Reactivity of Various Four-Coordinate Aluminum Alkyls towards Dioxygen: Evidence for Spatial Requirements in the Insertion of an Oxygen Molecule into the Al–C Bond

Janusz Lewiński,* Janusz Zachara, Piotr Goś, Elżbieta Grabska, Tomasz Kopeć, Izabela Madura, Wojciech Marciniak, and Igor Prowotorow[a]

Dedicated to Professor Stanisław Pasynkiewicz on the occasion of his 70th birthday

Abstract: The interaction of dioxygen with various tetrahedral aluminum alkyls, (tBu)$_3$Al·OEt$_2$ (**1**), tBu$_2$Al(μ-OtBu)$_2$AltBu$_2$ (**6**), (tBu)$_2$Al(mesal) (**2**) [mesal = methyl salicylate anion], R$_2$Al(μ-pz)$_2$AlR$_2$ [pz = deprotonated pyrazole, R = Me (**3a**), Et (**3b**), and tBu (**3c**)], R$_2$Al(μ-3,5-Me$_2$pz)$_2$AlR$_2$ [3,5-Me$_2$pz = deprotonated 3,5-dimethylpyrazole, R = Me (**4a**), and Et (**4b**)], and Et$_2$B(μ-pz)$_2$AlEt$_2$ (**5**), has been investigated. We were particularly interested in the effect of steric hindrances both caused by the metal-bonded substituents and those that result from the nature of the bifunctional ligand used in the oxygenation reaction. In the reaction of **1** with O_2, only the formation of the monoalkoxide compound **6** was observed. The latter di-*tert*-butyl compound as well as all planar aluminapyrazoles, that is, the *tert*-butyl derivative **3c** and lower alkylaluminum derivatives with the more demanding 3,5-dimethylpyrazoyl ligands **4a** and **4b**, are stable under an atmosphere of dry oxygen and ambient conditions. Inspection of the space-filling representation of these compounds has undoubtedly shown that the bulky *tert*-butyl groups or pyrazolyles ligands, respectively, provide steric protection for the metal center from the dioxygen attack. In contrast, the dialkylaluminum derivatives of pyrazole, **3a** and **3b**, and the diethylaluminum bis(1-pyrazolyl)borate complex **5**, all with the metal center eclipsed with respect to the plane defined by the four nitrogen atoms, react smoothly with O_2 to form the alkyl(alkoxy)aluminum complexes. In the reaction of **5** with O_2 for example, the Et–B bonds remained intact, and the dimeric five-coordinate compound [Et$_2$B(μ-pz)$_2$Al(μ-OEt)Et]$_2$ (**9**) was isolated in good yield. The interaction of mononuclear di-*tert*-butyl chelate complex **2** with O_2 at $-15\,^\circ$C gives (tBuOO)(tBuO)Al(μ-OtBu)$_2$Al(mesal)$_2$ (**7**) in high yield, and the presence of the alkylperoxo moiety is a particularly significant point in the resulting product. All the compounds have been characterized spectroscopically, and the structures of **3c**, **4a**, **6**, **7**, and **9** have been confirmed by X-ray crystallography. Structural features of **1**–**6** are discussed and are considered in relation to the possible approach pathways of the O_2 molecule to the four-coordinate metal center. This analysis and the observed apparent dissimilarity in the reactions of model four-coordinate aluminum alkyls with O_2 clearly show that the stereoelectronic prerequisites are responsible for the fundamentally different reactivity.

Keywords: alkoxides · alkylperoxides · aluminum · complexes · insertions · oxygenations

Introduction

The interaction of aluminum alkyls with O_2 has been investigated for decades because of their practical and fundamental importance.[1, 2] Mild oxidation of aluminum alkyls by controlled introduction of dioxygen leads usually to the formation of a complex mixture of alkoxide compounds. The mechanistic details of this reaction have been investigated by a number of authors, but a full understanding of the reaction has not been reached. In principle, for the autoxidation reactions of Group 13 organometallics two general mechanisms are considered: the polar mechanism that involves the coordination of O_2 to the metal and the radical-chain process.[1–5] However, it is difficult to prove beyond any doubt which in fact is responsible in a particular case. Some experimental results and theoretical investigations for Group 13 alkyls point to the formation of a labile R$_3$M·O$_2$ complex as the key feature in the activation of the three-

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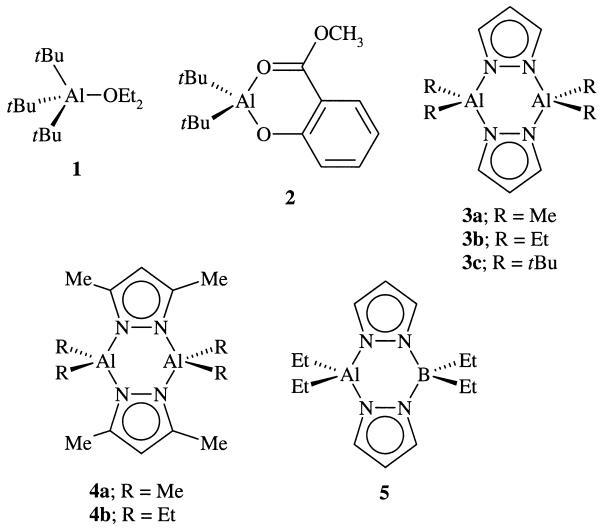
  0947-6539/00/0617-3215 $ 17.50+.50/0

coordinate Group 13 alkyls by dioxygen.[3, 4, 6, 7] However, very recently the formation of the $Me_3Al \cdot O_2$ adduct as the initial intermediate in the oxygenation reaction was questioned.[8] Furthermore, although the formation of Al–OOR intermediates has been proposed in a number of studies, only very recently we have disclosed the first example of a fully characterized alkylperoxide aluminum compound.[9] The first gallium[10] and indium[11] alkylperoxides have also been structurally characterized in the last decade. It should be noted that mechanistic considerations usually assumed the interaction of monomeric three-coordinate Group 13 alkyls with O_2. Hence, although high sensitivity four-coordinate aluminum alkyls towards dioxygen is commonly observed, the mechanism of the interactions that involve tetrahedral aluminum complexes is less certain.[9, 12, 13] In order to control more fully the Al–C bond oxidation, further insight into the dioxygen activation of organoaluminum compounds must be attained. Our preliminary study has shown that the interaction of O_2 with four-coordinate aluminum alkyls has strong geometric requirements.[13] Here we have examined the structure and reactivity of a variety of sterically encumbered four-coordinate organoaluminum compounds towards molecular oxygen. Four groups of compounds are considered: a simple tetrahedral trialkylaluminum Lewis acid–base adduct, a mononuclear dialkylaluminum chelate complex, dinuclear dialkylaluminum derivatives of pyrazole and 3,5-dimethylpyrazole, and a dialkylaluminum complex with the bis(pyrazolyl)borate co-ligand (see schematically depicted compounds **1**–**5**).. Steric hindrance is not always an obvious factor, especially if the reacting molecule is relatively small. Thus, we have been particularly interested in the effect of steric hindrances caused by the metal-bonded substituents and those that result from the nature of the bifunctional ligand used. The combined structural and chemical patterns described here provide compelling experimental evidence that the attack on the metal center by O_2 from a desired direction is the key feature in the dioxygen activations of tetrahedral organoaluminum complexes, followed by the insertion of O_2 into Al–C bond.

Abstract in Polish: *Badano reaktywność tlenu cząsteczkowego z różnorodnymi czterokoordynacyjnymi alkilowymi pochodnymi glinu: $(tBu)_3Al \cdot OEt_2$ (**1**), $tBu_2Al(\mu\text{-}OtBu)_2AltBu_2$ (**6**), $(tBu)_2Al(mesal)$ (**2**) (mesal = anion salicylanu metylu), $R_2Al(\mu\text{-}pz)_2AlR_2$ [pz = anion pirazolowy, R = Me (**3a**), Et (**3b**) i tBu (**3c**)], $R_2Al(\mu\text{-}3,5\text{-}Me_2pz)_2AlR_2$ [3,5-Me_2pz = anion 3,5-dimetylopirazolowy, R = Me (**4a**) i Et (**4b**)] oraz $Et_2B(\mu\text{-}pz)_2AlEt_2$ (**5**). W szczególności analizowano wpływ na przebieg reakcji utleniania zawady sterycznej wprowadzonej przez podstawniki alkilowe przy metalu jak i wynikającej z budowy dwufunkcyjnego ligandu. W reakcji **1** z O_2 obserwuje się wyłącznie tworzenie monoalkoksylowego związku **6**. Stwierdzono, że di-tert-butylowy związek **6**, jak i wszystkie glinowe pochodne pirazolu o płaskiej budowie, t.j. di-tert-butylowa pochodna **3c** oraz pochodne alkilowe **4a** i **4b** z bardziej rozbudowanym ligandem w postaci 3,5-dimetylopirazolu, są trwałe w atmosferze suchego tlenu w warunkach normalnych. Analiza czaszowych modeli tych związków wykazała niezbicie, że przestrzenne grupy tert-butylowe lub ligandy pirazolowe stanowią zawadę steryczną uniemożliwiającą atak cząsteczki tlenu na centrum koordynacji. Natomiast dialkilowe glinowe pochodne pirazolu **3a** i **3b**, oraz dietyloglinowy bis(1-pirazolylo)boranowy kompleks **5**, w których centrum glinowe jest wychylone nad płaszczyznę wyznaczoną przez atomy azotu, reagują łatwo z O_2 tworząc alkiloalkoksylowe kompleksy glinu, np. w reakcji **5** z O_2 wiązanie Et–B pozostaje nienaruszone i powstaje z dużą wydajnością dimeryczny pięciokoordynacyjny produkt $[Et_2B(\mu\text{-}pz)_2Al(\mu\text{-}OEt)Et]_2$ (**9**). Reakcja monocentrycznego di-tert-butylowego kompleksu chelatowego **2** z O_2 prowadzi do utworzenia z wysoką wydajnością związku (tBuOO)(tBuO)Al(μ-OtBu)$_2$Al(mesal)$_2$ (**7**) zawierającego, co jest szczególnie istotne, ugrupowanie alkilonadtlenkowe. Wszystkie związki zostały scharakteryzowane spektralnie a struktury molekularne **3c**, **4a**, **6**, **7** i **9** wyznaczono rentgenograficznie. Przedyskutowano budowę związków **1**–**6** w kontekście możliwych kierunków podejścia cząsteczki O_2 do tetraedrycznego centrum metalicznego. Analiza strukturalna i zaobserwowane różnice w przebiegu reakcji z O_2 modelowych czterokoordynacyjnych alkilo-pochodnych glinu dowodzą, że za zasadnicze różnice w ich reaktywności są odpowiedzialne czynniki stereoelektronowe.*

