DOI: 10.1002/ange.201005534

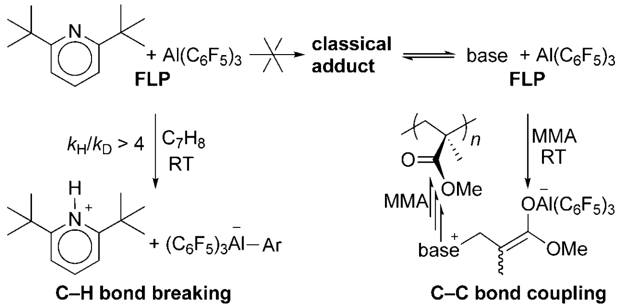
VIP **Polymer Synthesis**

Alane-Based Classical and Frustrated Lewis Pairs in Polymer Synthesis: Rapid Polymerization of MMA and Naturally Renewable Methylene Butyrolactones into High-Molecular-Weight Polymers**

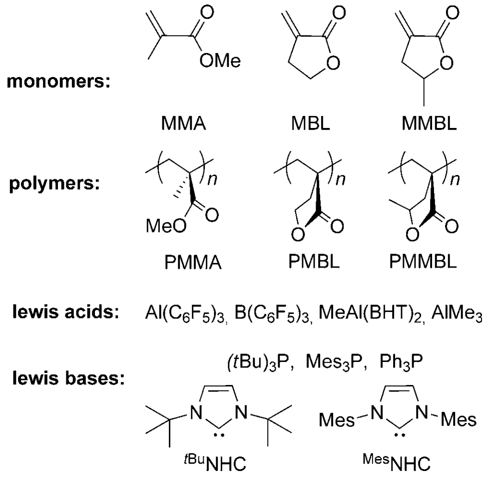
*Yuetao Zhang, Garret M. Miyake, and Eugene Y.-X. Chen**

The seminal works[1] by the research groups of Stephan and Erker uncovered the concept of "frustrated lewis pairs" (FLPs) to describe pairs formed by a sterically encumbered borane Lewis acid (most commonly $B(C_6F_5)_3$) and a base (e.g. $(tBu)_3P$), in which these two components are sterically precluded from forming classical donor/acceptor adducts Instead, the unquenched, opposite reactivity of FLPs can carry out unusual reactions or reactions that were previously known to be possible only by transition-metal complexes, such as activation of H_2, CO_2, N_2O, B–H bonds, alkenes and alkynes, as well as catalytic hydrogenation.[2] The direct use of FLPs in polymer synthesis and/or in polymerization catalysis is currently still missing from this list.[3]

Our research group reported in 2002[4] that strongly acidic, sterically encumbered alane $Al(C_6F_5)_3$[5] and bulky 2,6-di-*tert*-butyl pyridine, which do not form a classical acid/base adduct when the unsolvated alane is used, work cooperatively to activate and break arene C–H bonds when the toluene/alane adduct, $C_7H_8{\cdot}Al(C_6F_5)_3$,[6] is used, or when toluene is added to the above-mentioned mixture (Scheme 1). Preceding the current term FLP,[2] this result was an early example of the unusual reactivity of FLPs relative to what was generally recognized. Since then, our interest has continued to focus on utilizing the high Lewis acidity of $Al(C_6F_5)_3$ and, more importantly in many cases, the unique catalytic feature of the active species derived from this alane, for the polymerization of functionalized alkenes.[7] Reported herein is a significant development in this continuing effort: $Al(C_6F_5)_3$-based Lewis pairs rapidly polymerize polar vinyl monomers at room temperature (Scheme 2), including methyl methacrylate (MMA) and the naturally renewable methylene butyrolactones α-methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (MMBL),[8] to form high-molecular-weight (high MW) polymers. The bases examined herein include phosphines ($(tBu)_3P$, Mes_3P (Mes = 2,4,6-$Me_3C_6H_2$), and Ph_3P) as well as N-heterocyclic carbenes (NHCs; 1,3-di-*tert*-butylimidazolin-2-ylidene (^{tBu}NHC) and 1,3-di-mesityl-butylimidazolin-2-ylidene (^{Mes}NHC)). This polymerization is proposed to proceed via zwitterionic phosphonium or imidazolium enolaluminate active propagating species (Scheme 1). Intriguingly, although the borane congener can also form analogous zwitterionic species, they are inactive for such polymerization reactions.



Scheme 1. C–H bond breaking by an alane-based FLP reported earlier[4] and C–C bond coupling by alane-based classical and frustrated Lewis pairs described in this work.



