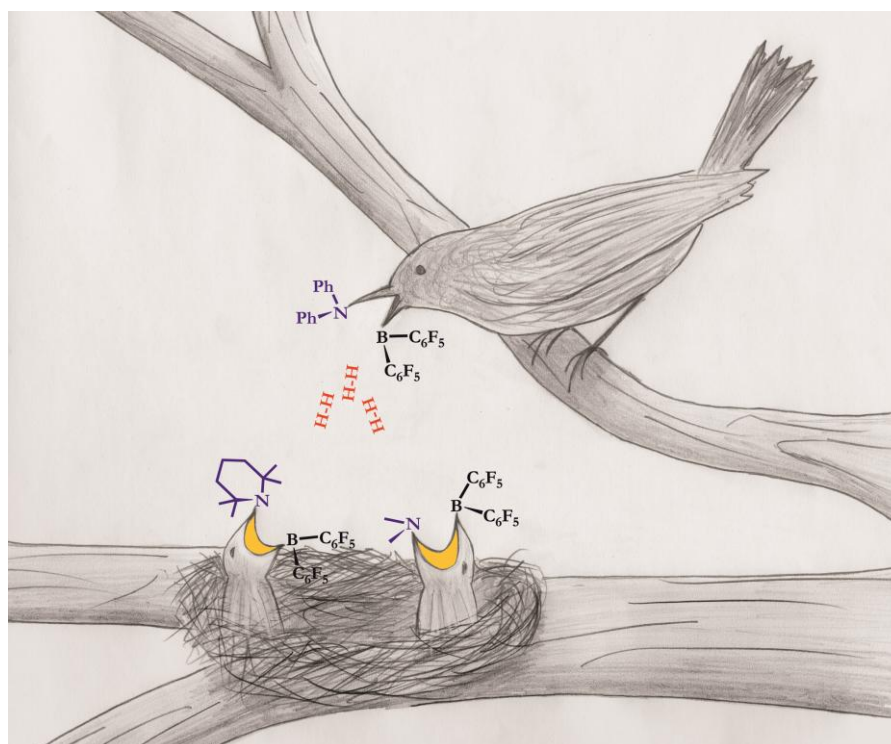


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# Frustrated Lewis Pairs

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PAPER

## Lewis pair polymerization by classical and frustrated Lewis pairs: acid, base and monomer scope and polymerization mechanism†

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Classical and frustrated Lewis pairs (LPs) of the strong Lewis acid (LA)  $\text{Al}(\text{C}_6\text{F}_5)_3$  with several Lewis base (LB) classes have been found to exhibit exceptional activity in the Lewis pair polymerization (LPP) of conjugated polar alkenes such as methyl methacrylate (MMA) as well as renewable  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL) and  $\gamma$ -methyl- $\alpha$ -methylene- $\gamma$ -butyrolactone ( $\gamma$ -MMBL), leading to high molecular weight polymers, often with narrow molecular weight distributions. This study has investigated a large number of LPs, consisting of 11 LAs as well as 10 achiral and 4 chiral LBs, for LPP of 12 monomers of several different types. Although some more common LAs can also be utilized for LPP,  $\text{Al}(\text{C}_6\text{F}_5)_3$ -based LPs are far more active and effective than other LA-based LPs. On the other hand, several classes of LBs, when paired with  $\text{Al}(\text{C}_6\text{F}_5)_3$ , can render highly active and effective LPP of MMA and  $\gamma$ -MMBL; such LBs include phosphines (e.g.,  $\text{P}^t\text{Bu}_3$ ), chiral chelating diphosphines, *N*-heterocyclic carbenes (NHCs), and phosphazene superbases (e.g.,  $\text{P}_4\text{-}^t\text{Bu}$ ). The  $\text{P}_4\text{-}^t\text{Bu}/\text{Al}(\text{C}_6\text{F}_5)_3$  pair exhibits the highest activity of the LP series, with a remarkably high turn-over frequency of  $9.6 \times 10^4 \text{ h}^{-1}$  (0.125 mol% catalyst, 100% MMA conversion in 30 s,  $M_n = 2.12 \times 10^5 \text{ g mol}^{-1}$ , PDI = 1.34). The polymers produced by LPs at RT are typically atactic ( $\text{P}_\gamma\text{MMBL}$  with ~47% mr) or syndio-rich (PMMA with ~70–75% rr), but highly syndiotactic PMMA with rr ~91% can be produced by chiral or achiral LPs at  $-78^\circ\text{C}$ . Mechanistic studies have identified and structurally characterized zwitterionic phosphonium and imidazolium enolaluminates as the active species of the current LPP system, which are formed by the reaction of the monomer- $\text{Al}(\text{C}_6\text{F}_5)_3$  adduct with  $\text{P}^t\text{Bu}_3$  and NHC bases, respectively. Kinetic studies have revealed that the MMA polymerization by the  $^t\text{Bu}_3\text{P}/\text{Al}(\text{C}_6\text{F}_5)_3$  pair is zero-order in monomer concentration after an initial induction period, and the polymerization is significantly catalyzed by the LA, thus pointing to a bimetallic, activated monomer propagation mechanism. Computational study on the active species formation as well as the chain initiation and propagation events involved in the LPP of MMA with some of the most representative LPs has added our understanding of fundamental steps of LPP. The main difference between NHC and  $\text{PR}_3$  bases is in the energetics of zwitterion formation, with the NHC-based zwitterions being remarkably more stable than the  $\text{PR}_3$ -based zwitterions. Comparison of the monometallic and bimetallic mechanisms for MMA addition shows a clear preference for the bimetallic mechanism.

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†Electronic supplementary information (ESI) available: Cartesian coordinates with BP86 and M06 solvent phase energies. CCDC 865899 (MMA-based zwitterion **1**), 865898 (MBL-based zwitterion **2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30427a

## Introduction

The “frustrated Lewis pair” (FLP) chemistry<sup>1</sup> has caught chemists’ imagination and thus attracted an explosive level of recent interest since the seminal works<sup>2</sup> of Stephan and Erker, which introduced the FLP concept to describe sterically encumbered Lewis acid (LA, most commonly  $\text{B}(\text{C}_6\text{F}_5)_3$ ) and Lewis base (LB, e.g.,  $\text{P}^t\text{Bu}_3$ ) pairs that are sterically precluded from forming classical donor–acceptor adducts. Instead, the unquenched, opposite LA/LB reactivity of a FLP can promote unusual reactions, or reactions that were previously known to be possible only by transition-metal complexes.<sup>1</sup> In its relatively short history, FLP

chemistry has achieved remarkable successes in many areas of chemistry, chiefly activation of small molecules,<sup>3</sup> catalytic hydrogenation,<sup>4</sup> and new reactivity/reaction development.<sup>5</sup>

Our interest in this area has been on the reactivity of the strongly acidic, sterically encumbered alane  $\text{Al}(\text{C}_6\text{F}_5)_3$ <sup>6</sup> towards LB substrates and subsequent application of the resulting active species to polymerization catalysis. This interest was prompted by several surprising findings during the period of 2000–2002 in the LA/LB chemistry associated with  $\text{Al}(\text{C}_6\text{F}_5)_3$ , which is in sharp contrast to the LA/LB chemistry with the borane congener  $\text{B}(\text{C}_6\text{F}_5)_3$ . Notable examples include: (a) unique “double activation” of group 4 metallocene dimethyl bases with  $\text{Al}(\text{C}_6\text{F}_5)_3$  to generate the corresponding highly active dicationic metallocene catalysts for olefin polymerization;<sup>7</sup> (b) formation of unusual  $\mu$ -alkyl dialuminate anions from the reaction of group 5 tantalocene trimethyl with  $\text{Al}(\text{C}_6\text{F}_5)_3$ ;<sup>8</sup> (c) high polymerization activity of the enolaluminate/ $\text{Al}(\text{C}_6\text{F}_5)_3$  LB/LA pair *versus* inactivity of the enolborate/ $\text{B}(\text{C}_6\text{F}_5)_3$  pair;<sup>9</sup> and (d) arene C–H bond activation taking place<sup>10</sup> when combining the strong LA  $\text{C}_7\text{H}_8\cdot\text{Al}(\text{C}_6\text{F}_5)_3$ <sup>11</sup> with a bulky LB, 2,6-di-*tert*-butyl pyridine, which does not form a classical acid–base adduct when unsolvated  $\text{Al}(\text{C}_6\text{F}_5)_3$  is used. Preceding the current term FLP,<sup>1</sup> this result (d) was an early example of the unusual reactivity of the FLP relative to what was generally recognized. Since then, our interest has continued to focus on utilizing the high Lewis acidity of  $\text{Al}(\text{C}_6\text{F}_5)_3$  and the unique catalytic feature of the active species derived from this alane for the polymerization of functionalized alkenes.<sup>12</sup> To this end, we recently communicated a significant development in this continuing effort:  $\text{Al}(\text{C}_6\text{F}_5)_3$ -based LPs rapidly polymerize conjugated polar alkenes, including methyl methacrylate (MMA) and naturally renewable methylene butyrolactones,<sup>13</sup>  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL)<sup>14</sup> and  $\gamma$ -methyl- $\alpha$ -methylene- $\gamma$ -butyrolactone ( $\gamma$ -MMBL),<sup>15</sup> at room temperature (RT) to high molecular weight (MW) polymers.<sup>16</sup> The bases examined therein included phosphines [ $\text{P}^t\text{Bu}_3$ ,  $\text{PMes}_3$  (Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ ), and  $\text{PPh}_3$ ] as well as *N*-heterocyclic carbenes (NHCs), 1,3-di-*tert*-butylimidazol-2-ylidene ( $I^t\text{Bu}$ ) and 1,3-di-mesityl-butylimidazol-2-ylidene (IMes). This Lewis pair polymerization (LPP) was proposed to proceed *via* zwitterionic phosphonium or imidazolium enolaluminate active species. Intriguingly, although the borane congener,  $\text{B}(\text{C}_6\text{F}_5)_3$ , can also form analogous zwitterionic species, it is inactive for LPP. Most recently, we found that reactive  $\alpha$ -methylene- $\gamma$ -butyrolactones (*e.g.*, MBL,  $\gamma$ -MMBL) can be directly and rapidly polymerized by the NHC base  $I^t\text{Bu}$  in DMF,<sup>17</sup> which represents the first conjugate-addition organopolymerization of polar alkenes by organic catalysts such as NHCs.<sup>18</sup>

This contribution presents a full account of our combined experimental and theoretical study on LPP, including experimental investigations into LA, LB and monomer scopes (Chart 1) and computational study of active species formation and polymerization mechanism. Notably, this study has examined a large number of classical and frustrated LPs, consisting of 11 LAs and 10 achiral and 4 chiral LBs, for the polymerization of 12 monomers of several different types, including methacrylates, an acrylate, acrylamides,  $\alpha$ -methylene- $\gamma$ -butyrolactones, a vinyl phosphonate, and cyclic monomers (lactones). Computational study of the active species formation as well as the chain initiation and propagation events involved in the polymerization

of MMA by the most representative LPP systems has added our understanding of fundamental steps involved in LPP.

## Experimental

### Materials, reagents, and methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an inert gas (Ar or  $\text{N}_2$ )-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes. HPLC-grade organic solvents were first sparged extensively with  $\text{N}_2$  during filling 20 L solvent reservoirs and then dried by passage through activated alumina (for  $\text{Et}_2\text{O}$ , THF, and  $\text{CH}_2\text{Cl}_2$ ) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Benzene- $d_6$  and toluene- $d_8$  were dried over sodium/potassium alloy and vacuum-distilled or filtered, whereas  $\text{CD}_2\text{Cl}_2$  and  $\text{CDCl}_3$  were dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on a Varian Inova 300 (300 MHz,  $^1\text{H}$ ; 75 MHz,  $^{13}\text{C}$ ; 282 MHz,  $^{19}\text{F}$ ), 400 MHz, or 500 MHz spectrometer. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  spectra were referenced to internal solvent resonances and are reported as parts per million relative to  $\text{SiMe}_4$ , whereas  $^{19}\text{F}$  NMR spectra were referenced to external  $\text{CFCl}_3$  and  $^{31}\text{P}$  NMR spectra to  $\text{H}_3\text{PO}_4$ .

Methyl methacrylate (MMA), furfuryl methacrylate (FMA), diethyl vinylphosphonate (DEVVP), *n*-butyl acrylate ( $n\text{BA}$ ),  $\epsilon$ -caporalactone ( $\epsilon\text{-CL}$ ),  $\gamma$ -valerolactone ( $\gamma\text{-VL}$ ),  $\gamma$ -butyrolactone ( $\gamma\text{-BL}$ ), and  $\alpha$ -angelica lactone ( $\alpha\text{-AL}$ ) were purchased from Sigma-Aldrich Chemical Co, while *N,N*-dimethylacrylamide (DMAA),  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL), and  $\gamma$ -methyl- $\alpha$ -methylene- $\gamma$ -butyrolactone ( $\gamma\text{-MMBL}$ ) were purchased from TCI America. These monomers were first degassed and dried over  $\text{CaH}_2$  overnight, followed by vacuum distillation; MMA was further purified by titration with neat tri(*n*-octyl)aluminum to a yellow end point and distillation under reduced pressure. A literature procedure was used to prepare *N,N*-diphenylacrylamide (DPAA).<sup>19</sup> The purified monomers were stored in brown bottles inside a glovebox freezer at  $-30\text{ }^\circ\text{C}$ .