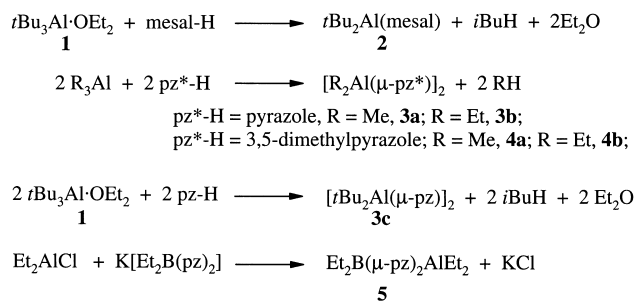


Results and Discussion

Synthesis and structure characterization of sterically encumbered four-coordinate organoaluminum compounds: The Lewis acid–base adduct $(tBu)_3Al \cdot OEt_2$ (**1**) was the starting reagent for the synthesis of *tert*-butylaluminum derivatives of the *O,O′* and *N,N* bifunctional ligands with varying steric demands. The interaction of **1** with 1 equivalent of methyl salicylate (mesal–H) in toluene permits the isolation of $(tBu)_2Al(mesal)$ (**2**) in high yield. The addition of 1 equivalent of pyrazole to a solution of **1** in toluene results in the quantitative formation of di-*tert*-butylaluminum complex **3c**. The interaction of Me_3Al with pyrazole (pz–H) has been reported to yield $[Me_2Al(\mu\text{-}pz)]_2$ (**3a**).[14] Hence the latter compound and other lower dialkylaluminum derivatives of pyrazole and 3,5-dimethylpyrazole (3,5-Me_2pz-H), that is,

  0947-6539/00/0617-3216 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

$[Et_2Al(\mu\text{-pz})]_2$ (**3b**), $[Me_2Al(\mu\text{-3,5-Me}_2\text{pz})]_2$ (**4a**), and $[Et_2Al(\mu\text{-3,5-Me}_2\text{pz})]_2$ (**4b**), were readily prepared by an analogous route in essentially quantitative yield (Scheme 1). The diethylaluminum bis(1-pyrazolyl)borate complex, $Et_2B(\mu\text{-pz})_2AlEt_2$ (**5**), was prepared in the reaction of $K[Et_2B(pz)_2]$ with Et_2AlCl.[15]



Scheme 1. Synthesis of sterically encumbered four-coordinate organoaluminum complexes **2**, **3a**, **3b**, **3c**, **4a**, **4b**, and **5**.

Compound **2** has been characterized by NMR and IR spectroscopy and by cryoscopic molecular weight determination. All the data are consistent with the monomeric four-coordinate chelate structure of **2** in solution (see Experimental Section). Several attempts to obtain monocrystals suitable for X-ray analysis failed. It should also be noted that previously we have demonstrated that dialkylaluminum derivatives of unsaturated hydroxy carbonyl compounds occur in solution as monomeric four-coordinate $R_2Al(O,O')$ chelate complexes (including the derivatives of methyl salicylate[16]), though they have a tendency to form five-coordinate $[R_2Al(O,O')]_2$ adducts in the solid state.[17, 18]

Alkylaluminapyrazoles **3a–c**, **4a**, and **b** have been characterized by NMR spectroscopy. The ^1H NMR spectra show no complexity, and single resonances of the corresponding protons are observed over a wide-temperature range. The ^{27}Al NMR spectra show a broad resonance in the range $\delta = 150-153$, which is consistent with a four-coordinate aluminum center. It is worthy to note that it has been previously suggested that dialkylaluminum derivatives of pyrazole with small alkyl substituents on aluminum have a boat conformation of the central ring in solution;[14] this is also consistent with the molecular structure of corresponding boron[19] and gallium compounds.[20] The paucity of structural data for aluminapyrazoles[21] and our attempts to rationalize the observed divergent behavior of various four-coordinate aluminum dialkyls with respect to molecular oxygen (vide infra), prompted us to investigate the X-ray structure of these complexes. Unfortunately, we were unable to obtain crystallographic structural data for **3a** and **3b** The molecular structure and space-filling representations of **3c** and **4a** are shown in Figures 1, 2, and 3, respectively. Selected bond lengths and angles are given in Table 1.

In contrast to the assumed boat conformation for low alkylaluminapyrazoles **3a** and **3b**, the complexes **3c** and **4a** are essentially planar with three fused heterocyclic rings, in which the aluminum atoms are four-coordinate and have a

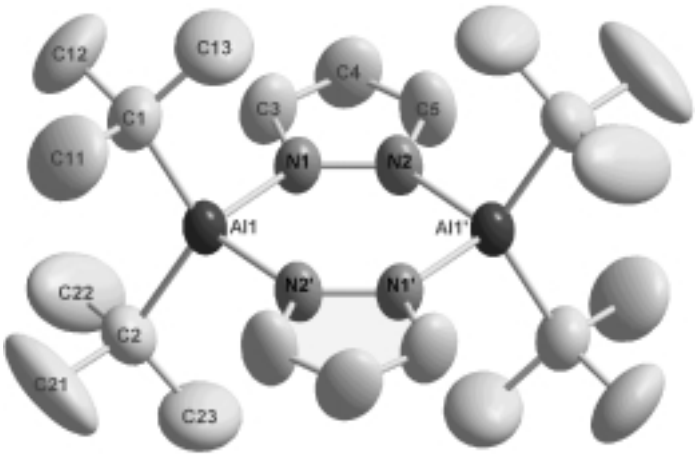


Figure 1. View of the molecular structure of $[(t\text{Bu})_2Al(\mu\text{-pz})]_2$ (**3c**) with thermal ellipsoids drawn at the 50% probability level.

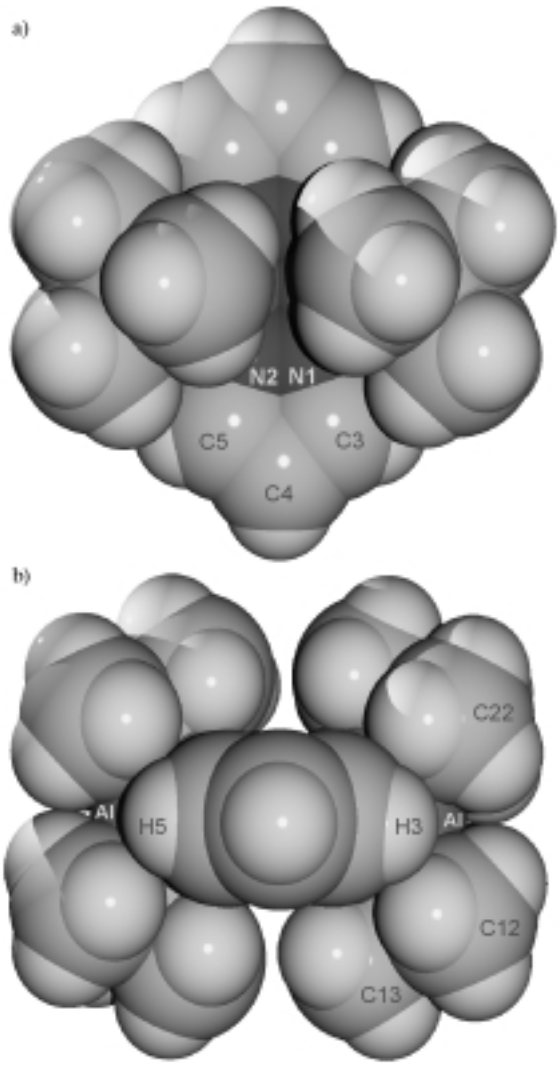


Figure 2. Space-filling representation of **3c**: a) view of the molecular Al_2N_4 mean plane; b) side view perpendicular to the Al–Al vector; this shows the steric hindrance imposed on the aluminum center.

distorted tetrahedral geometry.[22] For **3c**, the C1–Al1–C2 and N1–Al1–N(2′) angles are 121.50(14) and 100.08(9)°, respectively. For **4a**, the carbon atoms form the C–Al–C angle of

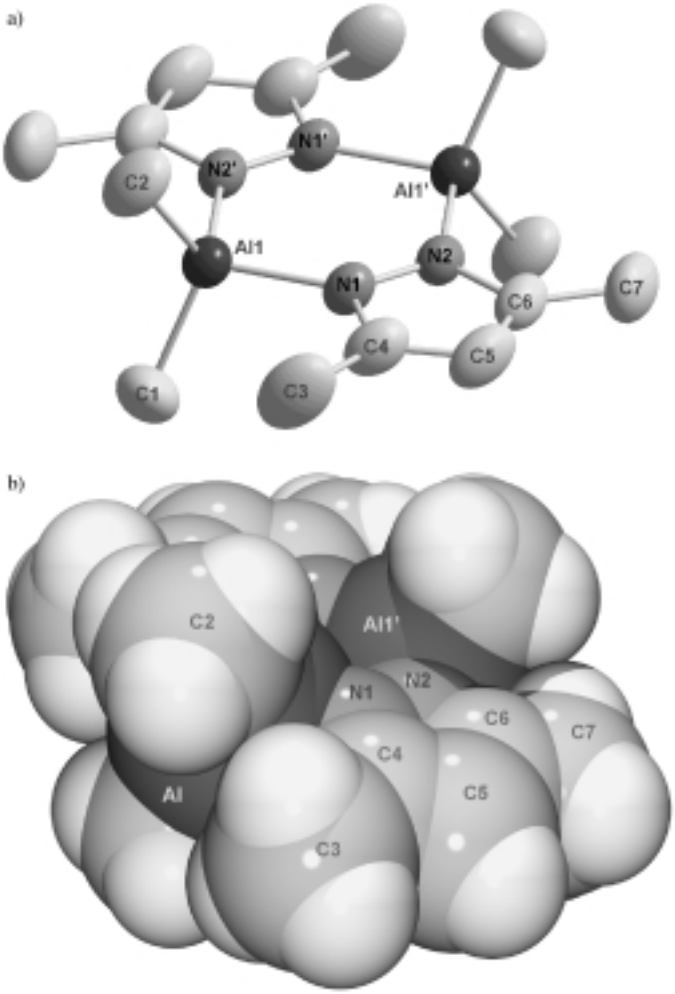


Figure 3. Molecular structure of $[Me_2Al(\mu\text{-}3,5\text{-}Me_2pz)]$ (**4a**): a) view with thermal ellipsoids drawn at the 50% probability level (all hydrogen atoms are omitted for clarity); b) space-filling representation; side view perpendicular to the Al–Al vector; this shows the steric hindrance imposed on the aluminum center.