Scheme 2. Chemical structures of monomers, polymers, Lewis acids, and Lewis bases investigated in this study.

Several features of the present acid/base polymerization system are noteworthy. First, control runs using $Al(C_6F_5)_3$, $(tBu)_3P$, Mes_3P, Ph_3P, ^{tBu}NHC, and ^{Mes}NHC for polymerization of MMA (200–800 equiv) at room temperature in toluene yielded no polymer formation for up to 24 hours. Second,

---

[*] Dr. Y. Zhang, G. M. Miyake, Prof. Dr. E. Y.-X. Chen
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523-1872 (USA)
Fax: (+1) 970-491-1801
E-mail: Eugene.Chen@colostate.edu

[**] This work was supported by the National Science Foundation.
MMA = methyl methacrylate

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201005534.

Table 1: Selected results of polymerization by base/Al(C_6F_5)$_3$ pairs.[a]

Run	Monomer	Solvent	Acid (adduct)	Base (1 equiv)	[acid]/[base]	*t* [min]	Conv. [%] (Yield [%])[c]	TOF [h^{-1}]	M_n×10^4 [g mol^{-1}]	MWD (M_w/M_n)	*rr* [%]	*mr* [%]	*mm* [%]
1	MMA	toluene	Al·MMA	(tBu)$_3$P	1:1	60	100	800	28.3	1.42	75.5	23.1	1.4
2	MMA	toluene	Al·MMA	(tBu)$_3$P	2:1	4	100	12000	39.7	1.52	73.5	25.0	1.5
3	MMA	toluene	Al·MMA	(tBu)$_3$P	2:1	7	100	6840	31.5	1.72	73.6	24.7	1.7
4	MMA	CH_2Cl_2	Al·TOL	(tBu)$_3$P	1:1	60	100	800	38.0	1.41	75.8	22.6	1.6
5	MMA	CH_2Cl_2	Al·MMA	(tBu)$_3$P	2:1	4	100	12000	36.9	1.47	75.0	23.0	2.0
6	MMA	toluene	Al·MMA	Mes_3P	2:1	1440	0	0	–	–	–	–	–
7	MMA	CH_2Cl_2	Al·MMA	Mes_3P	2:1	1440	0	0	–	–	–	–	–
8	MMA	toluene	Al·MMA	Ph_3P	2:1	1	100	48000	38.8; 13.3	1.04; 1.05	73.0	25.4	1.6
9	MMA	toluene	Al·MMA	^{Mes}NHC	2:1	1	100	48000	2.66	1.77	72.7	25.7	1.6
10	MMA	toluene	Al·MMA	^{tBu}NHC	2:1	15	100	3200	52.5	1.43	75.1	23.3	1.6
11	MMA	CH_2Cl_2	Al·MMA	^{tBu}NHC	2:1	15	100	3200	60.0	1.34	74.3	24.3	1.6
12	MBL	CH_2Cl_2	Al·TOL	(tBu)$_3$P	2:1	60	(90.5)	7660	4.48	2.18	n.d.	n.d.	n.d.
13	MBL	CH_2Cl_2	Al·TOL	^{tBu}NHC	2:1	60	(85.5)	704	16.3[b]	1.28	n.d.	n.d.	n.d.
14	MBL	CH_2Cl_2	Al·TOL	Ph_3P	2:1	60	(32.7)	262	20.3; 1.53	2.99; 1.33	n.d.	n.d.	n.d.
15	MMBL	CH_2Cl_2	Al·TOL	(tBu)$_3$P	2:1	10	100	4800	19.2	2.28	29.4	47.0	23.6
16	MMBL	CH_2Cl_2	Al·TOL	^{tBu}NHC	2:1	1	100	48000	13.9	1.15	33.8	46.9	19.3
17	MMBL	CH_2Cl_2	Al·TOL	^{Mes}NHC	2:1	1	100	48000	6.28	1.42	n.d.	n.d.	n.d.
18	MMBL	CH_2Cl_2	Al·TOL	Ph_3P	2:1	1	100	48000	13.9; 5.01	1.03; 1.04	n.d.	n.d.	n.d.

