DOI: 10.1002/zaac.201100352

Organoelement Complexes of a Dinucleating Double *β*-Diiminato Ligand – Precedent Cases from Groups 1, 2, and 13

Jan P. Falkenhagen,[a] Peter Haack,[a] Christian Limberg,*[a] and Beatrice Braun[a]

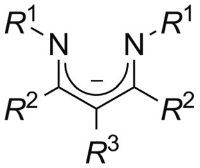
In Memory of Professor Kurt Dehnicke

Keywords: Rubidium; Aluminium; Magnesium; Coordination chemistry; Dinuclear complexes; Main group chemistry

Abstract. Main group chemistry of dinucleating ligands based on a xanthene backbone and two parallel diiminato binding sites (Xanthdim) has been investigated. To complement studies concerning the coordination modes adopted by Xanthdim in combination with alkali metal ions a di-rubidium complex with toluene co-ligands has been prepared. Its structural parameters lie in between those previously observed for corresponding K^+ and Cs^+ complexes. Furthermore, the complexes $[^{Me_2C_6H_3}Xanthdim](MgMe(thf))_2$ (**2**) and $[^{Me_2C_6H_3}Xanthdim](MgBr(thf))_2$ (**3**) were synthesised by reaction of $[^{Me_2C_6H_3}Xanthdim](K(thf)_2)_2$ and $[^{Me_2C_6H_3}Xanthdim]H_2$, respectively, with MeMgBr. Both compounds proved stable against ligand exchange according to the Schlenk equilibrium. After reaction of $[^{Me_2C_6H_3}Xanthdim]H_2$ and $[^{F_2C_6H_3}Xanthdim]H_2$, respectively, with $AlMe_3$ the complexes $[^{Me_2C_6H_3}Xanthdim](AlMe_2)_2$ (**4**) and $[^{F_2C_6H_3}Xanthdim](AlMe_2)_2$ (**5**) were isolated and fully characterised. They were found to be dynamic in solution and Al–CH_3···F-aryl interactions were detected in case of **5**. The solid-state structures and NMR spectroscopic properties of all compounds were determined and analysed.

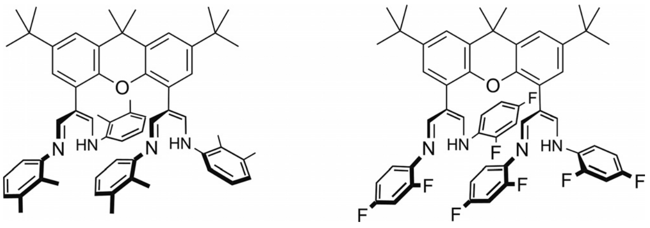
Introduction

β-Diketiminates (Scheme 1) have proved versatile ligand systems, both, in main group and transition metal chemistry. They stabilise high as well as low oxidation states, and they can also be employed for the synthesis of coordinatively unsaturated complexes, which often show interesting reactivities.[1–25]



Scheme 1.

As these reactivities are often based on the cooperation of two metal centres, we have synthesised two ligand precursors where two *β*-diiminato units are oriented parallel to each other: $[^{R}Xanthdim]H_2$ (Scheme 2) with *R* = 2,3-dimethylphenyl or 2,4-difluorophenyl.[26,27]

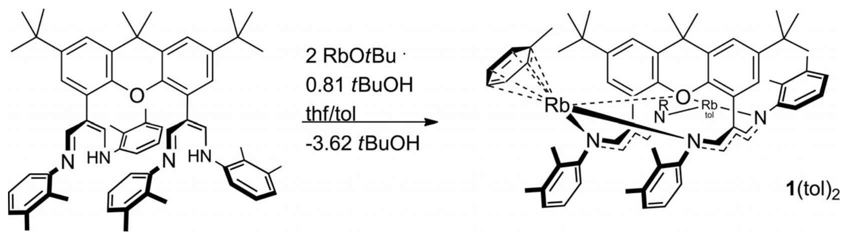


Scheme 2. The ligand precursors $[^{Me_2C_6H_3}Xanthdim]H_2$ (left) and $[^{F_2C_6H_3}Xanthdim]H_2$ (right).