Table 1. Selected bond lengths [Å], bond angles [°], and torsion angles [°] for **3c** and **4a**.

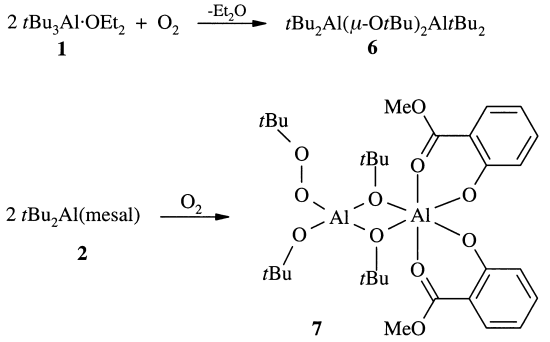
3c		**4a**	
Al1–N1	1.929(2)	Al1–N1	1.9244(17)
Al1–N2′	1.929(2)	Al1–N2′	1.9222(17)
Al1–C1	1.990(3)	Al1–C1	1.947(3)
Al1–C2	1.998(3)	Al1–C2	1.956(2)
N1–N2	1.348(3)	N1–N2	1.381(2)
N1–Al1–N2′	100.08(9)	N1–Al1–N2′	103.64(7)
C1–Al1–C2	121.50(14)	C1–Al1–C2	119.97(12)
N1–Al1–C1	107.67(12)	N1–Al1–C1	107.78(10)
N1–Al1–C2	108.78(13)	N1–Al1–C2	108.59(10)
N2′–Al1–C1	108.41(13)	N2′–Al1–C1	107.59(10)
N2′–Al1–C2	108.29(12)	N2′–Al1–C2	108.08(9)
Al1–N1–N2–Al1′	1.4(4)	Al1–N1–N2–Al1′	8.4(2)

roughly the same value [119.97(12)°], while the N–Al–N angle is somewhat larger [103.64(7)°] than that observed for **3c**. For steric reasons, the essentially planar geometry of both compounds is consistent with expectation, since in this geometry steric interactions of the bulky *tert*-butyl groups with α-C–H hydrogens of the pyrazolyl ligands or Al–Me groups with the methyl groups of the 3,5-substituted pyrazolyl ligand are reduced relative to a boat conformation (vide infra). The Al–N bond lengths in **3c** are slightly larger (1.929(2) Å) than those found for **4a** (average length of 1.923(2) Å).

The aluminapyrazobole $Et_2B(\mu\text{-}pz)_2AlEt_2$ (**5**) was isolated as an oil and therefore it has been characterized only by spectroscopic methods.[15] Unfortunately, aluminum poly(pyrazolyl)borate derivatives are also relatively scarce,[15, 23–26] and only complexes with tris(alkylpyrazolyl)hydroborato ligands in the η^2- or η^3-coordination mode have been characterized by X-ray crystallography.[23, 25, 26] However, it is reasonable to assume a boat conformation for **5** by analogy to the structurally characterized corresponding gallium and indium bis(pyrazolyl)borate complexes, $Me_2B(\mu\text{-}pz)GaMe_2$,[27] $H_2B(\mu\text{-}3,5\text{-}Me_2pz)GaMeCl$,[28] and $H_2B(\mu\text{-}pz)_2InMe_2$.[29]

Oxygenation of the aluminum alkyls

Interaction of $(tBu)_3Al\cdot OEt_2$ (***1***) *and* $(tBu)_2Al(mesal)$ (***2***) *with dioxygen*: In the following studies, we started with the simple trialkylaluminum Lewis acid–base adduct, $(t\text{Bu})_3\text{Al}\cdot\text{OEt}_2$ (**1**). When a solution of **1** was exposed to an excess (1 atm) of dry molecular oxygen, the white, crystalline mono-*tert*-butoxide compound, $t\text{Bu}_2\text{Al}(\mu\text{-O}t\text{Bu})_2\text{Al}t\text{Bu}_2$ (**6**), was isolated in good yield (Scheme 2). Compound **6** is stable as a solid in



Scheme 2. Autoxidation reactions of the Lewis acid–base adduct **1** and the chelate complex **2**.

air at ambient conditions for several days and it is stable indefinitely in solution under a dry oxygen atmosphere. It should be noted that the formation of **6** has also been observed in the reaction of three-coordinate $(t\text{Bu})_3\text{Al}$ with O_2.[4]

The molecular structure and the space-filling representation of **6** are shown in Figure 4. Selected bond lengths and angles are given in Table 2. The general structural features of the molecule are not surprising and are consistent with those observed for the sterically less demanding dimeric dialkylaluminum alkoxides.[30] The central $Al_2(\mu\text{-}O)_2$ is planar, and the molecule has a crystallographically imposed C_i symmetry. The coordination geometry of Al atoms is pseudotetrahedral, and the smallest O1–Al1–O(1′) angle is 78.28(6)°. The average Al–O bond length of 1.878 Å is longer than the Al–O bond lengths associated with the bridging O–*t*Bu ligands found in the dimeric dialkylaluminum alkoxides of lower steric bulk[30] and

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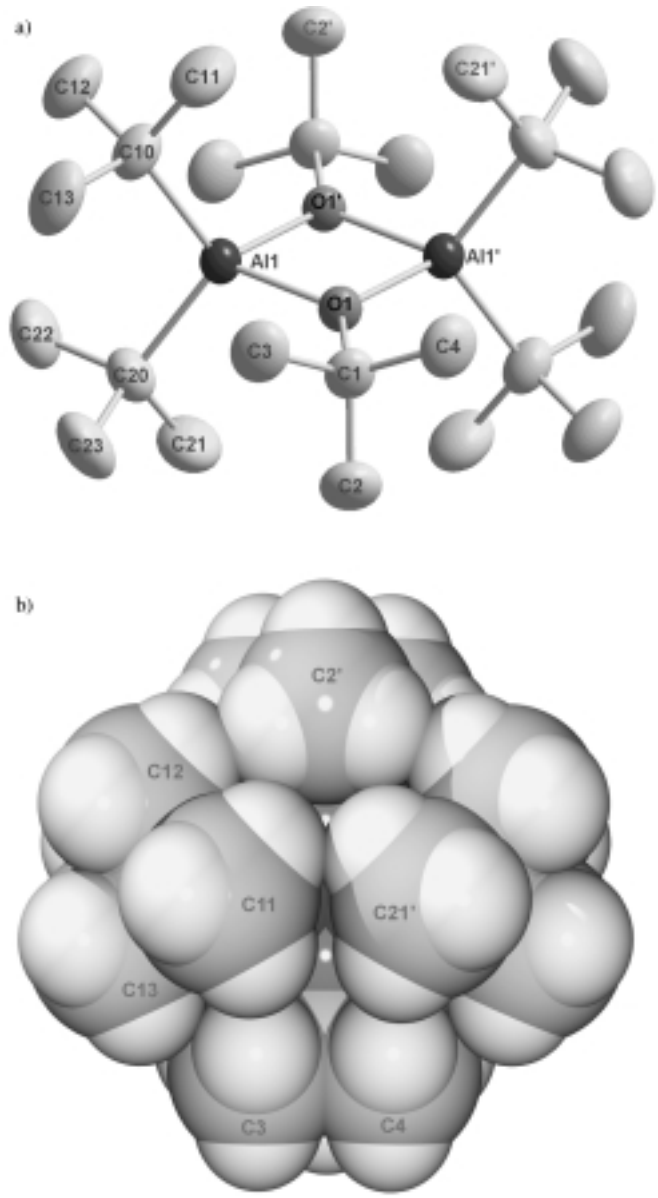


Figure 4. Molecular structure of $[t\mathrm{Bu}_2\mathrm{Al}(\mu\text{-}O t\mathrm{Bu})]_2$ (**6**): a) view with thermal ellipsoids drawn at the 50% probability level; b) space-filling representation.

inthe homoleptic *tert*-butoxide aluminum compound $(t\mathrm{BuO})_2\mathrm{Al}(\mu\text{-}O t\mathrm{Bu})_2\mathrm{Al}(O t\mathrm{Bu})_2$.[31] Examination of the molecular structure of **6** showed the existence of many repulsive steric interactions, which are close to van der Waals interactions.

The selective formation of the monoalkoxide product as a result of the oxidation of **1** is striking, and the stability of **6** towards further oxidation may seem unexpected in view of the highly reactive nature towards O_2 of the previously reported lower alkylaluminum compounds.[1] This subject will be discussed further in this paper. This behavior is also in marked contrast to that shown by the four-coordinate di-*tert*-butylaluminum chelate complex $(t\mathrm{Bu})_2\mathrm{Al}(\mathrm{mesal})$ (**2**). The interaction of **2** with dry oxygen at $-15\,^\circ\mathrm{C}$ leads to the formation of $(t\mathrm{BuOO})(t\mathrm{BuO})\mathrm{Al}(\mu\text{-}O t\mathrm{Bu})_2\mathrm{Al}(\mathrm{mesal})_2$ (**7**) in a high yield (Scheme 2). After a standard work-up, **7** was obtained as a colorless solid. Thus, in contrast to the results observed in an analogous reaction for **1**, the reaction proceeds with the oxidation of both *t*Bu–Al bonds. However, the presence of the alkylperoxo moiety is a particularly significant point of the product from the reaction of **2** with O_2. The structure of **7** in solution has been confirmed by NMR and IR spectroscopy, and the solid structure has been determined by X-ray crystallography. The ^{1}H NMR spectrum of **7** shows two singlets of the CH_3 protons of chelating mesal ligands and four singlets of $-C(CH_3)_3$ protons that correspond to one *t*BuOO group and three *t*BuO groups with different environments. The bridging alkoxides have different environments because there is no mirror plane in the molecule. The environment of one *tert*-butyl group is such that the alkoxide group and the *facial O,O′*-ligand are at the same side of the Al_2O_2 ring. In contrast, the second *tert*-butyl group has the peroxide and the *facial O,O′*-ligand at the same side of the Al_2O_2 ring. The presence of the Al–OO*t*Bu linkage has been confirmed by IR spectra, which show an absorption at 890 cm^{-1} attributable to the characteristic (O–O) peroxidic stretching vibration.[32]