[a] Reaction conditions: 800 equivalents of monomer relative to base; 10 mL total solution volume (solvent toluene (TOL)) or dichloromethane + monomer); room temperature (ca. 25 °C). [b] The GPC trace shows a small (ca. 4%) low MW tail peak. [c] Conversions and yields of the isolated polymer determined by using gravimetric methods. n.d. = not determined, conv. = % monomer conversions measured by ^{1}H NMR spectroscopy, *rr*, *mr*, *mm* = polymer methyl triads measured by ^{1}H (PMMA) or ^{13}C NMR (PMMBL) spectroscopy, M_n determined by GPC relative to PMMA standards.

premixing the alane (as a toluene adduct) with the base (tBu)$_3$P at room temperature for 10 minutes in either a 1:1 or 2:1 [Al]/[base] ratio, followed by addition of MMA (800 equiv), also caused no monomer consumption for up to 24 hours. Likewise, premixing the unsolvated Al(C_6F_5)$_3$ with (tBu)$_3$P in benzene for 10 minutes, followed by addition of MMA (800 equiv), resulted in minimum monomer conversion of 3.8 % after 26.5 hours. Excitingly, when the preformed alane/monomer adduct, MMA·Al(C_6F_5)$_3$,[9] was pretreated with the phosphine base in toluene at room temperature for ten minutes (which cleanly generates the zwitterionic phosphonium enolaluminate active propagating species, see below), followed by addition of MMA (800 equiv), rapid polymerization was observed, which consumed all monomer in 60 minutes and yielded high MW polymer ($M_n = 2.83 \times 10^5$ Da, MW distribution (MWD) = $M_w/M_n = 1.42$; Table 1, run 1). The resulting PMMA has a syndiotacticity of 75.5 % *rr*. The same polymerization was much more rapid with a [Al]/[base] ratio of 2:1, and converted all monomer into high MW polymer ($M_n = 3.97 \times 10^5$ Da, MWD = 1.52, *rr* = 73.5 %; run 2) in 4 minutes, thus giving a high turnover frequency (TOF) of 1.2×10^4 h^{-1}. Third, a more convenient procedure, which consists of simply premixing C_7H_8·Al(C_6F_5)$_3$ with MMA in toluene (i.e. generating MMA·Al(C_6F_5)$_3$ in situ), followed by addition of the base to start the polymerization, also led to a highly active polymerization system, thus achieving quantitative monomer conversion in seven minutes and yielding high MW polymer ($M_n = 3.15 \times 10^5$ Da, MWD = 1.72, *rr* = 73.6 %; run 3). Fourth, changing solvent polarity from relatively nonpolar toluene ($\varepsilon = 2.38$) to more polar dichloromethane (CH_2Cl_2, $\varepsilon = 8.93$)[10] did not noticeably affect the polymerization activity, although there were some variation in polymer MW (run 4 versus 1, run 5 versus 2; in runs 4 and 5, MMA·Al(C_6F_5)$_3$ was premixed with monomer, followed by addition of the base to begin the polymerization[11]). Fifth, replacing Al(C_6F_5)$_3$ with $AlMe_3$, MeAl(2,6-tBu$_2$-4-Me-C_6H_2O)$_2$, or B(C_6F_5)$_3$ for the same polymerizations yielded no polymer formation for up to 24 hours.[12]

Having achieved high polymerization activity of the (tBu)$_3$P/Al(C_6F_5)$_3$ pair with appropriate procedures, we were interested in examining the effectiveness of other sterically encumbered bases known to form FLPs with B(C_6F_5)$_3$. Intriguingly, the Mes_3P/Al(C_6F_5)$_3$ pair is completely ineffective for the polymerization of MMA in toluene or dichloromethane, for up to 24 hours (runs 6 and 7). On the other hand, the Ph_3P/Al(C_6F_5)$_3$ pair exhibits exceptional activity (TOF = 4.8×10^4 h^{-1}; run 8), despite the fact that Ph_3P forms a classic acid/base adduct.[11] However, the polymer produced by this pair has a bimodal MWD, which consists of approximately 41 % higher MW fraction ($M_n = 3.88 \times 10^5$ Da, MWD = 1.04) and approximately 59 % lower MW fraction ($M_n = 1.33 \times 10^5$ Da, MWD = 1.05), which is characteristic of the coexistence of two types of active species with rather similar catalytic activity. Interestingly, ^{Mes}NHC is extremely active for MMA polymerization, thereby consuming all 800 equivalents of MMA in less than one minute and giving a high TOF value of greater then 4.8×10^4 h^{-1} (run 9).[13] In comparison, the polymerization activity of ^{tBu}NHC is approximately 15 times lower, but the polymer MW is approximately 20 times higher ($M_n = 5.25 \times 10^5$ Da, MWD = 1.43; run 10) than that produced by ^{Mes}NHC ($M_n = 2.66 \times 10^4$ Da, MWD =

1.77; run 9). The polymerization carried out in dichloromethane performed similarly to that done in toluene (run 11 versus 10).

