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Full Paper

Synthesis, Characterization, and Catalytic Activity of a Series of Aluminium–Amidate Complexes*

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The aluminium complexes {[κ^2 -*N*,*O*-(*t*-BuNCOPh)]AlMe₂}₂ (**2**), [κ^2 -*N*,*O*-(*t*-BuNCOPh)]₂AlMe (**3**), and [κ^2 -*N*,*O*-(*t*-BuNCOPh)]₃Al (**4**) were prepared through the protonolysis reaction between trimethylaluminium and one, two, or three equivalents, respectively, of *N*-*tert*-butylbenzamide. Complex **2** was also prepared via a salt metathesis reaction between K(*t*-BuNCOPh) and dimethylaluminium chloride. Complexes **2**–**4** were characterized using ¹H and ¹³C NMR spectroscopy. Single-crystal X-ray diffraction analysis of the complexes corroborated ligand : metal stoichiometries and revealed that all the amidate ligands coordinate to the aluminium ion in a κ^2 fashion. The Al–amidate complexes **2**–**4** were viable catalyst precursors for the Meerwein–Ponndorf–Verley–Oppenauer reduction–oxidation manifold, successfully interconverting several classes of carbonyl and alcohol substrates.

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Introduction

The development of new catalytic systems for small molecule transformations that employ non-precious metal complexes is an important challenge.^[1] Aluminium is one of the most abundant elements in the earth's crust^[2] and is an attractive choice for such catalyst development because it is readily available, inexpensive, and non-toxic.^[3,4] The application of aluminium complexes as catalysts for high impact reactions is therefore very desirable. Indeed, aluminium complexes represent a privileged class of compounds in Lewis-acid catalysis^[5] and development of Al-based catalysts systems for processes such as the ring-opening polymerization of cyclic esters,^[6] the hydrofunctionalization reaction,^[7–10] epoxide coupling with carbon dioxide,^[6b,11–14] and transfer hydrogenation^[15–17] continues to be an active area of research.

We have been investigating the coordination chemistry of amidate ligands to aluminium(Π) ions with the goal of developing a new class of Al-based catalysts. Amidates represent a family of highly variable *N*,*O*-chelating, monoanionic ligands. The amide ligand precursors are easily prepared via the nucleophilic acyl substitution of an acid chloride with a primary amine^[18] in a variety of substitution patterns such that the steric and electronic properties of the amidate ligand can be readily modulated. Amidate ligand complexes have been shown to support a variety of transition^[19–23] and rare-earth metals^[24–28] that has resulted in a family of useful reagents for metalmediated transformations. The synthesis of Al–amidate

complexes was originally reported by Lappert and Horder^[29] and Wade et al.,^[30] and was expanded on by the Lin group to include various substituents in the amidate ligand.^[31,32] The MacBeth group has more recently reported the preparation of a tris(amidate)aluminium complex implementing a tripodal ligand.^[33] Despite these chemistries, the application of aluminium amidate complexes as catalysts has not been investigated. The Stahl group has reported the Al₂(NMe₂)₆-catalyzed transamidation of carboxamides,^[34] and has shown that aluminium amidate functional groups are important moieties under the reaction conditions,^[35,36] suggesting that Al-amidate complexes may be viable catalytic species. Herein, we report the synthesis of a series of Al-amidate complexes that vary in ligand: metal stoichiometry. We also demonstrate the viability of the complexes to serve as catalytic precursors for the Meerwein-Ponndorf-Verley (MPV) reduction of carbonyls and the related Oppenauer oxidation of alcohols.

Results and Discussion

Synthesis and Characterization of Aluminium–Amidate Complexes **2–4**

The 1:1 reaction between trimethylaluminium and various simple amides has been previously reported by the Lin group^[31,32] who showed that the bonding mode of the ligand and solid-state structure of the Al–amidate complexes were dependent on the substitution pattern of the amide precursor.

^{*}Dedicated to the memory of Professor Richard F. Langler, an inspirational teacher and mentor.



Scheme 1. Protonolysis routes to Al-amidate complexes with varying ligand/metal ratios.



Scheme 2. Salt metathesis route to Al-amidate complex 2.

