

Alumination of resorcinol and hydroquinone. An easy access to bifunctional Lewis acids

Franz A.R. Kaul, Martin Tschinkl, François P. Gabbai *

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Abstract

The reaction of trimethylaluminum with hydroquinone and resorcinol produces [(1,4-(Me₂AlO)₂C₆H₄)-THF]₂ (**1**) and [(1,3-(Me₂AlO)₂C₆H₄)-THF]₂ (**3**) respectively. Compounds **1** and **3** are poorly soluble in common solvents but readily dissolve in pyridine to give the corresponding adducts (1,4-(Me₂AlO)₂C₆H₄)-(Py)₂ (**2**) and (1,3-(Me₂AlO)₂C₆H₄)-(Py)₂ (**4**). The reaction of 4,6-dichlororesorcinol with trimethylaluminum produces the soluble chlorinated analog of compound **3** [(1,3-(Me₂AlO)₂-4,6-Cl₂C₆H₂)-THF]₂ (**5**). As indicated by NMR, the dimeric structure of **5** is fluxional in solution. Upon addition of chloride or t-butoxide anions to solution of **5** in THF, ²⁷Al NMR monitoring indicates that there is formation of anionic complexes but that the chelation of the anionic hosts by the two aluminum centers present in the [1,3-(Me₂AlO)₂-4,6-Cl₂C₆H₂] unit does not occur. © 1997 Elsevier Science S.A.

Keywords: Aluminium; Bifunctional Lewis acids; Resorcinol; Hydroquinone

1. Introduction

The cooperative binding of nucleophilic substrates by polydentate Lewis acids is becoming a phenomenon of prime importance both in organic and inorganic chemistry. In organic chemistry, recent reports indicate that the interaction of bifunctional aluminum derivatives with ketone results in the cooperative binding and increased electrophilic activation of the carbonyl function [1,2]. In inorganic chemistry and biochemistry [3] polyfunctional Lewis acids have been shown to be capable of selectively complex and transport anions [4]. It occurred to us that while the alumination of a large variety of phenols has been reported [5], the alumination of resorcinol and hydroquinone has to our knowledge no precedent. These latter reactions should in principle produce simple bifunctional Lewis-acids which could serve as bidentate ligands for nucleophiles. In this paper, we describe the reaction of two different resorcinols as well as that of hydroquinone with trimethylaluminum together with a study of the ligative behavior of one of those potentially bidentate Lewis-acids.

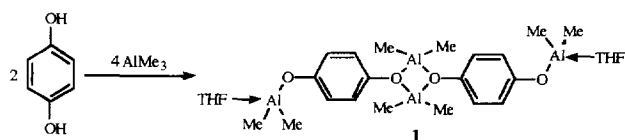
2. Results and discussion

2.1. Reaction of hydroquinone and resorcinol with AlMe₃

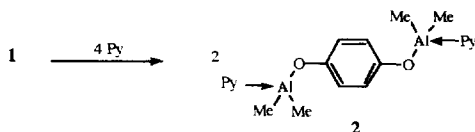
The addition of two equivalents of trimethylaluminum in hexane to a solution of hydroquinone in THF results in an exothermic reaction and instantaneous precipitation of a product (compound **1**) which can be easily isolated in high yield through filtration (Scheme 1). Compound **1** does not dissolve in classical solvents (THF, MeCN, CH₂Cl₂, Et₂O, toluene, hexane) which renders its characterization complicated. Elemental analysis data indicate that **1** contains one THF molecule per (1,4-dioxybenzene)bis(dimethylaluminum) unit. Based on the knowledge that non-sterically hindered phenoxyaluminumalkyl¹ derivatives have the strong tendency to form dimers both in solution and in the solid state through formation of intramolecular oxygen–aluminum donor–acceptor bonds [7], it is reasonable to postulate that **1** has the dimeric structure depicted in Scheme 1. Compound **1** dissolves in pyridine and is thus quantitatively converted into the (1,4-

* Corresponding author.

¹ For sterically hindered phenoxyaluminum derivatives, see Ref. [6].



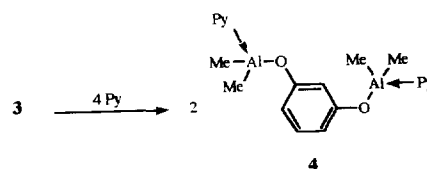
Scheme 1.



