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# Effect of ancillary (aminomethyl)phenolate ligand on efficacy of aluminum-catalyzed glucose dehydration to 5-hydroxymethylfurfural

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ABSTRACT

Air-stable dimethylaluminum complexes $L^RAlMe_2$ that contain (aminomethyl)phenolate ($L^R$) were prepared in high yield. NMR data and X-ray crystallographic characterization of the m structures of several of the complexes confirmed bidentate coordination of the (aminomethyl)ph ligand to aluminum. Efficient aluminum catalysts for glucose dehydration to HMF were gener modification of the (aminomethyl)phenolate ligand. $L^RAlMe_2$ complexes containing bidentate methyl)phenolate ligands with an aryl substituent on the amino moiety are efficient catalysts for dehydration to HMF in ionic liquid solvents. In [EMIM]Br and [BMIM]Br, the reaction proceeds a to very high conversion in 2 h to produce HMF with 60–63% selectivity and in 58–60% yield. Ev $L^RAlMe_2$ complexes catalyze glucose isomerization to fructose at ≥120 °C while the HMF yield on the degree of competing HMF loss to humins formation. These results indicate that additiona of ancillary ligand effects on aluminum-catalyzed glucose dehydration are needed to improve kn of structure–function relationships that are key to increasing the efficiency of aluminum cata dehydration of glucose (and ultimately cellulose) to HMF.

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## 1. Introduction

Glucose is the most abundant monosaccharide in cellulosic biomass hence efficient catalytic processes for its conversion into chemicals and biofuels are highly desirable [1–3]. Glucose dehydration is a promising method for synthesis of 5-hydroxymethylfurfural (HMF), an emerging bio-derived platform chemical that potentially could be used to produce a wide variety of high-value chemicals [4,5]. For example, HMF can be converted by selective oxidation into 2,5-furandicarboxylic acid (FDCA) which is attractive as a substitute for terephthalic acid in plastics production [6,7]. HMF can also undergo rehydration to produce levulinic acid (LA) which itself is a promising platform chemical that can be used as a feedstock for production of liquid hydrocarbon fuels [8,9].

give HMF in low yield and produce other byproducts, mod to-high yields of HMF have been reported in ionic liquids an boiling organic solvents with various Lewis acid metal salts as $CrCl_2$ [11–13], $SnCl_4$ [14,15], and $AlCl_3$ [10,16–18] as cat

Given the much lower toxicity and cheaper cost of Al in co ison to Cr and Sn, the development of efficient Al catalysts fo cose conversion to HMF is receiving increased attention [ 20]. For example, Abu-Omar and coworkers have reported tha exhibits high glucose conversion activity in water/THF bi medium to give HMF in 61% yield [16]. Dumesic and coworker found that catalytic conversion of glucose with the combina $AlCl_3$ and a Brønsted acid (such as HCl) in a biphasic water/alk nol solvent system gave 62% yield of HMF [10]. Rasrendra et a both $AlCl_3$ and $Al(OTf)_3$ in DMSO for glucose conversion to p

Investigations of glucose dehydration [5] using different catalysts (such as organic and inorganic acids, Lewis acids, salts, and zeolites) and solvents (including aqueous, organic, mixed aqueous/organic, and ionic liquids) have established that glucose conversion to HMF with Brønsted acids (such as HCl and $H_2SO_4$) typically proceeds via direct dehydration of glucose to HMF while with Lewis acid catalysts, the reaction typically proceeds via formation of fructose [6,10]. However, while mineral acids usually

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(aminomethyl)phenolate ligands as catalysts for the conversion of glucose to HMF in ionic liquids. We demonstrate that effective catalysts for glucose dehydration to HMF can be produced via modification of the (aminomethyl)phenolate ligand.

## 2. Experimental

### 2.1. General comments

All manipulations of air- and/or moisture-sensitive compounds were carried out under dry nitrogen atmosphere using standard Schlenk or glovebox techniques. All solvents were dried and distilled by standard methods [21] prior to use and stored in a glovebox over 4A molecular sieves that had been dried in a vacuum oven at 150 °C for at least 48 h. All other chemicals were used as received, unless otherwise stated. Toluene, THF, ethanol, petroleum ether, *n*-hexane, chloroform, methylene chloride, and methanol (all ACS grade) were purchased from Pharmco-Aaper. Ethyl acetate and acetonitrile were purchased from Fisher Scientific. 5-Hydroxymethylfurfural, (~99%), D-(−)-fructose, D-(+)-glucose (≥99.5%), $AlMe_3$ (2.0 M in hexane), 2-*tert*-butyl-4-methylphenol (99%), *N*-methylbenzylamino (97%), *N*-ethylbenzylamino (97%), *N*-isopropylbenzylamine (97%), *N*-phenylaniline (99%), 4-methylaniline (99.6%), 4-chloroaniline (98%), benzaldehyde (≥98%) and poly(methylhydrosiloxane) were purchased from Sigma–Aldrich. Paraformaldehyde (96%), 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl, 97%), and 1-ethyl-3-methylimidazolium bromide ([EMIM]Br, 97%) were purchased from Acros Organics. [EMIM]Cl and [EMIM]Br were purified before use, via recrystallization according to the literature method [22]. [BMIM]Br was synthesized and purified by following literature methods [22,23]. *N*-(*tert*-Butyl)benzylamino (99%) was purchased from Alfa Aesar. *N*-benzyl-4-chloroaniline [24], *N*-benzyl-*p*-toluidine [24], 2-[(*N*-benzyl-*N*-methyl)aminomethyl]-6-*tert*-butyl-4-methylphenol (**1a**) [25], 2-(*N*-benzyl-*N*-ethyl-aminomethyl)-4-methyl-6-*tert*-butyl-phenol (**1b**) [26], and $L^{Et}AlMe_2$ (**2b**, $L^{Et}$ = 2-(*N*-benzyl-*N*-ethyl-aminomethyl)-4-methyl-6-*tert*-butyl-phenolate) [26] were prepared by the literature methods or modification thereof.

$^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian VXR-400 spectrometer at room temperature. All chemical shifts are reported in units of $\delta$ (downfield from tetramethylsilane) and were referenced to residual solvent peaks. FTIR spectra were collected

HMF in 50% and 60% yield, respectively [19]. Liu and Chen s
that aluminum trialkyls (such as pyrophoric $AlMe_3$ and AlE
trialkoxides (such as $Al(OPr^i)_3$ and $Al(OBu^t)_3$) can give up
HMF yield from glucose conversion in [EMIM]Cl [20]. These s
indicate that aluminum species hold strong promise as Lew
catalysts for glucose conversion to HMF. However, the majo
studies used (10–30%) $AlCl_3$ in different solvents, and current
edge of ancillary ligand effects on the efficiency of glucose c
sion to HMF with aluminum Lewis acid catalysts is lacking. H
we report a systematic study of the efficacy of easily pre
air-stable dimethylaluminum complexes containing bid

29.97 mmol) were charged into a heavy-walled reaction ves
equipped with a magnetic stir bar. The vessel was capped tigh
then placed in an oil bath maintained at 105 °C, and heated w
stirring for 1 h. After cooling to room temperature, the light-yel
reaction mixture was dissolved in chloroform (50 mL). The solu
was washed with distilled water (5 × 15 mL) and dried over an
drous $Na_2SO_4$ for 12 h. After filtering off $Na_2SO_4$, the filtrate
evaporated under reduced pressure to give a pale-yellow oil, wh
was purified by silica gel column chromatography using 20:1
roleum ether:ethyl acetate as eluent. The solution was evapora
under reduced pressure to give **1c** as a colorless oil. The mate
was collected and dried under reduced pressure. Yield: 5.4
82.9%. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 11.15 (br s, 1H, O*H*), 7
7.15 (m, 5H, Ar*H*), 6.92 (d, $^4J$ = 2.0 Hz, 1H, Ar*H*), 6.64 (d, $^4J$ =
Hz, 1H, Ar*H*), 3.67 (s, 2H, Ar$CH_2$), 3.51 (s, 2H, Ph$CH_2$), 2.99 (s
1H, $^3J$ = 7.2 Hz, $CH(CH_3)_2$), 2.18 (s, 3H, Ar$CH_3$), 1.37 (s, 9H,
($CH_3$)$_3$), 1.06 (d, 6H, $^3J$ = 7.2 Hz, NCH($CH_3$)$_2$). $^{13}C\{H\}$ NMR (
MHz, $CDCl_3$): $\delta$ 154.7, 138.5, 136.4, 129.6, 128.7, 127.8, 12
127.1, 126.6, 122.4 (all Ar—*C*), 54.0 (Ar$CH_2$), 52.7 (Ph$CH_2$),
($CH(CH_3)_2$), 34.8 ($C(CH_3)_3$), 29.7 (ArC($CH_3$)$_3$), 21.0 (Ar$CH_3$),
(NCH($CH_3$)$_2$).