The molecular structure of **7** is shown in Figure 5, and selected bond lengths and angles are given in Table 2. The molecule has an unsymmetrical dinuclear structure with two aluminum atoms with a different coordination mode. The Al1 atom is bonded to a *tert*-butyl peroxide group and one terminal *tert*-butoxide group, and the Al2 is bonded to two chelating mesal ligands. Both aluminum sites are joined by bridging μ_2-*tert*-butoxide groups. A particularly significant point of the structure of **7** is the presence of the Al–OO*t*Bu moiety. The *tert*-butyl peroxide group is terminally bonded by the O3 atom with the Al1–O3 bond length of 1.725(7) Å. The peroxo O3–O4 bond length of 1.38(2) Å is slightly shorter than those found for other monodentate and bridging alkyl peroxides coordinated to main group[10, 11, 33, 34] and transition metals.[32] The Al1–O5 bond length associated with the terminal O*t*Bu ligand is 1.690(10) Å. The coordination geometry of Al1 is pseudotetrahedral with the smallest O1–Al1–O2 angle of 83.3(2)° associated with strains in the central $Al_2(\mu\text{-}O)_2$ ring. The location of the second oxygen atom of the alkylperoxo moieties and the geometry of the OO*t*Bu ligand are worthy of note with regard to the coordination modes of alkylperoxo moieties to main group metals (Figure 6). The O4 atom of the alkylperoxo group is situated at a distance of 2.50(2) Å from the Al1 atom.

This distance may be considered as quite long, however it is substantially shorter than the sum of the van der Waals radii (that is, 3.45 Å).[35] For comparison, the terminal Al–O(ether) contacts in the five-coordinate dihalogeno- and dialkylaluminum alkoxides derived from ether-functionalized alcohols, that is, $[X_2\mathrm{Al}(O,O)]_2$-type complexes, range from 2.001 to 2.999 Å.[17, 36] Other notable features of the alkyl peroxide **7** are the almost planar geometry of the AlOOC unit with a torsion angle of 176(1)° and that the OO*t*Bu ligand is bent in a plane perpendicular to the central $Al_2(\mu\text{-}O)_2$ ring. The planar geometry is in contrast to that observed in other nonbridging alkyl peroxides bonded to main group metals (Sb and Ge), in which the M–O–O–C torsion angles are in the range from 121.7° to 147.4°.[33] However, the Al1–O3–O4 and O3–O4–C4 angles of 106.9(7)° and 101(1)°, respectively, are comparable with corresponding values in the reported

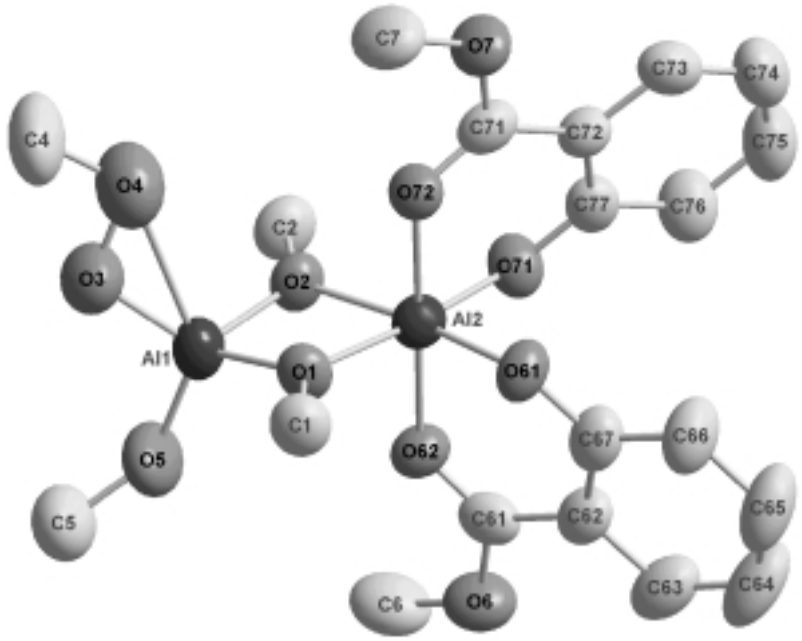


Figure 5. View of the molecular structure of (*t*BuOO)(*t*BuO)Al(μ-O*t*Bu)$_2$Al(mesal)$_2$ (**7**). Thermal ellipsoids are drawn at the 50% probability level. The methyl groups of all *tert*-butyl substituents are omitted for clarity.

Table 2. Selected bond lengths [Å], bond angles [°], and torsion angles [°] for **6**, **7**, and **9**.

6		**9**	
Al1−O1	1.8795(13)	Al1−O1	1.8773(15)
Al1−O1′	1.8757(13)	Al1−O1′	1.8888(15)
Al1−C10	2.036(2)	Al1−C9	1.984(2)
Al1−C20	2.036(2)	Al1−N1	2.0128(18)
O1−Al1−O1′	78.28(6)	Al1−N3	2.0159(18)
C10−Al1−C20	112.52(9)	B1−N2	1.574(3)
7		B1−N4	1.586(3)
Al1−O1	1.788(5)	B1−C11	1.613(3)
Al1−O2	1.787(5)	B1−C13	1.620(3)
Al1−O3	1.725(7)	O1−Al1−O1′	74.31(7)
Al1−O4	2.502(18)	O1−Al1−N1	145.71(8)
Al1−O5	1.691(10)	O1−Al1−N3	91.70(7)
O3−O4	1.378(18)	O1−Al1−C9	112.05(10)
Al2−O1	1.923(4)	O1′−Al1−C9	108.40(9)
Al2−O2	1.920(4)	O1′−Al1−N1	93.40(7)
Al2−O61	1.830(4)	O1′−Al1−N3	150.28(8)
Al2−O71	1.831(4)	C9−Al1−N1	102.17(10)
Al2−O62	1.925(4)	C9−Al1−N3	101.12(10)
Al2−O72	1.922(4)	N1−Al1−N3	83.53(7)
Al1−O3−O4	106.9(7)	N2−B1−N4	102.92(17)
O3−O4−C4	101.4(12)	Al1−O1−Al1′	105.69(7)
O1−Al1−O2	83.3(2)	Al1−N1−N2−B1	−8.9(3)
O5−Al1−O3	107.2(5)	B1−N4−N3−Al1	−7.5(3)
O1−Al2−O2	76.3(2)		

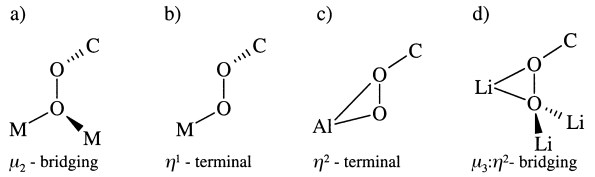
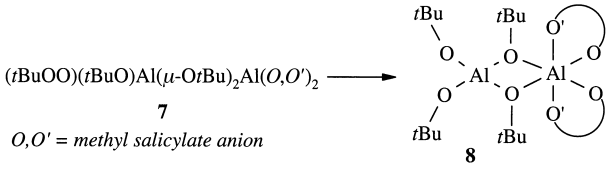


Figure 6. The previously observed coordination modes of the alkylperoxo moieties to main group metals: a) in gallium[10] and indium[11] alkylperoxides; b) in germanium and antimony alkylperoxides;[33] c) the ligation of Al−OO*t*Bu moiety in **7**; d) in the dodecameric aggregate [LiOO*t*Bu]$_{12}$.[34]

monodentatealkyl peroxides.[32, 33] The above observation indicates that in the solid state the mode of alkylperoxo moiety coordination in **7** may be considered as asymmetrical η^2-terminal, and the long-range Al−O interaction does not essentially affect the coordination geometry of the Al1 atom. It is reasonable to assume that this alkylperoxo moiety occurs as η^1-terminal in solution. It is worthy to note that the structurally characterized gallium and indium alkyl peroxides contained only bridging alkylperoxo groups,[10, 11] and in one case the spectroscopic characterization of a terminal alkyl peroxide of gallium was reported.[37] In addition, the overall structure of **7** is similar to that of dialkoxide aluminum chelate complexes [Al(OR)$_2$(β-diketonate)]$_2$,[38] and the other Al−O bond lengths and Al−O−Al angles in **7** are similar to those found for the latter. The coordination geometry of Al2 is almost ideally octahedral with a small deviation for the O1−Al2−O2 angle of 76.3(2)°; this is imposed by the strains in the central Al$_2$(μ-O)$_2$ ring.

Compound **7** is stable as a solid in air at ambient conditions. However, ^{1}H NMR spectra indicate that in solution it decomposes slowly at room temperature, that is, the signals of the peroxide compound decay, while new resonances appear in the spectra over time. We assume that the new set of signals arises from the decomposition of the *tert*-butyl peroxide group to the *tert*-butoxide with the formation of (*t*BuO)$_2$Al(μ-O*t*Bu)$_2$Al(mesal)$_2$ (**8**) (Scheme 3). We note that aluminum alkoxide complexes analogous to **8** have been obtained in the redistribution reaction of (RO)$_3$Al and Al(β-diketonate)$_3$.[38]



Scheme 3. Decomposition reaction of the *tert*-butylperoxide complex **7**.

Interaction of the dialkylaluminum derivatives of pyrazoles with dioxygen (*Scheme 4*): It was noted earlier that lower alkylaluminum derivatives of pyrazole are air- and moisture-sensitive,[14] however, to our knowledge no controlled oxidation of this group of compounds has been studied. We have found that **3a** and **3b** react smoothly with O$_2$ to form aluminum alkoxide compounds, and the oxidation of one Al−C bond from the R$_2$Al moieties is completed within several hours at ambient temperature. The remaining Al−C

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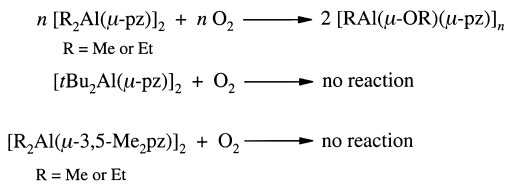
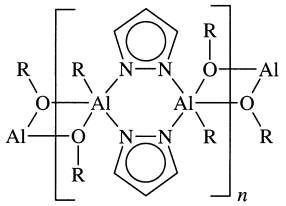


Scheme 4. Reactivity of the aluminapyrazoles towards dioxygen.