Scheme 2.

dioxybenzene)bis(dimethylaluminum)bis(pyridine) adduct (**2**) whose structure was confirmed by NMR spectroscopy (Scheme 2). The high symmetry of the molecule is consistent with the detection of a single aryl-proton and of a single aluminum-methyl resonance in the ^1H NMR spectrum. Along the same lines, in the ^{13}C NMR spectrum of **2**, in addition to the pyridine resonances, only three signals are detected, respectively corresponding to the (1/4) aryl-carbons, (2/3/5/6) aryl-carbons and methyl-carbons. The ^{27}Al NMR spectrum of **2** exhibits a peak at 141 ppm thus confirming the presence of a tetracoordinated aluminum center in **2**.

Resorcinol reacts with two equivalents of trimethylaluminum in a similar manner to that of hydroquinone to afford a high yield of compound **3** which is a structural isomer of **1** (Scheme 3). Like in the case of **1**, the elemental analysis data indicate the presence of one THF molecule per (1,3-dioxybenzene)bis(dimethylaluminum) unit. Unlike **1**, **3** is sparingly soluble in THF which allowed its NMR characterization. The ^1H NMR spectrum of **3** in THF- d_8 exhibits two methyl resonances, thus indicating the presence of two aluminum centers. The detection of two signals at 141 and 183 ppm in the ^{27}Al NMR spectrum of **3** constitutes further proof of the presence of two different but both tetracoordinated aluminum centers in **3**. These data clearly suggest that **3** has a dimeric structure analogous to that proposed for **1**. Addition of pyridine to **3** results in quantitative conversion to the (1,3-dioxybenzene)bis(dimethylaluminum)bis(pyridine) adduct (**4**) whose NMR data are fully consistent with the proposed structure (Scheme 4). The ^1H NMR spectrum exhibits three broad aryl-proton resonances with the expected intensity together with a



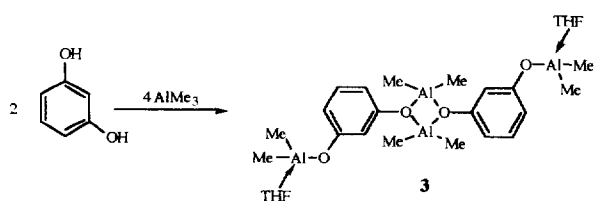
Scheme 4.

single methyl resonance. The ^{27}Al NMR spectrum of **4** resembles closely that of **2**, since a single resonance is detected at 141 ppm corresponding to the tetracoordinated aluminum center.

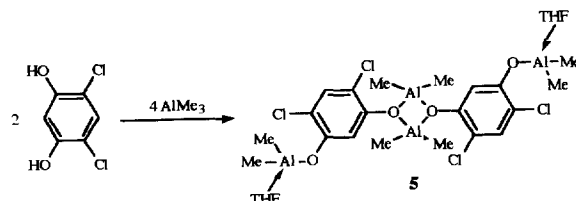
2.2. Reaction of 4,6-dichlororesorcinol with AlMe_3

Because of the favorable arrangement of the aluminum centers, the systems derived from the resorcinol appear as promising Lewis acidic ligands potentially capable of cooperatively binding nucleophiles. As mentioned above, compound **3** presents the inconvenience of being poorly soluble in organic solvents, thus strongly limiting the scope of the possible applications. In order to circumvent this problem, we became very eager to synthesize a highly soluble analog. The reaction of 4,6-dichlororesorcinol with two equivalents of trimethylaluminum in THF produces compound **5** which is highly soluble in THF, toluene, benzene (Scheme 5). As in the case of **3**, the analytical data suggest that **5** has a dimeric structure as depicted in Scheme 5.

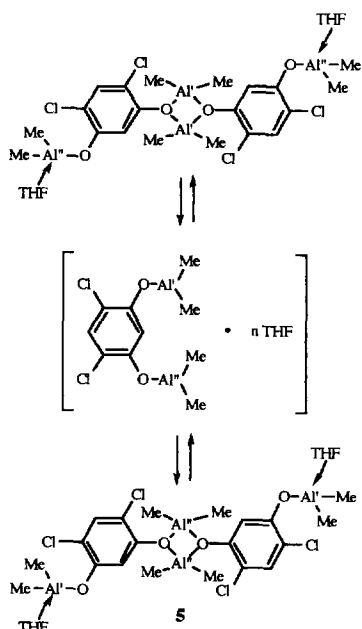
The presence of one THF molecule per (1,3-dioxy-4,6-dichlorobenzene)bis(dimethylaluminum) unit was confirmed by elemental analysis data and by the ^1H NMR spectrum of **5** in C_6D_6 which allowed the detection of the THF signals in the appropriate intensity ratio. In agreement with a dimeric structure and the existence of two different tetracoordinated aluminum centers is the detection by ^{27}Al NMR of two signals at 142 and 183 ppm. Unexpectedly however, only one methyl resonance is observed in the ^1H NMR spectrum of **5** (THF- d_8 , C_6D_6 or toluene- d_8). This apparent discrepancy between the ^{27}Al and the ^1H NMR data most probably indicates that the structure of **5** is fluxional in solution but that the rate at which the exchange process takes place is slow on the ^{27}Al NMR time scale and rapid on that of ^1H NMR (Scheme 6). Note that classically in FT NMR, the acquisition time necessary for the detection of a ^{27}Al nucleus is ten times smaller than that



Scheme 3.