#### 2.2.2. Synthesis of 2-[(N-benzyl-N-tert-butyl)aminomethyl]-6-tert-butyl-4-methylphenol (**1d**)

This compound was prepared following a similar procedur
that described for **1c**, from 2-*tert*-Butyl-4-methylphenol (3.2
19.98 mmol), *N*-*tert*-butylbenzylamine (3.27 g, 20.04 mmol)
paraformaldehyde (0.60 g, 19.98 mmol). After purification of
reaction product, a light-yellow oil, by silica gel column ch
matography (using 20:1 petroleum ether:ethyl acetate as elue
removal of the organic volatiles under reduced pressure furnis
a light-yellow oil that was recrystallized from hexane at −20
giving **1d** as white crystals. The material was collected and d
under reduced pressure. Yield: 4.46 g, 65.7%. $^1H$ NMR (400 M
$CDCl_3$): $\delta$ 10.98 (s, 1H, O*H*), 7.23–7.06 (m, 5H, Ar*H*), 6.88 (d,
1.6 Hz, 1H, Ar*H*), 6.61 (d, $^4J$ = 1.6 Hz, 1H, Ar*H*), 3.84 (s, 2H, ArC
3.70 (s, 2H, Ph$CH_2$), 2.19 (s, 3H, Ar$CH_3$), 1.37 (s, 9H, NC(CH
1.21 (s, 9H, ArC($CH_3$)$_3$). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 15
140.9, 136.4, 128.9, 128.3, 127.2, 127.1, 126.8, 126.3, 124.0
Ar—*C*), 57.1 (NC($CH_3$)$_3$), 54.6 (Ar$CH_2$), 54.4 (Ph$CH_2$) 34.7
($CH_3$)$_3$), 29.7 (NC($CH_3$)$_3$), 27.2 (ArC($CH_3$)$_3$), 21.0 (Ar$CH_3$).

on a Thermo Scientific Nicolet 6700 ATR-FTIR spectrometer fitted with a ZnSe crystal with a Smart iTR accessory. The resolution of the instrument was set to 4 $cm^{-1}$. The background of the IR spectrum of air was first collected, and then powdered samples were placed on the ZnSe crystal, pressed against the crystal using the inbuilt high-pressure clamp and their absorbance was measured. A total of 40 s scans were used for both background and the samples. Raman spectra were collected on a DXR Raman microscope (Thermo Fisher) spectrometer. The source of radiation was a laser operated at 532 nm. The excitation laser beam was focused on the sample using a microscope equipped with a 10× lens. The laser power at the sample surface was about 2 mW and the acquisition time for each spectrum was 20 s and recorded in the range of 50–3500 $cm^{-1}$. X-ray diffraction data were collected at 90.0(2) K on either a Nonius kappaCCD, Bruker-Nonius X8 Proteum, or a D8 Venture diffractometer. Elemental analysis for C, H, and N was performed by Robertson Microlit Laboratories, Ledgewood, NJ.

### 2.2. Synthesis of the proligands

#### 2.2.3. Synthesis of 2-[(N-benzyl-N-phenyl)aminomethyl]-6-tert-bu 4-methylphenol (**1e**)

This compound was prepared following a similar procedur that described for **1c**, from 2-*tert*-butyl-4-methylphenol (3.2 19.98 mmol), paraformaldehyde (0.60 g, 19.98 mmol), and phenylbenzylamine (3.67 g, 20.04 mmol). After purification of reaction product, a light-yellow oil, by silica gel column c matography (using 5:1 hexane:ethyl acetate as eluent), rem of the organic volatiles under reduced pressure gave **1e** as w crystals. Yield: 4.53 g, 63.1%. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ (br s, 1H, O*H*), 7.28–7.16 (m, 5H, Ar*H*), 7.10–6.96 (m, 6H, A 6.71 (d, $^{4}J$ = 1.6 Hz, 1H, Ar*H*), 4.26 (s, 2H, ArC$H_2$), 4.22 (s, PhC$H_2$), 2.24 (s, 3H, ArC$H_3$), 1.41 (s, 9H, C(C$H_3$)$_3$). $^{13}$C{H} (100 MHz, $CDCl_3$): $\delta$ 154.2, 149.4, 136.8, 136.3, 129.4, 12 128.4, 128.0, 127.9, 127.6, 127.2, 123.7, 122.1, 122.0 (all Ar- 57.6 (ArCH$_2$), 57.0 (PhCH$_2$), 34.8 (*C*(CH$_3$)$_3$), 29.8 (C(CH$_3$)$_3$), (ArCH$_3$).

#### 2.2.4. Synthesis of 2-[(N-benzyl-N-p-toluidine)aminomethyl]-6-te butyl-4-methylphenol (**1f**)

ture was heated for 6 h. After purification by silica gel column chromatography using 5:1 hexane:ethyl acetate as eluent, **1f** was obtained as a white powder. Yield: 1.63 g, 50.4%. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.99 (s, 1H, O*H*), 7.22–7.18 (m, 3H, Ar*H*), 7.06–6.95 (m, 7H, Ar*H*), 6.72 (d, $^{4}J$ = 1.6 Hz, 1H, Ar*H*), 4.23 (s, 2H, ArC$H_2$), 4.17 (s, 2H, ArC$H_2$), 2.27 (s, 3H, NArC$H_3$), 2.25 (s, 3H, ArC$H_3$), 1.42 (s, 9H, C(C$H_3$)$_3$). $^{13}$C{H} NMR (100 MHz, $CDCl_3$): $\delta$ 154.4, 146.8, 136.7, 136.5, 133.6, 129.9, 129.6, 128.4, 127.9, 127.7, 127.5, 127.1, 122.5, 122.2 (all Ar—*C*), 58.1 (ArCH$_2$), 57.7 (PhCH$_2$), 34.8 (*C*(CH$_3$)$_3$), 29.8 (C(CH$_3$)$_3$), 21.1 (NArCH$_3$), 21.0 (ArCH$_3$).

#### 2.2.5. Synthesis of 2-[(N-benzyl-N-(p-chlorophenyl))aminomethyl]-6-tert-butyl-4-methylphenol (**1g**)

This compound was prepared following a similar procedure to that described for **1c**, from 2-*tert*-butyl-4-methylphenol (0.37 g, 2.25 mmol), paraformaldehyde (0.10 g, 3.38 mmol), and *N*-benzyl-4-chloroaniline [24] (0.49 g, 2.25 mmol), except the reaction mixture was heated for 50 h. After purification by silica gel column chromatography using 20:1 petroleum ether:ethyl acetate as eluent, **1g** was obtained as a white powder. Yield: 0.66 g, 73.9%. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.26 (s, 1H, O*H*), 7.23–7.17 (m, 5H, Ar*H*), 7.03–6.96 (m, 5H, Ar*H*), 6.70 (d, 1H, $^{4}J$ = 1.6 Hz, Ar*H*), 4.23 (s, 2H, ArC$H_2$), 4.22 (s, 2H, ArC$H_2$), 2.24 (s, 3H, ArC$H_3$), 1.40 (s, 9H, C(C$H_3$)$_3$). $^{13}$C{H} NMR (100 MHz, $CDCl_3$): $\delta$ 154.0, 147.9, 136.9, 136.0, 129.4, 129.3, 128.6, 128.1, 127.9, 127.8, 127.4, 123.2, 121.8 (all Ar—*C*), 57.8 (ArCH$_2$), 56.8 (ArCH$_2$), 34.8 (*C*(CH$_3$)$_3$), 29.8 (C(CH$_3$)$_3$), 21.1 (ArCH$_3$).

### 2.3. Synthesis of aluminum complexes

#### 2.3.1. Synthesis of $L^{Me}AlMe_2$ complex (**2a**)

$AlMe_3$ (4.50 mL, 8.97 mmol, 2.0 M in hexane) was added dropwise to a toluene (20 mL) solution of 2-[(*N*-benzyl-*N*-methyl)aminomethyl]-6-*t*-butyl-4-methylphenol [25] (**1a**, 2.67 g, 8.97 mmol) at room temperature. Evolution of methane was immediately observed. The reaction mixture was stirred for 24 h at room temperature. All of the volatiles were removed under reduced pressure to give a foam-like white solid, which was dissolved in *n*-hexane

#### 2.3.2. Synthesis of $L^{i\text{-}pr}AlMe_2$ complex (**2c**)

Complex **2c** was obtained as a white powder, by follow similar procedure to that described for **2a**, from reaction be $AlMe_3$ (1.40 mL, 2.87 mmol, 2.0 M in hexane) and **1c** ( 2.87 mmol). Yield: 0.92 g, 83.9%. $^{1}$H NMR (400 MHz, CD 7.37–7.21 (m, 5H, Ar*H*), 7.03 (d, $^{4}J$ = 2.0 Hz, 1H, Ar*H*), 6.68 ( 2.0 Hz, 1H, Ar*H*), 4.23 (d, $^{2}J$ = 14.0, 1H, ArC$H_2$), 4.16 (d, $^{2}J$ Hz, 1H, ArC$H_2$), 3.95 (d, $^{2}J$ = 14.0 Hz, 1H, ArC$H_2$), 3.59 (d, $^{2}J$ Hz, 1H, ArC$H_2$), 3.17 (sept., 1H, $^{3}J$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 2.27 ArCH$_3$), 1.38 (s, 9H, C(C$H_3$)$_3$), 1.36 (d, 3H, $^{3}J$ = 7.2 Hz, CH( 1.25 (d, 3H, $^{3}J$ = 6.8 Hz, CH(C$H_3$)$_2$), −0.64 (AlC$H_3$), −0.68 ( $^{13}$C{H} NMR (100 MHz, $CDCl_3$): $\delta$ 156.6, 139.0, 132.2, 129.0, 128.7, 128.6, 128.1, 125.3, 120.8 (all Ar—*C*), 55.4 (A 53.8 (ArCH$_2$), 52.2 (*C*H(CH$_3$)$_2$), 35.0 (*C*(CH$_3$)$_3$), 29.7 (C(*C*H$_3$) (ArCH$_3$), 19.4 (CH(*C*H$_3$)$_2$), 19.1 (CH(*C*H$_3$)$_2$), −7.1 (AlCH$_3$ (AlCH$_3$). *Anal.* Calc. for $C_{24}H_{36}AlNO$: C, 74.55; H, 9.51; N Found: C, 74.50; H, 9.48; N, 3.64%.