Next, we investigated the effectiveness of these acid/base pairs for the polymerization of renewable monomers MBL and MMBL, which are cyclic analogues of MMA. α-Methylene-γ-butyrolactone (MBL), or tulipalin A, which is a natural substance found in tulips, and the MBL ring is an integral building block of many natural products.[14] The γ-methyl derivative, MMBL, is readily prepared by a two-step process from the cellulosic biomass-derived levulinic acid.[15] Despite being a heterogeneous process (because of the insolubility of the resulting polymer), the polymerization of MBL by $(t\mathrm{Bu})_3\mathrm{P}/\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$ in dichloromethane achieved greater than 90 % polymer yield in 1 hour (run 12). The PMBL produced has a medium M_n value of 4.48×10^4 Da and a relatively broad MWD of 2.18. Likewise, the $^{t\mathrm{Bu}}\mathrm{NHC}/\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$ pair is also quite effective for MBL polymerization, but the MW of the resulting PMBL is approximately four times higher (run 13 versus 12). Again, the use of $\mathrm{Ph}_3\mathrm{P}$ as the base brought about the formation of bimodal polymer products (ca. 32 % high MW fraction and ca. 68 % low MW fraction; run 14). Thanks to the good solubility of PMMBL in dichloromethane, the polymerization of MMBL by these acid/base pairs is homogeneous and highly effective. Specifically, the polymerization by $(t\mathrm{Bu})_3\mathrm{P}/\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$ achieved quantitative monomer conversion in ten minutes, thus giving a high MW polymer, essentially an atactic polymer ($M_n = 1.92 \times 10^5$ Da, MWD = 2.28, $mr = 47.0\,\%$; run 15). Both NHC bases are highly active for MMBL polymerization, with a high TOF value of $4.8 \times 10^4\ \mathrm{h}^{-1}$ (runs 16 and 17), but the M_n of 1.39×10^5 Da of the PMMBL produced by $^{t\mathrm{Bu}}$NHC is about twice that produced by $^{\mathrm{Mes}}$NHC, and the polymer also exhibits a much more narrow MWD (1.15 for run 16, see Figure 1 for GPC trace, versus 1.42 for run 17). The bimodal behavior of $\mathrm{Ph}_3\mathrm{P}$ is once again manifested in the MMBL polymerization (ca. 43 % high MW fraction and ca. 57 % low MW fraction; run 18, see Figure 1 for GPC trace)

To understand the above-described intriguing polymerization behavior observed for the base/alane pairs, which is a function of not only the form of the alane and the structure of the base, but also of the addition sequence of acid, base, and monomer, we examined a series of relevant reactions between the alane (in different forms) and five different bases employed in this study.