We were interested in examining how changing the number of equivalents of amide ligand precursor in the protonation chemistry with trimethylaluminium manifests in different aluminium coordination compounds. We focussed on the *N*-tert-butylbenzamide ligand (*t*-BuNHCOPh, **1-H**). The protonation reaction between **1-H** and Al₂(CH₃)₆ in a 1:0.5, 2:0.5, and 3:0.5 ratio in refluxing hexane was utilized to prepare the aluminium complexes {[κ^2 -*N*,*O*-(*t*-BuNCOPh)]AlMe₂}₂ (**2**), [κ^2 -*N*,*O*-(*t*-BuNCOPh)]₂AlMe (**3**), and [κ^2 -*N*,*O*-(*t*-BuNCOPh)]₃Al (**4**), respectively (Scheme 1).

A 1:1 reaction between amide 1-H and trimethylaluminium gives 2 as a dimer in the solid state in good isolated yield. The preparation and crystallization of compound 2 has previously been reported by Lin et al.^[31] Increasing the number of equivalents of amide to two results in protonation of two Al-CH₃ moieties to give compound 3 under analogous reaction conditions. Compound 3 was isolated in 79 % yield after crystallization from toluene at -25° C. Addition of a third equivalent of amide proved more difficult, with the third protonation reaction occurring only at an increased temperature (100°C). Compound 4 was isolated in 54% yield after crystallization from ether at -25° C. All three complexes 2–4 were prepared on a gram scale. The ¹H NMR spectra of the crude reaction products for all three compounds indicate that the protonation reactions are occurring essentially quantitatively with no apparent side products, and the isolated yields are a reflection of the solubility of the complexes under the crystallization conditions. Complexes 2-4 are stable in the solid state when stored under nitrogen at -25° C with no apparent decomposition even upon storage for longer than one year.

We were also able to utilize a salt metathesis route to form complex 2 (Scheme 2). Reaction of the potassium salt of the amidate ligand (1-K) with dimethylaluminium chloride in

toluene at room temperature gave 2 in 50 % yield after workup and crystallization from toluene at -25° C.^[37]

Complexes 2-4 are readily characterized by NMR spectroscopy analyses (see Supplementary Material for copies of the spectra). The ¹H NMR spectra of all the complexes lack the N-H resonance of the 1-H ligand precursor at ~6 ppm, indicating reaction between the amide hydrogen and the basic Al--CH3 moieties. The integration ratio between the tert-butyl groups in the ligand backbone and the unreacted Al-CH₃ groups helps support the formulation of the proposed compounds. In compound 2, the *tert*-butyl-to-Al-CH₃ ratio is 3:2, supporting the addition of one ligand per aluminium ion. In complex 3, a ratio 6:1 was observed, indicating that two ligands have reacted. Finally, complex 4 lacks a resonance below 0 ppm, supporting that all Al-CH₃ groups underwent protonolysis. The ¹³C NMR spectra of 2-4 also support these assignments: resonances for the Al-CH₃ group are observed at -8.5 and -11.7 ppm for complexes 2 and 3, respectively, whereas the ¹³C NMR spectrum of compound 4 lacks a signal in this range.

The structures of complexes **3** and **4** were corroborated by X-ray crystallography and crystallographic data are provided in Table 1. The structure of complex **2** has previously been reported.^[31] Single crystals of **3** were grown from a concentrated hexane solution at room temperature. The molecule crystallizes with two independent half-molecules in the asymmetric unit, where each lies on a crystallographic 2-fold rotation axis, thus generating the full molecules. A representation of one independent molecule is shown in Fig. 1. The two molecules are very similar and the bond distances and angles are effectively identical, so the discussion will only focus on the data for the molecule consisting of Al(1). The geometry of the aluminium ion in **3** is best described as square pyramidal based on a τ_5 of 0.16,^[38] with the two nitrogen atoms and two oxygen atoms

Table 1. Crystallographic data for complexes 3 and 4

	3	4(Et ₂ O) _{0.5}
Formula	C ₂₃ H ₃₁ AlN ₂ O ₂	C35H47AlN3O3.50
Formula weight [g mol ⁻¹]	394.48	592.74
<i>a</i> [Å]	18.6325(17)	30.729(3)
<i>b</i> [Å]	6.3247(6)	10.8742(11)
<i>c</i> [Å]	19.8089(19)	21.609(2)
α [°]	90	90
β [°]	108.812(2)	111.098(4)
γ [°]	90	90
V[Å ³]	2209.7(4)	6736.5(11)
Ζ	4	8
Space group	P2/n	C2/c
<i>T</i> [K]	100(2)	120(2)
λ [Å]	0.71073	0.71073
$D_{\rm calc} [{ m Mg} { m m}^{-3}]$	1.186	1.169
$\mu [\mathrm{mm}^{-1}]$	0.112	0.099
$R_1 (I > 2\sigma(I))$	0.0416	0.0503
wR_2 (all data)	0.1125	0.1219
$T_{\rm max}/T_{\rm min}$	1.07	1.01
GOF (F^2)	1.021	1.009