#### 2.3.3. Synthesis of $L^{t\text{-}Bu}AlMe_2$ complex (**2d**)

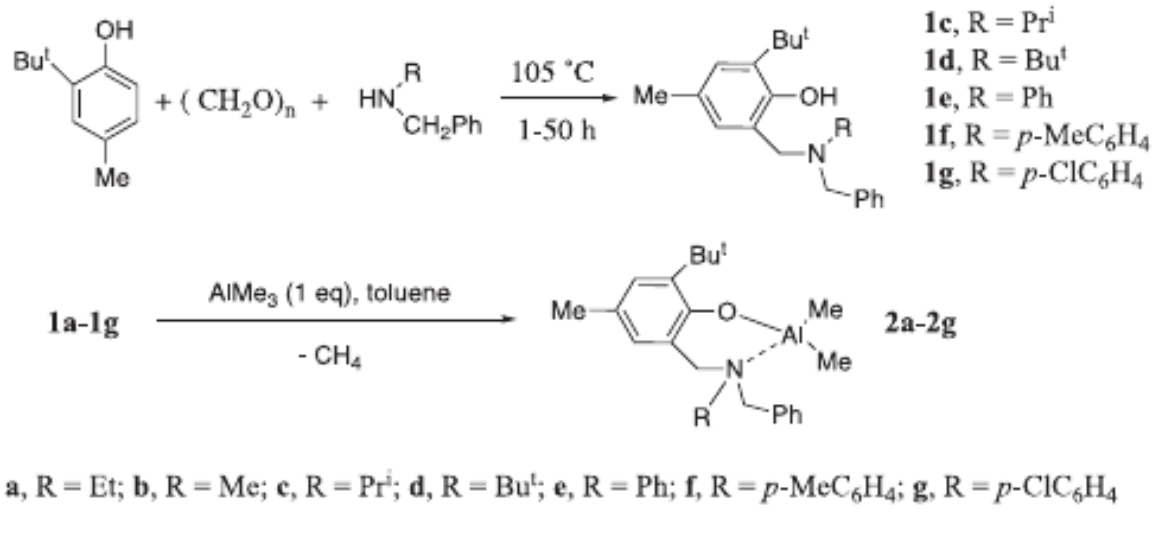
Complex **2d** was obtained as a light-yellow powder, by f ing a similar procedure to that described for **2a**, from re between $AlMe_3$ (1.0 mL, 2.00 mmol, 2.0 M in hexane) a (0.79 g, 2.00 mmol). Yield: 0.637 g, 80.5%. $^{1}$H NMR (40 $CDCl_3$): $\delta$ 7.37–7.31 (m, 2H, Ar*H*), 7.30–7.25 (m, 3H, Ar*H*), 7 $^{4}J$ = 2.0 Hz, 1H, Ar*H*), 6.72 (d, $^{4}J$ = 2.0 Hz, 1H, Ar*H*), 4.47 ( 14.8, 1H, ArC$H_2$), 4.36 (d, $^{2}J$ = 15.2 Hz, 1H, ArC$H_2$), 4.26 ( 15.2 Hz, 1H, ArC$H_2$), 4.11 (d, $^{2}J$ = 14.8 Hz, 1H, ArC$H_2$), 2.26 ArCH$_3$), 1.37 (s, 9H, NC(C$H_3$)$_3$), 1.26 (s, 9H, ArC(C$H_3$)$_3$),

and filtered to remove trace impurities. The filtrate was concentrated and kept at −20 °C overnight. Subsequently, **2a** was collected as a white precipitate and dried under reduced pressure. Yield: 2.32 g, 73.3%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44–7.37 (m, 3H, Ar*H*), 7.33–7.27 (m, 2H, Ar*H*), 7.04 (d, 1H, $^4J$ = 2.0 Hz, Ar*H*), 6.56 (d, $^4J$ = 2.0 Hz, 1H, Ar*H*), 3.97 (d, $^2J$ = 13.2 Hz, 1H, ArC$H_2$), (AlC$H_3$), −0.63 (AlC$H_3$). C{H} NMR (100 MHz, $CDCl_3$): $\delta$ 139.4, 135.1, 131.8, 128.8, 128.5, 128.1, 127.6, 125.4, 121 Ar—C), 62.4 (NC($CH_3$)$_3$), 52.6 (ArC$H_2$), 52.3 (PhC$H_2$) 3 ($CH_3$)$_3$), 29.6 (NC($CH_3$)$_3$), 28.2 (ArC($CH_3$)$_3$), 21.1 (ArC$H_3$ (AlC$H_3$), −7.3 (AlC$H_3$). *Anal.* Calc. for $C_{25}H_{38}$AlNO: C, 75. 9.68; N, 3.54. Found: C, 75.31; H, 9.97; N, 3.51%.

**Table 1**
Crystallographic Data for L$^R$AlMe$_2$ complexes **2a**–**c**, **2e**, and **2f**.

| Complex | **2a** | **2b** | **2c** | **2e** | **2f** |
|---|---|---|---|---|---|
| Formula | $C_{22}H_{32}$AlNO | $C_{23}H_{34}$AlNO | $C_{24}H_{36}$AlNO | $C_{27}H_{34}$AlNO | $C_{28}H_{36}$Al |
| Formula weight | 353.46 | 367.49 | 381.52 | 415.53 | 429.56 |
| *T* (K) | 90.0(2) | 90.0(2) | 90.0(2) | 90.0(2) | 90.0(2) |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic | monoclin |
| Space group | *P*2(1)/*n* | *P*2(1)/*n* | *P*2(1)/*n* | *P*2(1)/*c* | *P*2(1)/*c* |
| *Unit cell dimensions* | | | | | |
| *a* (Å) | 9.6557(2) | 11.1393(4) | 11.5303(4) | 12.0981(2) | 9.2418(3) |
| *b* (Å) | 12.6012(2) | 9.6143(3) | 18.1337(7) | 17.9578(4) | 21.7215( |
| *c* (Å) | 17.5369(3) | 20.1941(8) | 12.0678(5) | 12.0051(2) | 12.4113( |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 99.0269(8) | 91.854(3) | 117.291(2) | 116.0401(12) | 98.493(1) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 90 |
| *V* (Å$^3$) | 2107.35(7) | 2161.59(13) | 2242.36(15) | 2343.41(8) | 2464.19( |
| *Z* | 4 | 4 | 4 | 4 | 4 |
| $D_{Calc.}$ (g/cm$^3$) | 1.114 | 1.129 | 1.130 | 1.178 | 1.158 |
| Final *R* indices [$I > 2\sigma(I)$] | 0.0445, 0.1128 | 0.0548, 0.1458 | 0.0336, 0.0857 | 0.0430, 0.1053 | 0.0344, 0 |






**Scheme 1.** Synthesis of proligands **1c-g** and L$^R$AlMe$_2$ complexes **2a-g**.

*2.3.4. Synthesis of L$^{Ph}$AlMe$_2$ complex (**2e**)*

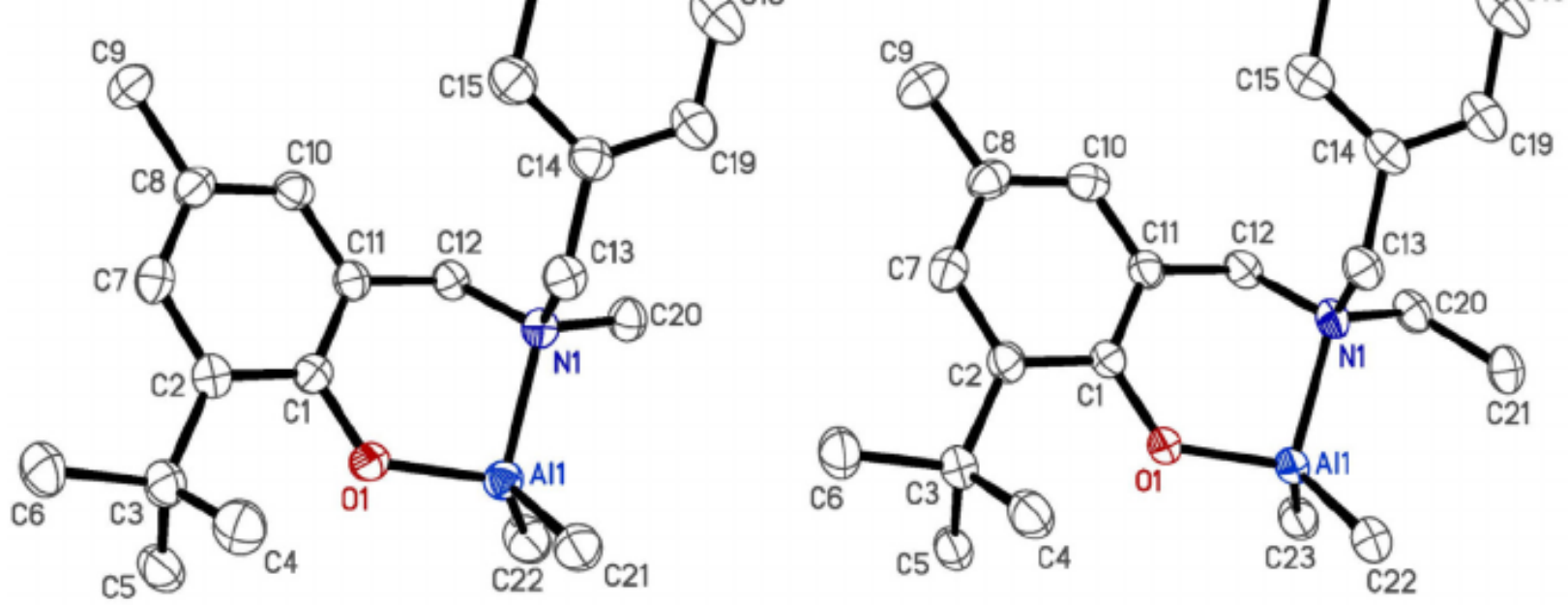
Complex **2e** was obtained as a white powder, by following a similar procedure to that described for **2a**, from reaction between $AlMe_3$ (1.74 mL, 3.48 mmol, 2.0 M in hexane) and **1e** (1.25 g, 3.48 mmol). Yield: 1.16 g, 79.9%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.48–7.36 (m, 4H, Ar*H*), 7.35–7.29 (m, 1H, Ar*H*), 7.25–7.19 (m, 1H, Ar*H*), 7.13–7.04 (m, 3H, Ar*H*), 6.59–6.52 (m, 3H, Ar*H*), 4.57 (d, $^2J$ = 14.0 Hz, 1H, ArC$H_2$), 4.43 (d, $^2J$ = 12.8 Hz, 1H, ArC$H_2$), 4.20 (d, $^2J$ = 14.0 Hz, 1H, ArC$H_2$), 3.81 (d, $^2J$ = 12.8 Hz, 1H, ArC$H_2$), 2.28 (s, 3H, ArC$H_3$), 1.44 (s, 9H, C(C$H_3$)$_3$), −0.43 (AlC$H_3$), −1.26 (AlC$H_3$). $^{13}$C{H} NMR (100 MHz, $CDCl_3$): $\delta$ 157.0, 145.8, 138.9, 131.5, 130.8, 129.9, 129.8, 129.0, 128.5, 128.0, 127.0, 125.0, 122.4, 119.5 (all Ar—*C*), 58.5 (ArC$H_2$), 53.3 (PhC$H_2$), 35.0 (*C*($CH_3$)$_3$), 29.7 (C(*C*$H_3$)$_3$), 21.0 (ArC$H_3$), −9.5 (AlC$H_3$), −10.4 (AlC$H_3$). *Anal.* Calc. for $C_{27}H_{34}$AlNO: C, 78.04; H, 8.23; N, 3.37. Found: C, 78.50; H, 8.71; N, 3.38%.