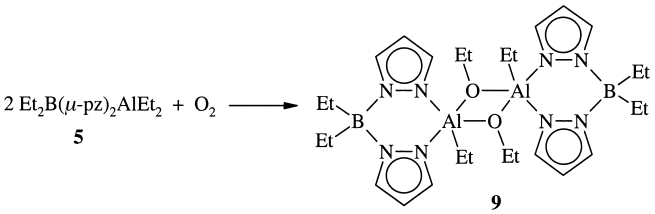
bonds are oxidized very slowly (in days, as monitored by ^{1}H NMR spectroscopy). The ^{1}H NMR spectra of the post reaction mixtures show two chemically inequivalent R groups, that is, Al–R and Al–OR groups. However, the ^{1}H NMR spectra were relatively complex, and at this stage of the studies we have assumed that the oxidation of **3a** and **3b** afforded a mixture of products with a basic structure unit expressed by **I**. This basic unit forms alkoxide bridges and



I

produces chain or cyclic structures with five-coordinate aluminum centers. Presumably the formation of five-coordinate alkylaluminum species inhibits the oxidation of the remaining Al–R groups. Unfortunately, the difficulties in the separation of products by fractional crystallization have precluded their structural characterization by X-ray crystallography. The *tert*-butylaluminum derivative of pyrazole **3c** as well as the alkylaluminum derivatives of 3,5-dimethylpyrazole **4a** and **4b** are stable indefinitely in solution under a dry oxygen atmosphere. This behavior is in strong contrast to that shown by the lower alkyls **3a** and **3b** as well as to the above mentioned four-coordinate di-*tert*-butylaluminum *O*,*O*′-chelate complex **2**, which readily reacts with dioxygen.

In order to confirm the structural motif of the alkyl(alkoxide)aluminum compounds derived from the reactions of the lower alkyl complexes **3a** and **3b** with O_2, that is, the oligomerization through alkoxide bridges, we have investigated an analogous reaction with $Et_2B(\mu\text{-pz})_2AlEt_2$ (**5**). While the controlled oxidations of dialkylaluminum complexes with bis(pyrazolyl)borate ligands have not been studied, their high sensitivity towards molecular oxygen has been previously indicated.[15] Moreover, attempts to prepare the alkyl(alkoxy)aluminum compounds in the reaction of $HB(3\text{-}t\text{Bupz})_3AlEt_2$ or $HB(3\text{-}t\text{Bupz})_2(5\text{-}t\text{Bupz})AlEt_2$ with O_2 were unsuccessful.[25] For the reaction of **5** with O_2, we assumed, in the light of the results of the **3a** and **3b** oxidation, that only one Et–Al bond will readily react, while the Et–B bonds will stay intact. Indeed, when a solution of **4** in hexane was exposed to dry oxygen at $-15\,^\circ$C, the crystalline ethyl(ethoxide)aluminum compound, $[Et_2B(\mu\text{-pz})_2Al(\mu\text{-OEt})Et]_2$ (**9**), was isolated in a good yield (Scheme 5). Compound **9** is freely soluble in aromatic hydrocarbon



Scheme 5. Reaction of the aluminapyrazobole **5** with O_2.

and halocarbon solvents. It is stable in the solid state under a nitrogen atmosphere; however, it decomposes readily in solution. The ambient-temperature ^{1}H NMR spectrum of **9** shows the pyrazolyl rings as equivalent and three chemically inequivalent ethyl groups, that is, those of the aluminum and boron bound groups and the Al–OEt group. The ^{27}Al NMR chemical shift at $\delta = 62$ is consistent with the presence of a five-coordinate aluminum center.[39]

The molecular structure of **9** was confirmed by X-ray crystallography, as illustrated in Figure 7. Selected bond lengths and angles are given in Table 2. The molecule has a centrosymmetric dimeric structure, in which two $Et_2B(\mu\text{-pz})_2Al(OEt)Et$ moieties are joined by the alkoxide oxygen O(1) and O(1′) atoms with the formation of a central four-membered $Al_2(\mu\text{-O})_2$ ring. Both aluminum atoms are five-coordinate with square pyramidal geometry. The basal plane consists of two alkoxide oxygen atoms and two nitrogen atoms of pyrazolyl ligands, and the ethyl group is in an apical position. The oxygen and nitrogen atoms deviate only slightly from the least-square basal plane; the highest deviation is 0.042(1) Å. The aluminum atom is displaced by 0.531(1) Å from the N_2O_2 basal plane. The natural bite angle of the diethylbis(pyrazolyl)borate ligand restricts the N1–Al1–N3 angle to 83.53(7)°. The extremely small O1–Al1–O1′ angle of 74.31(7)° is imposed by strains in the central $Al_2(\mu\text{-O})_2$ ring. The six-membered AlN_4B rings are in a boat configuration. The Al–O bond lengths within the $Al_2(\mu\text{-O})_2$ ring are of roughly the same value. The average Al–O bridging bonds length within the central Al_2O_2 ring (1.883 Å) is near the low end of the range observed for corresponding values of the five-coordinate $[R_2Al(O,O)]_2$-type adducts (1.850–1.999 Å).[17] The Al–N bond lengths in **9** (all bonds are roughly of the same value with a mean Al–N bond length of 2.014 Å) are slightly larger than those found for the four-coordinate compounds **3c** and **4a**.

Factors that determine divergent behavior of various four-coordinate dialkylaluminum complexes towards dioxygen: What are the stereoelectronic prerequisites for the observed fundamentally different reactivity? In an effort to address this question, we have examined the structural features of the studied compounds in the context of plausible approach pathways of molecular oxygen. Upon consideration of the space-filling representation of $t\text{Bu}_2Al(\mu\text{-O}t\text{Bu})_2Al t\text{Bu}_2$ (**6**) (Figure 4), it can be easily seen that the latter is sterically highly crowded, and the methyl groups are close to the van der Waals interactions. Thus, the presence of the four bulky *tert*-butyl groups situated around the metal center results in steric protection for the aluminum coordination

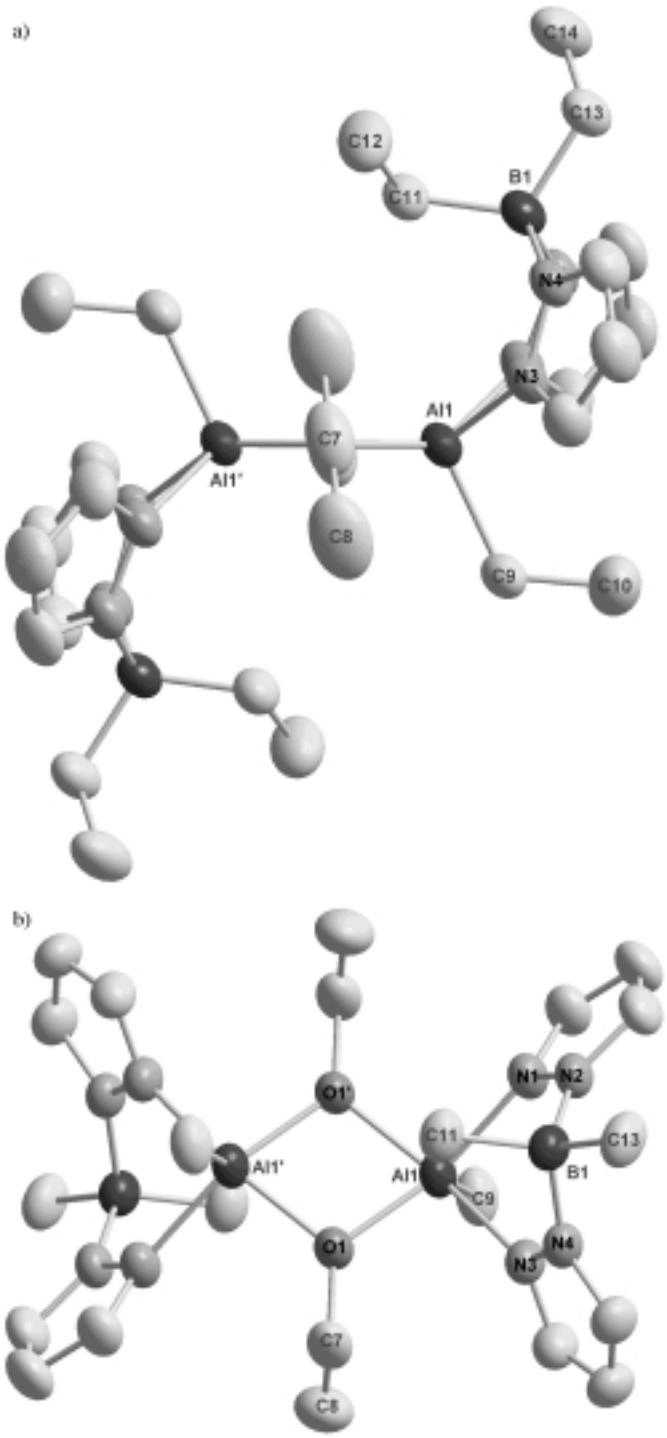


Figure 7. View of the molecular structure of $[Et_2B(\mu\text{-}pz)_2Al(\mu\text{-}OEt)Et]_2$ (**9**) with thermal ellipsoids drawn at the 50% probability level: a) side view perpendicular to the Al–Al vector; b) view of the molecular Al_2O_2 mean plane (the methyl groups of all ethyl substituents bonded to the metal centers are omitted for clarity).

sphere against O_2 attack.[40] In contrast, for dimeric, trimeric, or higher associated lower dialkylaluminum alkoxides, the metal center in R_2Al moieties is not sterically protected, and further oxidation may proceed; this is consistent with the well-known highly reactive nature of these compounds towards O_2. Furthermore, the space-filling representation of **3c** (Figure 2) shows that in this planar structure the bulky *tert*-butyl groups and α-CH groups of the pyrazolyl ligands provide steric bulk around the electrophile center, and this is sufficient to completely inhibit the molecular oxygen attack on the aluminum. Thus, the oxygenation does not occur. There is a completely different situation in the case of lower dialkylaluminum derivatives of pyrazole **3a** and **3b** and the aluminapyrazobole **5**. As we have discussed above, it is reasonable to assume a boat conformation for these compounds in solution. In the boat conformation (or if a steric effect dictates an alternate structural arrangement in some complexes like a chair-shaped central heterocyclic ring), the aluminum atom is eclipsed with respect to the plane defined by the four nitrogen atoms. In view of this geometry, it is apparent that the aluminum center is open to a dioxygen attack (Figure 8), and indeed the insertion of O_2 into the Al–C bond occurs for **3a**, **3b**, and **5**.