First, $(t\mathrm{Bu})_3\mathrm{P}$ and $\mathrm{C}_7\mathrm{H}_8{\cdot}\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$ react rapidly at room temperature in $\mathrm{C}_7\mathrm{D}_8$ to form at least five different products according to NMR spectroscopy. One product can be identified as the anticipated adduct $(t\mathrm{Bu})_3\mathrm{P}/\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$ (**1**), but only as a minor species in the product mixture. This rapid consumption (decomposition) of the acid and the base upon direct mixing as well as the formation of multiple undetermined products (presumably a result of several types of reactions occurring concurrently, such as C–H activation, nucleophilic attack of the aryl ring, etc.) explain why this acid/base pair, when premixed before addition of MMA, is inactive for the polymerization (see above). When the reaction was started at −75 °C, adduct **1** (a sharp signal at $\delta = 42.6$ ppm in the ^{31}P NMR spectrum) was formed as the major product (> 90 %), but upon warming many other products began to emerge. To avoid the complications brought about by toluene being coordinated to the alane, we also examined the reaction of the unsolvated $\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$ with $(t\mathrm{Bu})_3\mathrm{P}$ in $\mathrm{C}_6\mathrm{D}_6$ at room temperature, thus revealing the formation of the adduct (77 %), plus two other minor species.[11] This observation indicates that several products derived from the reaction using $\mathrm{C}_7\mathrm{H}_8{\cdot}\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$ must be related to toluene being coordinated to the alane. The broad signal appearing at $\delta = 48.7$ ppm in the ^{31}P NMR spectrum (and relevant signals in the ^{1}H NMR spectrum) for the adduct suggests an equilibrium established between the free acid/base FLP and the acid/base adduct.[16] Most significantly, the reaction of $(t\mathrm{Bu})_3\mathrm{P}$ with $\mathrm{MMA}{\cdot}\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$ at room temperature in $\mathrm{C}_6\mathrm{D}_6$ (or $\mathrm{CD}_2\mathrm{Cl}_2$) cleanly generates zwitterionic phosphonium enolaluminate $(t\mathrm{Bu})_3\mathrm{PCH}_2\mathrm{C}(\mathrm{Me}){=}\mathrm{C}(\mathrm{OMe})\mathrm{OAl}(\mathrm{C}_6\mathrm{F}_5)_3$ (**2**) as two isomers (*Z*/*E*) in a 7:3 ratio.[11,17] This addition pattern is similar to the 1,4-addition of FLPs to 1,3-dienes[18] and the 1,2-addition of FLPs to terminal alkynes.[19] Zwitterion **2** can be readily characterized by NMR spectroscopy (here using the major isomer as an illustration) for the phosphonium cation $(t\mathrm{Bu})_3\mathrm{P}^{+}$[18] [$\delta = 49.0$ ppm (s) in the ^{31}P NMR spectrum; $\delta = 1.52$ ppm (d, *tBu*) in the ^{1}H NMR spectrum)], for the enolaluminate anion $\mathrm{OAl}(\mathrm{C}_6\mathrm{F}_5)_3^{-}$[20] [$\delta = -123.4$ (m, 6F, *o*-F), −157.8 (t, 3F, *p*-F), −164.4 (m, 6F, *m*-F) in the ^{19}F NMR spectrum], and for the remaining ester enolate moiety $\mathrm{CH}_2\mathrm{C}(\mathrm{Me}){=}\mathrm{C}(\mathrm{OMe})\mathrm{O}$ [$\delta = 3.50$ (s, 3H, O*Me*), 3.19 (d, 2H, P*CH*$_2$), 1.63 ppm (s, 3H, =C*Me*) in the ^{1}H NMR spectrum], Figure 2. Phosphonium enolaluminate **2** is stable in solution at room temperature for up to 2 hours. Addition of an excess of MMA to this solution, with or without an additional equivalent of $\mathrm{Al}(\mathrm{C}_6\mathrm{F}_5)_3$, led to rapid polymerization, therefore confirming zwitterion **2** is the active species responsible for the rapid polymerization observed in the above polymerization procedure. Interestingly, although $(t\mathrm{Bu})_3\mathrm{P}$ reacts with $\mathrm{MMA}{\cdot}\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3$ to form analogous zwitterionic phosphonium enolborate $(t\mathrm{Bu})_3\mathrm{PCH}_2\mathrm{C}(\mathrm{Me}){=}\mathrm{C}(\mathrm{OMe})\mathrm{OB}(\mathrm{C}_6\mathrm{F}_5)_3$ (**3**),[11] it is inactive towards polymerization of MMA, with or without an additional equivalent of the borane. This observation is reminiscent of our previous

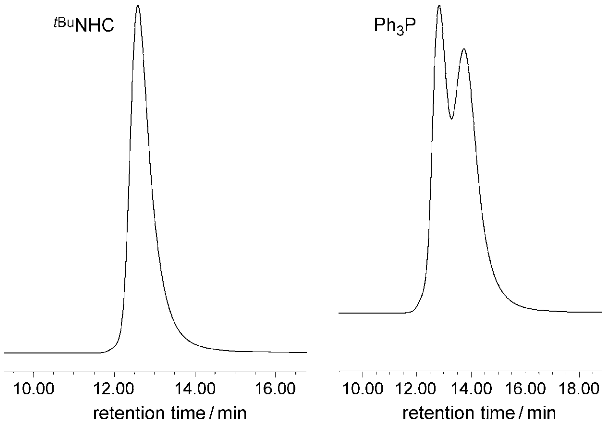


Figure 1. Gel permeation chromatography (GPC) traces of PMMBL produced by $^{t\mathrm{Bu}}$NHC (left trace, run 16) and by $(t\mathrm{Bu})_3\mathrm{P}$ (right trace, run 18).