Fig. 1. Solid-state structure of $[\kappa^2-N,O-(t\text{-BUNCOPh})]_2\text{AlMe}$ (3) with ellipsoids at the 30% probability level. H atoms have been omitted for clarity. Respective selected bond distances and angles: Al(1)–C(1), 1.9689 (17); Al(1)–N(1), 2.0032(9); and Al(1)–O(1), 1.8886(8) Å; and N(1)–Al(1)–O(1), 67.90(3); N(1)–Al(1)–C(1), 107.85(3); O(1)–Al(1)–C(1), 112.72(3); N(1)–Al(1)–N(1A), 144.31(6); O(1)–Al(1)–O(1A), 134.56(6); and N(1)–Al(1)–O(1A), 98.02(4)°.

coordinating in mutually *trans* relationships in the basal plane. At 1.9689(17) Å, the Al–C distance in **3** is longer than those in **2** (1.955(3) and 1.947(3) Å),^[31] but both are in the range of other reported Al–CH₃ distances. For example, the Salen^{*t*Bu}AlCH₃ complex prepared by Atwood et al. has an Al–C distance of 1.963(17) Å,^[39] whereas the {(BINOLate)AlCH₃(THF)}₂ complex (BINOLate = 1,1'-bi-2-naphtholate) reported by Nguyen et al. has an Al–C distance of 1.961(2) Å.^[40] The (formamidinate)Al(CH₃)₂ complex prepared by Deacon. Junk, Anwander et al. has Al–C bond distances of 1.950(3) Å,^[41] whereas the (β-ketiminate)Al(CH₃)₂ complexes reported by Peng et al. have Al–C distances of 1.964(4) and 1.984(3) Å depending on the specific ketiminate ligand employed.^[42] Finally, the (NON) AlCH₃ pincer complex (NON^{2–} = {CyNC₆H₄}₂O^{2–}) prepared by Dagorne et al. has an Al–C distance of 1.947(3) Å.^[43]

Single crystals of 4 were grown from diethyl ether at -25° C (Fig. 2). The aluminium ion is six-coordinated with a distorted octahedral geometry. The three nitrogen atoms and three oxygen atoms coordinate in mutually *meridional* arrangements. The average Al–N bond distance in 4 is 2.017 Å and the average Al–O distance is 1.901 Å, which are slightly longer than the corresponding distances in complex 3 (Al(1)–N(1)=2.0032 (9) Å and Al(1)–O(1)=1.8886(8) Å) although shorter than



Fig. 2. Solid-state structure of $[κ^2-N,O-(t-BuNCOPh)]_3A1$ (4) with ellipsoids at the 30% probability level. H atoms have been omitted for clarity. Respective selected bond distances and angles: Al(1)–N(1), 2.0248(13); Al(1)–O(1), 1.9037(11); Al(1)–N(2), 2.0131(13); Al(1)–O(2), 1.9056(12); and Al(1)–N(3), 2.0130(14); and Al(1)–O(3), 1.8939(12) Å; and N(1)–Al(1)–O(1), 67.25(5); N(2)–Al(1)–O(2), 67.21(5); N(3)–Al(1)–O(3), 67.59(5); N(1)–Al(1)–N(2), 105.46(5); N(1)–Al(1)–N(3), 154.16(6); N(2)–Al(1)–N(3), 97.96(5); O(1)–Al(1)–O(2), 94.06(5); O(1)–Al(1)–O(3), 98.08(5); O(2)–Al(1)–O(3), 165.72(5); N(1)–Al(1)–O(2), 94.94(5); N(1)–Al(1)–O(3), 96.67(5); N(2)–Al(1)–O(1), 159.81(6); N(2)–Al(1)–O(3); 101.54(5); N(3)–Al(1)–O(1); 93.87(5); and N(3)–Al(1)–O(2); 104.22(5)°.

those observed for **2** (Al–N = 2.157(2) Å and Al–O = 1.9096(17) Å).^[31] In all three complexes **2–4**, the N–Al–O angle formed between the aluminium ion and a given amidate ligand is in the range of 63.14(7)– $67.90(3)^{\circ}$ and is the smallest X–Al–Y angle (where X and Y are N or O) in the complexes.