In their deprotonated forms they have been employed successfully as ligands in transition metal chemistry, including dinuclear organozinc complexes that were investigated as epoxide/CO_2 copolymerisation catalysts,[27] diiron(II) complexes that proved to react with O_2 to give Fe^{III}–O–Fe^{III} compounds,[28] and a dicopper(I) complex, which activates O_2 involving a highly unusual Cu^{II}–O–Cu^{II} species.[29] Furthermore, an unprecedented binding and activation of CS_2 was realised by a dicopper(I) complex.[30] Recently, these studies were extended to alkali and alkaline-earth metal chemistry for various reasons:[31] First, alkali metal complexes represent valuable starting materials in the synthesis of transition metal complexes via salt metathesis, and we were interested, whether any structural differences occur on going from lithium to the higher homologues. Moreover, the questions arose, whether heteroleptic bimetallic complexes, $[Xanthdim](MR)_2$, are stable against ligand exchange through the Schlenk equilibrium and whether they can be employed as polymerisation catalysts. Initial work included the successful synthesis and characterisation

---

* Prof. Dr. C. Limberg
Fax: +49-30-2093-6966
E-Mail: christian.limberg@chemie.hu-berlin.de
[a] Humboldt-Universität zu Berlin
Institut für Chemie
Brook-Taylor-Str. 2
12489 Berlin, Germany



Scheme 3. Synthesis of $\mathbf{1}(\mathrm{tol})_2$ (R = 2,3-dimethylphenyl).

of lithium, potassium, caesium, magnesium and calcium complexes (whereas the second valences of magnesium and calcium were saturated by amido and diiminato ligands, respectively).[31]

The research described here expands these investigations to organometallic chemistry of the elements rubidium and magnesium. Moreover, for the first time a group 13 element, namely aluminium, has been included, as the Xanthdim ligand matrix may also be expected to support the cooperation of two aluminium atoms in polymerisation catalysis.

Results and Discussion

Group 1 Organometallics: Coordination of Rubidium Ions with Toluene Co-Ligands

Addition of RbO*t*Bu·0.81*t*BuOH to a solution of $[^{\mathrm{Me_2C_6H_3}}\mathrm{Xanthdim}]\mathrm{H}_2$ in thf caused a rapid colour change from yellow to orange indicating a spontaneous deprotonation of the ligand precursor. Subsequent addition of excessive hexane to a concentrated solution of the product in toluene led to the precipitation of $[^{\mathrm{Me_2C_6H_3}}\mathrm{Xanthdim}](\mathrm{Rb(tol)})_2$ ($\mathbf{1}(\mathrm{tol})_{2,}$ Scheme 3). It is noteworthy that the toluene molecules coordinated to the rubidium ions can be removed completely in vacuo, resulting in $[^{\mathrm{Me_2C_6H_3}}\mathrm{Xanthdim}](\mathrm{Rb})_2$ (**1**), which could be isolated in 81 % yield. Complex **1** is readily soluble in benzene, toluene, thf and dichloromethane; stability in dichloromethane is clearly limited, though, due to the not unexpected reactivity of **1** against halogenated solvents. However, NMR spectroscopic characterisation of a [D$_2$]dichloromethane solution was offhandedly possible, and the ^{1}H NMR spectrum showed characteristics that confirmed the quantitative formation of $[^{\mathrm{Me_2C_6H_3}}\mathrm{Xanthdim}]^{2-}$ and thus a complete conversion of $[^{\mathrm{Me_2C_6H_3}}\mathrm{Xanthdim}]\mathrm{H}_2$ to **1**: a singlet resonance at δ = 7.84 ppm for the diiminato protons instead of a doublet (as observed in case of $[^{\mathrm{Me_2C_6H_3}}\mathrm{Xanthdim}]\mathrm{H}_2$), and the absence of the signal at around 12 ppm corresponding to the acidic NH protons of the ligand precursor.