Phosphines, including  $\text{PPh}_3$ ,  $\text{P}^t\text{Bu}_3$ , and  $\text{PMes}_3$  were purchased from Alfa Aesar Chemical Co. Chiral phosphines, including (*S*)-(-)-(1,1'-binaphthalene-2,2'-diyl)bis(diphenylphosphine) (CP-1), (-)-1,2-bis[(2*S*,5*S*)-2,5-diisopropylphospholano]benzene (CP-2), (*S,S*)-1,2-bis[ $\alpha$ -naphthyl(phenylphosphino)]ethane (CP-3), and (2*S*,3*S*)-(-)-2,3-bis(diphenylphosphino)butane (CP-4) were purchased from Sigma-Aldrich. Superbases, 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2,2,4,4,4-pentakis(dimethylamino)-catenadi(phosphazene) ( $\text{P}_4\text{-}^t\text{Bu}$ , solution in hexane) and 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2,2,4,4,4-pentakis(dimethylamino)-catenadi(phosphazene) ( $\text{P}_2\text{-}^t\text{Bu}$ , solution in THF) were purchased from Sigma-Aldrich; the solvent was removed prior to use. *N*-Heterocyclic carbenes (NHCs), including 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) and 1,3-di-*tert*-butylimidazol-2-ylidene ( $I^t\text{Bu}$ ), were purchased from Strem Chemical Co. A literature procedure was used to prepare 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (TPT).<sup>20</sup> Trimethylaluminum, triethylaluminum, and tri(*n*-octyl)aluminum were purchased from Strem Chemical Co., while butylated

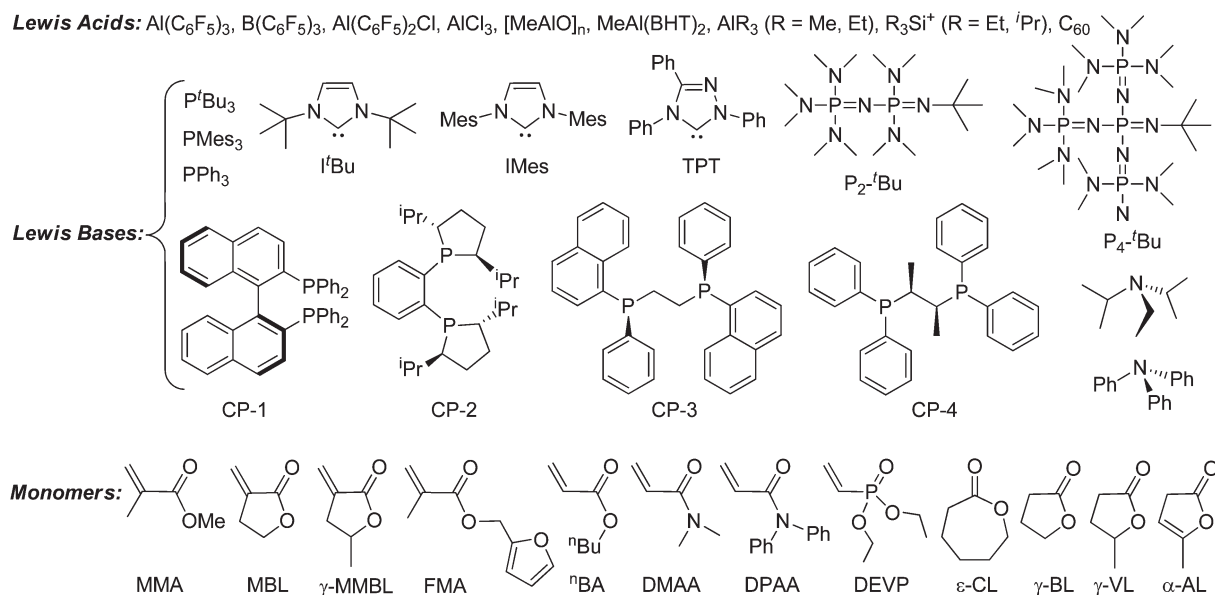


Chart 1 Scopes of LAs, LBs, and monomers investigated in this study.

hydroxytoluene (BHT-H, 2,6-di-*tert*-butyl-4-methylphenol) was purchased from Alfa Aesar Chemical Co. Methylaluminumoxane solution (10 wt% in toluene, MAO),  $\text{AlCl}_3$ , triisopropylsilane, and triethylsilane were purchased from Aldrich Chemical Co. All chemicals were used as received unless otherwise specified as follows.  $\text{C}_{60}$  (>99.95%) was purchased from Materials Technologies Research and dried *in vacuo* prior to use. BHT-H was recrystallized from hexanes prior to use;  $^t\text{Bu}_3\text{P}$  was first degassed and dried over  $\text{CaH}_2$  overnight, followed by vacuum distillation. Literature procedures were used to prepare  $\text{MeAl}(\text{BHT})_2$ <sup>21</sup> and  $\text{Al}(\text{C}_6\text{F}_5)_2\text{Cl}$ .<sup>22</sup> Tris(pentafluorophenyl)borane,  $\text{B}(\text{C}_6\text{F}_5)_3$ , and activator  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ <sup>23</sup> were obtained as research gifts from Boulder Scientific Co., and  $\text{B}(\text{C}_6\text{F}_5)_3$  was further purified by recrystallization from hexanes at  $-30^\circ\text{C}$ . Tris(pentafluorophenyl)alane,  $\text{Al}(\text{C}_6\text{F}_5)_3$ , as a (toluene)<sub>0.5</sub> or (toluene)<sub>1.0</sub> adduct, or in its unsolvated form, was prepared by ligand exchange reactions between  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{AlMe}_3$  or  $\text{AlEt}_3$  (for preparation of the unsolvated form).<sup>24</sup> (*Extra caution should be exercised when handling these materials, especially the unsolvated alane, due to its thermal and shock sensitivity!*) The  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  adduct<sup>9</sup> was prepared by addition of excess MMA to a toluene solution of the alane, followed by removal of the volatiles and drying *in vacuo*; its crystal structure was determined previously.<sup>25</sup> Zwitterionic species derived from the reaction of  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  with several phosphines and NHCs were previously described.<sup>16</sup>

**Generation, NMR data, and crystal structure of MMA-based phosphonium enolaluminate  $^t\text{Bu}_3\text{P}\text{-CH}_2\text{C}(\text{Me})=\text{C}(\text{OMe})\text{O-Al}(\text{C}_6\text{F}_5)_3$  (**1**).** A Teflon-valve-sealed J. Young-type NMR tube was charged with  $^t\text{Bu}_3\text{P}$  (10.1 mg, 0.05 mmol) and 0.3 mL of  $\text{C}_6\text{D}_6$  or  $\text{CD}_2\text{Cl}_2$ . A solution of  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  (31.4 mg, 0.05 mmol, 0.3 mL  $\text{C}_6\text{D}_6$  or  $\text{CD}_2\text{Cl}_2$ ) was added to this tube *via* pipette at ambient temperature, and the colorless mixture was allowed to react for 10 min before analysis by NMR, which showed the clean and quantitative formation of zwitterion **1** as

two isomers A (major) and B (minor) in a 7 : 3 ratio. These species undergo decomposition at RT after storing in solution for 2 h; a mixture of **1**, free  $^t\text{Bu}_3\text{P}$ , and other two unidentifiable species, but clearly no free  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  adduct or  $\text{Al}(\text{C}_6\text{F}_5)_3$  present, was formed after 20 h at RT.

<sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ) for major isomer **1A**:  $\delta$  3.63 (s, 3H, OMe), 2.49 (d,  $J = 9.9$  Hz, 2H,  $\text{PCH}_2$ ), 1.70 (s, 3H, =CMe), 0.74 (d,  $J = 13.2$  Hz, 27H,  $^t\text{Bu}$ ); minor isomer **1B**:  $\delta$  3.27 (s, 3H, OMe), 2.80 (d,  $J = 10.8$  Hz, 2H,  $\text{PCH}_2$ ), 1.60 (d,  $J = 1.8$  Hz, 3H, =CMe), 0.81 (d,  $J = 13.8$  Hz, 27H,  $^t\text{Bu}$ ). <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23^\circ\text{C}$ ) for **1A**:  $\delta$  3.50 (s, 3H, OMe), 3.19 (d,  $J = 9.6$  Hz, 2H,  $\text{PCH}_2$ ), 1.63 (s, br, 3H, =CMe), 1.52 (d,  $J = 13.2$  Hz, 27H,  $^t\text{Bu}$ ); **1B**:  $\delta$  3.23 (s, 3H, OMe), 3.32 (d,  $J = 11.1$  Hz, 2H,  $\text{PCH}_2$ ), 1.82 (d,  $J = 1.8$  Hz, 3H, =CMe), 1.55 (d,  $J = 13.5$  Hz, 27H,  $^t\text{Bu}$ ). <sup>13</sup>C NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23^\circ\text{C}$ ) for **1A**:  $\delta$  156.5 (d,  $^3J_{\text{C-P}} = 9.6$  Hz, OC(OMe)=), 150.3 (dm,  $^1J_{\text{C-F}} = 230$  Hz), 141.0 (dm,  $^1J_{\text{C-F}} = 246$  Hz), 136.9 (dm,  $^1J_{\text{C-F}} = 249$  Hz), 67.78 (d,  $^2J_{\text{C-P}} = 7.3$  Hz), 52.76, 39.94 (d,  $^1J_{\text{C-P}} = 25.9$  Hz,  $\text{CMe}_3$ ), 30.47 ( $\text{CMe}_3$ ), 24.46 (d,  $^1J_{\text{C-P}} = 31.8$  Hz,  $\text{CH}_2\text{P}$ ), 18.76 (OMe); **1B**:  $\delta$  160.6 (d,  $^3J_{\text{C-P}} = 11.5$  Hz, OC(OMe)=), 150.3 (dm,  $^1J_{\text{C-F}} = 230$  Hz), 141.0 (dm,  $^1J_{\text{C-F}} = 246$  Hz), 136.9 (dm,  $^1J_{\text{C-F}} = 249$  Hz), 75.69 (d,  $^2J_{\text{C-P}} = 8.0$  Hz), 57.49, 39.88 (d,  $^1J_{\text{C-P}} = 26.5$  Hz,  $\text{CMe}_3$ ), 30.43 ( $\text{CMe}_3$ ), 24.00 (d,  $^1J_{\text{C-P}} = 33.7$  Hz,  $\text{CH}_2\text{P}$ ), 17.93 (OMe). <sup>19</sup>F NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ) for **1A**:  $\delta$  -122.6 (m, 6F, *o*-F), -156.8 (t,  $J_{\text{F-F}} = 21.4$  Hz, 3F, *p*-F), -163.3 (m, 6F, *m*-F); **1B**:  $\delta$  -122.3 (m, 6F, *o*-F), -156.9 (t,  $J_{\text{F-F}} = 21.4$  Hz, 3F, *p*-F), -163.6 (m, 6F, *m*-F). <sup>19</sup>F NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23^\circ\text{C}$ ) for **1A**:  $\delta$  -123.4 (m, 6F, *o*-F), -157.8 (t,  $J_{\text{F-F}} = 21.4$  Hz, 3F, *p*-F), -164.3 (m, 6F, *m*-F); **1B**:  $\delta$  -123.2 (m, 6F, *o*-F), -157.8 (t,  $J_{\text{F-F}} = 21.4$  Hz, 3F, *p*-F), -164.4 (m, 6F, *m*-F). <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ) for **1A**:  $\delta$  47.8 (s,  $^t\text{Bu}_3\text{P}$ ); **1B**:  $\delta$  51.9 (s,  $^t\text{Bu}_3\text{P}$ ). <sup>31</sup>P NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23^\circ\text{C}$ ) for **1A**:  $\delta$  49.0 (s,  $^t\text{Bu}_3\text{P}$ ); **1B**:  $\delta$  52.6 (s,  $^t\text{Bu}_3\text{P}$ ).

The molecular structure of **1** (*E* isomer) has been confirmed by single-crystal X-ray diffraction analysis. Single crystals suitable for X-ray diffraction analysis, obtained by layering a



solution of  $t\text{Bu}_3\text{P}$  (0.1 mmol) in 4 mL hexanes on an equimolar solution of  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  in 1 mL  $\text{CH}_2\text{Cl}_2$  at  $-30\text{ }^\circ\text{C}$ , were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at  $120\text{ }^\circ\text{C}/10^{-6}$  Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker SMART CCD diffractometer. The structure was solved by direct methods and refined using the Bruker SHELXTL program library<sup>26</sup> and refined by full-matrix least-squares on  $F^2$  for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions. A disordered  $\text{CH}_2\text{Cl}_2$  solvent molecule was found in the crystal lattice, and the Platon Squeeze program was applied to take care of the solvent void ( $203\text{ \AA}^3$ ) in the structure refinement. The  $t\text{Bu}$  group in **1** was disordered and treated in part (C24 to C35, 59.20%; C24A to C35A, 40.80%). One perfluorophenyl ring (C13 to C18, F11 to F15, 60.36%; C13A to C18A, F11A to F15A, 39.64%) was disordered and the SAME command was implemented to restrain the bond distances and angles of the disordered perfluorophenyl ring. Selected crystallographic data for **1**:  $\text{C}_{35}\text{H}_{35}\text{AlF}_{15}\text{O}_2\text{P}$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.7749(4)\text{ \AA}$ ,  $b = 12.9668(4)\text{ \AA}$ ,  $c = 15.2829(5)\text{ \AA}$ ,  $\alpha = 92.432(2)^\circ$ ,  $\beta = 97.632(2)^\circ$ ,  $\gamma = 111.204(2)^\circ$ ,  $V = 1963.59(11)\text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calcd}} = 1.405\text{ Mg m}^{-3}$ ,  $\text{GOF} = 1.115$ ,  $R_1 = 0.0488$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1545$ . CCDC 865899 contains the supplementary crystallographic data.

