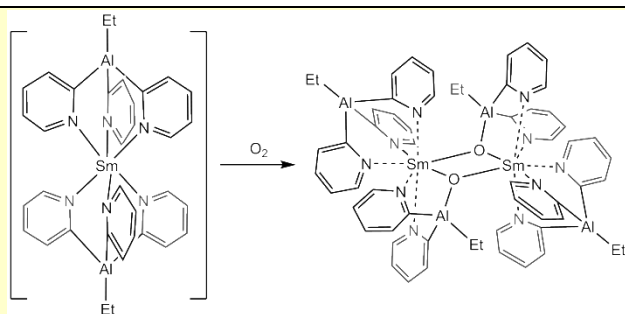


Formation of a heterometallic Al^{III}/Sm^{III} complex involving a novel [EtAl(2-py)₂O]²⁻ ligand (2-py = 2-pyridyl)

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ABSTRACT: Controlled O₂-oxidation of the Sm(II) sandwich compound [{EtAl(2-py)₃]₂Sm} (**1a**) gives the Sm(III)/Al(III) compound [{EtAl(2-py)₃}{EtAl(2-py)₂O}Sm]₂ (**2**), containing the novel multifunctional dianionic ligand [EtAl(2-py)₂O]²⁻. The formation of an O-bridged Al-O-Sm arrangement in the structure of **2** is potentially relevant to the catalytic epoxidation of styrene with dry air using heterobimetallic sandwich compounds like **1a**.

INTRODUCTION

The coordination chemistry of neutral *tris*-pyridyl ligands of the type [Y(2-py)₃] (Fig. 1, **A**)¹ has been investigated intensively in the past twenty or so years where Y is a non-metallic bridgehead atom or group [CX (X = H,² OR, NH₂³), N,⁴ P, or P=O⁵]. It has only been relatively recently, however, that attention has turned to Group 13 and 14 congeners containing metallic or semi-metallic bridgeheads.⁶⁻⁹ In addition to providing ligands with expanded bites, the incorporation of metallic and semi-metallic atoms provides the potential for redox activity and variable oxidation states at the bridgehead.^{6,7} The group 13 ligands [RAl(2-py)₃]⁻ (Fig. 1, **B**) are of particular interest in that they are the only anionic members of the *tris*-pyridyl family.⁹ Thus, like closely-related *tris*-pyrazolylborate¹⁰ and poly(pyrazolyl)aluminates,¹¹ the *tris*-pyridyl aluminates exhibit a strong affinity for metal complexation. The coordination of these aluminates to other metals provides a very simple systematic route to often useful heterometallic Al^{III} complexes, like the heterometallic sandwich compound [{MeAl(2-py)₃]₂Fe} (isoelectronic with ferrocene) which has been shown to be a highly active catalyst for the selective epoxidation of styrene using dry air.¹²

We present here a study of the reaction of O₂ with the Sm(II) sandwich compound [{EtAl(2-py)₃]₂Sm} (**1a**), showing that the product is the Sm(III)/Al(III) compound [{EtAl(2-py)₃}{EtAl(2-py)₂O}Sm]₂ (**2**), containing the novel multifunctional dianionic ligand [EtAl(2-py)₂O]²⁻ (Fig. 1, **C**). This selective reaction provides a potential explanation for the catalytic activity of the previously mentioned, closely related Fe(II) sandwich complex in the epoxidation of styrene.