*2.3.5. Synthesis of L$^{p\text{-}Tol}$AlMe$_2$ complex (**2f**)*

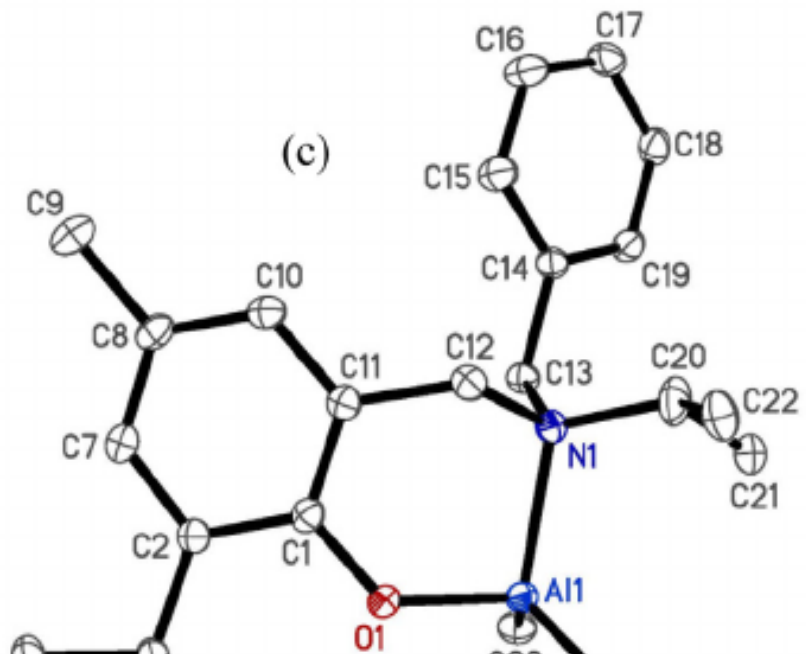
Complex **2f** was obtained as a white powder, by followin similar procedure to that described for **2a**, from reaction betw $AlMe_3$ (0.34 mL, 0.67 mmol, 2.0 M in hexane) and **1f** (0.24 g, 0 mmol). Yield: 0.21 g, 73.0%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7 7.18 (m, 5H, Ar*H*), 7.12–7.04 (m, 3H, Ar*H*), 6.58–6.52 (m, Ar*H*), 4.52 (d, $^2J$ = 14.4 Hz, 1H, ArC$H_2$), 4.39 (d, $^2J$ = 13.2 Hz, ArC$H_2$), 4.16 (d, $^2J$ = 14.4 Hz, 1H, ArC$H_2$), 3.76 (d, $^2J$ = 13.2 Hz, ArC$H_2$), 2.38 (s, 3H, NArC$H_3$), 2.27 (s, 3H, ArC$H_3$) 1.43 (s, 9 (C$H_3$)$_3$), −0.46 (AlC$H_3$), −1.26 (AlC$H_3$). $^{13}$C{H} NMR (100 M $CDCl_3$): $\delta$ 157.0, 143.1, 138.8, 136.7, 131.6, 130.8, 130.4, 12 128.9, 128.4, 127.9, 125.0, 122.2, 119.5, (all Ar—*C*), 58.4 (ArC 53.2 (PhC$H_2$), 35.0 (*C*($CH_3$)$_3$), 29.7 (C(*C*$H_3$)$_3$), 21.1 (NArC$H_3$), (ArC$H_3$), −9.5 (AlC$H_3$), −10.3 (AlC$H_3$). *Anal.* Calc. for $C_{28}H_{36}$A C, 78.29; H, 8.45; N, 3.26. Found: C, 77.82; H, 8.94; N, 3.17%.

*2.3.6. Synthesis of L$^{4\text{-}ClAr}$AlMe$_2$ complex (**2g**)*

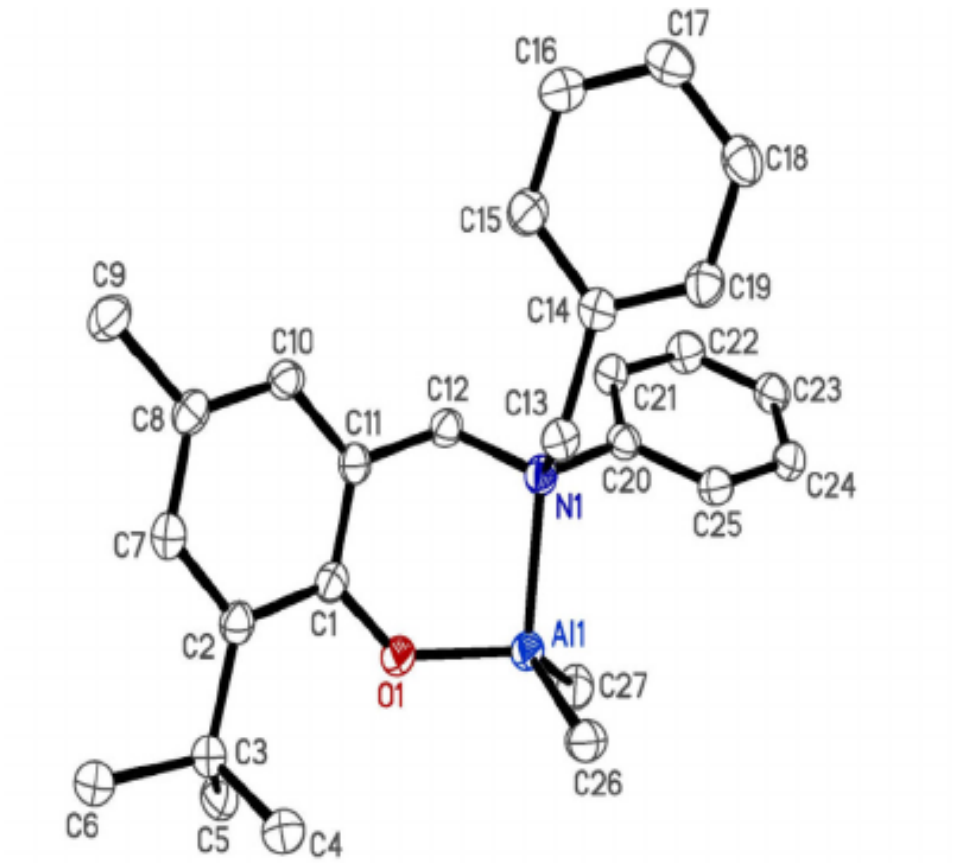
Complex **2g** was obtained as a white powder, by followin similar procedure to that described for **2a**, from reaction betw $AlMe_3$ (0.82 mL, 1.63 mmol, 2.0 M in hexane) and **1 g** (0.6 1.63 mmol). Yield: 0.63 g, 86.2%. $^1$H NMR ($CDCl_3$, 400 MHz 7.46–7.38 (m, 1H, Ar*H*), 7.36–7.29 (m, 2H, Ar*H*), 7.27–7.18 2H, Ar*H*), 7.16–7.07 (m, 3H, Ar*H*), 6.61–6.53 (m, 3H, Ar*H*), (d, $^2J$ = 14.4 Hz, 1H, ArC$H_2$), 4.39 (d, $^2J$ = 12.8 Hz, 1H, ArC$H_2$), (d, $^2J$ = 14.4 Hz, 1H, ArC$H_2$), 3.79 (d, $^2J$ = 12.8 Hz, 1H, ArC$H_2$), (s, 3H, ArC$H_3$), 1.43 (s, 9H, C(C$H_3$)$_3$), −0.44 (AlC$H_3$), −1.23 (AlC $^{13}$C{H} NMR ($CDCl_3$, 100 MHz): $\delta$ 156.9, 144.5, 139.1, 132.8, 13 130.5, 129.9, 129.8, 129.2, 128.7, 128.2, 125.3, 123.9, 119.2 Ar—*C*), 58.6 (ArC$H_2$), 53.7 (ArC$H_2$), 35.0 (*C*($CH_3$)$_3$), 29.8 (C(*C*H 21.0 (ArC$H_3$), −9.5 (AlC$H_3$), −10.1 (AlC$H_3$). *Anal.* Calc. for $C_{27}$

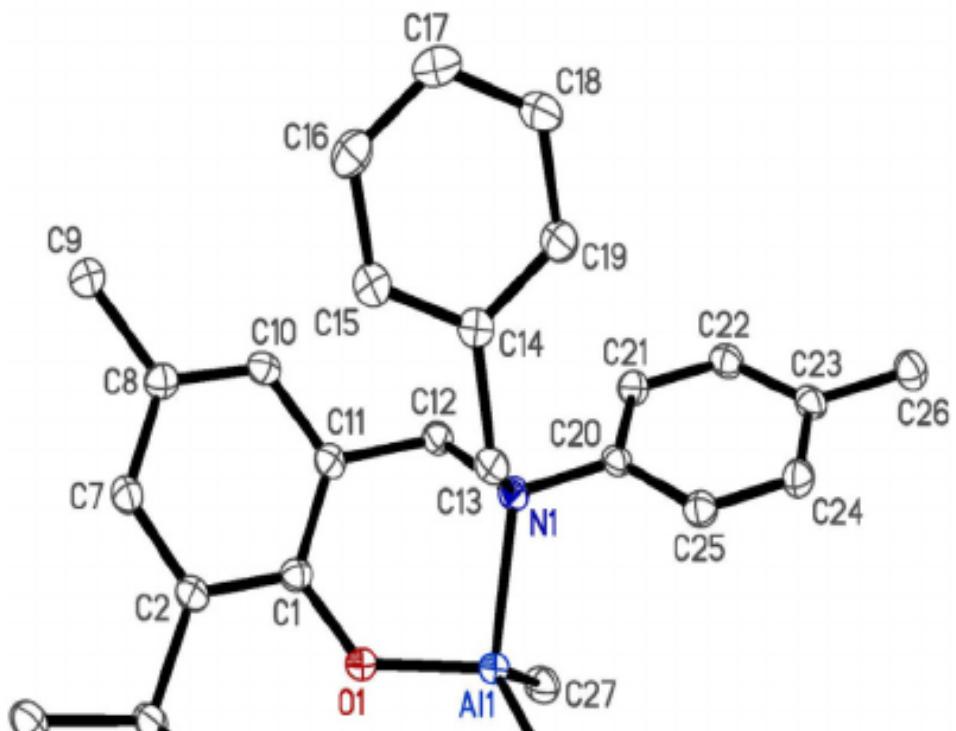



(c)






water, let stir for 5 min and centrifuged for 1 h. Subsequent supernatant was collected (via decantation to exclude ins solids) and analyzed by HPLC.