### Generation, NMR data, and crystal structure of MBL-based phosphonium enolaluminate $t\text{Bu}_3\text{P}\text{-MBL-Al}(\text{C}_6\text{F}_5)_3$ (**2**)

Zwitterion **2** derived from the reaction of MBL with  $t\text{Bu}_3\text{P}$  and toluene- $\text{Al}(\text{C}_6\text{F}_5)_3$  was carried out in the same manner as that described for **1**.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz,  $23\text{ }^\circ\text{C}$ ):  $\delta$  4.12 (t, 2H,  $J = 8.5\text{ Hz}$ ,  $\text{CH}_2\text{O}$ ), 3.19 (d, 2H,  $J = 8.8\text{ Hz}$ ,  $\text{CH}_2\text{P}$ ), 2.67 (t, 2H,  $J = 8.5\text{ Hz}$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.56 (d, 27H,  $J = 13.5$ ,  $t\text{Bu}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23\text{ }^\circ\text{C}$ ):  $\delta$  163.5 (d,  $^3J_{\text{C-P}} = 10.0\text{ Hz}$ ,  $\text{OC}(\text{OMe})=$ ), 150.3 (dm,  $^1J_{\text{C-F}} = 231\text{ Hz}$ ), 141.0 (dm,  $^1J_{\text{C-F}} = 246\text{ Hz}$ ), 136.9 (dm,  $^1J_{\text{C-F}} = 250\text{ Hz}$ ), 66.44, 61.32 (d,  $^2J_{\text{C-P}} = 4.6\text{ Hz}$ ), 39.29 (d,  $^1J_{\text{C-P}} = 26.7\text{ Hz}$ ,  $\text{CMe}_3$ ), 34.06, 30.12 ( $\text{CMe}_3$ ), 19.73 (d,  $^1J_{\text{C-P}} = 37.9\text{ Hz}$ ,  $\text{CH}_2\text{P}$ ).  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 282 MHz,  $23\text{ }^\circ\text{C}$ ):  $\delta$   $-123.5$  (m, 6F,  $o\text{-F}$ ),  $-157.9$  (t,  $J_{\text{F-F}} = 19.3\text{ Hz}$ , 3F,  $p\text{-F}$ ),  $-164.6$  (m, 6F,  $m\text{-F}$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23\text{ }^\circ\text{C}$ ):  $\delta$  47.4 (s,  $t\text{Bu}_3$ ).

The molecular structure of **2** has been confirmed by single-crystal X-ray diffraction analysis. A 20 mL glass vial was charged with toluene- $\text{Al}(\text{C}_6\text{F}_5)_3$  (0.16 mmol), MBL (0.16 mmol), and 4 mL toluene, while another vial was charged with  $t\text{Bu}_3\text{P}$  (0.16 mmol) and 10 mL hexanes. The two vials were cooled to  $-30\text{ }^\circ\text{C}$  and the solution of  $t\text{Bu}_3\text{P}$  was layered on the mixture of toluene- $\text{Al}(\text{C}_6\text{F}_5)_3$  and MBL *via* pipette at low temperature. The vial was stored in the freezer for one week and crystals of **2** were formed. The crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at  $120\text{ }^\circ\text{C}/10^{-6}$  Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker SMART CCD diffractometer. The structure was solved by direct methods and refined using the

Bruker SHELXTL program library<sup>26</sup> and refined by full-matrix least-squares on  $F^2$  for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions. Selected crystallographic data for **2**:  $\text{C}_{35}\text{H}_{34}\text{AlF}_{15}\text{O}_2\text{P}$ , monoclinic, space group  $P2_1/n$ ,  $a = 15.9769(3)\text{ \AA}$ ,  $b = 12.0995(2)\text{ \AA}$ ,  $c = 18.1623(3)\text{ \AA}$ ,  $\beta = 93.4810(10)^\circ$ ,  $V = 3504.52(11)\text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calcd}} = 1.572\text{ Mg m}^{-3}$ ,  $\text{GOF} = 1.013$ ,  $R_1 = 0.0442$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1483$ . CCDC 865898 contains the supplementary crystallographic data.

**Generation and NMR data of phosphonium enolaluminate  $t\text{Bu}_3\text{P}\text{-CH}_2\text{C}(\text{Me})=\text{C}(\text{OMe})\text{-AlCl}_3$  (**3**).** A Teflon-valve-sealed J. Young-type NMR tube was charged with  $\text{AlCl}_3$  (21.4 mg, 0.16 mmol) and 0.3 mL of  $\text{CD}_2\text{Cl}_2$ . MMA (16.1 mg, 0.16 mmol) was added to this tube *via* pipette at ambient temperature, and the colorless mixture was allowed to react for 10 min before analysis by NMR, which showed the clean and quantitative formation of  $\text{MMA}\cdot\text{AlCl}_3$  adduct. To this colorless solution was added  $t\text{Bu}_3\text{P}$  (32.5 mg, 0.16 mmol) and 0.3 mL of  $\text{CD}_2\text{Cl}_2$ . Two isomers A (major) and B (minor) in a 2 : 1 ratio were formed as predominant products. This reaction also produced other unidentified minor species, presumably a result of competing decomposition of **3** because it has limited stability at RT. A mixture containing phosphonium enolaluminate **3**, free  $t\text{Bu}_3\text{P}$ , and some other unidentifiable species was formed after sitting the solution at RT for 36 h.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23\text{ }^\circ\text{C}$ ) for the  $\text{MMA}\cdot\text{AlCl}_3$  adduct:  $\delta$  6.79 (s, 1H,  $\text{CH}_2=$ ), 6.28 (s, 1H,  $\text{CH}_2=$ ), 4.28 (s, 3H,  $\text{OMe}$ ), 2.09 (s, 3H,  $=\text{CMe}$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23\text{ }^\circ\text{C}$ ) for **3A**:  $\delta$  3.63 (s, 3H,  $\text{OMe}$ ), 3.22 (d,  $J = 10.2\text{ Hz}$ , 2H,  $\text{PCH}_2$ ), 1.83 (s, br, 3H,  $=\text{CMe}$ ), 1.61 (d,  $J = 13.5\text{ Hz}$ , 27H,  $t\text{Bu}$ ); **3B**:  $\delta$  3.60 (s, 3H,  $\text{OMe}$ ), 3.24 (d,  $J = 10.8\text{ Hz}$ , 2H,  $\text{PCH}_2$ ), 1.80 (d,  $J = 1.2\text{ Hz}$ , 3H,  $=\text{CMe}$ ), 1.62 (d,  $J = 13.5\text{ Hz}$ , 27H,  $t\text{Bu}$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $23\text{ }^\circ\text{C}$ ) for **3A**:  $\delta$  49.8 (s,  $t\text{Bu}_3$ ); **3B**:  $\delta$  52.3 (s,  $t\text{Bu}_3$ ).

**General polymerization procedures.** MMA polymerizations were performed either in 30 mL oven-dried glass reactors inside the glovebox under ambient conditions (*ca.*  $25\text{ }^\circ\text{C}$ ) or in 25 mL oven-dried Schlenk flasks interfaced to the dual-manifold Schlenk line for runs carried out at other temperatures. A predetermined amount of a Lewis acid (LA), such as  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$ , (toluene)<sub>0.5</sub> or 1.0- $\text{Al}(\text{C}_6\text{F}_5)_3$ ,  $\text{AlCl}_3$ ,  $\text{AlEt}_3$ ,  $\text{AlMe}_3$ ,  $\text{Al}(\text{C}_6\text{F}_5)_2\text{Cl}$  *et al.*, was first dissolved in the monomer MMA (1.00 mL, 9.35 mmol) and 5 mL of solvent ( $\text{CH}_2\text{Cl}_2$  or toluene) inside a glovebox, and the polymerization was started by rapid addition of a solution of a Lewis base (LB), such as phosphines  $\text{PR}_3$ , a chiral phosphines, NHCs, amines, superbases *et al.*, in 4 mL of solvent ( $\text{CH}_2\text{Cl}_2$  or toluene) *via* a gastight syringe to the above LA + MMA solution under vigorous stirring. The amount of the monomer (M) and the  $[\text{LA}]/[\text{LB}]$  ratio (2/1) were fixed for all polymerizations, whereas the  $[\text{M}]/[\text{LB}]$  ratio was varied in some experiments. After the measured time interval, a 0.2 mL aliquot was taken from the reaction mixture *via* syringe and quickly quenched into a 4 mL vial containing 0.6 mL of undried “wet”  $\text{CDCl}_3$  stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by  $^1\text{H}$  NMR to obtain the percent monomer conversion data. The procedures for obtaining the monomer conversion data *vs.* reaction time were detailed in

literature.<sup>25,27a</sup> The polymerization was immediately quenched after the removal of the aliquot by addition of 5 mL 5% HCl-acidified methanol. The quenched mixture was precipitated into 100 mL of methanol, stirred for 1 h, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight.

Polymerization of other monomers was performed using the same procedure already described for the MMA polymerization except for DEVP. In a typical DEVP polymerization procedure, the reactor was charged with a stir bar, a LB (P<sup>t</sup>Bu<sub>3</sub>, PPh<sub>3</sub>, or I<sup>t</sup>Bu), 200 equiv. of DEVP (2 mL, 0.013 mol), and 2 mL of CH<sub>2</sub>Cl<sub>2</sub>. The polymerization was started by rapid addition of (toluene)<sub>0.5</sub>·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (32.8 mg, 55.1 mmol) under vigorous stirring. The polymerization was quenched at the times specified in the polymerization table, by pouring the polymer solution into 100 mL of MeOH, and stirred for 1 h. Prior to quenching, a 0.2 mL aliquot was withdrawn from the solution and quenched into septum sealed vials containing 0.6 mL of undried “wet” CHCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR for monomer conversion data. Oily polymers were collected by decanting the solvents and dried in a vacuum oven at 50 °C to a constant weight.

**Polymer characterizations.** Polymer number-average molecular weights ( $M_n$ ) and molecular weight distributions (MWD =  $M_w/M_n$ ) were measured by gel permeation chromatography (GPC) analyses carried out at 40 °C and a flow rate of 1.0 mL min<sup>-1</sup>, with DMF (for PMBL and PMMBL samples) or CHCl<sub>3</sub> (for PMMA and other polymer samples) as the eluent, on a Waters University 1500 GPC instrument coupled with a Waters RI detector and equipped with four PLgel 5 μm mixed-C columns (Polymer Laboratories; linear range of molecular weight = 200–2 000 000). The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with Waters Empower software (version 2002). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for the analysis of PMMA<sup>27,28</sup> and PMMBL<sup>29</sup> microstructures were recorded and analyzed according to the literature methods.

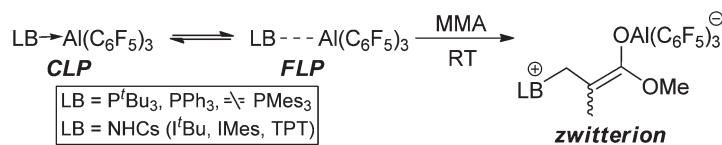
**Computational details.** All the density functional theory (DFT) calculations were performed using the Gaussian09 package.<sup>30</sup> Geometry optimizations were performed using the BP86 GGA functional of Becke and Perdew<sup>31</sup> with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers (SVP keyword in Gaussian).<sup>32</sup> Geometry optimizations were performed without symmetry constraints. Transition states (TSs) were approached through a linear transit procedure using the forming C–C bond as the reaction coordinate. Full TS searches were started from the maxima along the linear transit paths. All the geometries discussed in this work were confirmed as minima or TSs by frequency calculations. The reported energies have been obtained *via* single point energy calculations with the BP86 and M06<sup>33</sup> functionals with the triple- $\zeta$  basis set with one polarization function developed by Ahlrichs (TZVP keyword in Gaussian09). Solvent effects have been included in this single point energy calculation, based on the polarizable continuum solvation model PCM using toluene as the solvent.<sup>34</sup>

## Results and discussion

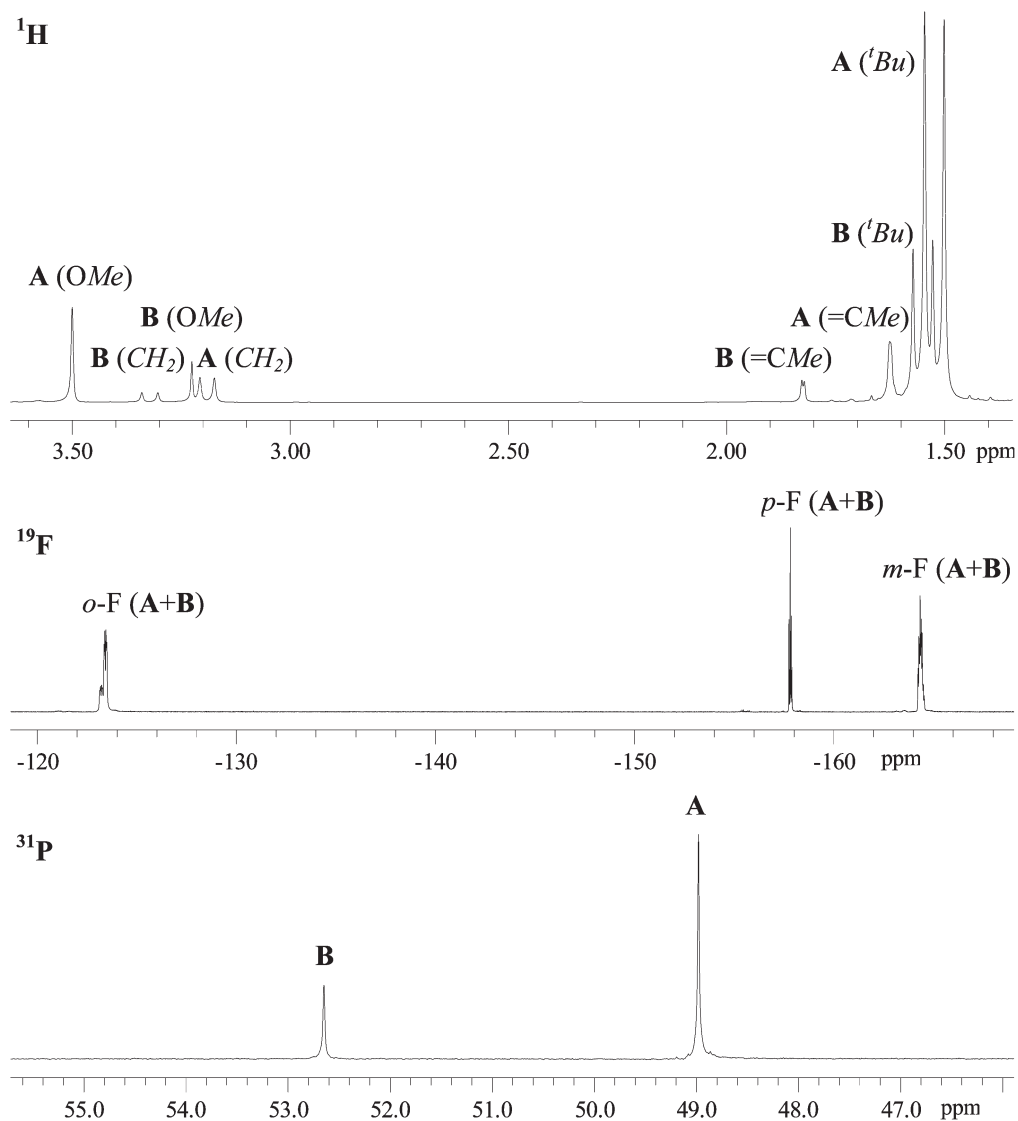
### Generation and characterization of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-based zwitterionic active species