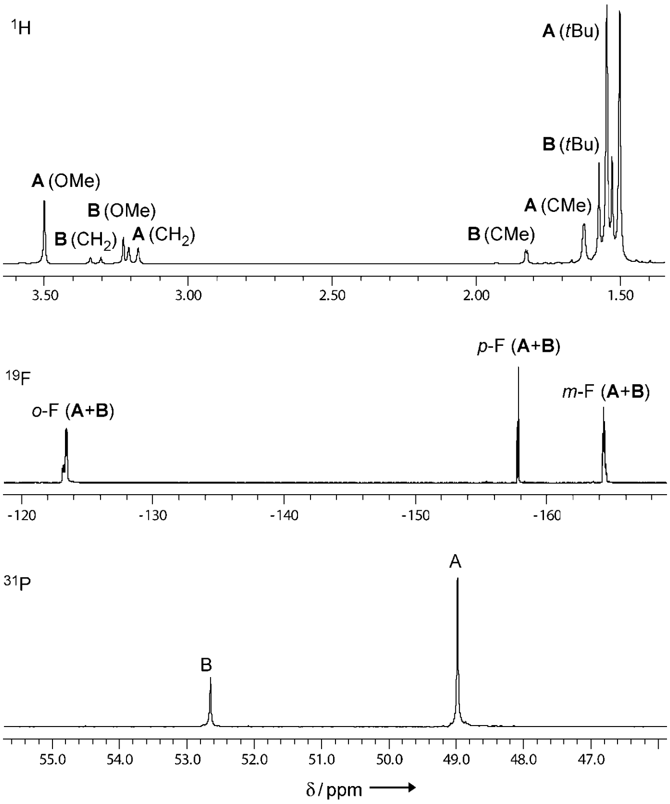


Figure 2. ^{1}H, ^{19}F, and ^{31}P NMR spectra (CD_2Cl_2, 23 °C) of $(tBu)_3PCH_2C(Me){=}C(OMe)OAl(C_6F_5)_3$ (**2**) as two isomers: major isomer **A** and minor isomer **B**.

findings regarding the high activity of enolaluminate versus the inactivity of enolborate species towards conjugate-addition polymerization.[9,20] This difference in reactivity can be attributed to the inability of the enolborate/borane pair to effect the bimolecular, activated-monomer anionic polymerization as does the enolaluminate/alane pair.[20]

Second, Mes_3P and $C_7H_8{\cdot}Al(C_6F_5)_3$ do not react in C_7D_8 at −75 °C and thus can be characterized as a FLP at this temperature. Upon warming to −40 °C, the identifiable major product was the adduct $Mes_3P{\cdot}Al(C_6F_5)_3$ (**4**), plus several other undetermined minor species. This reaction was also examined using the unsolvated $Al(C_6F_5)_3$, which led to formation of the weak adduct **4**[21] as the minor species (17 %),[11] and predominantly the unreacted phosphine and alane, which were readily identifiable by ^{31}P and ^{19}F NMR spectroscopy. Nevertheless, a key insight for the observed nonpolymerization activity of the $Mes_3P/Al(C_6F_5)_3$ pair is that there is no reaction between Mes_3P and $MMA{\cdot}Al(C_6F_5)_3$ at room temperature. Now it is clear that the lower nucleophilicity of Mes_3P, relative to $(tBu)_3P$, is responsible for its inability to attack the monomer activated by the alane, thus giving rise to no formation of the zwitterionic active species.

Third, Ph_3P and $C_7H_8{\cdot}Al(C_6F_5)_3$ cleanly formed adduct $Ph_3P{\cdot}Al(C_6F_5)_3$ (**5**),[11] but this classical adduct formation did not quench its reactivity as the $Ph_3P/Al(C_6F_5)_3$ pair was still highly active for MMA polymerization (see above). Obviously, in the presence of the MMA monomer, the alane forms a more stable adduct with MMA as a consequence of its high oxophilicity. Thus, examining the active species formation through the reaction of Ph_3P and $MMA{\cdot}Al(C_6F_5)_3$ revealed that the reaction never went to completion and the formed zwitterionic species, $Ph_3PCH_2C(Me){=}C(OMe)OAl(C_6F_5)_3$ (**6**) (two isomers in a 1:1 ratio), started to decompose at room temperature in less than 1 hour—such behavior presumably contributed to the above observed bimodal polymerization behavior.

Fourth, both NHC bases, ^{tBu}NHC and ^{Mes}NHC, react with $C_7H_8{\cdot}Al(C_6F_5)_3$ at room temperature in benzene to form clean, stable adducts $^{tBu}NHC{\cdot}Al(C_6F_5)_3$ (**7**) and $^{Mes}NHC{\cdot}Al(C_6F_5)_3$ (**8**), respectively.[11] In contrast, there is no reaction between ^{tBu}NHC and $B(C_6F_5)_3$ at −65 °C in toluene (i.e. forming a FLP),[22] but at room temperature the same reaction yields a zwitterionic product with $B(C_6F_5)_3$ being attached to the 4-position of the imidazole heterocycle.[23] The molecular structure of adduct **8** has been characterized by X-ray diffraction analysis (Figure 3).[24] Again, as both $^{tBu}NHC/Al(C_6F_5)_3$ and $^{Mes}NHC/Al(C_6F_5)_3$ pairs are highly active for MMA polymerization (see above), their stable classical adduct formation did not quench each other's reactivity towards this monomer. Indeed, the reaction of ^{tBu}NHC and ^{Mes}NHC with $MMA{\cdot}Al(C_6F_5)_3$ readily generates the corresponding zwitterionic imidazolium enolaluminate active species, $^{tBu}NHC\text{-}CH_2C(Me){=}C(OMe)OAl(C_6F_5)_3$ (**9**) and $^{Mes}NHC\text{-}CH_2C(Me){=}C(OMe)OAl(C_6F_5)_3$ (**10**), respectively, which is consistent with the polymerization results already discussed.