### 2.6. Product analysis

Quantitative analysis of the products was performed by using a Thermo Scientific Dionex Ultimate 3000 HPLC s equipped with a Dionex quaternary pump, a Shodex RI-101 tive index detector, and a Biorad Aminex HPX-87H column ( 7.8 mm). 5.0 mM $H_2SO_4$ was used as the mobile phase at rate of 0.6 mL/min, and the column temperature was main at 50 °C. The injection volume was 20 μL. All concentrations cose, fructose, and HMF in the aqueous phase were determi comparison to standard calibration curves.

Glucose conversion and products selectivity are defi follows:

$$\textit{Glucose conversion} = (\textit{moles of glucose reacted})/(\text{initial } \textit{moles of gl}$$

$$\textit{HMF selecti vity} = (\textit{moles of HMF produced})/(\text{initial } \textit{moles of g} - \textit{moles of glucose unreacted})$$

$$\textit{HMF yield} = (\textit{moles of HMF produced})/(\text{initial } \textit{moles of glu}$$

## 3. Results and discussion

### 3.1. Synthesis and characterization of proligands and complexe

The new (aminomethyl)phenol derivatives **1c–g** (Sche


**Fig. 2.** ORTEP diagrams of **2e**, (left) and **2b** (right). Thermal ellipsoids are drawn at 50% probability level. Hydrogens are omitted for clarity.

AlClNO: C, 72.07; H, 7.39; N, 3.11. Found: C, 71.51; H, 7.25; N, 3.08%.

### 2.4. Crystallographic studies

Single crystals of $L^{R}AlMe_2$ complexes **2a**–**2c** (R = Me, Et, *i*-Pr), **2e** (R = Ph), and **2f** (R = *p*-tolyl) suitable for X-ray crystallographic analysis were obtained by slow recrystallization from a 1:1 *n*-hexane:toluene solution of the complex in the glovebox at room temperature. Colorless single crystals of each complex were placed in dry and degassed paratone oil on a glass plate and used for X-ray diffraction analysis. Crystallographic data for the complexes are collected in Table 1. Further details of the crystallographic study are given in the Supplementary Material.

### 2.5. General procedure for catalytic dehydration of glucose

All the reactions were performed in a 5-mL reaction vial sealed with a solid cap with PTFE faced silicone septum. In a typical experiment, D-(+)-glucose (50 mg, 0.28 mmol), [EMIM]Cl (500 mg, 3.41 mmol), and a specified amount of aluminum precatalyst were charged into the reaction vial along with a magnetic stir bar under

were synthesized in good yield by modification of the m
reported by Kim and Ishida [27], via neat reaction of 2-*tert*-
4-methylphenol with paraformaldehyde and appropriate
at 105 °C. In addition, compounds **1a** [25] and **1b** [26] wer
pared by literature methods. $L^{R}AlMe_2$ complexes **2a**–**g** (Sch
were obtained in good yield via modification of the m
reported by Wang and Ma [26] for preparation of $L^{Et}AlMe$
by treatment of proligands **1a**–**g** with one equivalent of Al
toluene at room temperature for 24 h. The reaction proc
cleanly with evolution of methane to produce **2a**–**g** which
isolated as moisture-sensitive light-yellow or white powder
compounds are readily soluble in nonpolar and polar a
hydrocarbon solvents, such as chloroform, methylene ch
diethyl ether, and THF, as well as aromatic hydrocarbon so
such as benzene and toluene. However, the compounds ar
moderately soluble in aliphatic hydrocarbon solvents, and
could be recrystallized from hexane at low temperatures.

The formulation and molecular structure of $L^{R}AlMe_2$ com
**2a** and **2c**–**g** were established by microanalysis and solution
data. Their $^{1}H$ NMR spectra did not show the downfield reso
characteristic of the phenolic OH group of the proligands, su
ing coordination of phenolate oxygen with aluminum. Con
with bidentate coordination of the (aminomethyl)phe
ligand, with tight binding of the amino nitrogen to alu
resulting in hindered rotation of *N*-benzyl group on the NMR
scale at room temperature, the $^{1}H$ NMR spectra of $L^{R}AlMe$
plexes **2a** and **2c**–**g** contained four doublet resonances
4.57–3.55 ppm range for the four benzylic protons. Similarl
chemically inequivalent methyl resonances were observed
*N*-isopropyl group of **2c**, consistent with coordination of



| | 2e | | 2f | |
|---|---|---|---|---|
| 1.7616(9) | Al(1)—O(1) | 1.7589(8) | Al(1)—O(1) | 1.7571(11) |
| 1.9570(14) | Al(1)—C(27) | 1.9619(11) | Al(1)—C(28) | 1.9560(16) |
| 1.9638(13) | Al(1)—C(26) | 1.9647(11) | Al(1)—C(27) | 1.9589(16) |
| 2.0532(10) | Al(1)—N(1) | 2.0727(9) | Al(1)—N(1) | 2.0802(13) |
| 110.42(5) | O(1)—Al(1)—C(27) | 110.95(4) | O(1)—Al(1)—C(28) | 111.47(6) |
| 113.27(5) | O(1)—Al(1)—C(26) | 113.86(4) | O(1)—Al(1)—C(27) | 110.67(6) |
| 118.92(6) | C(27)— Al(1)—C(26) | 113.74(5) | C(28)—Al(1)—C(27) | 116.50(7) |
| 94.95(4) | O(1)—Al(1)—N(1) | 97.36(3) | O(1)—Al(1)—N(1) | 97.09(5) |
| 110.52(5) | C(27)—Al(1)—N(1) | 110.30(4) | C(28)—Al(1)—N(1) | 110.12(6) |
| 105.97(5) | C(26)—Al(1)—N(1) | 106.45(4) | C(27)—Al(1)—N(1) | 109.26(6) |
| 109.24(7) | C(20)—N(1)—Al(1) | 106.59(7) | C(20)—N(1)—Al(1) | 106.78(8) |

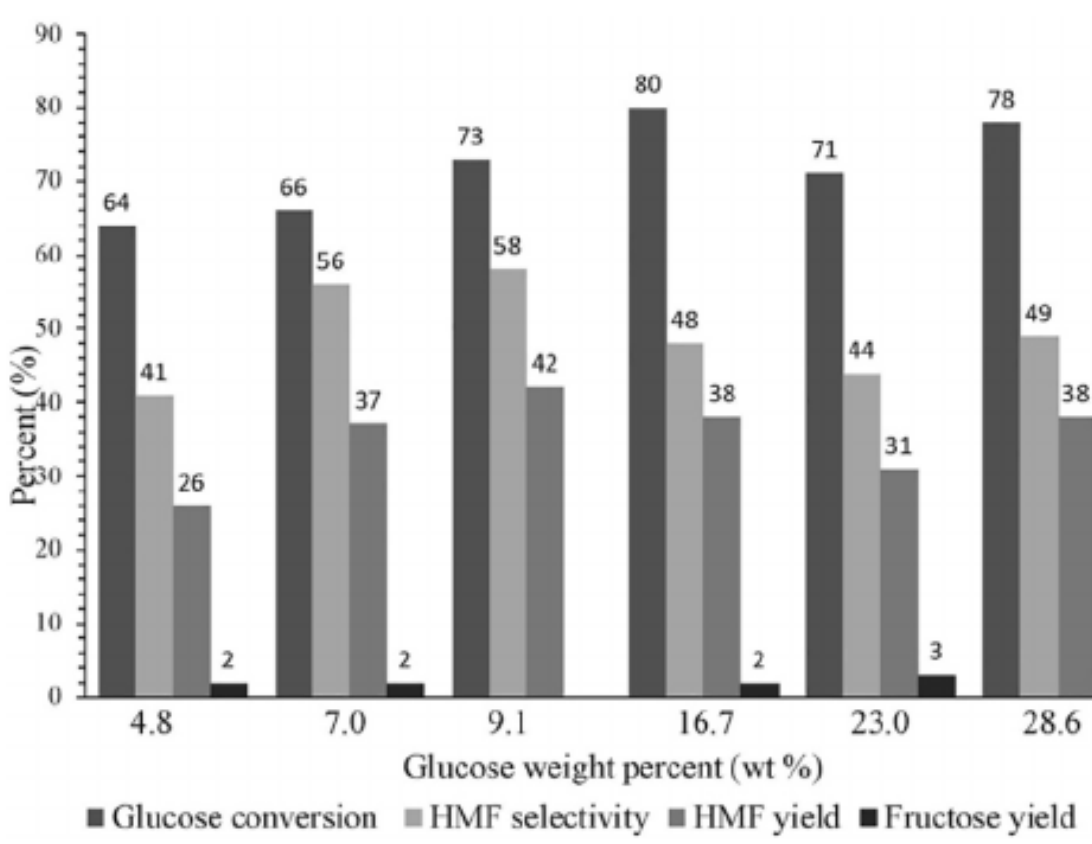



**Fig. 3.** The effect of glucose weight percent in [EMIM]Cl on the proc
distribution. Reaction conditions: 50 mg glucose using 5 mol% [$L^{Ph}AlMe_2$] (
120° C for 2 h.