Reaction of MMA·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with P<sup>t</sup>Bu<sub>3</sub> at RT in C<sub>6</sub>D<sub>6</sub> or CD<sub>2</sub>Cl<sub>2</sub> cleanly generates the corresponding zwitterionic phosphonium enolaluminate, <sup>t</sup>Bu<sub>3</sub>P–CH<sub>2</sub>C(Me)=C(OMe)O–Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**1**), as two isomers (*E/Z*) in a 7 : 3 ratio (Scheme 1).<sup>16</sup> This addition pattern is similar to additions of FLP to non-polar substrates, such as 1,4-addition of FLPs to 1,3-dienes<sup>35</sup> and 1,2-addition of FLPs to terminal alkynes,<sup>36</sup> as well as 1,4-additions of the ethylene-bridged intramolecular frustrated P/B (phosphine/borane) Lewis pair to ynones.<sup>37</sup> Zwitterion **1** can be readily characterized by NMR (here using the major isomer for illustration) for the phosphonium cation [<sup>t</sup>Bu<sub>3</sub>P<sup>+</sup>]<sup>35</sup> [ $\delta$  49.0 (s) ppm in <sup>31</sup>P NMR; 1.52 (d, <sup>t</sup>Bu) in <sup>1</sup>H NMR], for the enolaluminate anion [OAl(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup><sup>25,38</sup> [ $\delta$  –123.4 (m, 6F, *o*-F), –157.8 (t, 3F, *p*-F), –164.4 (m, 6F, *m*-F) in <sup>19</sup>F NMR], and for the remaining ester enolate moiety –CH<sub>2</sub>C(Me)=C(OMe)O– [ $\delta$  3.50 (s, 3H, *OMe*), 3.19 (d, 2H, *PCH*<sub>2</sub>), 1.63 (s, 3H, =*CMe*) in <sup>1</sup>H NMR], as depicted in Fig. 1. The molecular structure (the *E* isomer) of **1** has been confirmed by X-ray diffraction analysis, as shown in Fig. 2. It is worth noting that phosphonium enolaluminate **1** starts to undergo decomposition after sitting in solution at RT for 2 h, forming a mixture containing **1**, free P<sup>t</sup>Bu<sub>3</sub>, and other two unidentifiable species, but clearly no free MMA·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> present, after 20 h. Addition of excess MMA to a freshly generated solution of phosphonium enolaluminate **1** led to immediate polymerization, but the polymerization with an additional equiv. of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is much more rapid due to monomer activation (*vide infra*).

Intriguingly, *no reaction* took place between PMes<sub>3</sub> and MMA·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at RT, although PMes<sub>3</sub>/Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> can be described as an FLP.<sup>16</sup> Importantly, this observation correlates to the *non-polymerization* activity of this FLP in the presence of excess MMA (*vide infra*). On the other hand, PPh<sub>3</sub> and Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> cleanly form a CLP adduct, Ph<sub>3</sub>P·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, but this adduct formation did not quench its reactivity toward polymerization, as this CLP is still highly active for MMA polymerization (*vide infra*); it is worth noting that the stoichiometric reaction of PPh<sub>3</sub> and MMA·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> never went to completion, and the formed zwitterionic species, Ph<sub>3</sub>P–CH<sub>2</sub>C(Me)=C(OMe)O–Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (two isomers in a 1 : 1 ratio), started to decompose at RT in less than 1 h.<sup>16</sup> As NHCs, such as I<sup>t</sup>Bu and IMes, are strong bases, they react with C<sub>7</sub>H<sub>8</sub>·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at RT in benzene to form cleanly stable adducts, I<sup>t</sup>Bu·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and IMes·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, and the reaction between I<sup>t</sup>Bu or IMes with MMA·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> readily generates the corresponding zwitterionic imidazolium enolaluminate active species, I<sup>t</sup>Bu–CH<sub>2</sub>C(Me)=C(OMe)O–Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or IMes–CH<sub>2</sub>C(Me)=C(OMe)O–Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, which also correlates to the observed high polymerization activity of the I<sup>t</sup>Bu/Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and IMes/Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> pairs in the presence of a large excess of MMA.<sup>16</sup> In contrast, there is no reaction between I<sup>t</sup>Bu and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at –60 °C in toluene (*i.e.*, forming a FLP),<sup>39</sup> but at RT the same reaction yields a zwitterionic product with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> being attached to the 4-position of the imidazole heterocycle.<sup>40</sup> TPT, a weaker nucleophile than I<sup>t</sup>Bu or IMes, but still a strong base, reacts with MMA·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at RT to give a mixture



**Scheme 1**  $\text{Al}(\text{C}_6\text{F}_5)_3$ -based classical Lewis pair (CLP) and frustrated Lewis pair (FLP) examples and their reaction with conjugated polar vinyl monomers such as MMA leading to zwitterionic species that are active for polymerization.



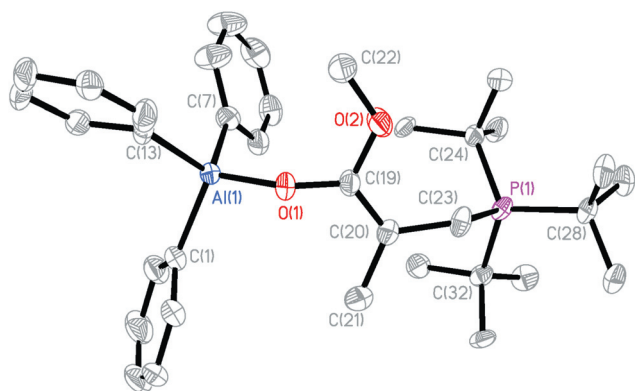
**Fig. 1**  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR spectra ( $\text{CD}_2\text{Cl}_2$ , 23 °C) of  $^t\text{Bu}_3\text{P}-\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{OMe})\text{O}-\text{Al}(\text{C}_6\text{F}_5)_3$  (**1**) as two isomers: major isomer A and minor isomer B.

containing the zwitterionic species, PMMA, and other minor species. Nevertheless, addition of excess MMA to this mixture rapidly converted all monomer to PMMA.

Likewise, replacing MMA with the cyclic MBL having fixed *s-cis*-conformation in the reaction with the  $\text{P}^t\text{Bu}_3/\text{Al}(\text{C}_6\text{F}_5)_3$  pair affords the corresponding zwitterionic phosphonium enolaluminate as a single isomer ( $^{31}\text{P}$  NMR:  $\delta$  47.4),  $^t\text{Bu}_3\text{P}-\text{MBL}-\text{Al}(\text{C}_6\text{F}_5)_3$  (**2**). This zwitterion has been characterized spectroscopically by NMR (Fig. 3) and also structurally by X-ray diffraction analysis (Fig. 4). Also noteworthy is that phosphonium

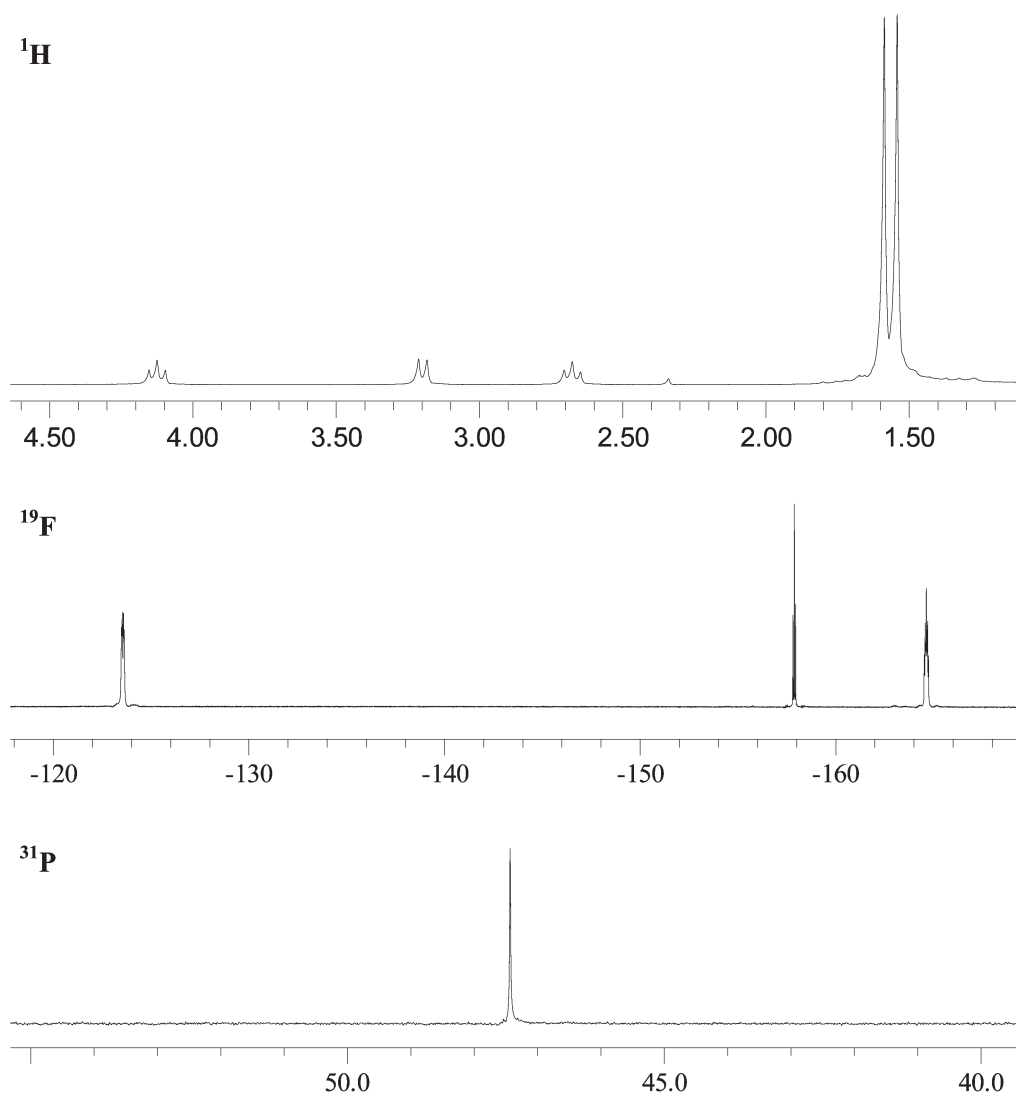
enolaluminate **2** is active for MBL polymerization, but this polymerization becomes much more rapid with an additional equiv. of  $\text{Al}(\text{C}_6\text{F}_5)_3$  (*vide infra*).

**Polymerization of MMA by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{LB}$  (LB = phosphines and NHCs) pairs.** Control runs using  $\text{Al}(\text{C}_6\text{F}_5)_3$  (as a toluene or MMA adduct), phosphines ( $\text{P}^t\text{Bu}_3$ ,  $\text{PMe}_3$ , and  $\text{PPh}_3$ ), and NHCs ( $^t\text{Bu}$ , IMes, and TPT) individually for polymerization of MMA (200–800 equiv.) at RT in toluene yielded no polymer formation up to 24 h. (Note that TPT catalyzes tail-to-tail



**Fig. 2** X-ray crystal structure of  $t\text{Bu}_3\text{P}-\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{OMe})\text{O}-\text{Al}(\text{C}_6\text{F}_5)_3$  (**1**) with thermal ellipsoids drawn at the 50% probability. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Al(1)–O(1), 1.7513(11); O(1)–C(19), 1.3167(16); C(19)–O(2), 1.3718(18); C(19)–C(20), 1.345(2); C(20)–C(23), 1.5155(19); C(23)–P(1), 1.8487(15); Al(1)–O(1)–C(19), 142.69(11); O(1)–C(19)–C(20), 126.13(14); O(1)–C(19)–O(2), 116.33(13); O(2)–C(19)–C(20), 117.52(12); C(19)–C(20)–C(23), 118.56(13); C(20)–C(23)–P(1), 124.86(11).