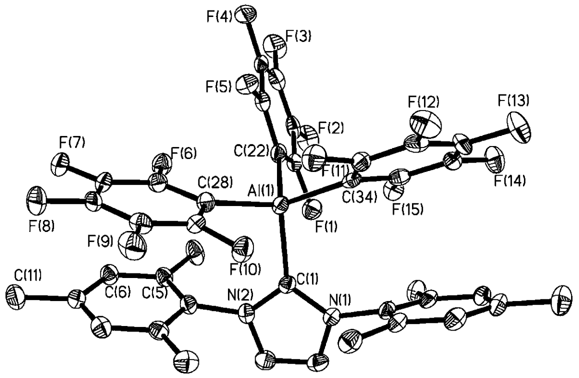


Figure 3. X-ray crystal structure of $^{Mes}NHC{\cdot}Al(C_6F_5)_3$ (**8**). Hydrogen atoms have been omitted for clarity, ellipsoids are drawn at 50 % probability. Selected bond lengths [Å] and angles [°]: Al–C1 2.060(4), Al–C22 2.017(4), Al–C28 2.019(4), Al–C34 2.014(4); C1-Al-C22 112.03(16), C1-Al-C28 104.70(15), C1-Al-C34 110.47(15), C22-Al-C28 110.24(16), C22-Al-C34 101.62(15), C28-Al-C34 117.99(16).

In conclusion, select phosphine or NHC base/$Al(C_6F_5)_3$ pairs have been found to rapidly convert MMA and naturally renewable MBL and MMBL monomers into high MW polymers. The polymerization is proposed to proceed via zwitterionic phosphonium or imidazolium enolaluminate active species. Formation of FLPs is not a prerequisite for achieving high polymerization activity, as the base/$Al(C_6F_5)_3$ pairs that readily form stable classical adducts can still exhibit exceptional polymerization activity (e.g. Ph_3P, ^{tBu}NHC, and

${}^{\mathrm{Mes}}$NHC). However, one requirement that persists in all the systems investigated here is that the base must be nucleophilic enough to attack the monomer activated by the alane to effectively generate the zwitterionic active species. The addition sequence of acid, base, and monomer can also be critically important for achieving a highly active system, as a consequence of the potential side reactions caused by FLP reactivity of acid/base pairs in certain situations. The structure of the base can drastically impact the MW of the polymer; for example, the PMMA produced by ${}^{t\mathrm{Bu}}$NHC has a M_n of 5.25×10^5 Da, which is about 20 times higher than the PMMA produced by ${}^{\mathrm{Mes}}$NHC under otherwise identical conditions. It appears that this polymerization system can be readily extended to other monomers (e.g. acrylamides). Our studies on the monomer scope as well as on the polymerization kinetics and mechanism are underway.

Received: September 3, 2010
Published online: November 24, 2010

Keywords: alanes · frustrated Lewis pairs · N-heterocyclic carbenes · phosphines · polymerization

---

[1] a) J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 5056–5059; *Angew. Chem. Int. Ed.* **2007**, *46*, 4968–4971; b) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 8196–8199; *Angew. Chem. Int. Ed.* **2007**, *46*, 8050–8053; c) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881; d) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Frohlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, 5072–5074; e) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[2] D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76, and references therein.

[3] The use of bulky phosphine–boranes as activators and additives in titanium-catalyzed olefin polymerization has been reported: J. S. L. McCahill, G. C. Welch, D. W. Stephan, *Dalton Trans.* **2009**, 8555–8561.

[4] D. Chakraborty, E. Y.-X. Chen, *Macromolecules* **2002**, *35*, 13–15.

[5] a) S. Feng, G. R. Roof, E. Y.-X. Chen, *Organometallics* **2002**, *21*, 832–839; b) C. H. Lee, S. J. Lee, J. W. Park, K. H. Kim, B. Y. Lee, J. S. Oh, *J. Mol. Catal. A* **1998**, *132*, 231–239; c) P. Biagini, G. Lugli, L. Abis, P. Andreussi, US 5602269, **1997**.