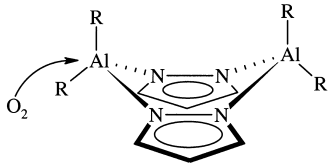


Figure 8. Schematic representation of a boat conformation of aluminapyrazoles, which leaves the aluminum center open to O_2 attack.

Further insight into the dioxygen activations of tetrahedral aluminum alkyls is gained upon consideration of the molecular structure of the low alkylaluminum complexes derived from 3,5-dimethyl substituted pyrazole and their reactivity towards O_2 (unlike the case for **3a** and **3b**, no reactions with O_2 were observed for **4a** and **4b**). From the space-filling representations of **4a** (Figure 3b), it can be seen that the presence of the two methyl groups in the 3,5-positions results in steric protection of the metal center against O_2 attack. This protection is along vectors coplanar to the central Al_2N_4 ring that pass through approximately the middle of the trigonal faces of the Al tetrahedral coordination sphere formed by the two carbon atoms and the nitrogen atom (approach pathways **A** and **A′**, Figure 9). The only available space for the

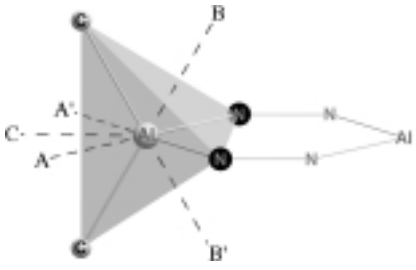


Figure 9. View of the possible approach pathways of molecular oxygen towards the tetrahedral metal center in planar dialkylaluminum derivatives of pyrazoles.

approach of O_2 is from both sides of the central Al_2N_4 ring on the CNN faces and along a vector coplanar to the Al_2N_4 ring and perpendicular to the tetrahedron CC edge (approach pathways **B** and **B′**, and **C**, respectively, Figure 9). In fact, the observed lack of reactivity of compounds **4a** and **4b** towards O_2 undoubtedly indicates that these approach pathways are

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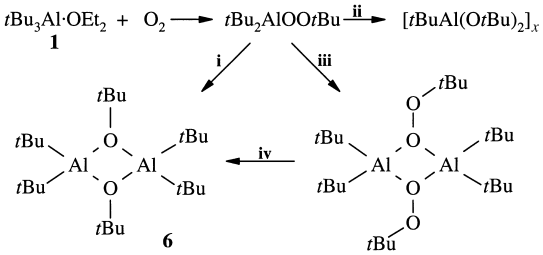
not effective in the oxygenation reactions of tetrahedral dialkylaluminum chelate complexes. We presume, therefore, that the enhanced stability of the planar dialkylaluminum complexes derived from pyrazoles towards oxygenation results from the steric bulk, which precludes the initial approach of a dioxygen molecule to the metal from the tetrahedron CCN face (**A** and **A′**, Figure 9). These observations clearly indicate that the stereoelectronic prerequisites of the four-coordinate metal center are responsible for the fundamentally different reactivity of dialkylaluminum derivatives of pyrazoles towards O_2.

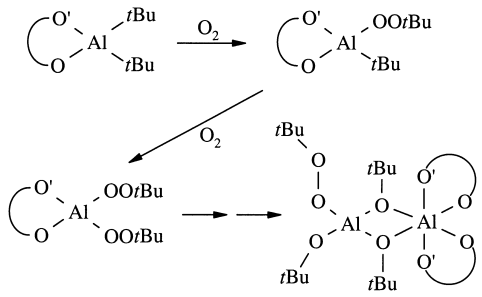
Additional evidence for the hypothesis relating to an attack on the metal center by O_2 from a desired direction as the key feature in the dioxygen activations of tetrahedral organoaluminum compounds is provided by the comparison of the results obtained for two other di-*tert*-butylaluminum complexes, $t\mathrm{Bu}_2\mathrm{Al}(\mu\text{-}O t\mathrm{Bu})_2\mathrm{Al}t\mathrm{Bu}_2$ (**6**) and $(t\mathrm{Bu})_2\mathrm{Al}(\mathrm{mesal})$ (**2**). As mentioned above, unlike the reaction of **6** with O_2, the oxidation of both Al–C bonds readily occurs for **2**. In the latter case, the chelating mesal ligand does not provide the steric hindrance during the tetrahedron CCO facial attack of O_2, and a dioxygen molecule may approach the metal center for subsequent interactions. Furthermore, the oxidation of only one *tert*-butyl group in **1** and all *tert*-butyl groups in **2** is also worthy to be noted. The presence of only the monoalkoxide product in the reaction of **1** with O_2 indicates that the reaction of the alkylperoxide $t\mathrm{Bu}_2\mathrm{AlOO}t\mathrm{Bu}$ intermediate formed in the first reaction step by intermolecular oxygen transfer (Scheme 6) with a second molecule of the parent compound is preferred (path i). This is rather than intramolecular autoxidation, which leads to higher oxidized alkoxide compounds (path ii). However, we cannot exclude



Scheme 6. Considered pathways of the oxygenation reaction of the *tert*-butyl derivative **1**.

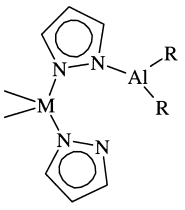
the possibility that the $t\mathrm{Bu}_2\mathrm{AlOO}t\mathrm{Bu}$ moiety initially forms dimeric species (path iii), which further decompose to the monoalkoxide dimer (path iv). The latter path would be consistent with the isolation and structure characterization of the corresponding gallium and indium alkylperoxides.[10, 11]

Although we have no direct evidence for the mechanism of the reaction that leads to **7**, we tentatively propose the following: the product of the first insertion of O_2 into the tBu–Al bond, $t\mathrm{Bu}(t\mathrm{BuOO})\mathrm{Al}(\mathrm{mesal})$, does not undergo intermolecular autoxidation or dimerization as a result of steric hindrances, but the insertion of dioxygen into the second Al–C bond occurs (Scheme 7). Further **7** is formed presumably by subsequent decompositions of alkylperoxo moieties and intermolecular rearrangements similar to those for aluminum dialkoxide chelate complexes.[38]



Scheme 7. A proposed course of oxygenation of $t\mathrm{Bu}_2\mathrm{Al}(O,O')$ chelate complex.

Based on the results presented above we infer that the initial step in the oxygenation reactions is the O_2 attack on the four-coordinate metal center. However, one may argue that the insertion of O_2 into the Al–C bond is preceded by a dissociation of the four-coordinate complex to three-coordinate intermediate, for example, a dissociation of one Al–N bond in the aluminapyrazoles that leads to a three-coordinate η^1-N–AlEt_2 intermediate depicted by structure **II**.



II

Thus, if a dissociative mechanism with a three-coordinate metal center is involved in the reaction, then we would expect that all the aluminapyrazoles studied, independently of their molecular structure, that is, planar or boat conformations, would react with O_2 to form alkoxide compounds. As we have demonstrated above, this is not the case for the planar aluminapyrazoles. Moreover, the dissociation of the Al–N bond of the aluminapyrazoboles has been found to be highly dependent on temperature;[24, 25] this is not the case for the reaction of the aluminapyrazobole **5** with O_2. Though we cannot rule out the involvement of a dissociative mechanism in the reaction of the adduct $(t\mathrm{Bu})_3\mathrm{Al}\cdot\mathrm{OEt}_2$ (**1**) with O_2 (in the latter case, the Al–O dative bond is relatively weak), generally the dissociative mechanism with a transiently three-coordinate metal center seems to be of minor importance in the reactions of O_2 with four-coordinate aluminum alkyls, and especially in the reactions carried out at relatively low temperatures.

Our view is fully consistent with the results obtained by Chisholm et al. for the interaction of O_2 with the four-coordinate diethylaluminum complexes with tris(alkylpyrazolyl)hydroborato ligands.[25] In the latter report, it has been shown that although the complex $[\mathrm{H}(3\text{-}t\mathrm{Bupz})\mathrm{B}(3\text{-}t\mathrm{Bupz})_2\text{-}\eta^2]\mathrm{AlEt}_2$ readily isomerizes to $[\mathrm{H}(3\text{-}t\mathrm{Bupz})\mathrm{B}(3\text{-}t\mathrm{Bupz})(5\text{-}t\mathrm{Bupz})\text{-}\eta^2]\mathrm{AlEt}_2$ in solution, no oxidation products were evident for the former compound after a 24 h reaction period at 20 °C. In contrast, the second compound reacted immediately, as has been reported, with O_2 under similar conditions. In our opinion (the authors have not discussed the observed dissimilarity) for $[\mathrm{H}(3\text{-}t\mathrm{Bupz})\mathrm{B}(3\text{-}t\mathrm{Bupz})_2\text{-}\eta^2]\mathrm{AlEt}_2$, the bulky *tert*-butyl groups provide a steric shielding of the metal center (structure **III**, Figure 10). Furthermore, inspection of the molecular structure of $[\mathrm{H}(3\text{-}t\mathrm{Bupz})\mathrm{B}(3\text{-}t\mathrm{Bupz})(5\text{-}t\mathrm{Bupz})\text{-}\eta^2]$-

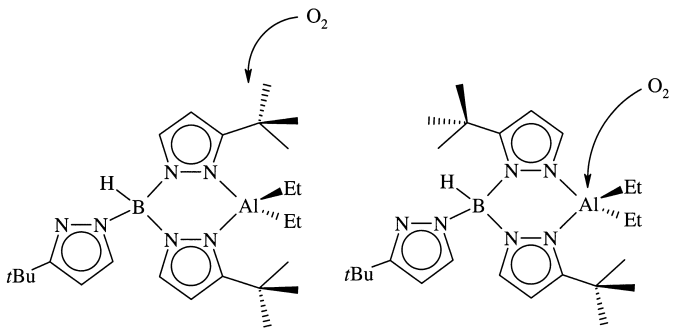


Figure 10. Schematic representation of both the aluminum center shielding in [H(3-*t*Bupz)B(3-*t*Bupz)$_2$-η^2]AlEt$_2$ (**III**) and the open face in [H(3-*t*Bupz)B(3-*t*Bupz)(5-*t*Bupz)-η^2]AlEt$_2$ (**IV**) towards O_2 attack.