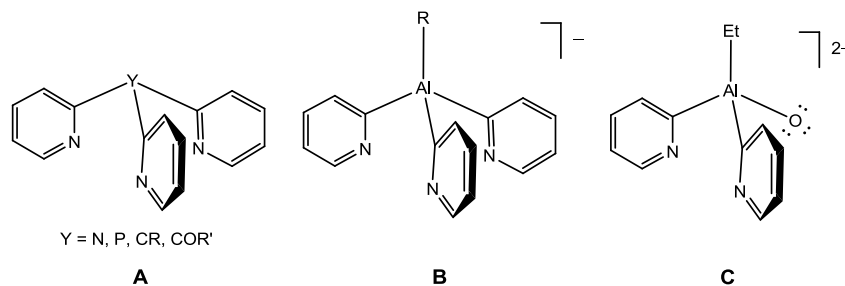


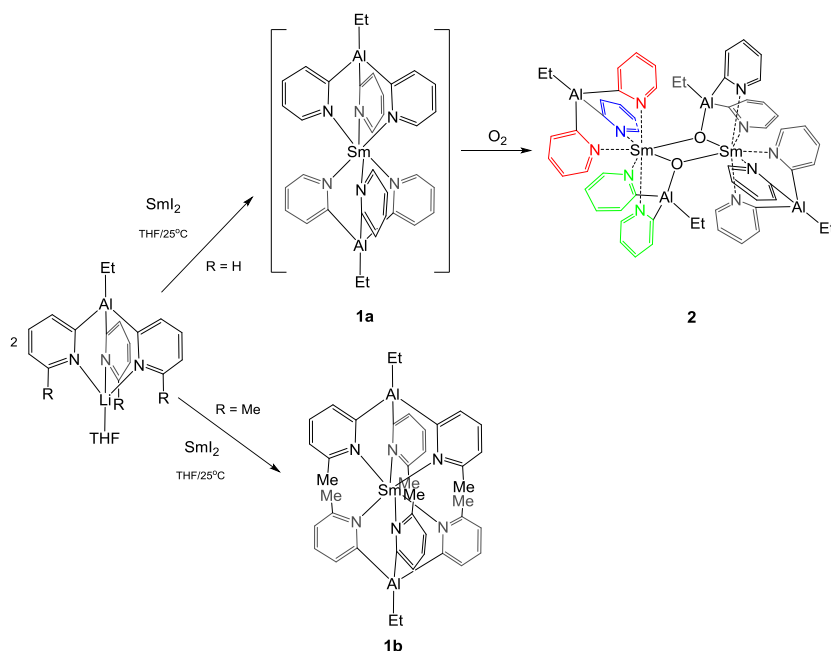
Figure 1 a) Framework found in the family of tris-2-pyridyl ligands, b) the tris-2-pyridyl aluminate family of ligands, c) the new $[\text{EtAl}(\text{2-py})_2\text{O}]^{2-}$ anion in **2**.

RESULTS AND DISCUSSION

In preliminary studies, the room-temperature 2 : 1 stoichiometric reaction of the lithium aluminate precursor $[\text{EtAl}(\text{2-py})_3\text{Li}\cdot\text{THF}]^{\text{9d}}$ with SmI_2 was undertaken in THF in an attempt to obtain the Sm(II) sandwich compound $[\{\text{EtAl}(\text{2-py})_3\}_2\text{Sm}]$ (**1a**). However, **1a** proved to be so air-sensitive that it could not be isolated in solid/crystalline form. Indeed, storage of the reaction solution at ambient temperature led to gradual fading of the initial intense deep-purple color to yellow and the formation of a crop of colorless crystals after several days.¹³ These were identified by X-ray crystallography as the Al(III)/Sm(III) dimer $[\{\text{EtAl}(\text{2-py})_3\}\{\text{EtAl}(\text{2-py})_2\text{O}\}\text{Sm}]_2$ (**2**) (see later discussion). *In situ* ^1H NMR spectroscopic experiments support the conclusion that **2** is formed by O_2 oxidation rather than H_2O hydrolysis, since the addition of H_2O to **1a** results in hydrolysis to pyridine whereas the addition of O_2 leads to the formation of detectable amounts of **2**. It is clear from these experiments, however, that **2** is only formed in low yield. Subsequently it was shown that crystalline **2** can be obtained reproducibly by the reaction of the *in situ* prepared solution of **1a** with dry excess O_2 gas in low (ca. 3-6%) crystalline yield (Scheme 1).

Elemental analysis of **2** was hampered by contamination of crystalline samples with LiI and toluene (ca. two molecules of each per molecule of **2**). However, despite the presence of (f^7) Sm^{3+} , the ^1H and ^{13}C NMR spectra of **2** exhibit relatively little paramagnetic shifting or signal broadening. Significantly, the ^1H NMR spectra in THF or toluene show the presence of three separate 2-py environments in a relative ratio of 2 : 2 : 1, consistent with the retention of the solid-state structure in solution (see the color-coded structural formula in Scheme 1). This conclusion and the full assignment of the ^1H and ^{13}C resonances are supported by in-depth 2D NMR experiments (^1H - ^{13}C HMBC, ^1H - ^{13}C HMQC, ^1H - ^1H COSY and ^1H - ^1H NOESY) (see experimental section and supporting information).

Scheme 1. Synthetic routes to the new complexes 1b and 2. The color-coding of the structure of 2 indicates the presence of three 2 : 2 : 1 2-py environments.



In order to verify the intermediacy of the sandwich compound **1a** in the formation of **2**, the reaction with SmI_2 was repeated using the more sterically hindered precursor $[\text{EtAl}(6\text{-Me-}2\text{-py})_3\text{Li}\cdot\text{THF}]$,^{9d} reasoning that the presence of the 6-Me substituents on the aluminate ligand might result in steric shielding of the Sm(II) ion and greater resistance to oxidation. This strategy proved successful and storage of the 2 : 1 reaction of $[\text{EtAl}(6\text{-Me-}2\text{-py})_3\text{Li}\cdot\text{THF}]$ with SmI_2 at ambient temperature produced black crystals of the sandwich compound $[\{\text{EtAl}(6\text{-Me-}2\text{-py})_3\}_2\text{Sm}]$ (**1b**) in *ca.* 30% crystalline yield (Scheme 1).