Scheme 5.



Scheme 6.

needed for a ^1H nucleus [8]. In order to verify this hypothesis, a VT ^1H NMR experiment was undertaken on a solution of **5** in toluene- d_8 . At -40°C , the signal corresponding to the methyl resonance of **5** decoalesces and starts splitting into two distinct peaks at -50°C . Cooling to -90°C results in a more acute splitting of the two peaks which, however, remain broad, thus indicating that the exchange process is not completely frozen even at -90°C . Presumably, and in agreement with the ^{27}Al NMR data, the two different methyl resonances detected at low temperature correspond to the two different aluminum centers present in the dimeric structure of **5**. Altogether, these findings indicate that the Lewis acidic aluminum centers of **5** are always coordinated by a base (THF or phenoxyoxygen) but that this coordination is labile so that exchange takes place (Scheme 6).

2.3. Anion complexation studies

It can be expected that the (1,3-dioxy-4,6-dichlorobenzene)bis(dimethylaluminum) unit contained in **5** will be able to act as bidentate Lewis acid for anions (Fig. 1). In order to investigate this possibility, two simple experiments have been undertaken.

Incremental addition of tetraphenylphosphonium chloride to a solution of **5** in THF results in dramatic

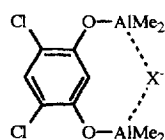


Fig. 1.

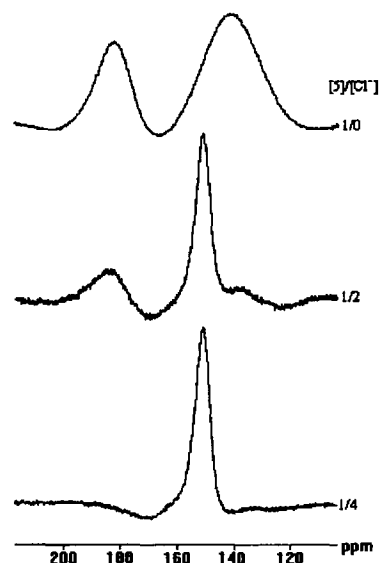
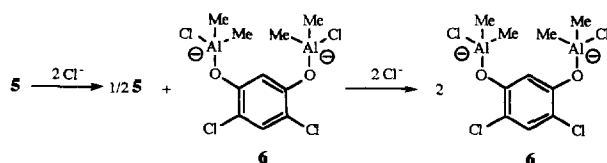


Fig. 2. ^{27}Al NMR spectra showing the effect of the incremental addition of Ph_4PCl to a THF solution of **5**.

changes of the ^{27}Al NMR spectrum (Fig. 2). By a molar ratio of $1/2$ ($5/\text{Cl}^-$), in addition to the detection of the two resonances at 142 and 183 ppm corresponding to **5**, a new signal is detected at 152 ppm, thus indicating that a new species (**6**) coexists in solution with **5**. By a molar ratio of $1/4$ ($5/\text{Cl}^-$), the signals corresponding to **5** have completely disappeared to leave solely **6** in solution. These results suggest that the cooperative binding of chloride anions does not occur but that the compound (**6**) detected in solution is most probably a dianionic complex containing two aluminate centers (Scheme 7).

A different behavior is observed when $t\text{-BuOK}$ is added to a solution of **5** in THF (Fig. 3). By a molar ratio of $1/2$, the spectrum exhibits two signals at 126 and 153 ppm indicating that **5** is not present any longer in solution. Most probably, this spectrum corresponds to that of a species (**7**) in which the two labile THF molecules of **5** have been displaced by the two $t\text{-BuO}^-$ anions. The structure of the compound thus formed corresponds to that of a dimer with terminal aluminate centers as depicted in Scheme 8. In any cases, the chelation of a $t\text{-BuO}^-$ anion by the (1,3-dioxy-4,6-dichlorobenzene)bis(dimethylaluminum) unit can be ruled out since two ^{27}Al NMR signals are detected. Indeed, a symmetrical chelate complex as shown in Fig. 1 would be expected to give rise to only one ^{27}Al resonance. By



Scheme 7.