Catalytic Activity of the Al–Amidate Complexes

We were interested in investigating the ability of the Al-amidate complexes 2-4 to serve as catalysts. As a starting point, we focussed on the MPV reduction of carbonyls, ^[15,44-46] a benign and chemoselective reduction protocol for the conversion of carbonyls into their alcohol equivalents utilizing alcohols, most often 2-propanol, as the hydrogen source.^[47] Given the importance of carbonyl reduction in organic chemistry, the development of new MPV protocols applicable for a wide range of carbonyls is attractive. The MPV reduction has been shown to proceed through internal hydrogen transfer between an aluminium alkoxide and a coordinated carbonyl.^[48,49] We envisioned that the Al–CH $_3$ groups in complexes 2 and 3 would be readily protonated by 2-propanol to generate catalytically viable Al-alkoxide species under MPV reaction conditions. Indeed, at 10 mol-% in total aluminium,^[50] complexes **2** and **3** are both pre-catalysts for the reduction of various carbonyl compounds at 50°C using 8 equivalents of 2-propanol as the reductant^[51] (Table 2). The catalyst system was applicable to the reduction of ketones to secondary alcohols. Acetophenone was cleanly reduced to sec-phenethyl alcohol in 60 % and 71 % conversions using 2 and 3, respectively (entries 1 and 2). The related 2napthanone was reduced to 1-(2-naphthyl)ethanol, although the conversions were lower for both aluminium compounds (entries 4 and 5). The reduction of both alkenyl and alkynyl substrates proved more difficult. 4-Phenyl-3-buten-2-one was reduced to the alcohol 4-phenyl-3-buten-2-ol in 29% (for 2, entry 6) and 41 % (for 3, entry 7) conversion and 4-phenyl-3-butyne-2-one was only reduced in 8% conversion using either pre-catalyst



Table 2. MPV reduction of carbonyls catalyzed by 2 and 3

^AReactions were run on a 1-mmol scale in carbonyl.

^BAmounts of catalyst used were 0.05 mmol of **2**, 0.1 mmol of **3**, or 0.1 mmol of **4**.

^CDetermined by GC by relative integrations of the starting material to the product.

(entries 8 and 9). The aliphatic ketone cyclohexanone was readily reduced to cyclohexanol in excellent conversion (entries 10 and 11). Finally, both benzylic (entries 12 and 13) and aliphatic (entries 14 and 15) aldehydes could also be reduced under our reaction conditions to give the corresponding primary alcohols in excellent conversions. The aluminium tris(amidate) complex 4 does not have an Al-CH₃ functional group and hence should lack the ability to form an Al-alkoxide with 2-propanol, rendering the complex catalytically inactive. However, acetophenone is readily reduced using 4 as the pre-catalyst (entry 3), suggesting that the solid-state structure of 4 may not be reflective of the solution dynamics of the complex under the reaction conditions. Stahl demonstrated that a tris(amidate) aluminium species was the resting state of the catalyst in his transamidation chemistry and that catalytically viable species were generated through facile ligand substitution reactions under the reaction conditions.^[35,36] We suggest similar fluxionality here, where one of the amidate ligands is protonated off of the aluminium ion by an equivalent of 2-propoanol to generate a catalytically viable Al–alkoxide under the reaction conditions.^[52]

We also investigated the competency of the Al–amidate complexes to serve as catalysts for the Oppenauer oxidation^[53] of alcohols to the corresponding carbonyl compounds.^[16] The Oppenauer oxidation is the reverse of the MPV reduction, again proceeding through an Al–alkoxide where a sacrificial carbonyl serves as the oxidant. The Al–amidate complexes are viable catalysts for the Oppenauer oxidation conditions relative to the reduction protocol developed above. At 5 mol-% total aluminium^[54] and using pivaldehyde as the oxidant, various alcohols were oxidized in good-to-excellent conversions at room temperature (Table 3). Using 1.5 equivalents of pivaldehyde, *sec*-phenethyl alcohol was oxidized to acetophenone in good conversions of 81% and 91% using **2** or **3** as the catalytic



Table 3. Oppenauer oxidation of alcohols catalyzed by 2-4

C

^AReactions were run on a 1-mmol scale in alcohol.

^BAmounts of catalyst used were 0.025 mmol of **2**, 0.05 mmol of **3**, or 0.05 mmol of **4**.

^CDetermined by GC by relative integrations of the starting material to the product.

^DObtained after 24 h.