The ^1H and ^{13}C NMR spectrum of **1b** in THF exhibits paramagnetic shifting of the resonances. However, these resonances are nonetheless sharp enough to allow the unambiguous assignment of *all* of the ^1H and ^{13}C environments, with the aid of 2-D NMR experiments (see experimental section and the supporting information). These studies strongly support the conclusion that the solid-state sandwich structure of **1b** (later confirmed by single-crystal X-ray analysis) is maintained in solution. The assignment of the ^1H NMR spectrum of **1b** is illustrated in Fig. 2, where it is compared to the precursor $[\text{EtAl}(6\text{-Me-}2\text{-py})_3\text{Li}\cdot\text{THF}]$. An interesting feature is the particularly strong influence of the Sm^{2+} ion on the chemical shifts for the 6-Me groups of the $[\text{EtAl}(6\text{-Me-}2\text{-py})_3]^-$ ligand (shifted upfield to δ -9.0) and the Al-bonded Et-group [shifted downfield to δ 9.4 (q.) and 6.4 (t.)]. Also worthy of note is the down-field shift of the Al-bonded C-atom of the pyridine ligands in the ^{13}C NMR spectrum (δ 320) (see experimental section and supporting information).

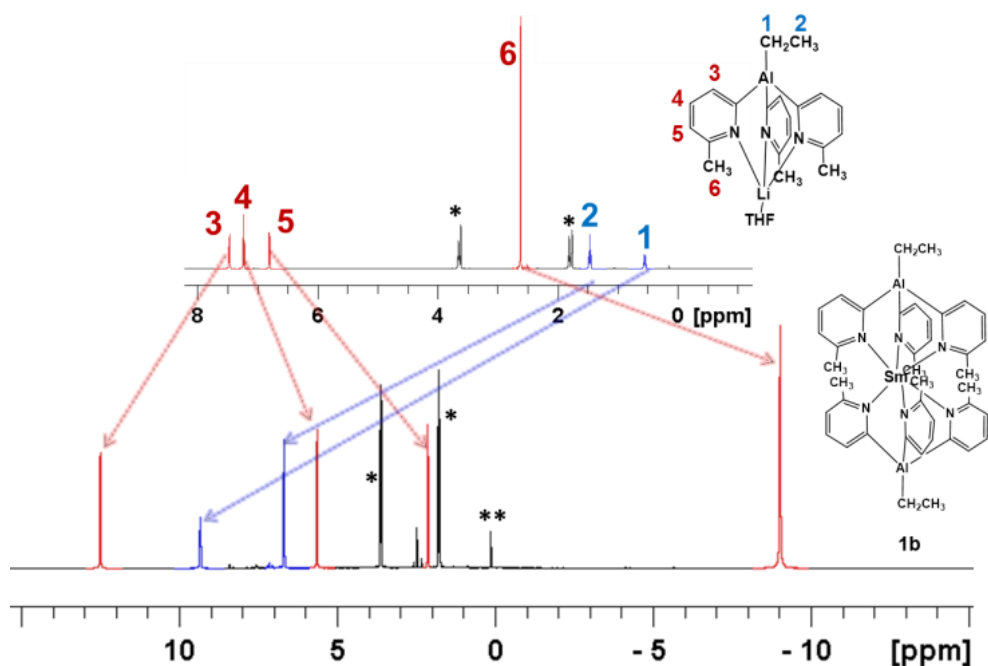


Fig. 2 ^1H NMR spectrum of **1b** in THF-d_8 (bottom) and the spectrum of the precursor $[\text{EtAl}(6\text{-Me-}2\text{-py})_3\text{Li}\cdot\text{THF}]$ in THF-d_8 (top) (note that the scale is different in both spectra). [* residual $\text{THF-d}_8/\text{THF}$, ** silicon grease].

Interestingly, prolonged reaction of **1b** with O_2 does not result in the formation of an oxo-complex analogous to **2**. Instead a mixture of products is observed by ^1H NMR spectroscopy, from which a small quantity of crystals of the bipyridine complex [6,6'-dimethyl-2,2'-bipyridyl-Li] were isolated. The coupling of the 6-Me-2-py ligands of **1b** in the oxidation reaction provides evidence of a radical pathway in this reaction, and potentially in the oxidation of **1a** to **2**.