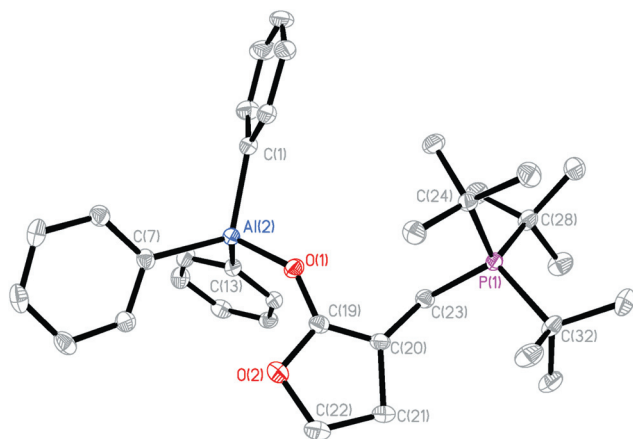
dimerization of MMA in this or other solvents or in bulk at  $80^\circ\text{C}$ .<sup>41</sup> Premixing  $\text{C}_7\text{H}_8\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  with  $t\text{Bu}_3\text{P}$  at RT for 10 min in either a 1 : 1 or 2 : 1 [LA]/[LB] ratio, followed by addition of MMA (800 equiv.), also led to no monomer consumption up to 24 h, due to the FLP-induced C–H activation and other decomposition of this Lewis pair.<sup>16</sup> On the other hand, addition of MMA (800 equiv.) to the preformed zwitterionic phosphonium enolaluminate active species **1** by pre-treating the alane–monomer adduct,  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$ , with this phosphine LB in toluene at RT for 10 min (*vide infra*), brought about rapid polymerization, consuming all monomer in 60 min and yielding high molecular weight (MW) polymer ( $M_n = 2.83 \times 10^5 \text{ g mol}^{-1}$ , polydispersity index (PDI) =  $M_w/M_n = 1.42$ ; run 1, Table 1). The resulting PMMA exhibited a syndiotacticity of 75.5% rr. The same polymerization was *much more rapid* in a 2 : 1 [LA]/[LB] ratio, which converted all monomer to high MW polymer in 4 min ( $M_n = 3.97 \times 10^5 \text{ g mol}^{-1}$ , MWD = 1.52, rr = 73.5%, run 2), thus giving a high turn-over frequency (TOF) of  $1.2 \times 10^4 \text{ h}^{-1}$ . A more convenient procedure by simply premixing  $\text{C}_7\text{H}_8\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  with MMA in toluene (*i.e.*, generating  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  *in situ*), followed by addition of the base to



**Fig. 3**  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR spectra ( $\text{CD}_2\text{Cl}_2$ ,  $23^\circ\text{C}$ ) of  $t\text{Bu}_3\text{P}-\text{MBL}-\text{Al}(\text{C}_6\text{F}_5)_3$  (**2**).



start the polymerization, also led to a highly active polymerization system, achieving quantitative monomer conversion in 7 min and yielding similarly high MW polymer ( $M_n = 3.15 \times 10^5 \text{ g mol}^{-1}$ , PDI = 1.72,  $rr = 73.6\%$ , run 3). The same polymerization carried out at 0 °C was still highly effective (100% conversion in 1 h), producing PMMA with higher syndiotacticity of 77.9%  $rr$  (run 4). The PMMA with high syndiotacticity of 88.1%  $rr$  can be produced at -78 °C, at expense of polymerization activity (consuming all 80 equiv. of MMA in 100 min). Changing solvent polarity from relatively non-polar toluene ( $\epsilon = 2.38$ ) to more polar  $\text{CH}_2\text{Cl}_2$  ( $\epsilon = 8.93$ )<sup>42</sup> did not noticeably affect the polymerization activity, although there was some variation in polymer MW (run 5 vs. 1, 6 vs. 2).



**Fig. 4** X-ray crystal structure of  ${}^t\text{Bu}_3\text{P-MBL-Al}(\text{C}_6\text{F}_5)_3$  (**2**) with thermal ellipsoids drawn at the 50% probability. Selected bond lengths (Å) and angles (°): Al(2)–O(1), 1.7599(11); O(1)–C(19), 1.3073(17); C(19)–O(2), 1.3666(18); C(19)–C(20), 1.342(2); C(20)–C(23), 1.496(2); C(23)–P(1), 1.8332(15); Al(2)–O(1)–C(19), 138.81(10); O(1)–C(19)–C(20), 128.77(13); O(1)–C(19)–O(2), 115.97(13); O(2)–C(19)–C(20), 115.27(13); C(19)–C(20)–C(23), 120.81(13); C(20)–C(23)–P(1), 123.32(11).

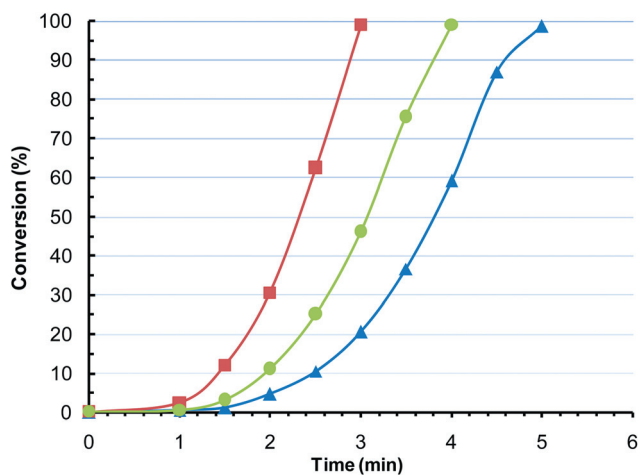
Having achieved high polymerization activity with the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  pair using appropriate procedures (*i.e.*, by avoiding direct contact of the FLP in absence of monomer or by pre-forming zwitterion **1**), we examined the effectiveness of other sterically encumbered bases known to form FLPs with  $\text{B}(\text{C}_6\text{F}_5)_3$ . As suggested from the no reaction between  $\text{PMes}_3$  and  $\text{MMA} \cdot \text{Al}(\text{C}_6\text{F}_5)_3$  at RT (*vide supra*), the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{PMes}_3$  pair is indeed *ineffective* for MMA polymerization in toluene or  $\text{CH}_2\text{Cl}_2$ , up to 24 h (runs 7 and 8, Table 1). Interestingly, the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{PPh}_3$  pair exhibits exceptional activity (TOF =  $4.8 \times 10^4 \text{ h}^{-1}$ , run 9), despite the fact that  $\text{PPh}_3$  forms a classic acid–base adduct with the alane.<sup>16</sup> However, the polymer produced by this pair had a bimodal MW distribution (MWD) consisting of ~41% higher MW fraction ( $M_n = 3.88 \times 10^5 \text{ g mol}^{-1}$ , PDI = 1.04) and ~59% lower MW fraction ( $M_n = 1.33 \times 10^5 \text{ g mol}^{-1}$ , PDI = 1.05), characteristic of co-existing two types of active species with rather similar catalytic activity; this polymerization behavior is consistent with the incomplete reaction of  $\text{PPh}_3$  with  $\text{MMA} \cdot \text{Al}(\text{C}_6\text{F}_5)_3$  and instability of the resulting zwitterion (*vide supra*).

Excitingly, the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{NHC}$  pairs are not only extremely active for MMA polymerization (runs 10–14), they also produce PMMA with narrow and unimodal MWDs. Thus, the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{IMes}$  pair consumed all 800 equiv. of MMA in less than 1 min, giving a high TOF of  $>4.8 \times 10^4 \text{ h}^{-1}$  (run 10). In comparison, the polymerization activity of  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{I}^t\text{Bu}$  is ~15 times lower, but the resulting polymer MW is ~20 times higher ( $M_n = 5.25 \times 10^5 \text{ g mol}^{-1}$ , PDI = 1.43, run 11) than that produced by IMes ( $M_n = 2.66 \times 10^4 \text{ g mol}^{-1}$ , PDI = 1.77, run 10). The polymerization by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{I}^t\text{Bu}$  in  $\text{CH}_2\text{Cl}_2$  performed similarly to that in toluene (run 12 vs. 11). Likewise, the polymerization by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{TPT}$  in either toluene (run 13) or  $\text{CH}_2\text{Cl}_2$  (run 14) is highly active, achieving quantitative monomer conversion in less than 1 min. An interesting and welcoming feature of the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{TPT}$  pair is that it produced structurally more defined polymers with considerably narrower MWDs (PDI = 1.17, run 13; PDI = 1.23, run 14) than those achieved by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{IMes}$  and  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{I}^t\text{Bu}$  pairs.

**Table 1** Selected results of MMA polymerization by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{LB}$  pairs<sup>a</sup>

Run no.	LA (adduct)	LB (1 eq.)	[LA]/[LB]	Solvent	Temp (°C)	Time (min)	Conv. <sup>b</sup> (%)	TOF (h <sup>-1</sup> )	$10^{-4} M_n^c$ (g mol <sup>-1</sup> )	PDI <sup>c</sup> ( $M_w/M_n$ )	[rr] <sup>d</sup> (%)	[mr] <sup>d</sup> (%)	[mm] <sup>d</sup> (%)
1	Al-MMA	P <sup>t</sup> Bu <sub>3</sub>	1 : 1	Toluene	25	60	100	800	28.3	1.42	75.5	23.1	1.4
2	Al-MMA	P <sup>t</sup> Bu <sub>3</sub>	2 : 1	Toluene	25	4	100	12 000	39.7	1.52	73.5	25.0	1.5
3	Al-TOL	P <sup>t</sup> Bu <sub>3</sub>	2 : 1	Toluene	25	7	100	6840	31.5	1.72	73.6	24.7	1.7
4	Al-TOL	P <sup>t</sup> Bu <sub>3</sub>	2 : 1	Toluene	0	60	100	800	13.8	2.39	77.9	20.9	1.2
5	Al-MMA	P <sup>t</sup> Bu <sub>3</sub>	1 : 1	CH <sub>2</sub> Cl <sub>2</sub>	25	60	100	800	38.0	1.41	75.8	22.6	1.6
6	Al-MMA	P <sup>t</sup> Bu <sub>3</sub>	2 : 1	CH <sub>2</sub> Cl <sub>2</sub>	25	4	100	12 000	36.9	1.47	75.0	23.0	2.0
7	Al-MMA	PMes <sub>3</sub>	2 : 1	toluene	25	1440	0	0	—	—	—	—	—
8	Al-MMA	PMes <sub>3</sub>	2 : 1	CH <sub>2</sub> Cl <sub>2</sub>	25	1440	0	0	—	—	—	—	—
9	Al-MMA	PPh <sub>3</sub>	2 : 1	Toluene	25	1	100	48 000	38.8; 13.3	1.04	73.0	25.4	1.6
10	Al-MMA	IMes	2 : 1	Toluene	25	1	100	48 000	2.66	1.77	72.7	25.7	1.6
11	Al-MMA	I <sup>t</sup> Bu	2 : 1	Toluene	25	15	100	3200	52.5	1.43	75.1	23.3	1.6
12	Al-MMA	I <sup>t</sup> Bu	2 : 1	CH <sub>2</sub> Cl <sub>2</sub>	25	15	100	3200	60.0	1.34	74.3	24.3	1.4
13	Al-MMA	TPT	2 : 1	Toluene	25	1	100	24 000	15.9	1.17	71.6	26.7	1.7
14	Al-MMA	TPT	2 : 1	CH <sub>2</sub> Cl <sub>2</sub>	25	1	100	24 000	12.5	1.23	74.2	23.7	2.1

<sup>a</sup> Conditions:  $[\text{MMA}]/[\text{LB}] = 800$ , except for runs 13 and 14 where LB = TPT and  $[\text{MMA}]/[\text{TPT}] = 400$ ; 10 mL total solution volume. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup> Number-average molecular weight ( $M_n$ ) and polydispersity index (PDI) determined by GPC relative to PMMA standards. <sup>d</sup> Polymer methyl triads (rr, mr, mm) measured by <sup>1</sup>H NMR.



**Fig. 5** Plots of monomer conversion (%) vs. reaction time (min) for MMA polymerization in toluene at RT by the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  pair with two different procedures and LA catalyst concentrations. Line ▲: procedure A,  $[\text{MMA}]/[\text{LA}]/[\text{LB}] = 800/2/1$ ;  $[\text{MMA}]_0 = 0.935 \text{ M}$ ,  $[\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3] = 2.34 \text{ mM}$ ,  $[\text{P}^t\text{Bu}_3] = 1.17 \text{ mM}$ . Line ●: procedure B,  $[\text{MMA}]/[\text{LA}]/[\text{LB}] = 800/1.8/1$ . Line ■: procedure B,  $[\text{MMA}]/[\text{LA}]/[\text{LB}] = 800/2/1$ .

Concentrating on the highly active  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  pair for polymerization of MMA, we examined kinetic profiles of the polymerization in toluene at RT using two different procedures and the LA catalyst concentrations. Specifically, in procedure A, 2 equiv. of  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  was dissolved in 800 equiv. MMA and toluene, followed by addition of 1 equiv.  $\text{P}^t\text{Bu}_3$  in toluene solution to start the polymerization. As can be seen from Fig. 5 (▲ line), after an initial slow induction period ( $\sim 2$  min), the monomer conversion increased almost linearly with reaction time till completion of the reaction, thus showing a zero-order dependence on  $[\text{MMA}]$ ; this type of polymerization kinetics was also observed in the MMA polymerization by other nucleophile/electrophile pairs, such as zirconocene enolate/zirconocenium cation,<sup>43</sup> enolaluminate anion/organoaluminum,<sup>44</sup> and silyl ketene acetal/silylium cation<sup>45</sup> pairs. On the other hand, in procedure B, 1 equiv.  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$  was first premixed with 1 equiv.  $\text{P}^t\text{Bu}_3$  in toluene for 10 min (to form the zwitterionic species 1), followed by addition of another equiv.  $\text{MMA}\cdot\text{Al}(\text{C}_6\text{F}_5)_3 + 800$  equiv. of MMA, and the resulting polymerization system was considerably faster (by 55%); hence, after now a much shorter induction period ( $\sim 1$  min), the kinetic plot showed a linear increase of monomer conversion with time, see Fig. 5 (■ line). There also showed a significant effect of the LA concentration on the polymerization rate. For example, using the same procedure (B) but lowering the total amount of the alane from 2 equiv. to 1.8 equiv., the polymerization was slowed by 23%, see Fig. 5 (● line); consistent with this observation, increasing the amount of the alane to 2.5 equiv., the polymerization became faster by approximately 50%. These results showed that this polymerization is strongly catalyzed by LA, which is consistent with the proposed bimolecular, activated monomer propagation mechanism (*vide infra*).