Crystals of $\mathbf{1}(\mathrm{tol})_2$·2(tol) suitable for single-crystal X-ray diffraction analysis could be obtained by slow evaporation of the solvent from a concentrated solution of **1** in toluene at room temp. The molecular structure is shown in Figure 1. As recently reported for dinuclear potassium as well as caesium complexes of the $[^{\mathrm{Me_2C_6H_3}}\mathrm{Xanthdim}]^{2-}$ ligand,[31] also in $\mathbf{1}(\mathrm{tol})_2$·2(tol) the β-diiminato binding pockets have a W-conformation. This is not surprising since the ion radius of Rb$^+$ (148 pm) lies between the radii of K$^+$ (133 pm) and Cs$^+$ (167 pm). The two β-diiminato units are doubly bridged by the two Rb$^+$ ions, which complete their coordination spheres by interactions with the central oxygen atom of the xanthene-based backbone and by toluene ligands binding in a η^6 mode. The Rb···Rb distance of 6.0492(5) Å lies exactly between the distances of the corresponding dinuclear potassium (5.662(1) Å) and caesium (6.284(2) Å) complexes.[31] As found for the molecular structures of those, also in the structure of $\mathbf{1}(\mathrm{tol})_2$·2(tol) each metal ion binds to the β-diiminato units with one short (Rb1–N3: 2.854(2) Å and Rb2–N1: 2.868(2) Å) and one long (Rb1–N2: 3.01(2) Å and Rb2–N4: 2.924(2) Å) contact. The C–N and C–C distances within the binding pockets match the ones determined for the potassium and caesium complex, respectively, quite well, too.

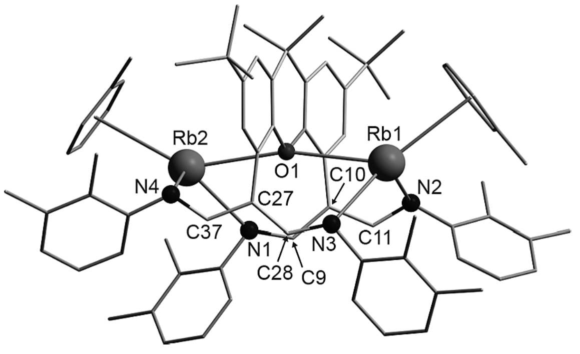
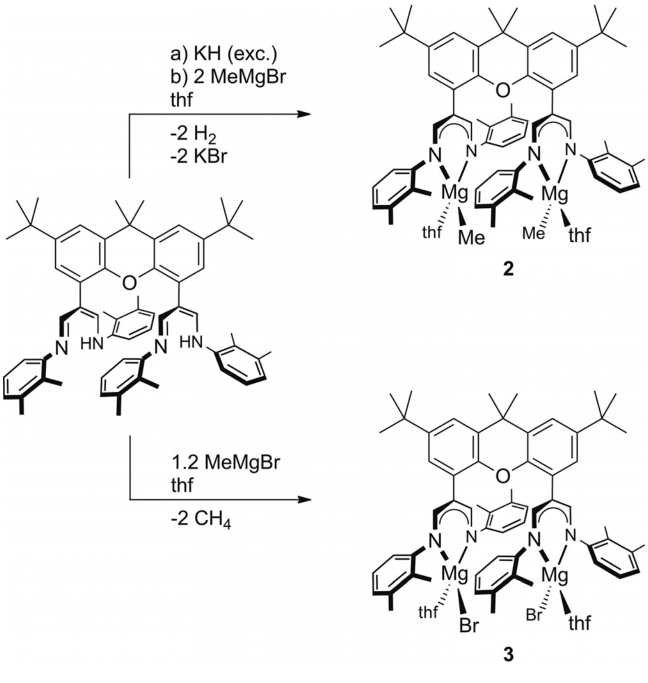