The solid-state structure of **2** is that of a centrosymmetric dimer composed of a central $\text{Sm}_2(\mu\text{-O})_2$ ring unit (Fig. 3). The metal ions are coordinated by an *intact* $[\text{EtAl}(2\text{-py})_3]^-$ anion (**B**, R = Et) as well as by a $[\text{EtAl}(2\text{-py})_2\text{O}]^{2-}$ dianion (**C**). Compound **2** bears a close similarity to the Sm^{III} pyrazolylborate complex $[\{\text{HB}(\text{pz}^{\text{Me}2})_3\}\{\text{HB}(\text{pz}^{\text{Me}2})_2\text{O}\}\text{Sm}]_2$ ($\text{pz}^{\text{Me}2}$ = 3,5-dimethylpyrazole), containing both an *intact* $[\text{HB}(\text{pz}^{\text{Me}2})_3]^-$ and an O-substituted $[\text{HB}(\text{pz}^{\text{Me}2})_2\text{O}]^{2-}$ ligand.^{14,15} Unlike the $[\text{EtAl}(2\text{-py})_2\text{O}]^{2-}$ dianion of **2**, however, this O-substituted boron dianion is thought to result from hydrolysis in the presence of adventitious water. The ligand behaviour of the $[\text{EtAl}(2\text{-py})_2\text{O}]^{2-}$ dianion in **2** is related to that found in a series of complexes in which β -diketimide $[(\text{HC}^{\text{Me}}\{\text{C}(\text{Me})\text{NAr}\}_2)\text{Al}(\text{Me})(\text{O})]^-$ anions function as monodentate or bidentate O-donors to a range of metals (commonly forming Al-O-metal heterometallic arrangements).¹⁶

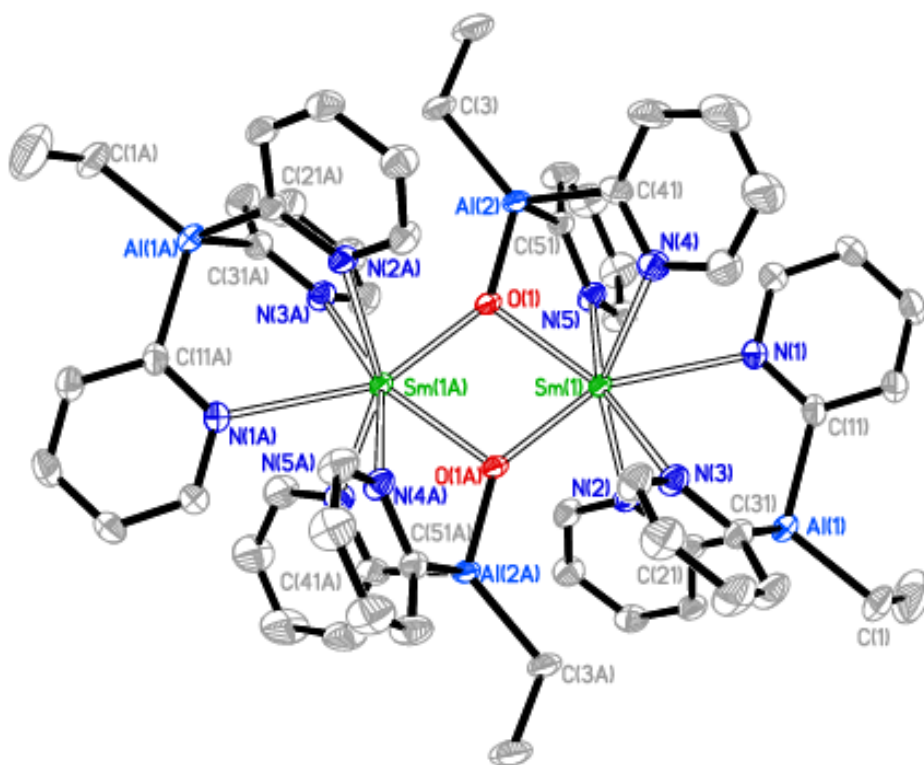


Fig. 3 Dimer structure of **2**. Thermal ellipsoids are drawn at the 40 % probability level. H-atoms and the lattice solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°); Sm(1)–O(1) 2.209(2), Sm(1)–O(1A) 2.283(2), Sm(1)–N(1) 2.697(3), Sm(1)–N(2) 2.578(2), Sm(1)–N(3) 2.564(3), Sm(1)–N(4) 2.577(3), Sm(1)–N(5) 2.585(3), Sm(1)⋯Sm(1A) 3.6226(3), Al(1)–C(1,3) 1.982(3)–1.988(4), Al(1,2)–Cpy 2.013(4)–2.039(3), Al(2)–O(1) 1.762(2), O(1)–Sm(1)–O(1A) 72.49(8), Sm(1)–O(1)–Sm(1A) 107.51(8), O(1)–Al(2)–Cpy 97.7(1)–98.1(1), Cpy–Al(2)–Cpy 107.4(1), Cpy–Al(1)–Cpy 104.6(1)–106.5(1).