**Scope of monomer.** To expand the utility of LPP in polymer synthesis, we examined the polymerization of 11 other

monomers by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{LB}$  pairs, the result of which were summarized in Table 2. First, we investigated the effectiveness of  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{LB}$  pairs for polymerization of renewable monomers MBL and  $\gamma$ -MML, cyclic analogs of MMA. Despite being a heterogeneous process (due to insolubility of the resulting polymer in the reaction medium), the polymerization of MBL by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  in  $\text{CH}_2\text{Cl}_2$  with  $[\text{MBL}]/[\text{LB}] = 800$  achieved greater than 90% polymer yield in 1 h (run 1, Table 2). The PMBL produced had a medium  $M_n$  of  $4.48 \times 10^4 \text{ g mol}^{-1}$  and a relatively high PDI of 2.18. Likewise, the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{I}^t\text{Bu}$  pair is also quite effective for MBL polymerization, but the  $M_n$  (which contained a small,  $\sim 4\%$  low MW tail peak) of the resulting PMBL is  $\sim 4$  times higher than that by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  (run 2 vs. 1, Table 2). Owing to good solubility of PMMML in  $\text{CH}_2\text{Cl}_2$ , the polymerization of MMBL by such LPs is homogeneous and highly effective. Specifically, the polymerization by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  achieved quantitative monomer conversion in 10 min, giving a high MW, essentially atactic polymer ( $M_n = 1.92 \times 10^5 \text{ g mol}^{-1}$ , PDI = 2.28,  $\text{mr} = 47.0\%$ , run 3, Table 2). All LPs with three NHC bases are highly active for MMBL polymerization, with a high TOF of  $4.8 \times 10^4 \text{ h}^{-1}$  (runs 4–6, Table 2), but  $M_n$  of  $1.39 \times 10^5 \text{ g mol}^{-1}$  of the PMMML produced by  $\text{I}^t\text{Bu}$  is about twice of that produced by IMes, and the polymer also exhibits a much more narrow MWD (PDI = 1.15 for run 4, vs. PDI = 1.42 for run 5). The bimodal behavior of the LP with  $\text{PPH}_3$  is once again manifested in the MMBL polymerization, resulting in the polymer product with  $\sim 43\%$  high MW fraction and  $\sim 57\%$  low MW fraction (run 7).

Neither the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  pair nor the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{IMes}$  pair exhibited any reactivity toward polymerization of a bulky methacrylate, FMA, up to 24 h (runs 8–9, Table 2). Moving to an acrylate monomer, polymerization of  $^n\text{BA}$  by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  achieved 33% conversion in 1 h (run 10); however, there was no further significant increase in conversion, even after 24 h at which point the conversion was still only 35%, indicating substantial catalyst deactivation in this acrylate polymerization. On the other hand, polymerization of an acrylamide monomer, DMAA, by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  with  $[\text{DMAA}]/[\text{LB}] = 800$  achieved quantitative monomer conversion in 1 min, affording a high TOF of  $4.8 \times 10^4 \text{ h}^{-1}$  and a high MW polymer with  $M_n = 2.93 \times 10^5 \text{ g mol}^{-1}$ , PDI = 1.43 (run 11, Table 2). Likewise, the  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{I}^t\text{Bu}$  pair is also highly active for DMAA polymerization, producing PDMAA with even higher MW of  $M_n = 3.69 \times 10^5 \text{ g mol}^{-1}$  and lower PDI of 1.28 (run 12). In comparison, the polymerization of DPAA by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  ( $[\text{DPAA}]/[\text{LB}] = 200$ ) was much slower, requiring 24 h to achieve quantitative monomer conversion. Nonetheless, the PDPAA produced has a high MW of  $M_n = 3.57 \times 10^5 \text{ g mol}^{-1}$  and PDI = 1.31 (run 13, Table 2). Polymerization of a vinyl phosphonate monomer, DEVP, by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  was active but sluggish (run 14), while the polymerization by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{IMes}$  was significantly faster (run 15).

Moving onto cyclic esters and lactones,  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  (0.125 mol% catalyst) exhibited moderate activity toward polymerization of  $\epsilon$ -CL, achieving 58% conversion after 20 h (run 16, Table 2). On the other hand, none of the five-membered lactones investigated, including  $\gamma$ -BL,  $\gamma$ -VL, and  $\alpha$ -AL, were polymerized by the current LPs, such as  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{P}^t\text{Bu}_3$  and  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{IMes}$ , under current ambient conditions (runs 17–20, Table 2).

**Table 2** Polymerization results by Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/LB pairs<sup>a</sup>

Run no.	Monomer (M)	LB (1 eq.)	[M]/[LB]	Solvent	Time (min)	Conv. <sup>b</sup> (%)	TOF (h <sup>-1</sup> )	10 <sup>-4</sup> M <sub>n</sub> <sup>c</sup> (g mol <sup>-1</sup> )	PDI <sup>c</sup> (M <sub>w</sub> /M <sub>n</sub> )
1	MBL	P <sup>t</sup> Bu <sub>3</sub>	800	CH <sub>2</sub> Cl <sub>2</sub>	60	(90.5)	760	4.48	2.18
2	MBL	I <sup>t</sup> Bu	800	CH <sub>2</sub> Cl <sub>2</sub>	60	(85.5)	704	16.3 (>96%)	1.28
3	γ-MMBL	P <sup>t</sup> Bu <sub>3</sub>	800	CH <sub>2</sub> Cl <sub>2</sub>	10	100	4800	19.2	2.28
4	γ-MMBL	I <sup>t</sup> Bu	800	CH <sub>2</sub> Cl <sub>2</sub>	1	100	48 000	13.9	1.15
5	γ-MMBL	IMes	800	CH <sub>2</sub> Cl <sub>2</sub>	1	100	48 000	6.28	1.42
6	γ-MMBL	TPT	400	CH <sub>2</sub> Cl <sub>2</sub>	0.5	100	48 000	7.35 (>95%)	1.22
7	γ-MMBL	PPh <sub>3</sub>	800	CH <sub>2</sub> Cl <sub>2</sub>	1	100	48 000	13.9; 5.01	1.03; 1.04
8	FMA	P <sup>t</sup> Bu <sub>3</sub>	400	Toluene	1440	0	0	—	—
9	FMA	IMes	400	Toluene	1440	0	0	—	—
10	<sup>n</sup> BA	P <sup>t</sup> Bu <sub>3</sub>	800	Toluene	60	33.0	264	n.d.	n.d.
11	DMAA	P <sup>t</sup> Bu <sub>3</sub>	800	Toluene	1	100	48 000	29.3	1.43
12	DMAA	I <sup>t</sup> Bu	800	Toluene	1.5	100	32 000	36.9	1.28
13	DPAA	P <sup>t</sup> Bu <sub>3</sub>	200	Toluene	300	100	67	35.7	1.31
14	DEVP	P <sup>t</sup> Bu <sub>3</sub>	200	CH <sub>2</sub> Cl <sub>2</sub>	1740	79.3	6	n.d.	n.d.
15	DEVP	IMes	200	CH <sub>2</sub> Cl <sub>2</sub>	960	75.6	10	2.79	2.11
16	ε-CL	P <sup>t</sup> Bu <sub>3</sub>	800	Toluene	1200	58.0	23	7.37	2.76
17	γ-BL	P <sup>t</sup> Bu <sub>3</sub>	400	Toluene	120	0	0	—	—
18	γ-BL	IMes	400	Toluene	120	0	0	—	—
19	γ-VL	P <sup>t</sup> Bu <sub>3</sub>	400	Toluene	120	0	0	—	—
20	α-AL	P <sup>t</sup> Bu <sub>3</sub>	400	Toluene	120	0	0	—	—

<sup>a</sup> Conditions: [LA]/[LB] = 2; room temperature (~25 °C); n.d. = not determined. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR; values in parentheses were isolated yields. <sup>c</sup> Number-average molecular weight (M<sub>n</sub>) and polydispersity index (PDI) determined by GPC relative to PMMA standards; values (percentages) in parentheses were the percentage of the major peak when the other minor shoulder peak showed up on the GPC trace.

**Table 3** Polymerization results by LA/LB pairs<sup>a</sup>

Run no.	LA (2 eq.)	LB (1 eq.)	Monomer (M)	[M]/[LB]	Solvent	Temp (°C)	Time (min)	Conv. <sup>b</sup> (%)	TOF (h <sup>-1</sup> )	10 <sup>-4</sup> M <sub>n</sub> <sup>c</sup> (g mol <sup>-1</sup> )	PDI <sup>c</sup> (M <sub>w</sub> /M <sub>n</sub> )	[rr] <sup>d</sup> (%)
1	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	P <sup>t</sup> Bu <sub>3</sub>	MMA	400	Toluene	25	1440	0	0	—	—	—
2	MeAl(BHT) <sub>2</sub>	P <sup>t</sup> Bu <sub>3</sub>	MMA	800	Toluene	25	1440	0	0	—	—	—
3	AlMe <sub>3</sub>	P <sup>t</sup> Bu <sub>3</sub>	MMA	400	Toluene	25	1440	Trace	~0	—	—	—
4	AlEt <sub>3</sub>	PPh <sub>3</sub>	MMA	40	Toluene	25	1440	97.3	1.6	1.17	2.25	67.8
5	AlEt <sub>3</sub>	PPh <sub>3</sub>	MMA	40	Toluene	-78	1440	100	1.7	3.86	1.60	87.5
6	AlCl <sub>3</sub>	P <sup>t</sup> Bu <sub>3</sub>	MMA	800	Toluene	25	1440	66.7	22	2.55	1.91	68.9
7	AlCl <sub>3</sub>	P <sup>t</sup> Bu <sub>3</sub>	MMA	800	Toluene	-78	600	100	80	27.3	2.12	91.1
8	ClAl(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	P <sup>t</sup> Bu <sub>3</sub>	MMA	400	Toluene	25	1440	32.8	5.5	1.84 (98%)	1.42	n.d.
9	ClAl(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	IMes	MMA	400	Toluene	25	1440	36.4	6.1	0.52	1.43	n.d.
10	ClAl(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	P <sup>t</sup> Bu <sub>3</sub>	γ-MMBL	400	CH <sub>2</sub> Cl <sub>2</sub>	25	1440	22.5	3.8	1.64 (98%)	1.36	n/a
11	ClAl(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	IMes	γ-MMBL	400	CH <sub>2</sub> Cl <sub>2</sub>	25	1440	45.4	7.6	2.47	2.06	n/a
12	MAO	none	γ-MMBL	n.a.	CH <sub>2</sub> Cl <sub>2</sub>	25	1440	30.6	n/a	1.35 (99%)	1.29	n/a
13	MAO	P <sup>t</sup> Bu <sub>3</sub>	γ-MMBL	400	CH <sub>2</sub> Cl <sub>2</sub>	25	1440	93.2	15	0.79 (99%)	1.26	n/a
14	MAO	I <sup>t</sup> Bu	γ-MMBL	400	CH <sub>2</sub> Cl <sub>2</sub>	25	1440	95.6	16	0.79 (99%)	1.27	n/a
15	Et <sub>3</sub> Si <sup>+</sup>	P <sup>t</sup> Bu <sub>3</sub>	MMA	400	CH <sub>2</sub> Cl <sub>2</sub>	25	1440	0	0	—	—	—
16	<sup>t</sup> Pr <sub>3</sub> Si <sup>+</sup>	P <sup>t</sup> Bu <sub>3</sub>	MMA	400	CH <sub>2</sub> Cl <sub>2</sub>	25	1440	0	0	—	—	—
17	C <sub>60</sub>	IMes	MMA	800	Toluene	25	1440	0	0	—	—	—
18	C <sub>60</sub>	I <sup>t</sup> Bu	γ-MMBL	200	DMF	25	1080	0	0	—	—	—

<sup>a</sup> Conditions: [LA]/[LB] = 2, except for runs by MAO (12–14) where 100 equiv. was used. Silylium ions R<sub>3</sub>Si<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> were generated *in situ* from R<sub>3</sub>SiH + Ph<sub>3</sub>C[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. n/a = not applicable; n.d. = not determined. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup> Number-average molecular weight (M<sub>n</sub>) and polydispersity index (PDI) determined by GPC relative to PMMA standards; values (percentages) in parentheses were the percentage of the major peak when the other minor (trace) shoulder peak showed up on the GPC trace. <sup>d</sup> Polymer methyl triads (rr, mr, mm) measured by <sup>1</sup>H NMR.

**Scope of Lewis acids and bases.** As described above, LPs based on the strong LA Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> are highly active for polymerization of conjugated polar alkenes such as methacrylates, acrylamides, and α-methylene-γ-butyrolactones. An interesting fundamental and practical question is whether this LA could be replaced by other more common LAs without compromising polymerization activity. To address this question, we initially examined common LAs such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, MeAl(BHT)<sub>2</sub>, and AlMe<sub>3</sub>, in combination with the highly effective LB partner,

P<sup>t</sup>Bu<sub>3</sub>, for MMA polymerization, but observed none to negligible polymer formation, up to 24 h (runs 1–3, Table 3). The finding of the inactivity of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/P<sup>t</sup>Bu<sub>3</sub> pair, even with another equiv. of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, is intriguing because MMA·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> readily reacts with P<sup>t</sup>Bu<sub>3</sub> to form zwitterionic phosphonium enolborate <sup>t</sup>Bu<sub>3</sub>P–CH<sub>2</sub>C(Me)=C(OMe)O–B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>16</sup> This observation is reminiscent of our previous findings regarding the high activity of enolaluminate vs. inactivity of enolborate species toward conjugate-addition polymerization, attributed to



the inability of the enolborate/borane pair to effect the bimolecular, activated-monomer anionic polymerization as does the enolate/alane pair.<sup>9,38</sup> With a 10-fold increase in the LP loading (2.5 mol%), the AlEt<sub>3</sub>/PPh<sub>3</sub> pair is active for MMA polymerization at both RT and -78 °C, albeit the TOF numbers were low (<2 h<sup>-1</sup>, runs 4–5), which is consistent with the results reported by Hatada *et al.*<sup>46</sup> The syndiotacticity of the PMMA produced at -78 °C, 87.5% rr, is considerably higher than that produced at RT, 67.8% rr, so is the polymer molecular weight (run 5 vs. 4).