AlEt$_2$ reveals that the aluminum atom is eclipsed with respect to the plane defined by the four pyrazole nitrogens, and only one CCN face is shielded by the *tert*-butyl group (structure **IV**, Figure 10). The second CCN face is open to O_2 attack, and indeed the reaction can take place.

Finally, the same morphology observed by us for the structures of the alkylperoxo compound **7** and the alkoxide compound **8** as well as the structures of dimer **6** that involve bridging alkoxides, and both types of dimers *t*Bu$_2$Ga(μ-OO*t*Bu)(μ-O*t*Bu)Ga*t*Bu$_2$ and *t*Bu$_2$M(μ-OO*t*Bu)$_2$M*t*Bu$_2$ (M = Ga or In) with bridging alkylperoxides,[10, 11, 37] leads to another reasonable presumption that Group 13 alkylperoxides can form species similar to the well-known alkoxide compounds. This is usually neglected when an autoxidation mechanism of Group 13 organometallic compounds is considered.

Conclusion

This report deals with an investigation of the reactivity of sterically encumbered four-coordinate aluminum alkyls with molecular oxygen. Although mechanistic considerations have usually assumed the interaction of monomeric three-coordinate aluminum alkyls with dioxygen, our study has shown that four-coordinate complexes can be readily oxidized to alkoxide compounds via alkyl peroxide intermediates. We have also demonstrated the feasibility of the attack on the metal center by O_2, followed by an insertion of O_2 into the Al–C bond to generate an Al–OOR moiety, and this is the key feature in the dioxygen activations of four-coordinate organoaluminum complexes. For the first time we have fully structurally characterized the aluminum alkylperoxo compound, (*t*BuOO)(*t*BuO)Al(μ-O*t*Bu)$_2$Al(mesal)$_2$, which was derived from the insertion of O_2 into the Al–C bond in the dialkylaluminum *O*,*O*′-chelate complex. Moreover, the current results indicate that the initial approach of molecular oxygen to the metal center has strong geometric requirements, that is, for R$_2$Al(X,X) complexes (where X,X = nitrogen–nitrogen or oxygen–oxygen chelating ligand), the effective approach pathway is on one of the two tetrahedron CCX planes. Evidence for this view has been provided after consideration of both structural features of various four-coordinate aluminum alkyls, and the observed divergent behavior of these compounds towards dioxygen. Thus, all aluminapyrazoles of planar structure, the *tert*-butyl derivative of pyrazole, and lower alkylaluminum derivatives supported by the more demanding 3,5-dimethylpyrazoyl ligand, are stable under an atmosphere of dry oxygen at ambient temperature. The space-filling representation of these compounds has undoubtedly shown that the bulky *tert*-butyl groups or pyrazolyles ligands, respectively, provide steric protection for the metal center against an effective O_2 attack. In contrast, the low alkylaluminum complexes derived from pyrazole and the diethylaluminapyrazobole, and all compounds with the metal center eclipsed with respect to the plane defined by the four nitrogen atoms, smoothly react with O_2 to form aluminum alkoxides. However, only one aluminum alkyl group from the R$_2$Al moieties readily reacted, for example, the reaction of Et$_2$B(μ-pz)$_2$AlEt$_2$ with O_2 allows for the isolation of the five-coordinate ethyl(ethoxide)aluminum dimer [Et$_2$B(μ-pz)$_2$Al(μ-OEt)Et]$_2$. In fact, a plausible hypothesis relating to the interaction mechanism of four-coordinate aluminum alkyls with O_2 has certainly been advanced. Further studies are required in order to achieve an intimate understanding of the stereoelectronic effects that control the insertion of O_2 into the Al–C bond and the subsequent transformation of alkylperoxides.

Experimental Section

General methods: All operations were carried out under a nitrogen atmosphere with a standard Schlenk and high-vacuum techniques. Solvents were purified and dried by standard techniques. The NMR spectra were recorded from a solution in C_6D_6 (300 MHz, 20 °C) on a Varian 300VXL spectrometer, and the IR spectra (1800–350 cm^{-1}) were recorded from a solution in CH_2Cl_2 on a Specord 75IR spectrophotometer. Molecular weight measurements were carried out using cryoscopic methods in benzene. Commercially available reagents were used as purchased. The compounds (*t*Bu)$_3$Al · OEt$_2$ (**1**)[41] and K[Et$_2$B(pz)$_2$][42] were prepared by the literature methods.

(*t*Bu)$_2$Al(mesal) (2): Methyl salicylate (4 mmol) was slowly added at 0 °C to a solution of *t*Bu$_3$Al · OEt$_2$ (4 mmol) in toluene (15 cm^3). The solution was warmed up to room temperature over 0.5 h. The solvent was evaporated in vacuo at ambient temperature. The resulting white product was recrystallized from toluene/hexane solution; yield approximately 96%. ^{1}H NMR: δ = 1.27 (s, 18H; Al–*t*Bu), 3.05 (s, 3H; OCH$_3$), 6.34 (td, 1H; Ar–H), 6.92 (dd, 1H; Ar–H), 7.02 (td, 1H; Ar–H), 7.47 (dd, 1H; Ar–H); ^{27}Al NMR: δ = 153 ($w_{1/2}$ = 1750 Hz).

General procedure for the synthesis of aluminapyrazoles: The compound R$_3$Al (R = Me, Et) (≈4 mmol) was added dropwise by syringe at −78 °C to a suspension of pyrazole or 3,5-dimethylpyrazole in toluene. The resulting solution was allowed to warm up to room temperature and was then stirred for 2 h. The solvent was removed under vacuum to leave a white solid in essentially quantitative yield.

[*Me*$_2$*Al*(μ-*pz*)]$_2$ (***3a***): ^{1}H NMR: δ = −0.29 (s, 12H; Al–CH$_3$), 5.88 (t, 2H; CH), 7.36 (d, 4H; CH); ^{27}Al NMR: δ = 153 ($w_{1/2}$ = 3480 Hz); $C_{10}H_{18}Al_2N_4$: calcd C 48.38, H 7.31, N 22.57; found C 48.32, H 7.52, N 22.47.

[*Et*$_2$*Al*(μ-*pz*)]$_2$ (***3b***): ^{1}H NMR: δ = 0.28 (q, 8H; Al–C*H*$_2$CH$_3$), 1.13 (t, 12H; Al–CH$_2$C*H*$_3$), 5.90 (t, 2H; CH), 7.45 (d, 4H; CH); ^{27}Al NMR: δ = 151 ($w_{1/2}$ = 3540 Hz); $C_{14}H_{26}Al_2N_4$: calcd C 55.25, H 8.61, N 18.41; found C 55.08, H 8.72, N 18.30.

[*Me*$_2$*Al*(μ-*3,5-Me*$_2$*pz*)]$_2$ (***4a***): ^{1}H NMR: δ = −0.29 (s, 12H; Al–CH$_3$), 2.17 (s, 12H; CH$_3$), 5.55 (s, 2H; CH); ^{27}Al NMR: δ = 150 ($w_{1/2}$ = 3240 Hz); $C_{14}H_{26}Al_2N_4$: calcd C 55.25, H 8.61, N 18.41; found: C 55.20, H 8.75, N 18.33.

[*Et*$_2$*Al*(μ-*3,5-Me*$_2$*pz*)]$_2$ (***4b***): ^{1}H NMR: δ = 0.33 (q, 8H; Al–C*H*$_2$CH$_3$), 1.08 (t, 12H; Al–CH$_2$C*H*$_3$), 2.20 (s, 12H; CH$_3$), 5.63 (s, 2H; CH); ^{27}Al NMR: δ = 151 ($w_{1/2}$ = 3360 Hz); $C_{18}H_{34}Al_2N_4$: calcd C 59.98, H 9.51, N 15.54; found C 59.88, H 9.60, N 15.45.

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$[(tBu)_2Al(\mu\text{-}pz)]_2$ (**3c**): A solution of pyrazole (4 mmol) in toluene at 0 °C was added dropwise to a solution of $t\text{Bu}_3\text{Al}\cdot\text{OEt}_2$ (4 mmol) in toluene. The resulting solution was warmed up to room temperature and then was stirred for 5 h. The solvent was removed under vacuum to leave a white solid in quantitative yield. ^{1}H NMR: $\delta = 0.98$ (s, 36H; Al–*t*Bu), 6.01 (t, 2H; CH), 7.68 (d, 4H; CH); ^{27}Al NMR: $\delta = 150$ ($w_{1/2} = 3800$ Hz); $C_{22}H_{42}Al_2N_4$: calcd C 63.43, H 10.16, N 13.45; found C 63.34, H 10.21, N 13.38.

Synthesis of $Et_2B(\mu\text{-}pz)_2AlEt_2$ (5): The preparation of **5** was carried out following the published method.[15] The compound $K[Et_2B(pz)_2]$ (12 mmol) was suspended in toluene (30 cm^3), and Et_2AlCl (12 mmol) was added dropwise by syringe at room temperature. The resulting white slurry was stirred for 3 h and filtered. The solvent was removed under vacuum to leave a colorless oil: yield approximately 98%. ^{1}H NMR: $\delta = 0.06$ (q, 4H; Al–CH_2CH$_3$), 0.5–0.8 (m, 5H; B–C$_2$H$_5$), 0.96 (t, 6H; Al–CH$_2$CH_3), 6.39 (t, 2H; CH), 7.72 (d, 2H; CH) 7.76 (d, 2H; CH); ^{27}Al NMR: $\delta = 153$ ($w_{1/2} = 3750$ Hz); ^{11}B NMR: $\delta = 2.3$.

General procedure for the reaction of 1 and 2 with O_2: In a typical oxygenation reaction, a solution of the appropriate aluminum alkyl ($\approx$3 mmol) in hexane or a hexane/toluene mixture (7 cm^3) was exposed to dry atmospheric oxygen at -15 °C ($CaCl_2$ was placed at the inlet of the Schlenk flask to prevent the access of moisture). The reaction was carried out for approximately 3 h. The solvent was removed under vacuum to yield a white crystalline solid. The resulting products were characterized by elemental analysis and NMR spectroscopy.