Each of the Sm³⁺ cations in the structure of **2** is coordinated by all three N atoms of a [EtAl(2-py)₃][−] anion as well as by the two 2-py N atoms of a [EtAl(2-py)₂O]^{2−} dianion and the two μ₂-O atoms within the central Sm₂(μ-O)₂ ring. This results in both of the symmetry-related metal ions having a seven coordinate, capped trigonal prismatic coordination geometry in which one of the coordinating N-atoms of a [EtAl(2-py)₃][−] anion [N(1)] forms the cap. The N–Sm [range 2.564(3)–2.644(3) Å] and O–Sm bond lengths [range 2.209(2)–2.283(2) Å] fall in similar ranges to those found in the previously reported, closely-related pyrazolylborate complex [{HB(pz^{Me2})₃}{HB(pz^{Me2})₂O}Sm]₂ (pz^{Me2} = 3,5-dimethylpyrazole) mentioned earlier [N–Sm range 2.519(2)–2.590(2), O–Sm range 2.239(1)–2.317(1) Å],¹⁴ which also contains Sm^{III} in a capped trigonal pyramidal geometry. The metric parameters found in the [Sm(μ-O)]₂ ring unit of **2** are also similar to those present in the related pyrazolylborate complex, only with greater O–Sm–O angles at the Sm^{III} centres of **2** [73.17(7)°] resulting in a much shorter Sm⋯Sm separation [3.6226(3) Å; cf 3.7142(3) Å in [{HB(pz^{Me2})₃}{HB(pz^{Me2})₂O}Sm]₂].¹⁴ The Al–O bonds in the [EtAl(2-py)₂O]^{2−} dianion of **2** [1.762(2) Å] are similar to those found in complexes containing the [(HC≡C(Me)[−]NAr]₂)Al(Me)(O)][−] anion [range 1.690(6)–1.77(1) Å] and typical of Al–O single bonds.¹⁶

The structural characterisation of the Sm(II) sandwich compound [{EtAl(6-Me-2-py)₃]₂Sm] (**1b**) (Fig. 4a) supports the intermediacy of [{EtAl(2-py)₃]₂Sm] (**1a**) in the formation of **2**. The structure is as expected for a compound of this type, being similar to the closely-related recently characterized Ca complex [{EtAl(6-Me-2-py)₃]₂Ca].^{9d} The complex is also related to a number of lanthanide(II) sandwich complexes containing [E(py')₃][−] anionic ligands (E = Sn, Pb; py' = 2-pyridyl groups bearing various substituents).¹⁷ It is notable, however, that these ligands only appear to be robust enough to coordinate the most stable Eu(II) (f⁷) and Yb(II) (f¹⁴) ions and that an attempt to coordinate Sm(II) using the Sm(II) anions [Et₃M–Sm(5-Me-2-py)₃][−] (M = Ga, In) resulted in extensive rearrangement of the ligand and oxidation Sm(II) to Sm(III).^{17c} Presumably, one of the key factors responsible for the ability of the [EtAl(6-Me-2-py)₃][−] ligand to coordinate Sm²⁺ is the

redox stability of its Al(III) bridgehead. As illustrated in Fig. 4b, the 6-Me-substituents of the pyridyl ring units of the [EtAl(6-Me-2-py)₃]⁻ ligands of **1b** interdigitate, resulting in the steric shielding of the Sm²⁺ ion. This situation is identical to that found in the Ca complex [{EtAl(6-Me-2-py)₃]₂Ca}, and provides a plausible reason as to why **1b** (based on qualitative observations) is apparently more stable to aerial oxidation than unsubstituted **1a**.