For LPP of MMA, AlCl<sub>3</sub> is much more effective than AlR<sub>3</sub>. Thus, even in a low catalyst loading of 0.125 mol%, the AlCl<sub>3</sub>/P<sup>t</sup>Bu<sub>3</sub> pair exhibited modest activity in MMA polymerization, achieving 66.7% conversion in 24 h (run 6). Kinetic profiling of this polymerization showed that 66.4% conversion was already achieved within 1.5 min and there was no noticeable increase in conversion thereafter (up to 24 h), the observation of which indicated rapid catalyst deactivation, as indicated by the instability of the AlCl<sub>3</sub>-derived zwitterionic species (see Experimental). Keeping this in mind, we ran the same polymerization at -78 °C and achieved quantitative monomer conversion in 10 h (run 7). More significantly, the MW of the PMMA produced at -78 °C ( $M_n = 2.73 \times 10^5$  g mol<sup>-1</sup>) is more than 10 times higher than that produced at RT (run 7 vs. 6). Impressively, this low temperature polymerization produced highly syndiotactic PMMA (91.1% rr).

Compared to Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, ClAl(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> based LPs are much less active for both polymerizations of MBL and  $\gamma$ -MMBL (runs 8–11, Table 3). Specifically, the ClAl(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>/LB pairs achieved low monomer conversions of <50%, even after extended times (14 h). Based on kinetic profiling experiments, there was substantial catalyst deactivation after an initial stage of polymerization (1 min), after which no significant increase in monomer conversion occurred. Considering methylaluminoxane (MAO) as a potent Lewis acidic activator for olefin polymerization by metal-based catalysts,<sup>47</sup> we examined MAO-based LPs for  $\gamma$ -MMBL polymerization. In absence of a LB, MAO (100 equiv.) itself is active for  $\gamma$ -MMBL (400 equiv.) polymerization at RT, achieving 30.6% conversion after 24 h (run 12). With an additional of 1 equiv. of P<sup>t</sup>Bu<sub>3</sub>, the conversion was enhanced to 93.2% in the same period, producing the polymer with a relatively low MW of  $M_n = 7.89 \times 10^3$  g mol<sup>-1</sup> (run 13, Table 3). Using an NHC base, the MAO/<sup>t</sup>Bu pair performed similarly in this polymerization (run 14 vs. 13, Table 3).

Interestingly, strongly Lewis acidic silylium ions R<sub>3</sub>Si<sup>+</sup>-[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>, generated *in situ* from the reaction of R<sub>3</sub>SiH + Ph<sub>3</sub>C[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], are inactive as LAs for LPP of MMA polymerization in either toluene or CH<sub>2</sub>Cl<sub>2</sub> at RT, when combined with P<sup>t</sup>Bu<sub>3</sub> (runs 15–16, Table 3). We also examined C<sub>60</sub>, a known Lewis acid,<sup>48</sup> in combination with NHC bases, for LPP of MMA and  $\gamma$ -MMBL; no polymerization was observed up to 24 h in different solvents (runs 17–18, Table 3).

Turning our attention to the scope of Lewis bases and considering the success of the Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/P<sup>t</sup>Bu<sub>3</sub> pair for LPP of various types of monomers, we were interested in the potential of chiral chelating phosphines for enhancements in activity and/or stereoselectivity in LPP. To this end, four chiral phosphines (Chart 1) were selected and investigated for MMA polymerization as LB components of LPs with Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. In comparison, CP-1, a chiral biNAP diphosphine, is much less active (TOF = 224 h<sup>-1</sup>,

run 1, Table 4) than P<sup>t</sup>Bu<sub>3</sub> (TOF =  $1.2 \times 10^4$  h<sup>-1</sup>). In addition, the polymer produced exhibited a bimodal MWD, with  $M_n = 3.70 \times 10^5$  g mol<sup>-1</sup>, PDI = 1.13 (56%) and  $M_n = 1.29 \times 10^6$  g mol<sup>-1</sup>, PDI = 1.01 (44%). CP-2, a benzene-bridged diphosphine, showed a 3.5-fold activity enhancement over CP-1 (run 2 vs. 1), but it is still less active than the simple P<sup>t</sup>Bu<sub>3</sub>. Impressively, CP-3, an ethylene-bridged diphosphine, is 4 times more active than P<sup>t</sup>Bu<sub>3</sub>, achieving a high TOF of  $4.8 \times 10^4$  h<sup>-1</sup> (run 3, Table 4). The PMMA produced also had a high MW of  $M_n = 2.74 \times 10^5$  g mol<sup>-1</sup> and a unimodal MWD (PDI = 1.40). The analogous 2,3-butane-bridged chiral diphosphine, CP-4, is also highly active, achieving a high TOF of  $1.6 \times 10^4$  h<sup>-1</sup> and a high MW of  $M_n = 3.68 \times 10^5$  g mol<sup>-1</sup> (PDI = 1.48, run 4, Table 4). In all cases, the syndiotacticity of PMMA produced by these chiral LB/LA pairs was about 74–75% rr, showing no enhancement over the PMMA produced by the achiral Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/P<sup>t</sup>Bu<sub>3</sub> pair.

Superbases, P<sub>4</sub><sup>-t</sup>Bu and P<sub>2</sub><sup>-t</sup>Bu (Chart 1), were also investigated as LBs for LPP of MMA. The Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/P<sub>4</sub><sup>-t</sup>Bu pair exhibited the *highest* activity amongst all LPs investigated in this study, giving the highest TOF of  $9.6 \times 10^4$  h<sup>-1</sup> (*i.e.*, consuming all 800 equiv. of monomer in 30 s!) and also producing high MW PMMA with  $M_n = 2.12 \times 10^5$  g mol<sup>-1</sup> and narrow MWD of PDI = 1.34 (run 5, Table 4). The Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/P<sub>2</sub><sup>-t</sup>Bu pair is also highly active with TOF =  $4.8 \times 10^4$  h<sup>-1</sup> (run 6, Table 4). On the other hand, the LPs of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with two tertiary amines, NPh<sub>3</sub> and NEt<sup>t</sup>Pr<sub>2</sub>, showed no activity toward polymerization of MMA up to 24 h (runs 7–8). The Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/NPh<sub>3</sub> pair is also inactive for the polymerization of the more reactive monomer  $\gamma$ -MMBL (run 9), but the Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/NEt<sup>t</sup>Pr<sub>2</sub> pair exhibits good activity for polymerization of  $\gamma$ -MMBL, achieving quantitative conversion in 5 h and giving a TOF of 160 h<sup>-1</sup> (run 10, Table 4).

### Computational studies of zwitterionic active species formation, chain initiation and propagation

This section focuses on the mechanistic aspects of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-based LPs as catalysts in MMA polymerization. The LB/Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> pairs, LB = phosphines (P<sup>t</sup>Bu<sub>3</sub>, PMes<sub>3</sub> and PPh<sub>3</sub>) and NHC (IMes), were examined for their formation of the active species upon reaction with the monomer MMA as well as subsequent MMA addition to the formed zwitterionic active species.

**Zwitterion formation and stability.** We started from MMA coordination to the Al atom of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to form the alane-activated monomer adduct [Al]-MMA. Next, we considered the reaction of the adduct with different LBs to form the zwitterionic active species [Al]-MMA-LB. The energetics of these steps is shown in Scheme 2. Here we report the energy values obtained with both BP86 and M06 functionals. The former is known to underestimate binding energy but offers a balanced approach when the binding of different large ligands is compared. Conversely, the latter predicts much more reasonable binding energies, but has some tendency to overestimate the binding energy of large ligands in solution.<sup>49</sup>

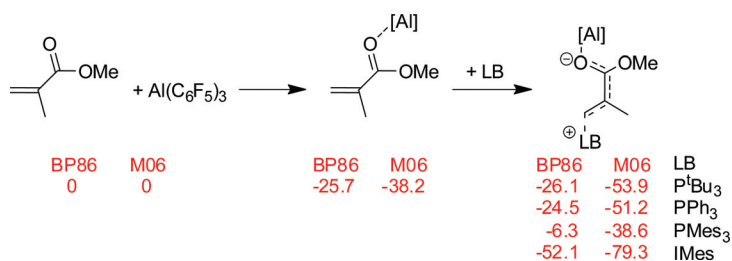
Despite the unfavorable entropic contribution due to MMA coordination to Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, formation of the [Al]-MMA adduct, which was previously isolated and structurally characterized,<sup>9,25</sup> is strongly favored, with a binding energy of the alane to MMA of 25.7 and 38.2 kcal mol<sup>-1</sup> at the BP86 and M06 levels,



**Table 4** Polymerization results by Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/LB pairs<sup>a</sup>

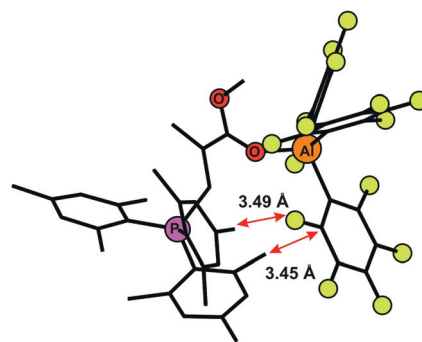
Run no.	LB (1 eq.)	Monomer (M)	[M]/[LB]	Solvent	Time (min)	Conv. <sup>b</sup> (%)	TOF (h <sup>-1</sup> )	10 <sup>-4</sup> M <sub>n</sub> <sup>c</sup> (g mol <sup>-1</sup> )	PDI <sup>c</sup> (M <sub>w</sub> /M <sub>n</sub> )	[rr] <sup>d</sup> (%)
1	CP-1	MMA	800	Toluene	210	98.0	224	37.0 (56%)	1.13	74.7
2	CP-2	MMA	800	Toluene	60	98.3	786	25.8	1.83	73.8
3	CP-3	MMA	800	Toluene	1	100	48 000	27.4	1.40	73.7
4	CP-4	MMA	800	Toluene	3	100	16 000	36.8	1.48	74.2
5	P <sub>4</sub> - <sup>t</sup> Bu	MMA	800	Toluene	0.5	100	96 000	21.2	1.34	72.4
6	P <sub>2</sub> - <sup>t</sup> Bu	MMA	400	Toluene	0.5	100	48 000	4.82	1.64	72.8
7	NPh <sub>3</sub>	MMA	800	CH <sub>2</sub> Cl <sub>2</sub>	1440	0	0	—	—	—
8	NEt <sup>t</sup> Pr <sub>2</sub>	MMA	800	CH <sub>2</sub> Cl <sub>2</sub>	1440	0	0	—	—	—
9	NPh <sub>3</sub>	γ-MMBL	800	CH <sub>2</sub> Cl <sub>2</sub>	1440	0	0	—	—	—
10	NEt <sup>t</sup> Pr <sub>2</sub>	γ-MMBL	800	CH <sub>2</sub> Cl <sub>2</sub>	300	100	160	9.77	1.90	n/a

<sup>a</sup> Conditions: [LA]/[LB] = 2, LA = Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as a toluene adduct; RT (~25 °C). n/a = not applicable. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup> Number-average molecular weight (M<sub>n</sub>) and polydispersity index (PDI) determined by GPC relative to PMMA standards; values (percentages) in parentheses were the percentage of the major peak when the other minor shoulder peak showed up on the GPC trace. <sup>d</sup> Polymer methyl triads (rr, mr, mm) measured by <sup>1</sup>H NMR.



**Scheme 2** Energetics (kcal mol<sup>-1</sup>) of zwitterion formation with different LBs, as predicted by the BP86 and M06 functionals. Separated MMA, Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and LB is assumed as the reference system at 0 kcal mol<sup>-1</sup>.

respectively (Scheme 2). This result was expected considering the extremely high Lewis acidity of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>7,11,50</sup> The energetics of the zwitterion formation largely depends on the LB and the functional considered. In fact, as shown in Scheme 2, binding of IMes to the [Al]-MMA adduct is strongly favored, with the zwitterionic species [Al]-MMA-IMes more than 50 kcal mol<sup>-1</sup> below the starting species, with a net gain of roughly 26 kcal mol<sup>-1</sup> from the [Al]-MMA adduct, while phosphines bind much less strongly to the [Al]-MMA adduct, with the binding strongly influenced by the functional. For instance, the BP86 functional predicts an energy gain of only 0.4 for P<sup>t</sup>Bu<sub>3</sub>, whereas binding of PPh<sub>3</sub> and PMes<sub>3</sub> to the [Al]-MMA adduct is unfavored by 1.2 and 19.4 kcal mol<sup>-1</sup>, respectively. Considering an unfavorable entropic contribution, not considered in the present case, the [Al]-MMA-PR<sub>3</sub> zwitterion is predicted to be unstable at the BP86 level. Differently, a sizeable zwitterion energy formation is predicted by the M06 functional, with the binding of all the LBs to the [Al]-MMA moiety being roughly 15 kcal mol<sup>-1</sup> stronger. Consequently, even including an unfavorable entropic contribution, formation of [Al]-MMA-PR<sub>3</sub> (R = <sup>t</sup>Bu, Ph) zwitterions is favored with the M06 functional, while PMes<sub>3</sub> is unbound to the adduct, in agreement with experiments. It is worth noting that the relative stability of the phosphine zwitterion species predicted by both the BP86 and the M06 functionals is in good agreement with the experimental results, which showed somewhat greater stability of the P<sup>t</sup>Bu<sub>3</sub> zwitterion species relative to the PPh<sub>3</sub> zwitterion as well as no zwitterion formation in the case of PMes<sub>3</sub> and no polymerization activity by the Mes<sub>3</sub>P/Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> pair. The instability of the



**Fig. 6** DFT optimized geometry of the Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-MMA-PMes<sub>3</sub> zwitterion.

PMes<sub>3</sub> zwitterion can be easily explained considering the optimized geometry shown in Fig. 6, where repulsive steric interaction between the methyl substituents on the mesityl rings and the phenyl groups of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, due to the short distances between these groups, are responsible for the zwitterion instability.