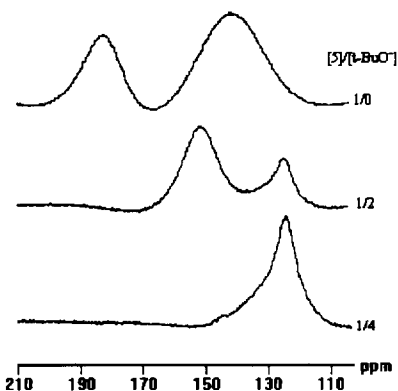
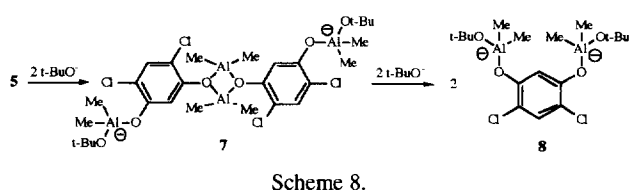


Fig. 3. ^{27}Al NMR spectra showing the effect of the incremental addition of $t\text{-BuOK}$ to a THF solution of **5**.



a molar ratio of 1/4 only one species (**8**) remains in solution with a ^{27}Al chemical shift of 122 ppm. This species is very likely to be a dianionic complex similar to **6**.

3. Conclusion

The present results indicate that the reaction of aromatic diols with aluminum alkyls constitutes a valid route to the synthesis of bifunctional Lewis acids. The anion complexation experiments undertaken in this work with the (1,3-dioxy-4,5-dichlorobenzene)bis(dimethylaluminum) unit as a receptor indicate that anion chelation is hard to achieve. This might result from the too distant location of the Lewis acidic centers in this molecular framework which renders their concomitant ligation to an identical anion difficult. It must also be noted that the Lewis acidic centers of the (1,3-dioxy-4,5-dichlorobenzene)bis(dimethylaluminum) unit are neutralized through the coordination of solvent molecules and through intramolecular dative bond formation. As a result, the incoming anions are competing with coordinated bases which would have to be simultaneously displaced before chelation can occur.

4. Experimental

All experiments were carried out under an atmosphere of dry, purified nitrogen inside a glove box or using Schlenk techniques. All solvents were dried, dis-

tilled and kept under nitrogen. All NMR data were obtained using Jeol GX 400 instrument at 399.8 MHz (^1H), 100.5 MHz (^{13}C) and 104.4 MHz (^{27}Al). TMS was used as an external standard for ^1H and ^{13}C NMR. A molar aqueous solution of $\text{Al}(\text{NO}_3)_3$ was used as external standard for ^{27}Al NMR. Microanalyses: in-house analyzers (by combustion). Trimethylaluminum (2 M in hexane), hydroquinone, resorcinol and 4,6-dichlororesorcinol were purchased from Aldrich Chemicals and were used without further purification.

4.1. Synthesis of $[(1,4\text{-(Me}_2\text{AlO)}_2\text{C}_6\text{H}_4)\text{-THF}]_2$ (**1**)

Addition of a 0.5 M hydroquinone solution in THF (7 ml, 3.5 mmol) to a stirred 2 M trimethylaluminum solution in hexane (4 ml, 8 mmol) at 25 °C resulted in a vigorous reaction, precipitation of a colorless product and gas evolution. After stirring for 24 h, the precipitate was isolated through filtration, washed with two 5 ml portions of Et_2O , and dried under vacuum to afford an 87% (0.89 g, 1.55 mmol) yield of compound **1** (m.p.: no apparent physical changes under 400 °C). Anal. Calcd: C, 57.1; H, 8.2. Found: C, 56.4; H, 8.3. Compound **1** was too insoluble to analyze by NMR.

4.2. Synthesis of $(1,4\text{-(Me}_2\text{AlO)}_2\text{C}_6\text{H}_4)\text{-(Py)}_2$ (**2**)

Addition of an excess of pyridine to **1** resulted in complete dissolution of the product. The resulted solution was exposed to a vacuum until a dry solid remained. This solid was analyzed by ^1H NMR and was found to be pure compound **2** which had therefore formed quantitatively **1** (m.p.: no apparent physical changes under 400 °C). Anal. Calcd: C, 63.1; H, 6.8; N, 7.4. Found: C, 62.7; H, 6.8; N, 7.3. ^1H NMR ($\text{Py-}d_5$) δ -0.32 (s, 12H, CH_3), 6.99 (s, 4H, aryl- H). ^{13}C NMR ($\text{Py-}d_5$) δ -8.7 (br, CH_3), 120.1 (s, $\text{C}2/3/5/6$), 153.0 (s, $\text{C}1/4$). ^{27}Al NMR ($\text{Py-}d_5$) δ 141.