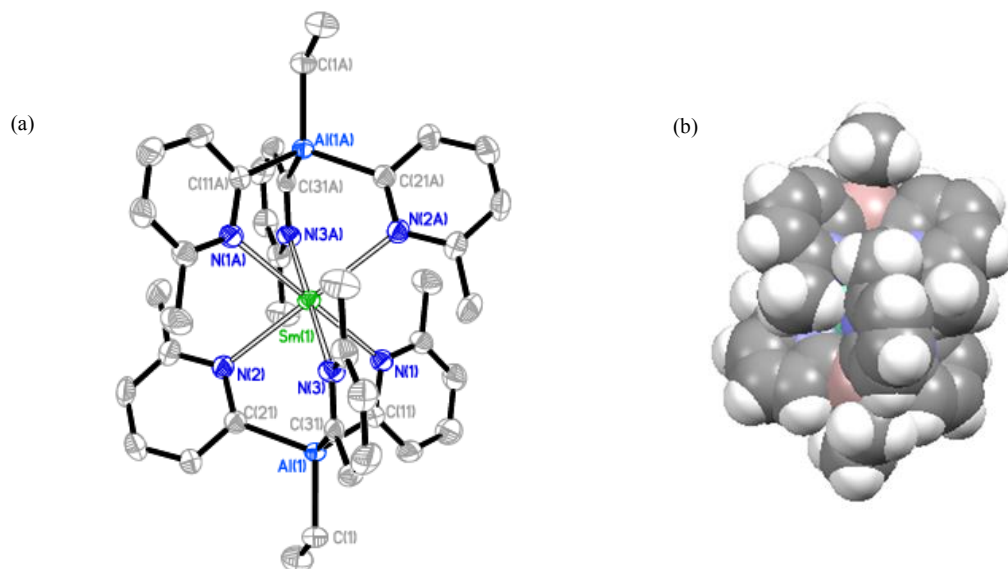


Figure 4 a) Dimer structure of **1b**. Thermal ellipsoids are drawn at the 40 % probability level. H-atoms and the lattice solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)-N(1) 2.668(3), Sm(1)-N(2) 2.666(3), Sm(1)-N(3) 2.721(3), Al(1)-C(1) 1.981(4), N-Sm-N range 88.45(9)-90.98(9), Cpy-Al-Cpy range 105.8(2)-113.1(1), Al-N-Sm range 119.9(3)-125.0(3); b) space-filling diagram, showing the interdigitation of the 6-Me-groups (the view is the same as that shown in (a)).

CONCLUSION

In summary, we have shown that reaction of molecular O₂ with the Sm(II) sandwich compound [{EtAl(2-py)₃]₂Sm (**1a**) gives the Al(III)/Sm(III) complex [{EtAl(2-py)₃}{EtAl(2-py)₂O}Sm]₂ (**2**), containing a [EtAl(2-py)₂O]²⁻ ligand. This study is not just of interest in regard to the formation of this novel ligand arrangement, but also in respect to its relevance to the previously reported application of the Al(III)/Fe(II) sandwich compound [{MeAl(2-py)₃]₂Fe in the catalytic epoxidation of styrene using dry air. In this context **2** can be regarded as a potential model intermediate in this type of reaction by which molecular O₂ is transferred into active O-atoms prior to reaction with the alkene. The synergic involvement of both of the metal centers in O₂ activation and transfer would be an interesting feature of this reaction. Further investigations of the reactions of sandwich compounds of this type with O₂ are underway, as is the study of the reactions of species like **2** with alkenes in order to elucidate the mechanism of epoxidation further.

EXPERIMENTAL SECTION

General Methods. All syntheses and manipulations were carried out on a vacuum-line under an argon atmosphere or with the aid of a N₂-filled glove box (Saffron type α). Toluene and THF were dried under nitrogen over Na and Na/benzophenone, respectively. The lithium precursors, [EtAl(6-Me-2-py)₃Li·THF] and [EtAl(2-py)₃Li·THF] were synthesized as previously reported.^{9b,9c} Elemental analysis was obtained on a Perkin Elmer 240 Elemental Analyser. ¹H, ¹³C{¹H}, ⁷Li and ²⁷Al NMR spectra were recorded on a Bruker Advance 500 MHz Cryo spectrometer. Direct observation of Al-bonded C atoms (Al-CH₂ and Al-C²py) in the ¹³C{¹H} spectra, although easy through ¹H-¹³C HMQC and ¹H-¹³C HMBC experiments, was challenging due to their low intensity broad resonances and typically required the use of line broadening (lb) of 15-20Hz in the processing of the spectra. The unambiguous assignment of ¹H and ¹³C NMR resonances was accomplished with the help of additional 2D NMR experiments (¹H-¹H COSY, ¹H-¹³C HMQC, ¹H-¹³C HMBC and ¹H-¹H NOESY experi-

ments). For instance, H³ pyridinic protons were unambiguously identified on the basis of the ¹H-¹³C- heteronuclear multiple-bond correlation spectroscopy (HMBC) and ¹H-¹H Nuclear Overhauser effect spectroscopy (NOESY) spectra. ¹H-¹H NOESY experiments were particularly informative not only in the correct assignment of H³ py (the only pyridinic proton showing a cross peak with AlCH₂CH₃ protons) but also in confirming the presence of an Et-Al-Py linkage. In particular, in the case of **1b** the ¹H-¹³C HMBC spectrum (see Fig. S4, SI) showed a crosspeak correlating the broad carbon peak at 321.38 ppm (C² py), with a doublet at 12.49 ppm in the ¹H spectrum (H³ py), resulting from a 2-bond ¹H-¹³C coupling. An additional support of this assignment is the fact that the ¹H-¹H NOESY experiment (Fig. S5, SI) showed crosspeaks between the H³ pyridinic protons and the protons of Al-CH₂CH₃, evidencing their spatial proximity. No other cross peak between pyridinic and Al-CH₂CH₃ protons was observed. In the case of **2**, three separate 2-pyridyl environments in a relative ratio of 2 : 2 : 1 were clearly observed in the ¹H-¹H COSY spectrum (see Fig. S10, SI), along with two ethyl environments. Again, the correct assignment of the resonances of each system was done with the help of 2D NMR experiments. The H³ py resonance of each of the three pyridyl rings was identified on the basis of ¹H-¹³C HMBC and ¹H-¹H NOESY experiments (Fig. S11-S12, SI), as previously illustrated for compound **1b**. Importantly, the presence of cross-peaks in the ¹H-¹H NOESY spectrum (Fig. S12, SI) between H³ py and H³ py' with only one of the two sets of ethyl resonances, while the H³ (py'')₂O protons only showed cross peaks with the other set of ethyl resonances, allowed the correct assignment of the three different pyridyl systems (py, py' and (py'')₂O refer, respectively, to the pyridyl environments shown in blue, red and green in the figures in the SI, see Scheme 1 and S1 in the SI). Compound **2** was only slightly soluble in toluene preventing its study by ¹³C NMR spectroscopy. Reported ¹³C signals for **2** in d₈-toluene were extracted from a ¹H-¹³C HMQC experiment. While compound **2** was more soluble in THF, it was found to be less stable in THF than in toluene, as evidenced by the presence of a significant amount of free pyridine and other unidentified impurities in the spectra recorded in d₈-THF. Therefore, all of the NMR spectra shown in the SI were carried out in d₈-toluene with the exception of the ¹H-¹³C HMBC experiment shown in Fig. S12 of the SI which was carried out in d₈-THF, showing a ¹³C{¹H} spectrum as the 'external projection'.