^EAmount of catalyst **2** employed was 0.05 mmol.

precursor, respectively, in 3 h (entries 1 and 3). Increasing the amount of oxidant to 3 equivalents increased the conversions to 98% (for 2, entry 2) and 97% (for 3, entry 4) under otherwise identical conditions and time. As with the reduction protocol, despite lacking an Al–CH₃ functional group, complex 4 was a viable option as a catalytic precursor for this oxidation protocol. In fact, complex 4 gave the highest conversion of alcohol into carbonyl in the *sec*-phenethyl oxidation (entry 5). The Al–amidate complexes did not perform as well in the oxidation of 1-(2-naphthyl)ethanol, giving only low conversions into ketone even with 3 equivalents of pivaldehyde and after longer reaction times (entries 6–8). The alkenyl alcohol 4-phenyl-3-buten-2-ol

was readily oxidized using all three Al–amidate complexes as catalysts, giving 4-phenyl-3-buten-2-one in good conversions. Oxidations using **3** and **4** as catalyst precursors were complete in 3 h, giving the ketone product in >95 % conversion (entries 10 and 11). The corresponding oxidation with **2** was more sluggish (entry 9), proceeding in only 46 % conversion in 3 h, although increasing the reaction time to 24 h did provide the ketone product in comparable conversions to those obtained using the other pre-catalysts. The alkynyl alcohol 4-phenyl-3-butyne-2-ol was oxidized to the ketone 4-phenyl-3-butyne-2-one, although the conversions were low. For Al–amidate complexes **2** and **4**, conversions of 29 % and 30 % (entries 12 and 15), respectively,

were obtained which increased slightly with longer reaction times. Increasing the amount of complex 2 to 10 mol-% total aluminium did provide reasonable conversion (64%) into the ketone product after 24 h (entry 13). The oxidation using 3 as the catalyst precursor was unsuccessful, giving product in less than 10% conversion even with longer reaction times (entry 14). Cyclohexanol was readily oxidized to cyclohexanone; using either 2 or 4 as the catalyst precursor gave the ketone product in <50% conversion after 3h using 1.5 equivalents of pivaldehyde, although higher conversions were obtained after 24 h (entries 16 and 19). Using Al-amidate complex 3 as the precatalyst gave cyclohexanone in 72 % conversion under identical reaction conditions (entry 17), and increasing the amount of pivaldehyde to 3 equivalents increased the conversion to 88% after 3 h (entry 18). Our catalyst system was also applicable to the oxidation of benzylic primary alcohols. Benzaldehyde was formed in 74-90% conversion from the oxidation of benzyl alcohol using 1.5 equivalents of pivaldehyde and 2-4 as the catalyst precursor (entries 20-22). The Al-amidate complexes were unsuccessful catalyst precursors for the oxidation of primary aliphatic alcohols (entries 23-26), giving only trace amounts of product for all three Al-amidate complexes. Increasing the amount of catalyst precursor to 10 mol-% total aluminium did increase the conversion into the product to 20 %.

Both the reduction and oxidation procedures could be scaled and reaction products isolated; acetophenone could be reduced on a 5-mmol scale with 2-propanol using **2** as the catalyst to give *sec*-phenethyl alcohol in 52 % yield after purification (Eqn 3). Similarly, oxidation of 5 mmol of *sec*-phenethyl alcohol to acetophenone could be carried out with **2** as the catalyst in 80 % isolated yield (Eqn 4).



Conclusions

We have demonstrated that aluminium–amidate complexes with varying ligand-to-metal ratios can be prepared systematically through the protonation reaction between trimethylaluminium and amide ligand precursor. We have also demonstrated that salt metathesis is a viable route to install amidate ligands at the aluminium ion. The structural and spectroscopic characterization of the complexes support the ligand-to-metal stoichiometry observed. Our investigations into the catalytic chemistry of Al–amidate complexes have shown that **2–4** are all viable catalyst precursors for the Meerwein–Ponndorf– Verley–Oppenauer manifold for a variety of carbonyl and alcohol substrates. We are currently investigating how changes in the amidate ligand backbone affect the Al–amidate coordination complexes and how these changes manifest in differences in catalytic activity. We are also expanding the use of the Al-amidate complexes in other types of catalytic processes.

Experimental

Physical Measurements

¹H and ¹³C NMR spectra were recorded at ambient temperature in deuterated solvents using a Varian 400 MHz spectrometer (399.78 MHz for ¹H, 100.52 MHz for ¹³C). Chemical shifts were referenced to residual solvent; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Melting points were determined with a DigiMelt SRS capillary melting point apparatus using capillary tubes plugged with silicon grease under nitrogen; values are uncorrected. Elemental analyses were performed either at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer Series II 2400 CHNS analyzer (for 3 and 4) or at Complete Analysis Laboratories on a CHN analyzer by Thermo Electron (for 1-K). Gas chromatography (GC) analyses were carried out on a computerinterfaced Varian 3800 instrument equipped with an flame ionization detector (FID). A 30-m Zebron capillary column with a 0.25-mm inner diameter and a 0.25-µm film thickness was used. The flow rate was $1.2 \,\mathrm{mL}\,\mathrm{min}^{-1}$.