[6] G. S. Hair, A. H. Cowley, R. A. Jones, B. G. McBurnett, A. Voigt, *J. Am. Chem. Soc.* **1999**, *121*, 4922–4923.

[7] a) E. Y.-X. Chen, *Chem. Rev.* **2009**, *109*, 5157–5214; b) E. Y.-X. Chen, *Dalton Trans.* **2009**, 8784–8793.

[8] a) G. M. Miyake, Y. Zhang, E. Y.-X. Chen, *Macromolecules* **2010**, *43*, 4902–4908; b) G. M. Miyake, S. E. Newton, W. R. Mariott, E. Y.-X. Chen, *Dalton Trans.* **2010**, *39*, 6710–6718; c) R. A. Cockburn, T. F. L. McKenna, R. A. Hutchinson, *Macromol. Chem. Phys.* **2010**, *211*, 501–509; d) J. Mosnáček, K. Matyjaszewski, *Macromolecules* **2008**, *41*, 5509–5511.

[9] A. D. Bolig, E. Y.-X. Chen, *J. Am. Chem. Soc.* **2001**, *123*, 7943–7944.

[10] Direct contact of CH_2Cl_2 with $Al(C_6F_5)_3$ must be avoided as it would result in decomposition leading to the formation of $[ClAl(C_6F_5)_2]_2$: D. Chakraborty, E. Y.-X. Chen, *Inorg. Chem. Commun.* **2002**, *5*, 698–701. However, alane/monomer adducts (isolated or generated in situ) are inert towards CH_2Cl_2.

[11] See the Supporting Information for details.

[12] Some activity (TOF value $< 2\,h^{-1}$) was observed for MMA polymerization by R_3P/Et_3Al at low temperatures (−78 °C or −93 °C): T. Kitayama, E. Masuda, M. Yamaguchi, T. Nishiura, K. Hatada, *Polym. J.* **1992**, *24*, 817–827.

[13] Group-transfer polymerization of MMA initiated by silyl ketene acetals and catalyzed by nucleophilic NHCs, ${}^{i\mathrm{Pr}}$NHC and ${}^{t\mathrm{Bu}}$NHC, was recently reported: a) J. Raynaud, Y. Gnanou, D. Taton, *Macromolecules* **2009**, *42*, 5996–6005; b) J. Raynaud, A. Ciolino, A. Baceiredo, M. Destarac, F. Bonnette, T. Kato, Y. Gnanou, D. Taton, *Angew. Chem.* **2008**, *120*, 5470–5473; *Angew. Chem. Int. Ed.* **2008**, *47*, 5390–5393; c) M. D. Scholten, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2008**, *41*, 7399–7404.

[14] H. M. R. Hoffmann, J. Rabe, *Angew. Chem.* **1985**, *97*, 96–112; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 94–110.

[15] a) L. E. Manzer, *ACS Symp. Ser.* **2006**, *921*, 40–51; b) L. E. Manzer, *Appl. Catal. A* **2004**, *272*, 249–256.

[16] S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476–3477.

[17] MMBL reacts with $(t\mathrm{Bu})_3P$ and $Al(C_6F_5)_3$ to generate the analogous zwitterionic phosphonium enolaluminate as a single isomer (^{31}P NMR spectrum: $\delta = 45.8$ ppm) as a result of the fixed *S-cis* conformation of this monomer.

[18] M. Ullrich, K. S.-H. Seto, A. J. Lough, D. W. Stephan, *Chem. Commun.* **2009**, 2335–2337.

[19] M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397.

[20] a) Y. Ning, H. Zhu, E. Y.-X. Chen, *J. Organomet. Chem.* **2007**, *692*, 4535–4544; b) A. Rodriguez-Delgado, E. Y.-X. Chen, *J. Am. Chem. Soc.* **2005**, *127*, 961–974.

[21] Formation of weak Lewis adducts between Mes_3P and AlX_3 (X = Cl, Br) was recently reported: G. Ménard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 1796–1797.

[22] D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem.* **2008**, *120*, 7538–7542; *Angew. Chem. Int. Ed.* **2008**, *47*, 7428–7432.

[23] P. A. Chase, D. W. Stephan, *Angew. Chem.* **2008**, *120*, 7543–7547; *Angew. Chem. Int. Ed.* **2008**, *47*, 7433–7437.

[24] CCDC 791461 (**8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.