X-ray Crystallographic Studies. Data were collected on a Nonius Kappa CCD Diffractometer equipped with an Oxford Cryostream cooling device or, in the case of **1b**, on Bruker SMART X2S diffractometer using a monochromatic Mo-K α microfocus source with a BREEZE CCD detector, and equipped with an Oxford Cryosystem Desk 65 Top cooler at 200 K. Crystals were mounted directly from solution using perfluorohydrocarbon oil¹⁸ to prevent atmospheric oxidation, hydrolysis and solvent loss. Data were collected by Bruker GIS, processed using Bruker SAINT and were refined using the SHELXTL-97 suite of programs by full-matrix least squares on F².¹⁹ Details of the data collections and structural refinements are given in Table S1 in the SI.

Synthesis of **1b** and **2**

Synthesis of 1b. In a glove box, [EtAl(6-Me-2-py)₃Li·THF] (200 mg, 0.49 mmol) and SmI₂ (102 mg, 0.25 mmol) were added to a Schlenk tube which was later transferred to a vacuum line. After the addition of THF (15ml) the mixture was stirred at room temperature for 36h and then filtered through celite[®]. After that, to the resultant deep-purple solution 20 ml of toluene was added. The majority of the solvent was removed *in vacuo* until the precipitation of a black solid was observed, which was heated gently back into solution. The solution was then stored at -15°C to give extremely air-sensitive black crystals of **1b** (60mg, 0.074 mmol, 30.2%). Elem. anal. calc. for **1b**: C 58.9, H 5.7, N 10.3; found: C 57.9, H 5.7, N 10.2 %. ¹H NMR (298K, d₈-THF, 500 MHz), δ = 12.49 (d, JHH = 7.5 Hz, 6H, H³ py), 9.31 (q, JHH = 7.8 Hz, 4H, CH₂), 6.66 (t, J HH = 8.0 Hz, 6H, CH₂CH₃), 5.61 (t, JHH = 7.1 Hz, 6H, H⁴ py), 2.11 (d, JHH = 7.0 Hz, 6H, H⁵ py), -9.05 (s, 18H, CH₃). ¹³C{¹H} NMR (298K, d₈-THF, 100.6 MHz), δ = 321.38 (br, C² py), 193.43 (C⁶ py), 156.98 (C³py), 152.88 (C⁴ py), 70.16 (C⁵ py), 66.63 (CH₃, overlapped with d₈-THF resonance), 34.84 (br, AlCH₂), 18.18 (AlCH₂CH₃). ²⁷Al NMR (298K, d₈-THF, 130.3 MHz, rel. solution of AlCl₃·6H₂O/D₂O), δ = 154.48 (br, s). Note: compound **1b** can also be prepared by reacting equimolar amounts of [EtAl(6-Me-2-py)₃Li·THF] and SmI₂ (0.49 mmol) in THF (5 ml) and toluene (20 ml).