$t\text{Bu}_2\text{Al}(\mu\text{-O}t\text{Bu})_2\text{Al}t\text{Bu}_2$ (6): The reaction was performed as described in the general procedure with **1** (0.45 g); yield approximately 98%. ^{1}H NMR: $\delta = 1.23$ (s, 36H; *t*Bu), 1.33 (s, 18H; *t*BuO); $C_{24}H_{54}Al_2O_2$: calcd C 67.25, H 12.70; found C 67.15, H 12.78.

$(t\text{BuOO})(t\text{BuO})\text{Al}(\mu\text{-O}t\text{Bu})_2\text{Al(mesal)}_2$ (7): The reaction was performed as described in the general procedure with **2** (0.86 g); yield approximately 90%. When the reaction was carried out at room temperature, the formation of an inseparable complex mixture of products was observed. White crystals of **7** were isolated from a solution in toluene/pentane at -30 °C. IR (CH_2Cl_2): $\tilde{\nu}_{O-O} = 890$ cm^{-1}; ^{1}H NMR: $\delta = 1.38$ (s, 9H; *t*BuO), 1.49 (s, 9H; *t*BuO), 1.60 (s, 9H; *t*BuO), 1.61 (s, 9H; *t*BuO), 3.77 (s, 3H; OCH$_3$), 3.82 (s, 3H; OCH$_3$), 6.38 (t, 2H; Ar–H), 6.57 (t, 2H; Ar–H), 6.92 (t, 2H; Ar–H), 7.79 (d, 2H; Ar–H); $C_{32}H_{50}Al_2O_{11}$: C 57.82, H 7.58; found: C 57.91, H 7.74.

$(t\text{BuO})_2\text{Al}(\mu\text{-O}t\text{Bu})_2\text{Al(mesal)}_2$ (8): A solution of **7** in toluene was stirred for 2 h at ambient temperature. The solvent was removed under vacuum, and a white crystalline solid was produced. ^{1}H NMR: $\delta = 1.53$ (s, 18H; *t*BuO), 1.59 (s, 18H; *t*BuO), 3.74 (s, 6H; OCH$_3$), 6.37 (t, 2H; Ar–H), 6.55 (t, 2H; Ar–H), 6.92 (t, 2H; Ar–H), 7.83 (d, 2H; Ar–H), $C_{32}H_{50}Al_2O_{10}$: C 59.25, H 7.77; found C 59.34, H 7.82. Attempts to obtain crystals suitable for X-ray analysis failed.

Reaction of $[R_2Al(\mu\text{-}pz)]_2$ (R = Me, Et) with O_2: A solution of $[R_2Al(\mu\text{-}pz)]_2$ (2.6 mmol) in toluene (7 cm^3) was exposed at ambient temperature to atmospheric oxygen, which was dried by passage over KOH pellets. The reaction was carried out for 3–6 h. The solvent was removed under vacuum, and a white crystalline solid was produced. The resulting product was characterized by elemental analysis and NMR spectroscopy.

Reaction of $[(t\text{Bu})_2\text{Al}(\mu\text{-pz})]_2$ with O_2: The reaction was carried out in a manner analogous to that for the lower alkyl aluminapyrazoles. No reaction products were evident after 24 h at ambient temperature (monitored by ^{1}H NMR).

Reaction of $[R_2Al(\mu\text{-}3,5\text{-}Me_2pz)]_2$ (R = Me, Et) with O_2: In a typical oxygenation reaction, no reaction products were evident after 24 h at ambient temperature (monitored by ^{1}H NMR).

$[Et_2B(\mu\text{-}pz)_2Al(\mu\text{-OEt})Et]_2$ (9): A solution of **5** (2.6 mmol) in hexane (7 cm^3) was exposed to dry atmospheric oxygen for approximately 4 h at -15 °C, and a slow precipitation of colorless crystals occurred. The crystals were filtered and dried under vacuum; the yield was approximately 96%. ^{1}H NMR: $\delta = -0.05$ (q, 4H; Al–CH_2CH$_3$), 0.5–0.8 (m, 5H; B–C$_2$H$_5$), 0.98 (t, 6H; Al–CH$_2$CH_3), 1.08 (t, 6H; OCH$_2$CH_3), 3.88 (q, 4H; OCH_2CH$_3$), 6.18 (t, 2H; CH), 7.68 (d, 2H; CH), 7.74 (d, 2H; CH); ^{27}Al NMR: $\delta = 62$ ($w_{1/2} = 1200$ Hz); ^{11}B NMR: $\delta = 1.8$; $C_{28}H_{52}Al_2B_2N_8O_2$: calcd C 55.28, H 8.62, N 18.42; found C 55.10, H 8.70, N 18.35.

X-ray crystallographic study: Crystal data for X-ray structure determinations were collected with a Siemens P3 diffractometer ($Mo_{K\alpha}$, $\lambda =$ 0.71073 Å, graphite monochromated). Suitable single crystals of **3c**, **4a**, **6**, **7**, and **9** were placed in a thin-walled capillary (Lindemann glass) in an inert atmosphere. The crystal class and the orientation matrix were obtained from the least-square refinement of randomly found reflections. The intensities were recorded in the $\omega - 2\theta$ scan mode. A meaningful crystal decay of 15.1% was recorded for **3c**. After correction for the Lorentz polarization effect and the crystal decay, the equivalent reflections were averaged (absorption corrections were not necessary). The structures were solved by direct methods using SHELXS-86.[43] The full-matrix least-squares refinement method against F^2 values was carried out by using the SHELXL-93 program (for **7**) and the SHELXL-97 program[44] for the remaining compounds. Except for the partial occupancy group of the disordered part of the molecule **7**, all non-hydrogen atoms throughout all five structures were refined with anisotropic displacement parameters. The hydrogen atoms of all methyl groups in **4a** were refined as idealized disordered groups, with two positions rotated from each other by 60° and refined occupancy factors. For **3c**, **6**, and **9**, the hydrogen atoms of the methyl groups were placed in calculated positions and were allowed to ride on their parent C atoms. The H–C bond lengths in **9** were also allowed to vary. The positional and isotropic thermal parameters for hydrogen atoms bonded to the pyrazole rings in **3c** and **4a** were refined. The monocrystals of **7** were weakly diffracted, and a considerable disorder was observed. As we found in the refinement process, the peroxide and alkoxide ligands were disordered over two opposite sites that almost mirrored against a plane defined by the central Al_2O_2 ring. The disorder was modeled in terms of two sets of Al(O*t*Bu)(OO*t*Bu) atoms with refined occupancy factors 0.75(1) and 0.25(1). The non-hydrogen atoms of the group with SOF = 0.25(1) were refined isotropically with geometrical restraints, and we assumed that the chemically equivalent lengths in both groups were nearly equal. Hydrogen atoms in **7** were placed in calculated positions with assigned thermal parameters $[U(H) = 1.2 \times U_{eq}(C)]$. Crystal data, data collection, and refinement parameters for **3c**, **4a**, **6**, **7**, and **9** are given in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136351, and CCDC-136470 to CCDC-136473. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Financial support for this work was provided by the State Committee for Scientific Research (Grant No. 3T09A 10812 and 3T09A 01615).

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Table 3. Crystal data, data collection, and refinement parameters.

	3c	**4a**	**6**	**7**	**9**
formula	$C_{22}H_{42}Al_2N_4$	$C_{14}H_{26}Al_2N_4$	$C_{24}H_{54}Al_2O_2$	$C_{32}H_{50}Al_2O_{11}$	$C_{28}H_{52}Al_2B_2N_8O_2$
M_r	416.56	304.35	428.63	664.68	608.36
crystal size [mm]	$0.45 \times 0.20 \times 0.16$	$0.19 \times 0.15 \times 0.12$	$0.22 \times 0.15 \times 0.10$	$0.32 \times 0.28 \times 0.12$	$0.42 \times 0.26 \times 0.24$
crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	triclinic
space group, number	$P2_1/c$, 14	$P2_1/c$, 14	*Pbca*, 61	*Pbca*, 61	$P\bar{1}$, 2
temperature [K]	293(2)	293(2)	293(2)	293(2)	293(2)
a [Å]	8.6495(8)	8.6716(12)	15.056(3)	15.171(3)	8.6856(16)
b [Å]	13.7690(13)	13.6052(17)	9.825(3)	18.542(6)	9.0990(16)
c [Å]	11.9096(11)	8.4960(13)	18.344(4)	26.827(7)	11.6497(19)
α [°]	90	90	90	90	85.603(14)
β [°]	109.209(7)	111.842(11)	90	90	86.492(14)
γ [°]	90	90	90	90	67.915(14)
V [Å^3]	1339.4(5)	930.4(2)	2713.8(12)	7546.5(34)	850.1(3)
Z	2	2	4	8	1
ρ_{calcd} [g cm^{-3}]	1.033	1.086	1.049	1.170	1.188
F(000)	456	328	960	2848	328
radiation used			$Mo_{K\alpha}$, $\lambda = 0.71073$ Å		
μ [mm^{-1}]	0.122	0.153	0.123	0.129	0.123
2θ range [°]	4.68 – 50.14	5.06 – 50.10	4.44 – 50.10	4.0 – 47.2	3.50 – 50.10
reflections collected	3267	1755	3668	4669	3235
unique data	2352, $R_{int} = 0.036$	1637, $R_{int} = 0.017$	2397, $R_{int} = 0.015$	4669, $R_{int} = 0.00$	3012, $R_{int} = 0.021$
obs. data [$I > 2\sigma(I)$]	1470	1144	1634	2136	2310
data/parameters	2352/175	1637/107	2397/145	4659/464	3012/227
$R1$, $wR2$[a]	0.0529, 0.1329	0.0386, 0.0884	0.0380, 0.0970	0.0698, 0.1026	0.0428, 0.1096
weights a, b[b]	0.0832, 0.0000	0.0497, 0.0212	0.0599, 0.0000	0.0211, 10.8828	0.0668, 0.1744
largest resid. [e Å^{-3}]	+0.197/−0.167	+0.159/−0.126	+0.223/−0.114	+0.168/−0.177	+0.299/−0.185

[a] $R1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

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Received: November 2, 1999 [F2112]