X-Ray Structure Determination

X-Ray diffraction data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å $Mo_{K\alpha}$ radiation. Cell parameters were retrieved using *APEX II* software^[55] and further refined on all observed reflections during integration using *SAINT*+.^[56] Each dataset was treated with *SADABS*^[57] absorption corrections based on redundant multi-scan data. The structures were solved by direct methods and refined by leastsquares method on F^2 using the *SHELXTL* program package.^[58] All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were treated as idealized contributions. Details regarding specific solution refinement for each compound are provided in the following paragraphs.

X-Ray structural analysis for 3: A single colourless plate $(0.41 \times 0.13 \times 0.07 \text{ mm}^3)$ was mounted using NVH immersion oil onto a nylon fibre and cooled to the data collection temperature of 100(2) K. The systematic absences in the data were consistent with the centrosymmetric, monoclinic space group P2/n. The asymmetric unit contains two independent half molecules of 1_2 AlMe for Z' = 1 and Z = 4.

X-Ray structural analysis for 4: A single colourless block $(0.20 \times 0.14 \times 0.06 \text{ mm}^3)$ was mounted using NVH immersion oil onto a nylon fibre and cooled to the data collection temperature of 120(2) K. The systematic absences in the data were consistent with the centrosymmetric, monoclinic space group $C^{2/c}$. The asymmetric unit contains one molecule of $\mathbf{1_3Al}$ and a half molecule of diethyl ether solvent located on the inversion centre.

Preparation of Compounds

All reactions and manipulations were performed under an inert atmosphere (N₂) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X/Q5 Cu-0226S catalyst purifier system. Glassware was dried overnight at 150°C before use. CDCl₃ was purchased from Sigma Aldrich and was degassed and stored over 4 Å molecular sieves before use. [D8]THF was purchased from Sigma Aldrich and dried over sodium metal before use. Toluene, hexanes, and diethyl ether were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexanes) or two columns of neutral alumina (for toluene and Et₂O). Celite was purchased from Sigma Aldrich and was dried under reduced pressure at 250°C for 48 h before use. N-tert-Butylbenzamide (1-H) was prepared through the nucleophilic acyl substitution reaction of benzyl chloride with tert-butyl amine according to literature methods.^[18] Complex 2 was prepared via a protonolysis route between **1-H** and trimethylaluminium as reported by Lin et al.^[31] on a 5.6-mmol total aluminium scale in 74 % yield. 2-Propanol was dried and distilled over calcium oxide before use. Pivaldehyde was dried and distilled over CaH₂ before use. 4-Phenyl-3-buten-2-ol was prepared by sodium borohydride reduction of 4-phenyl-3-buten-2-one. Silica gel (230-400 mesh) was purchased from Fisher Scientific. All other reagents were purchased from commercial sources and used as received.

K(t-BuNCOPh) (1-K)

An Erlenmeyer flask equipped with a magnetic stir bar was charged with *N*-tert-butylbenzamide (2.50 g, 14.1 mmol). The reagent was dissolved in diethyl ether (50 mL). To the rapidly stirring solution was added KN(SiMe₃)₂ (2.80 g, 14.1 mmol) in small portions over 0.5 h. The resulting mixture was stirred for 12 h at room temperature after which a white solid was collected by filtration over a medium-porosity frit. The solid was washed with diethyl ether (25 mL) followed by hexanes (25 mL) and then dried under vacuum. **1-K** was collected as a white powder (2.67 g, 88 %). $\delta_{\rm H}$ ([D8]THF) 8.11(2H, m), 7.12 (3H, m), 1.33 (9H, s, C(*CH*₃)₃). $\delta_{\rm C}$ ([D8]THF) 164.5 (*C*=O), 128.5, 127.1, 126.8, 51.6 (N-*C*(CH₃)₃), 31.6 (N-*C*(*CH*₃)₃). Anal. Calc. for C₁₁H₁₄KNO: C 61.36, H 6.55, N 6.50. Found: C 57.97, H 7.34, N 6.48 %.