Synthesis of 2. In a glove box, [EtAl(2-py)₃Li·THF] (181 mg, 0.49 mmol) and SmI₂ (102 mg, 0.25 mmol) were added to a Schlenk tube which was later transferred to a vacuum line. After the addition of THF (15ml) the mixture was stirred at room temperature for 36h. To the resultant very dark deep-blue solution, portions of 0.2 ml of O₂ were injected, allowing ca. 30 min between injections, until the formation of a lighter, brownish mixture was observed (typically a total volume of 1-3ml of O₂ was necessary). Filtration of the mixture through celite[®] and addition of toluene (20ml) gave a yellow solution. The majority of the solvent was removed *in vacuo* until the precipitation of a white solid was observed, which was heated gently back into solution. The solution was then stored at -15°C to give colorless crystals of **2** (5-10 mg, 0.0037-0.0074 mmol, 3-6%). Elem. anal. calc. for 2·2tol·2lil: C 48.3, H 4.3, N 7.8; found: C 47.7, H 4.6, N 7.5 %. We also note the presence of pyridine contamination in samples (as seen in the NMR spectra). ¹H NMR (298K, d₈-toluene, 500 MHz), δ = 13.64 [d, JHH = 4.5 Hz, 2H, H⁶ py], 9.74 [d, JHH = 7 Hz, 2H, H³ py], 8.96 [d, JHH = 7.5 Hz, 4H, H³ py'], 8.55 [d, JHH = 7.3 Hz, 4H, H³ (py'')₂O], 8.07 [t, JHH = 7.2 Hz, 2H, H⁴ py], 7.64 [m, 2H, H³ py], 6.56 [t, JHH = 7.5 Hz, 4H, H⁴ py'], 6.50 [t, JHH = 7.5 Hz, 4H, H⁴ (py'')₂O], 4.46 [m, 4H, H⁵ (py'')₂O], 3.38 [m(br), 4H, H³ py'], 3.05 [t, J HH = 8.0 Hz, 6H, CH₃], 2.67-2.60 [m, 10H, 2CH₃' and CH₂], 2.28 [q, JHH = 8 Hz, 4H, CH₂'], 0.39 [d(br), J HH = 4 Hz, 4H, H⁶ (py'')₂O], -4.51 [br, 4H, H⁶ py']. ¹³C NMR (298K, d₈-toluene, as determined through a ¹H-¹³C HMQC experiment), 157.3 (2C⁶ py), 144.4 (4C⁶ py'), 144.2 (4C⁶ (py'')₂O), 134.4 (2C⁴ py), 134.3 (2C³ py), 133.8 (4C₃ py'), 133.6 (4C⁴ py'), 133.0 (4C³ (py'')₂O), 132.7 (4C⁴ (py'')₂O), 121.8 (2C⁵ py), 117.4 (4C⁵(py'')₂O), 117.0 (4C⁵ py'), 12.5 (CH₃'), 12.3 (CH₃), 2.3 (CH₂'), 0.4 (CH₂). ¹H NMR (298K, d₈-THF, 500 MHz), δ = 13.45 (d, JHH = 4 Hz, 2H, H⁶ py), 9.52 (d, JHH = 7 Hz, 2H, H³ py), 8.76 (d, JHH = 7.8 Hz, 4H, H₃ py'), 8.42 (d, JHH = 7.7 Hz, 4H, H³ (py'')₂O), 8.34 (t, JHH = 7.2 Hz, 2H, H⁴ py), 7.81 (m, 2H, H⁵ py), 6.90 (t, JHH = 7.5 Hz, 4H, H⁴ py'), 6.85 (t, JHH = 7.5 Hz, 4H, H⁴ (py'')₂O), 4.90 (m, 4H, H⁵ (py'')₂O), 3.62 (overlapped with THF signal, 4H, H⁵ py'), 2.68 (t, J HH = 8.0 Hz, 6H, CH₃), 2.28-2.20 (m, 10H, 2CH₃' and CH₂), 1.94 (q, JHH = 8 Hz, 4H, 2CH₂'), 0.16 (d(br), J HH = 4 Hz, 4H, H⁶ (py'')₂O), -4.76 (br, 4H, H⁶ py'). ¹³C{¹H} NMR (298K, d₈-THF, 125.7 MHz), δ = 198.32 (br, 4C²(py'')₂O), 194.34 (br, 2C² py), 192.21 (br, 4C² py'), 157.74 (2C⁶ py), 144.46 (4C⁶ (py'')₂O), 142.87 (4C⁶ py'), 134.71 (2C⁴ py), 134.26 (2C³ py), 133.92 (4C⁴ py'), 133.82 (4C³ py'), 133.19 (4C³ (py'')₂O), 133.21 (4C⁴(py'')₂O), 122.13 (2C⁵ py), 117.86(4C⁵ (py'')₂O), 117.44 (4C⁵ py'), 12.07 (CH₃'), 11.92 (CH₃), 2.31 (br, CH₂'), 0.21 (br, CH₂). ²⁷Al NMR (298K, d₈-THF, 130.3 MHz, rel. solution of AlCl₃·6H₂O/D₂O), δ = 139.32 (br, s). py, py' and (py'')₂O refer, respectively, to the pyridyl rings in blue, red and green in the figures (See Scheme 1). CH₃ and CH₂ refer to the ethyl group attached to the tris-pyridyl system whereas CH₂' and CH₃' refer to the ethyl group attached to the (py'')₂O moiety.

ASSOCIATED CONTENT

Supporting Information

NMR spectra of **1b** and **2**, crystallographic data and cif files for **1b**, **2**, $[\{\text{MeAl}(\text{2-py})_3\}\{\text{EtAl}(\text{2-py})_2\text{O}\}\text{Sm}]_2$ and 6,6'-Me(2)bipy.LiI. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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