$C_1$ symmetry expected for tetrahedral $L^{R}AlMe_2$ complexes **2a**
**2c**–**g**, two different Al—$CH_3$ resonances were observed in thei
NMR spectra in the upfield region of −0.56 to −0.86 ppm for co
plexes **2a**–**2d** (with *N*-alkyl substituent), and −0.43 to −1.26 p
for **2e**–**g** (with *N*-aryl substituent). $^{13}C\{^{1}H\}$ NMR spectra of
complexes are also consistent with their $C_1$ symmetry; toge
with two Al—$CH_3$ and two benzylic carbon resonances, **2a**,
and **2d** each displayed ten aromatic carbon resonances while
**g** each displayed fourteen aromatic carbon resonances.

l lengths (Å) and bond angles (°) for L $^{R}$AlMe$_2$ complexes **2a–2c**, **2e**, and **2f**.

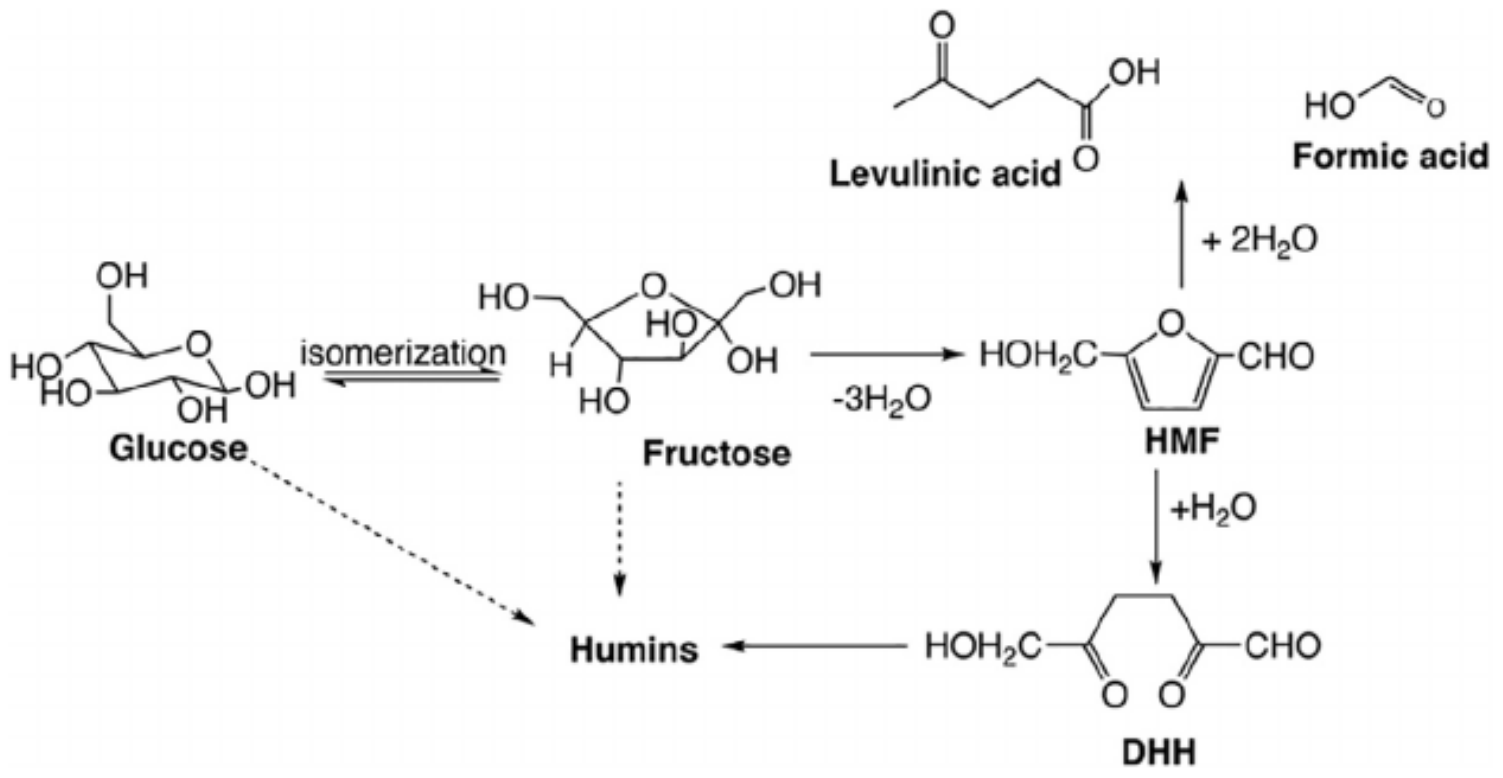
| **2b** | | **2c** | |
|---|---|---|---|
| Al(1)—O(1) | 1.7474(16) | Al(1)—O(1) | 1.7 |
| Al(1)—C(22) | 1.965(3) | Al(1)—C(23) | 1.9 |
| Al(1)—C(23) | 1.966(3) | Al(1)—C(24) | 1.9 |
| Al(1)—N(1) | 2.027(2) | Al(1)—N(1) | 2.0 |
| O(1)—Al(1)—C(22) | 109.99(10) | O(1)—Al(1)—C(23) | 110 |
| O(1)—Al(1)—C(23) | 110.45(10) | O(1)—Al(1)—C(24) | 108 |
| C(22)—Al(1)—C(23) | 119.21(12) | C(23)—Al(1)—C(24) | 113 |
| O(1)—Al(1)—N(1) | 97.17(8) | O(1)—Al(1)—N(1) | 97. |
| C(22)—Al(1)—N(1) | 110.44(10) | C(23)—Al(1)—N(1) | 109 |
| C(23)—Al(1)—N(1) | 107.31(10) | C(24)—Al(1)—N(1) | 115 |
| C(20)—N(1)—Al(1) | 109.88(15) | C(20)—N(1)—Al(1) | 111 |

| **2e** | | **2f** | |
|---|---|---|---|
| Al(1)—O(1) | 1.7559(10) | Al(1)—O(1) | 1.7 |
| Al(1)—C(22) | 1.9470(16) | Al(1)—C(23) | 1.9 |
| Al(1)—C(23) | 1.9542(16) | Al(1)—C(24) | 1.9 |
| Al(1)—N(1) | 2.0284(12) | Al(1)—N(1) | 2.0 |
| O(1)—Al(1)—C(22) | 111.53(7) | O(1)—Al(1)—C(23) | 110 |
| O(1)—Al(1)—C(21) | 111.66(6) | O(1)—Al(1)—C(24) | 108 |
| C(22)—Al(1)—C(21) | 117.33(8) | C(23)—Al(1)—C(24) | 113 |
| O(1)—Al(1)—N(1) | 96.53(5) | O(1)—Al(1)—N(1) | 97. |
| C(22)—Al(1)—N(1) | 108.36(6) | C(23)—Al(1)—N(1) | 109 |
| C(23)—Al(1)—N(1) | 109.35(6) | C(24)—Al(1)—N(1) | 115 |
| C(20)—N(1)—Al(1) | 109.58(8) | C(20)—N(1)—Al(1) | 111 |

X-ray diffraction analysis on single-crystals of **2a**–**2c**, **2e**, an
confirmed the structure assigned by spectroscopy. Structure
the complexes are depicted in Figs. 1 and 2, and crystallogra
data and selected metrical parameters for the complexes are
lected in Tables 1 and 2. The compounds adopt a distorted tetra
dral structure with the (aminomethyl)phenolate lig
coordinated to aluminum in bidentate fashion, via phenolate o
gen and amino nitrogen atoms. The aluminum center is also co
dinated by two carbon atoms from two methyl groups.
distortion from idealized tetrahedral geometry arises from
acute bite angle of the chelating (aminomethyl)phenolate lig
[O(1)—Al(1)—N(1) bond angles range from ca. 95° to 97°], wh
is compensated for by opening of the C—Al—C, C—Al—O,
C—Al—N bond angles (Table 2). All of the Al—O, Al—N and A
bond distances are within the range reported for related co
plexes [28–30]. However, **2a** and **2b** (with NMe(CH$_2$Ph) or
($CH_2$Ph) moiety, respectively) possessed shorter Al—N bond
tances (<2.03 Å) than were observed (>2.05 Å, Table 2) for **2c** (w
N(*i*-Pr)(CH$_2$Ph) moiety), **2e** (with NPh(CH$_2$Ph) moiety) or **2f** (w
N(*p*-Me$C_6H_4$)($CH_2$Ph) moiety). Presumably, this is because e
tron-releasing methyl and ethyl substituents increase elect
donation by amino nitrogen atom to aluminum, relative to
bulkier isopropyl substituent or less electron donating aryl s
stituents. The molecular structures (Figs. 1 and 2) confirmed
in **2e** and **2f** the two Al—CH$_3$ groups reside in a more dissim
chemical environment than in **2a**–**c**, consistent with $^1$H NMR
(*vide supra*). In **2e** and **2f**, one Al—Me group lies in close proxim
to the *N*-aryl ring; for **2e**, the torsion angle between Al—Me and
phenyl ring (C27—Al(1)—N1—C20) is 27.52° and the C20—C27
tance is 3.297 Å.