{ $[\kappa^2-N,O-(t-BuNCOPh)]AlMe_2$ } (2)

K(t-BuNCOPh) (1.20 g, 5.6 mmol) was added to an Erlenmeyer flask equipped with a magnetic stir bar. The reagent was suspended in toluene (50 mL) after which dimethylaluminium chloride was added as a 1.0 M solution in hexanes (5.6 mL, 5.6 mmol) using a syringe. The reaction vessel was sealed and the reaction mixture was stirred at room temperature for 12 h after which it was filtered over a Celite-padded frit and washed with toluene (10 mL). Solvents were removed and crude product was dissolved in boiling hexanes (50 mL) and filtered over a Celite-padded frit. Solvents were removed from the filtrate and the crude product was dissolved in toluene and filtered over a Celite-padded frit, and the filtrate was concentrated to ~ 20 mL. Colourless crystals were obtained after 24 h at -25° C, and were collected by filtration, washed with cold toluene $(3 \times 5 \text{ mL})$, and dried under vacuum (0.65 g, 50 %). The ¹H and ¹³C NMR data of this material match those reported by Lin et al. as follows.^[31] δ_H (CDCl₃) 7.41 (10H, m, Ph), 1.09 (18H, s, C(CH₃)₃), -0.87 (12H, s, Al-CH₃). δ_C (CDCl₃) 167.8 (C=O), 133.8, 129.8, 128.1, 127.2, 52.9 ((C(CH₃)₃), 31.1 (C(CH₃)₃), -8.5 (Al-CH₃).

$[\kappa^2-N,O-(t-BuNCOPh)]_2AIMe(3)$

A Schlenk flask equipped with a magnetic stir bar was charged with *N-tert*-butylbenzamide (1.99 g, 11.2 mmol) and hexane (50 mL). A 1.0 M solution of trimethylaluminium in heptane (5.6 mL, 5.6 mmol) was added to the stirring solution

and the reaction vessel was sealed. The reaction was heated at 68°C for 24 h after which volatiles were removed under vacuum. Crude materials were dissolved in toluene and filtered over a Celite-padded frit, and the filtrate was concentrated to ~20 mL. Colourless crystals were obtained after 24 h at -25° C, and were collected by filtration, washed with cold toluene (3 × 5 mL), and dried under vacuum (1.76 g, 79%), mp 141–143°C. $\delta_{\rm H}$ (CDCl₃) 7.42 (10H, m, Ph), 1.40 (18H, s, C(CH₃)₃), -0.55 (3H, s, Al-CH₃). $\delta_{\rm C}$ (CDCl₃) 177.0 (C=O), 135.4, 129.4, 128.1, 126.8 (Ph), 51.8 (N-C(CH₃)₃), 31.3 (N-C(CH₃)₃), -11.7 (Al-CH₃). Anal. Calc. for C₂₃H₃₁AlN₂O₂: C 70.03, H 7.92, N 7.10. Found: C 69.89, H 7.94, N 7.50%.

$[\kappa^2-N,O-(t-BuNCOPh)]_3AI$ (4)

A Schlenk flask equipped with a magnetic stir bar was charged with *N-tert*-butylbenzamide (2.99 g, 16.9 mmol) and hexane (50 mL). A solution of trimethylaluminium in heptane (5.6 mL, 5.6 mmol) was added to the stirring solution and the reaction vessel was sealed. The reaction was heated at 100°C for 24 h after which volatiles were removed under vacuum. Crude materials were dissolved in ether and filtered over a Celitepadded frit, and the filtrate was concentrated to ~20 mL. Colourless crystals were obtained after 24 h at -25° C, which were collected by filtration, washed with cold ether (3 × 5 mL), and dried under vacuum (1.69 g, 54 %), mp 130–134°C. $\delta_{\rm H}$ (CDCl₃) 7.41 (15H, m, Ph), 1.26 (27H, s, C(CH₃)₃). $\delta_{\rm C}$ (CDCl₃) 160.3 (C=O), 136.1, 128.9, 128.0, 126.7 (Ph), 52.0 (N-*C* (CH₃)₃), 31.9 (N-C(CH₃)₃). Anal. Calc. for C₃₃H₄₂AlN₃O₃: C 71.33, H 7.62, N 7.56. Found: C 71.29, H 7.46, N 7.62 %.