If similar stability of the [Al]-MMA-PPh<sub>3</sub> and [Al]-MMA-P<sup>t</sup>Bu<sub>3</sub> zwitterionic species was expected, there would be no meaningful steric interaction between the alane and the base that can justify the different stability of the zwitterions derived from IMes and PR<sub>3</sub>. Indeed, the energy gain associated with addition of the small PMe<sub>3</sub> to the [Al]-MMA adduct is 7.4 and 14.6 kcal mol<sup>-1</sup> at the BP86 and M06 levels, which indicates that steric repulsion somewhat destabilizes the binding of the larger P<sup>t</sup>Bu<sub>3</sub>

**Table 5** Natural bond orbital and bond strength analysis of [Al]-MMA-PPh<sub>3</sub> and [Al]-MMA-IMes zwitterionic species

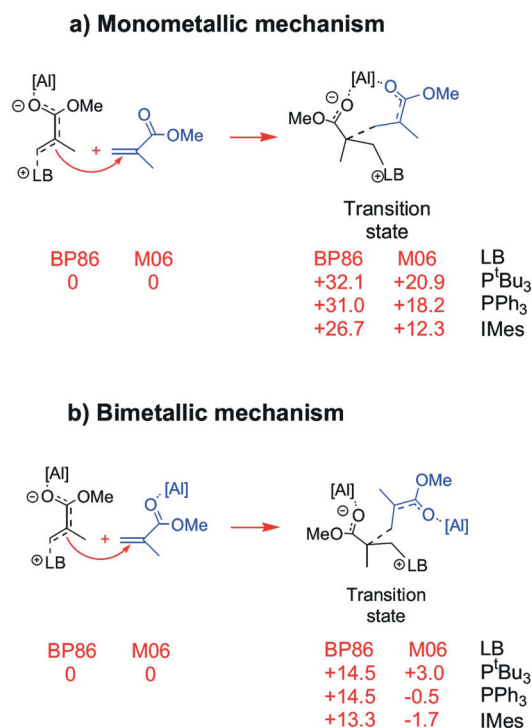
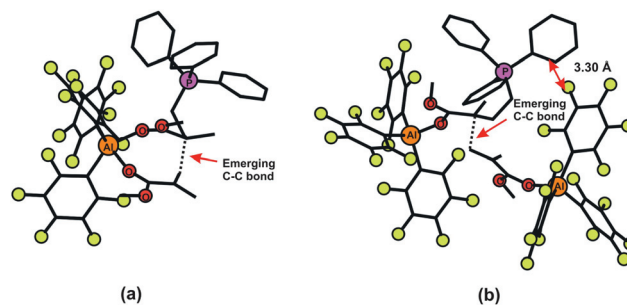
	[Al]-MMA-PPh <sub>3</sub>	[Al]-MMA-IMes
Bond length C <sub>MMA</sub> -LB (Å)	1.94	1.50
Bond order C <sub>MMA</sub> -LB	0.83	1.04
Bond length O <sub>MMA</sub> -Al (Å)	1.83	1.83
Bond order O <sub>MMA</sub> -Al	0.32	0.33
Charge on Al(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (electrons)	-0.21	-0.21
Charge on MMA (electrons)	-0.70	-0.60
Charge on LB (electrons)	0.91	0.81

and PPh<sub>3</sub> phosphines with the BP86 functional, and that the main source of stabilization with the M06 functional is dispersive in nature (at the M06 level P<sup>t</sup>Bu<sub>3</sub> binds more strongly than PMe<sub>3</sub> to [Al]-MMA). Analysis of the bond strength and charge distribution on PPh<sub>3</sub> and IMes zwitterions clearly show that the higher stability of the NHC zwitterion mainly arises from electronic effects (see Table 5). As shown in Table 5, for both the PPh<sub>3</sub> and IMes zwitterions the distance between the coordinated C atom of MMA and the coordinating P or C atom of the PPh<sub>3</sub> and IMes is close to a classical P-C or C-C σ bond, 1.84 and 1.54 Å, respectively. However, the C<sub>NHC</sub>-C<sub>MMA</sub> bond order is 1.04 in case of IMes, whereas, in case of the P-C<sub>MMA</sub> bond with PPh<sub>3</sub>, the order is lower, around 0.83. This result indicates that the MMA-IMes interaction in the zwitterion has a very strong covalent character, while the MMA-PPh<sub>3</sub> interaction in the zwitterion is more dative in nature. The Al-MMA interaction in the zwitterion, instead, is quite similar for both PPh<sub>3</sub> and IMes. Natural Population Analysis (NPA) shows a slightly larger charge separation for the [Al]-MMA-PPh<sub>3</sub> with a greater positive charge on PPh<sub>3</sub>, compared to the charge on IMes in the corresponding zwitterionic species. This analysis is consistent with a greater ionic character of the C<sub>MMA</sub>-PPh<sub>3</sub> bond relative to the C<sub>MMA</sub>-IMes bond.

The weaker stability of the PR<sub>3</sub>-based zwitterions could be related to the experimentally observed bimodal molecular weight distribution of the PMMA obtained when the Ph<sub>3</sub>P/Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> pair is employed as catalyst.<sup>16</sup> The formation of more than one active species could just arise from the decomposition of the [Al]-MMA-PPh<sub>3</sub> zwitterion.

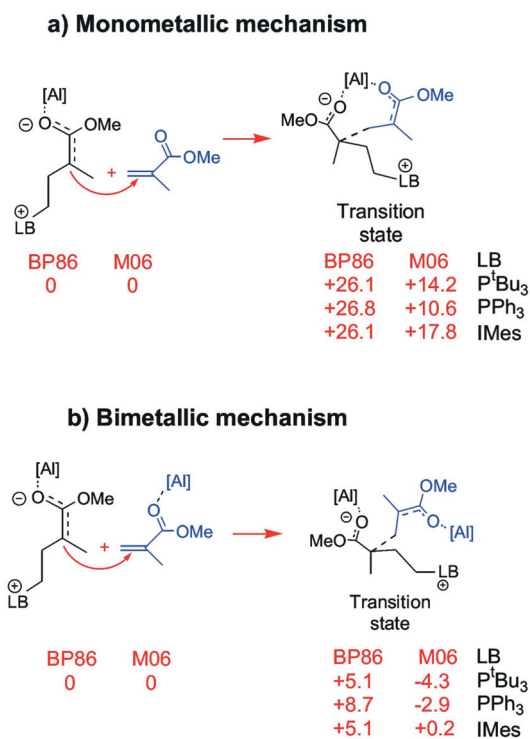
**MMA chain initiation.** We move now to the addition of the first MMA molecule to the active [Al]-MMA-LB species for LB = PPh<sub>3</sub>, P<sup>t</sup>Bu<sub>3</sub> and IMes, considering the two most probable mechanisms shown in Scheme 3. In the first pathway the zwitterion attacks an Al-free MMA molecule (monometallic mechanism, Scheme 3a), while in the second the zwitterion attacks an Al-activated MMA molecule, namely the preformed alane-monomer adduct (bimetallic mechanism, Scheme 3b). The energy barriers obtained with the BP86 and M06 functionals for the two mechanisms are also reported in Scheme 3.

The most stable transition states for MMA addition along the two reaction pathways shown in Scheme 3 are compared in Fig. 7 for the case of PPh<sub>3</sub>-based zwitterionic species. Although the bimetallic TS displays a more crowded geometry, see the short distance between the LB and the Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> moiety coordinated to the monomer in Fig. 7b, the numbers in the Scheme 3 show clearly that whatever LB is considered, the bimetallic

**Scheme 3** Energetics (kcal mol<sup>-1</sup>) of the first MMA addition to a preformed zwitterion with the BP86 and the M06 functionals.**Fig. 7** Transition state geometries of MMA addition to the Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-MMA-PPh<sub>3</sub> zwitterion proceeding *via* the monometallic (a) and bimetallic (b) mechanisms.

mechanism is strongly favored, with an energy barrier roughly 15–20 kcal mol<sup>-1</sup> lower than the energy barrier calculated for the monometallic mechanism. Both the BP86 and the M06 functionals performed consistently in this case.

The most notable difference between the M06 and BP86 results is that the BP86 functional, for both mechanisms, predicted energy barriers roughly 10–15 kcal mol<sup>-1</sup> higher than the corresponding energy barriers predicted by the M06 functional. Furthermore, the M06 functional predicted a negligible or even negative (LB = PPh<sub>3</sub> and IMes) energy barrier in case of the bimetallic mechanism. This result is expected based on the previously discussed differences between the two functionals, with a tendency of the M06 functional to overestimate the dispersive interactions, which are generated at the level of the TS by the close proximity of the zwitterions and the monomer.<sup>51</sup> However,



**Scheme 4** Energetics (kcal mol<sup>-1</sup>) of the generic MMA addition to a preformed zwitterion with the BP86 and the M06 functionals.

of paramount relevance here is the calculated preference for the bimetallic mechanism, whatever functional is considered, which is in agreement with the experimental data showing that the rate of MMA polymerization increases significantly by increasing the [Al]/LB ratio, and that the MMA reaction starts with a negligible induction period when the preformed zwitterion and [Al]-MMA adduct is employed (*vide supra*).

**MMA chain propagation step.** In this section we describe the reaction profile for MMA addition in a propagation step in the case of a long PMMA chain. The generic propagating active species was simulated by adding a methylene unit between the LB and the last inserted MMA molecule with a coordinated [Al] moiety, see Scheme 4. The addition of the methylene unit breaks connection between the LB and the [Al] through  $\pi$ -bonds, leaving only a  $\sigma$ -bond connection. The energy profiles for the mono- and the bimetallic MMA additions using PPh<sub>3</sub>, P<sup>t</sup>Bu<sub>3</sub> and IMes LBs are schematically shown in Scheme 4.

As anticipated, also in the chain growth step addition of the [Al]-MMA adduct is strongly favored, compared to the addition of non-activated MMA for all the LP systems considered. In fact, the numbers in Scheme 4 show a clear preference for the bimetallic mechanism with both functionals considered.<sup>52</sup> Comparison between the initiation step, Scheme 3, and the generic chain growth step, Scheme 4, indicates that in the generic chain growth step there is a reduction of roughly 10 kcal mol<sup>-1</sup> in the energy barriers for both the mono and the bimetallic mechanisms, although this decrease is somewhat smaller in case of the M06 functional. The reduction of repulsive steric interaction between the Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> moiety coordinated to the monomer and the LB bonded to the growing chain, the latter being pushed

away from the reacting atoms by the added methylene unit on the growing chain, mainly contributes to the reduced energy barrier for MMA addition.

## Conclusions

Highly active and effective LPP systems have been achieved with classical and frustrated LPs based on the strong Lewis acid Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Such CLPs and FLPs are especially effective for polymerizing conjugated polar alkenes such as MMA, acrylamides and especially renewable  $\alpha$ -methylene- $\gamma$ -butyrolactones MBL and  $\gamma$ -MMBL, into high MW polymers with relatively narrow MWDs. Investigations into the scope of LAs show that although some common LAs can also be utilized for LPP, Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-based LPs are far more active and effective than other LA-based LPs. On the other hand, the scope of LBs is not limited, and several types of LBs can also be utilized for establishing highly active and effective LPP systems employing Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Such highly effective LBs include (listed here only MMA polymerization data for comparison): achiral phosphine P<sup>t</sup>Bu<sub>3</sub> (TOF =  $1.2 \times 10^4$  h<sup>-1</sup>,  $M_n = 3.97 \times 10^5$  g mol<sup>-1</sup>, PDI = 1.52), chiral ethylene-bridged diphosphine CP-3 (TOF =  $4.8 \times 10^4$  h<sup>-1</sup>,  $M_n = 2.74 \times 10^5$  g mol<sup>-1</sup>, PDI = 1.40), NHC bases IMes (TOF =  $4.8 \times 10^4$  h<sup>-1</sup>,  $M_n = 2.66 \times 10^4$  g mol<sup>-1</sup>, PDI = 1.77), I<sup>t</sup>Bu (TOF =  $3.2 \times 10^3$  h<sup>-1</sup>,  $M_n = 5.25 \times 10^5$  g mol<sup>-1</sup>, PDI = 1.43), and TPT, as well as the superbases P<sub>4</sub>-<sup>t</sup>Bu, which is most active (TOF =  $9.6 \times 10^4$  h<sup>-1</sup>,  $M_n = 2.12 \times 10^5$  g mol<sup>-1</sup>, PDI = 1.34). These LPs are also highly active and effective for polymerization of  $\gamma$ -MMBL, observing the similar effect of the NHC base structure on the resulting polymer MW (*e.g.*, the MW of the polymer by I<sup>t</sup>Bu is much higher than that by IMes). In terms of stereoselectivity of these LPP systems, the polymers produced at RT are typically atactic (PMMBL with ~47% *mr*) or syndio-rich (PMMA with ~70–75% *rr*). The use of chiral chelating phosphine bases did not noticeably affect the stereoselectivity. However, highly syndiotactic PMMA with 91% *rr* can be produced by chiral or achiral LPs at -78 °C.

Mechanistic studies have identified and structurally characterized zwitterionic phosphonium and imidazolium enolaluminate species, formed by the reaction of the monomer-Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct with P<sup>t</sup>Bu<sub>3</sub> and NHCs, respectively. Such zwitterions were proposed to be the active species for the polymerization because they rapidly polymerize the subsequently added monomer. Kinetic studies have revealed that the MMA polymerization by the most representative LP of the current systems, <sup>t</sup>Bu<sub>3</sub>P/Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is zero-order in monomer concentration after an initial induction period and the polymerization is significantly catalyzed by the LA, conforming to a bimolecular, activated monomer propagation mechanism.

Computational work has examined the energetics of the zwitterionic active species formation as well as chain initiation and propagation fundamental steps involved in LPP. Consistent with experimental results, formation of the zwitterion is favored with all the LBs considered, with the exception of PMes<sub>3</sub>, due to the bulkiness of the mesityl groups. Analysis of the chain initiation step indicated that the bimetallic mechanism, with addition of a LA-activated MMA molecule to the zwitterion, is clearly favored over the monometallic mechanism involving addition of a non-activated MMA. Analysis of a model of the MMA



propagation step confirmed the preference for the bimetallic mechanism, with an overall reduction of the addition energy barrier, which is a consequence of the reduced steric stress induced by the more spatially separated LA and LB centers. The main difference between the NHC and the PR<sub>3</sub> based LPP systems is in the relative stability of the zwitterion, while the behavior in MMA addition is remarkably similar.

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