### 3.2. Glucose dehydration studies






**Scheme 2.** Possible pathways for glucose conversion to HMF and other products.

sion and the product distribution of glucose dehydration at 120 °C for 2 h using 5 mol% (relative to moles of glucose) L $^{Ph}$AlMe$_2$ (**2e**) as catalyst. The glucose conversion ranged between 73% and 80% for glucose concentrations in [EMIM]Cl ranging between 9.1 and 28.6 wt%. However, the highest HMF selectivity and yield (58% and 42%, respectively) were both obtained when 9.1 wt% glucose was employed. It is known that Lewis acid-catalyzed glucose dehy-

#### 3.2.2. Effect of temperature and time

Table 3 shows the effects of temperature and time on g
dehydration in [EMIM]Cl using [L $^{Ph}$AlMe$_2$] (**2e**, 5 mol%) as c
The reaction was investigated in the absence and presence
alyst over the 100–140 °C temperature range. At all temper
in the absence of a catalyst, both the glucose conversion (3
and the HMF yield (<1%) were quite poor, consistent with pr

dration generally proceeds via glucose isomerization to fructose, followed by fructose dehydration to HMF (Scheme 2) [6]. Predictably, all of the product mixtures also contained a small amount of fructose (2–3%) except for when 9.1 wt% glucose in [EMIM]Cl was employed, whereupon fructose was present only in trace amount. No other soluble products were detected by HPLC analysis in the supernatants obtained after aqueous extraction of any of the dark brown reaction mixtures; these results and all other results reported herein were reproduced at least 3 times. Since glucose concentrations ≥9.1 wt% resulted in comparable conversions while both the HMF selectivity and HMF yield decreased when >9.1 wt% glucose in [EMIM]Cl was employed, all other experiments reported herein were conducted using 9.1 wt% sugar in ionic liquid solvent, unless otherwise indicated.

literature reports.[11,31] For example, Zhao et al. reported 40
cose conversion and <4% HMF yield when 9.1 wt% gluc
[EMIM]Cl was heated at 180 °C for 3 h in the absence of a
lyst.[11] In the presence of [L$^{Ph}$AlMe$_2$] (**2e**), the conversion
cose at 100 °C increased gradually with time, reaching a max
of 59% after 6 h (Table 3, entries 3–6). The HMF sele
increased up to 56% over four hours of reaction, and remai
56% after 6 h, resulting in 33% HMF yield. As expected, glucos
version increased with an increase in temperature. Consequ
95% glucose conversion was achieved at 120 °C after 6 h. Ho
as the data in Table 3 (entries 11–14) show, glucose conversi
wed dramatically as the reaction progressed, with only a
increase in glucose conversion observed after 4 h. While this
reflects the reduction in reaction rate as the concentration

**Table 3**
Temperature and time effects on glucose dehydration in [EMIM]Cl in absence and presence of a catalyst. [a]

| Entry | Temp (°C) | Time (min) | Cat.[b] | Glucose Conv. (%) | HMF selectivity (%) |
|---|---|---|---|---|---|
| 1 | 100 | 1 | – | 3 | 0 |
| 2 | 100 | 2 | – | 4 | 0 |
| 3 | 100 | 1 | **2e** | 17 | 38 |
| 4 | 100 | 2 | **2e** | 31 | 43 |
| 5 | 100 | 4 | **2e** | 46 | 56 |
| 6 | 100 | 6 | **2e** | 59 | 56 |
| 7 | 120 | 1 | – | 4 | 0 |
| 8 | 120 | 2 | – | 6 | 0 |
| 9 | 120 | 4 | – | 8 | 5 |
| 10 | 120 | 6 | – | 15 | 5 |
| 11 | 120 | 1 | **2e** | 52 | 53 |
| 12 | 120 | 2 | **2e** | 69 | 54 |
| 13 | 120 | 4 | **2e** | 88 | 53 |
| 14 | 120 | 6 | **2e** | 95 | 49 |
| 15 | 140 | 1 | – | 23 | <1 |
| 16 | 140 | 0.33[c] | **2e** | 70 | 47 |
| 17 | 140 | 0.66[d] | **2e** | 85 | 45 |
| 18 | 140 | 1 | **2e** | 92 | 48 |



**Table 4**
The effect of catalyst ([L$^{Ph}$AlMe$_2$], **2e**) loading on glucose dehydration in [EMIM]Cl. [a]

| Entry | Temp (°C) | Catalyst mol% | Glucose conv. (%) | HMF selectivity (%) | HMF yield (%) |
|---|---|---|---|---|---|
| **1** | 100 | 5 | 46 | 56 | 26 |
| **2** | 100 | 10 | 65 | 42 | 27 |
| **3** | 100 | 15 | 69 | 43 | 30 |
| **4** | 100 | 20 | 71 | 39 | 28 |
| **5** | 120 | 5 | 88 | 53 | 46 |
| **6** | 120 | 10 | 94 | 45 | 42 |
| **7** | 120 | 15 | 95 | 45 | 43 |
| **8** | 120 | 20 | 97 | 42 | 40 |

[a] Reaction conditions: 9.1 wt% glucose at the indicated temperature for 4 h.

cose decreases, it is noteworthy that the HMF selectivity remained more or less constant (53–54%) over 4 h, and decreased only slightly (to 49%) after 6 h. This result argues against significant catalyst deactivation occurring during the reaction since the HMF selectivity remained essentially constant as the glucose conversion increased. Accordingly, the HMF yield increased up to 46% after 4 h and was essentially unchanged after 6 h.

Raising the reaction temperature to 140 °C resulted in 92% glucose conversion after 1 h, along with 48% HMF selectivity and 44%

increase in the catalyst loading resulted in unchanged or slig
decreased HMF selectivity and yield. Thus, it appears that cata
loadings higher than 5 mol% enhance side reactions that lea
formation of humins (*vide infra*).

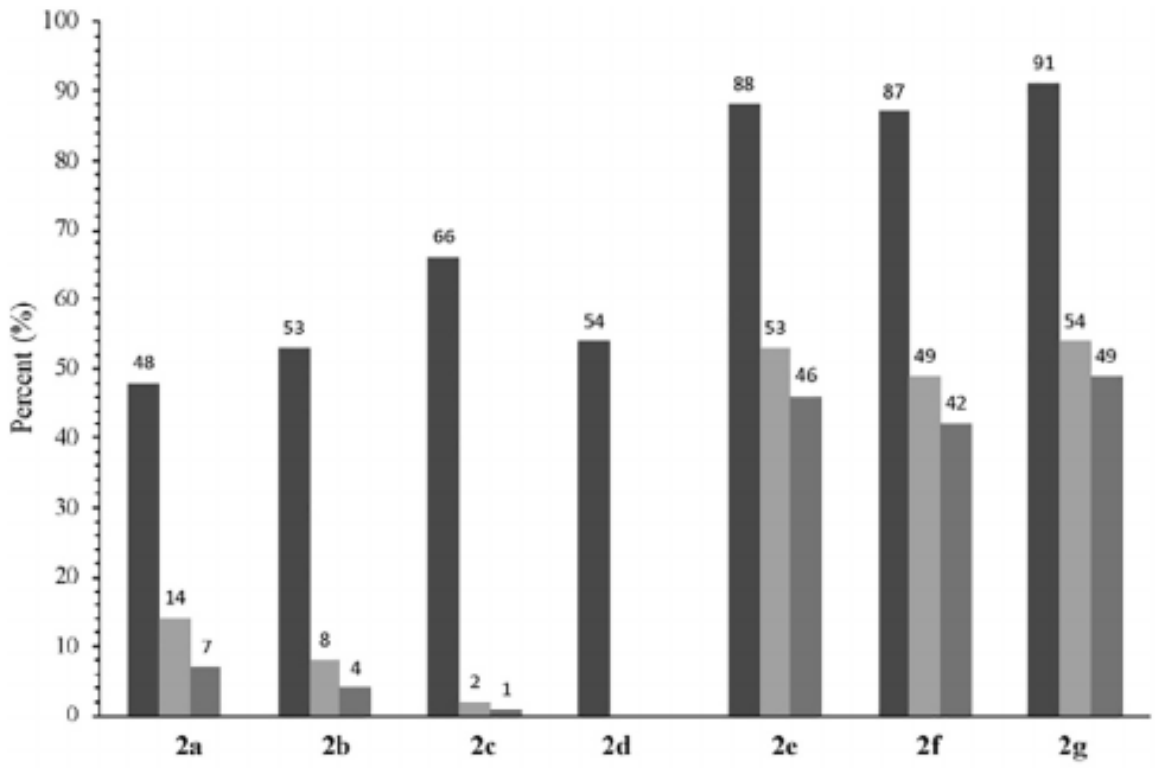
### 3.2.4. Ligand effects

The potential of L$^{R}$AlMe$_2$ complexes **2a**–**g** as catalysts for
cose dehydration to HMF was investigated by conducting the re
tion in [EMIM]Cl at 120 °C for 4 h using 5 mol% of **2a**–**g** as catal

HMF yield. Consequently, we investigated the effect of shorter reaction time for [$L^{Ph}AlMe_2$] (**2e**)-catalyzed glucose conversion at 140 °C (Table 3, entries 16 and 17). 70% glucose conversion was observed after 20 min but the reaction progress slowed dramatically once again, with only 15% additional glucose conversion observed after another 20 min of reaction. However, while glucose conversion increased on raising the reaction temperature from 120 to 140 °C, the HMF selectivity and hence the HMF yield decreased slightly although shorter time was required to reach high conversion (Table 3).

### 3.2.3. Effect of catalyst loading

Table 4 shows results of our study of the effect of catalyst loading on glucose conversion and the product distribution for [$L^{Ph}AlMe_2$] (**2e**)-catalyzed dehydration of glucose in [EMIM]Cl at both 100 and 120 °C for 4 h; the catalyst loading was varied in 5% increments from 5 to 20 mol%. At both temperatures, a modest increase in glucose conversion accompanied an increase in the catalyst loading from 5 to 10 mol% while further increase in the catalyst loading had little effect on the extent of reaction. Conversely, both the HMF selectivity and yield decreased significantly upon increasing the catalyst loading from 5 to 10 mol% while further




As shown by the glucose conversion and product distribution in Fig. 4, $L^{R}AlMe_2$ complexes **2a**–**d** for which the R substituent an alkyl group (Scheme 1) were ineffective catalysts for selec formation of HMF. The glucose conversion was modest (~5 even if significantly higher than in absence of a catalyst (Tabl entry 9). But more importantly, both the HMF selectivity and y were extremely poor. The HMF yield in fact decreased as size of amino moiety's alkyl substituent increased, with only a t amount of HMF produced when **2d** ($L^{R}AlMe_2$, R = $Bu^t$) was catalyst.