General Procedure for the Al–Amidate-Catalyzed Reduction of Ketone Substrates by 2-Propanol

An 8-mL vial equipped with a magnetic stirring bar was charged with pre-catalyst (0.05 mmol for **2**; 0.01 mmol for **3** or **4**) and toluene (4 mL). 2-Propanol (610 μ L, 8.0 mmol) was added and the vial was capped with a Teflon-lined silicone septum, and the reaction was stirred for 0.5 h. Carbonyl substrate (1.0 mmol) was added neat and the reaction was heated to 50°C. After 24 h, an aliquot (100 μ L) of the reaction was collected with a gas-tight syringe, loaded onto a plug of alumina, rinsed with methanol (15 mL), and analyzed directly by GC. The GC retention times of the products were confirmed with those of commercially available samples.

General Procedure for the Al–Amidate-Catalyzed Oxidation of Alcohol Substrates by Pivaldehyde

An 8-mL vial equipped with a magnetic stirring bar was charged with pre-catalyst (0.025 mmol for **2**; 0.05 mmol for **3** or **4**) and toluene (4 mL). Alcohol (1.0 mmol) was added neat and the vial was capped with a Teflon-lined silicone septum, and the reaction was stirred for 0.5 h. Pivaldehyde (163 μ L, 1.5 mmol or 325 μ L, 3.0 mmol) was added and the reaction was stirred at room temperature. After 3 h, an aliquot (100 μ L) of the reaction was collected with a gas-tight syringe, loaded onto a plug of alumina, rinsed with methanol (15 mL), and analyzed directly by GC. The GC retention times of the products were confirmed with those of commercially available samples.

Synthesis of sec-Phenethyl Alcohol

To a flask equipped with a magnetic stir bar was added 2 (0.12 g, 0.25 mmol) and toluene (25 mL). 2-Propanol (3.0 mL, 40.0 mmol) was added to the solution and the reaction was

stirred for 0.5 h after which acetophenone (0.60 g, 5.0 mmol) was added. The reaction vessel was sealed and the reaction heated to 50°C with stirring. After 24 h, the reaction was cooled to room temperature and quenched with 3 M HCl (25 mL). The resultant mixture was extracted with diethylether $(3 \times 50 \text{ mL})$ and the combined organics were washed with saturated sodium bicarbonate (3 \times 25 mL) and brine (25 mL), and then dried over anhydrous Na₂SO₄. The drying agent was removed by filtration and solvents were removed from the filtrate under reduced pressure to give the crude products. The product was purified by column chromatography on silica gel with hexane/ethyl acetate (8:2) eluent.^[59] sec-Phenethyl alcohol was collected as a colourless oil (0.32 g, 52 %) and characterized by ¹H NMR spectroscopy, with the data matching that of commercial samples. $\delta_{\rm H}$ (CDCl₃) 7.34 (5H, m, Ph), 4.90 (1H, q, *J*7, *H*C-OH), 1.78 (1H, b, OH), 1.50 (3H, d, J 7, CH₃).

Synthesis of Acetophenone

To a 125-mL flask equipped with a magnetic stir bar was added 2 (0.058 g, 0.125 mmol). Toluene (25 mL) was added to the flask followed by sec-phenethyl alcohol (0.61 g, 5.0 mmol). The resultant solution was stirred for 0.5 h after which pivaldehyde (1.63 mL, 15.0 mmol) was added. The reaction was stirred for 3 h at room temperature after which the reaction was guenched with 3 M HCl (25 mL). The resultant mixture was extracted with diethylether $(3 \times 50 \text{ mL})$ and the combined organics were washed with saturated sodium bicarbonate $(3 \times 25 \text{ mL})$ and brine (25 mL), and then dried over anhydrous Na₂SO₄. The drying agent was removed by filtration and solvents were removed from the filtrate under reduced pressure to give the crude products. The product was purified by column chromato graphy on silica gel with hexane/ethyl acetate (8:2) eluent.^[59] Acetophenone was collected as a colourless oil (0.48 g, 80 %) and characterized by ¹H NMR spectroscopy, with the data matching that of commercial samples. $\delta_{\rm H}$ (CDCl₃) 7.96 (2H, d, J 8, Ph), 7.56 (1H, t, J 8, Ph), 7.46 (2H, t, J 8, Ph), 2.60 (3H, s, CH₃).

Supplementary Material

¹H and ¹³C NMR spectra of compounds **2**, **3**, and **4**, GC methods and traces for the carbonyl and alcohol substrates, and ¹H NMR spectra of *sec*-phenethyl alcohol and acetophenone from the large-scale reactions are available from the Journal's website. CCDC 1020534 and CCDC 1020533 contain the supplementary crystallographic data for complexes **3** and **4**. The data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or data can be obtained from http://www.ccdc.cam.ac.uk/data_request/cif.

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