4.3. Synthesis of $[(1,3\text{-(Me}_2\text{AlO)}_2\text{C}_6\text{H}_4)\text{-THF}]_2$ (**3**)

Addition of a 0.5 M resorcinol solution in THF (7 ml, 3.5 mmol) to a stirred 2 M trimethylaluminum solution in hexane (4 ml, 8 mmol) at 25 °C resulted in a vigorous reaction, precipitation of a colorless product and gas evolution. After stirring for 24 h, the precipitate was isolated through filtration, washed with two 5 ml portions of Et_2O , and dried under vacuum to afford an 82% (0.84 g, 1.45 mmol) yield of compound **3** (m.p. 285 °C). Anal. Calcd: C, 57.1; H, 8.2. Found: C, 56.4; H, 8.2. ^1H NMR ($\text{THF-}d_8$) δ -0.99, -0.83 (br, 24H, CH_3), 6.20 (br, 6H, aryl4/5/6- H), 6.80 (br, 1H, aryl-2- H). ^{27}Al NMR, ($\text{THF-}d_8$) δ 141, 183. Because of the low solubility of compound **3**, no ^{13}C NMR data could be obtained.

4.4. Synthesis of $(1,3-(Me_2AlO)_2C_6H_4)-(Py)_2$ (**4**)

Addition of an excess of pyridine to **3** resulted in complete dissolution of the product. The resulting solution was exposed to a vacuum until a dry solid remained. This solid was analyzed by 1H NMR and was found to be pure compound **4** which had therefore formed quantitatively (m.p. 88 °C). Anal. Calcd: C, 63.1; H, 6.8; N, 7.4. Found: C, 62.7; H, 6.8; N, 7.3. 1H NMR (Py- d_5) δ -0.30 (s, 12H, CH_3), 6.65 (br, 2H, aryl-4/6-*H*), 6.80 (s, 1H, aryl-2-*H*), 7.20 (br, 1H, aryl-5-*H*). ^{13}C NMR (Py- d_5) δ -8.6 (br, CH_3), 110.1 (s, C5), 111.4 (s, C4/6), 130.0 (s, C2), 162.9 (s, C1/3). ^{27}Al NMR (Py- d_5) δ 141.

4.5. Synthesis of $[(1,3-(Me_2AlO)_2-4,6-Cl_2C_6H_2)-THF]_2$ (**5**)

Slow addition of 4,6-dichlororesorcinol (1.8 g, 10 mmol) solution in THF (20 ml) to a stirred 2 M trimethylaluminum solution in hexane (10 ml, 20 mmol) at 25 °C resulted in a vigorous reaction and gas evolution. The resulting brown solution was stirred for 24 h after which time the solvents were evaporated. To the resulting residue was added 10 ml of toluene and 20 ml of hexane which resulted in the precipitation of a dark brown oil which was separated from the solution through decanting. The solution was concentrated to a volume of 5 ml following which 15 ml of pentane were added to it. Cooling to -25 °C for 1 week afforded a 46% yield (1.68 g) of compound **5** (m.p. 83 °C). Anal. Calcd: C, 46.3; H, 6.1; Cl, 19.6. Found: C, 47.2; H, 6.3; Cl, 18.3. 1H NMR (THF- d_8) δ -0.89 (s, 24H, CH_3), 6.28 (br, 2H, aryl-5-*H*), 7.00 (br, 2H, aryl-2-*H*). ^{13}C NMR (THF- d_8) δ -11.0 (br, CH_3), 112.1, (s, C5), 113.3 (s, C4/6), 128.8 (s, C2), 156.0 (s, C1/3). ^{27}Al NMR (THF- d_8) δ 142, 183.

4.6. Anion complexation experiments

The NMR samples used for the chloride complexation study were prepared by mixing 18 mg of **5**

(0.025 mmol) with respectively 19 mg (0.05 mmol, ratio 1/2) and 38 mg (0.1 mmol, ratio 1/4) of tetraphenylphosphonium chloride in 1 ml of THF. Similarly, the samples used for the t-butoxide complexation study were prepared by mixing 36 mg of **5** (0.05 mmol) with respectively 11 mg (0.1 mmol, ratio 1/2) and 22 mg (0.2 mmol, ratio 1/4) of t-BuOK in 1 ml of THF.

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