The difference in catalytic efficiency of $L^{R}AlMe_2$ complexes taining alkyl-substituted amino group (**2a**–**d**) versus aryl-sub tuted amino group (**2e**–**g**) is remarkable. All of the a substituted aluminum (aminomethyl)phenolate complexes **2** afforded much higher glucose conversion (>87%) and much be HMF selectivity (49–54%) and yield (42–49%) than alkyl-sub tuted aluminum (aminomethyl)phenolate complexes **2** (Fig. 4). As the data in Table 2 show, bond angles about the and N atoms are similar for all of the complexes. However, Al bond distances for **2a** and **2b** are significantly shorter than th for **2e** and **2f**, due presumably to stronger sigma electron donat to aluminum by alkyl-substituted nitrogen relative to aryl-sub tuted nitrogen. On the other hand, the significantly longer Al bond distance for **2c** (compared to **2a** and **2b**) is most proba due to its sterically more crowded coordination sphere. Thus, presume that the markedly decreased efficiency of **2a**–**d** as gluc dehydration catalysts (versus **2e**–**g**) is due to the reduced Le acidity of **2a**–**d**, and/or greater steric hindrance at the alumin center in complexes **2c** and **2d**. In this regard, a slight increas both the HMF selectivity and yield was observed as electron do tion from aryl-substituted amino group was decreased by decre ing the electron releasing ability of the para substituent of the group (Fig. 4), that is, from R = *p*-$MeC_6H_4$ (**2f**) to R = $C_6H_5$ (**2e**) = *p*-$ClC_6H_4$ (**2g**) [32]. Clearly, the different (aminomethyl)phenc ligands impose different chemical (coordination) environme about the Al center, consistent with the different chemical sh observed for the Al—Me groups of **2a**–**d** versus **2e**–**g** Section 3.1).



**Table 5**
Ionic liquid effects on glucose dehydration with [$L^{Ph}AlMe_2$] (**2e**) as catalyst.

| Entry | Ionic liquid (IL) | Time (h) | Glucose conv. (%) | HMF selectivity (%) |
|---|---|---|---|---|
| **1**[a] | [EMIM]Br | 1 | 56 | 56 |
| **2**[a] | [EMIM]Br | 2 | 74 | 59 |
| **3**[a] | [EMIM]Br | 4 | 84 | 64 |
| **4**[a] | [EMIM]Br | 6 | 91 | 55 |
| **5**[a] | [BMIM]Br | 1 | 92 | 56 |
| **6**[a] | [BMIM]Br | 2 | 97 | 60 |
| **7**[a] | [BMIM]Br | 4 | 100 | 55 |
| **8**[b] | [BMIM]Br | 2 | 95 | 63 |

[a] Reaction conditions: 9.1 wt% glucose with 5 mol% [$L^{Ph}AlMe_2$] (**2e**) at 120 °C.
[b] 4.8 wt% glucose and 5 mol% [$L^{Ph}AlMe_2$] (**2e**) at 120 °C.

during dehydration of sugars [9,35,36]. In this regard, Lunc [37,38] have proposed a mechanism for humin formation in 2,5-dioxo-6-hydroxyhexanal (DHH), formed by HMF rehyd is a key intermediate (Scheme 2). Humins were proposed

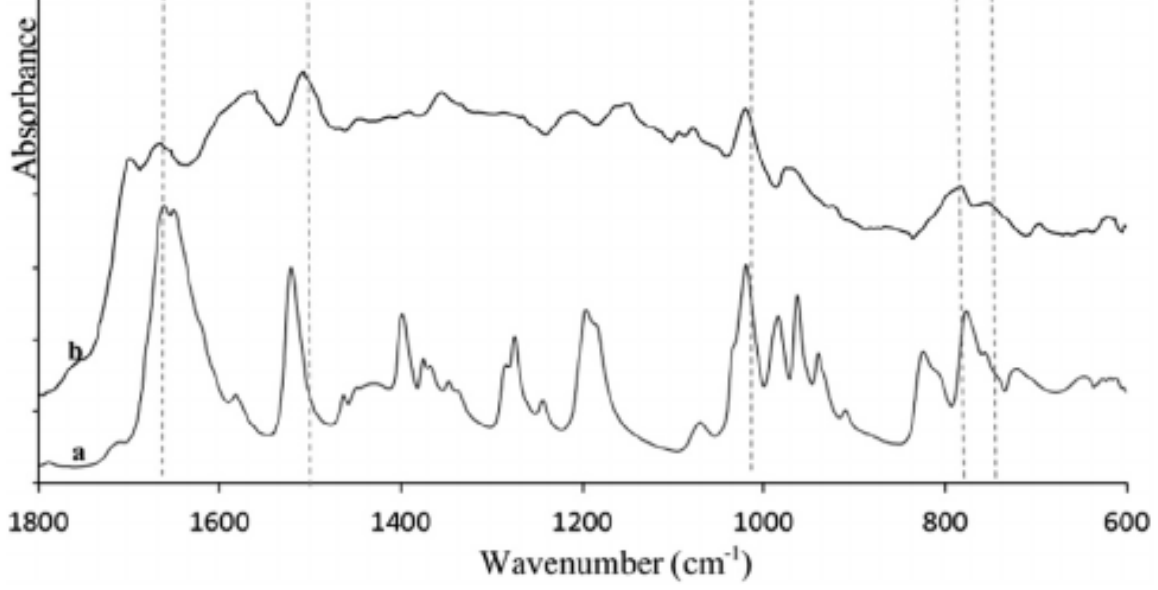



**Fig. 5.** ATR-IR spectra of (a) HMF and (b) humins formed during L $^{Ph}$AlMe$_2$ (**2e**)-catalyzed glucose dehydration in [EMIM]Cl at 120 °C for 4 h.

as in [EMIM]Cl (Table 3, entries 11–14), the HMF selectivity and yield were significantly higher in [EMIM]Br, peaking after 4 h at 64% and 54%, respectively. Higher HMF selectivity and yield have previously being observed in the presence of bromide ion relative to chloride ion, and have been attributed to acceleration of fructose dehydration as a result of better nucleophilicity and leaving group properties of bromide ion [33,34]. As mentioned earlier, fructose is the only other soluble product observed in our reactions, and Lewis acid-catalyzed glucose dehydration generally occurs via glucose isomerization to fructose [6].

Glucose conversion progressed significantly faster in [BMIM]Br (1-butyl-3-methylimidazolium bromide) than in [EMIM]Br, reaching 92% in 1 h, and giving HMF selectivity and yield of 56% and 52%, respectively. Increasing the reaction time to 2 h resulted in slightly higher glucose conversion and an increase in the HMF selectivity and yield to 60% and 58%, respectively. However, further increase in the reaction time resulted in a decrease in the HMF selectivity and yield (Table 5, entry 7). Since glucose conversion was much faster in [BMIM]Br, we investigated the effect of lowering the concentration of glucose in [BMIM]Br from 9.1 wt% to 4.8 wt% on the HMF selectivity and yield: 95% glucose conversion was achieved after 2 h, along with slight increases in the HMF selectivity and yield, up to 63% and 60%, respectively (Table 5, entry 8).

### *3.3. Humins analysis*

formed via subsequent aldol condensations of DHH with th
bonyl group of HMF, with the extent of HMF incorporation
humin structure being dependent on the accumulation o
during the reaction. Furthermore, it was suggested that h
could not be directly formed from sugars. Zandvoort et a
have similarly suggested that humins are mainly derived
HMF based on their finding that addition of HMF to the g
feed barely changed the elemental composition of the
obtained from acid-catalyzed dehydration of glucose. HPLC
sis of the product mixtures from glucose and fructose dehyd
catalyzed with aluminum (aminomethyl)phenolate complex
**g** detected HMF as well as glucose and/or fructose as the only
ucts. Thus, formation of humins rather than HMF rehydrat
form levulinic acid (LA) and formic acid (FA) appears to
main route for HMF loss in these reactions (Scheme 2).

The nature of the insoluble brown solids produced durin
AlMe$_2$ (**2e**)-catalyzed dehydration of glucose (for 4 h) in [
Cl at 120 °C was investigated by Raman and ATR–FTIR
troscopy. The Raman data are suggestive of the presence
matic groups with oxygen-rich functionalities. The sign
1385 and 1585 cm$^{-1}$ are characteristic of the D and G bands
ordered graphite-like carbon [37,39,40]. Fig. 5 compares AT
spectra of the humins with the IR spectrum of HMF. The h
show broad absorbance peaks in ca. 1100–1400 cm$^{-1}$ range
with peaks that arise from the furan ring of HMF [37,41]. S
cally, the two peaks in the 750–850 cm$^{-1}$ range, the p
1020 cm$^{-1}$, and the peak at 1512 cm$^{-1}$ have been attribut
furan ring of HMF. These data strongly support significant in
ration of HMF into the humin structure.

## 4. Conclusions

L$^R$AlMe$_2$ complexes **2e**–**g**, which contain a bidentate (a
methyl)phenolate ligand with an aryl substituent on the
group, are efficient catalysts for glucose dehydration in ionic
solvents to give HMF. In [EMIM]Br and [BMIM]Br, the reactio
ceeds at 120 °C with very high conversion in 2 h to produc
with 60–63% selectivity and in 58–60% yield. Both the HMF
tivity and yield were lower in [EMIM]Cl, up to 54% and 49%, r
tively. The HMF selectivity of glucose dehydration decreased
concentration of the aluminum catalyst was increased fro
20 mol%. Giving that no other soluble products (besides gl

incorporation of HMF in their structure, the HMF selectivity of L $^R$-AlMe$_2$-catalyzed glucose dehydration appears to be limited by competing loss of HMF to humins formation.

The reasonably high yield of HMF (60%) obtained herein from L$^{Ph}$AlMe$_2$-catalyzed glucose dehydration in ionic liquids is encouraging, as is our finding that the catalytic efficiency of L $^R$AlMe$_2$ complexes can be tuned via modification of the (aminomethyl) phenolate ligand. To date, the vast majority of studies of aluminum-catalyzed glucose conversion to HMF have focused on AlCl$_3$. The findings from this study are useful toward developing better understanding of the relationship between the structure and function of aluminum catalysts for glucose (and ultimately cellulose) conversion into HMF. Towards this end, we have recently initiated a study of the reactions of L$^{Me}$AlMe$_2$ (**2a**) and L$^{Ph}$AlMe$_2$ (**2e**) with glucose and cycloalkane diols in ionic liquid solvents.

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## Appendix A. Supplementary data

CCDC 1489633, 1489630, 1812487, 1489632, and 1489631 contains the supplementary crystallographic data for complexes **2a–c**, **2e** and **2f**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.poly.2018.03.035.

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