Figure 1. Molecular structure of $\mathbf{1}(\mathrm{tol})_2$ co-crystallised with two molecules of toluene. All hydrogen atoms and solvent molecules were omitted for clarity. Selected bond lengths in Å and angles in deg: Rb1···Rb2 6.0492(5), Rb1–N2 3.01(2), Rb1–N3 2.854(2), Rb2–N1 2.868(2), Rb2–N4 2.924(2), Rb1–O1 3.0503(18), Rb2–O1 3.0530(18), Rb1···Ar$_{\mathrm{centre}}$ 3.1407(3), Rb2···Ar$_{\mathrm{centre}}$ 3.1599(3), N1–C9 1.309(4), C9–C10 1.401(4), C10–C11 1.409(4), N2–C11 1.308(4), N3–C28 1.312(4), C27–C28 1.399(4), C27–C37 1.410(4), N4–C37 1.310(4), Rb1–O1–Rb2 164.74(7), N3–Rb1–N2 111.03(6), N3–Rb1–O1 68.75(6), N3–Rb1–Ar$_{\mathrm{centre}}$ 149.16(5), N1–Rb2–N4 109.15(7), N1–Rb2–O1 64.53(6), N1–Rb2–Ar$_{\mathrm{centre}}$ 138.79(5).

A First Organoelement Representative from Group 2: Methyl Magnesium Chemistry

Having confirmed the stability of a dinuclear amido magnesium Xanthdim complex against ligand exchange through the Schlenk equilibrium[32–34] in a previous study[31] we now focused on the investigation of an analogous species coordinated by alkyl functionalities. Corresponding mononuclear complexes bearing β-diketiminato ligands were shown to be accessible via two different routes: either by direct reaction between the ligand precursor [$^{Me_2}L^{iPr}$]H ($^{Me_2}L^{iPr}$ = CH{(CMe)(2,6-iPr$_2$C$_6$H$_3$N)}$_2$) and Me$_2$Mg[35] or by deprotonation with the aid of an external base (nBuLi) followed by treatment of the resulting lithium β-diketiminate, [$^{Me_2}L^{iPr}$]Li, with MeMgCl.[36]

Following the latter strategy, but with KH instead of nBuLi as the deprotonation agent, we set out, reacting [^{Me_2C_6H_3}Xanthdim]H$_2$ with KH in thf to access [^{Me_2C_6H_3}Xanthdim](K(thf)$_2$)$_2$ as described previously.[31] Subsequent treatment of this solution with MeMgBr in thf caused an immediate colour change from orange to yellow accompanied by a clouding of the reaction mixture. After workup [^{Me_2C_6H_3}Xanthdim](MgMe(thf))$_2$ (**2**) could be isolated as an orange solid in 71 % yield (Scheme 4). The ^{1}H NMR spectrum recorded for a [D$_2$]dichloromethane solution showed the complete set of signals expected for [^{Me_2C_6H_3}Xanthdim]$^{2-}$. The absence of a signal at around 12 ppm again indicated successful deprotonation of the precursor. Moreover, a singlet at –1.54 ppm corresponding to the six protons of the Mg bound methyl groups ensured selective formation of **2**.



Scheme 4. Synthesis of **2** and **3**.

Slow evaporation of the volatiles from a concentrated solution of **2** in a mixture of thf and hexane (1:2) led to crystals suitable for single-crystal X-ray diffraction analysis. However, these represented disordered binary crystals, in which the magnesium bound methyl groups were partly substituted by bromide anions. The latter applied to 5 % of the magnesium bound methyl groups as determined by population refinements of these sites. Two independent complex molecules which only exhibit minor differences (except for the observed metal-to-metal distance, vide infra) were found in the asymmetric unit. Therefore only one molecule will be discussed below. The degree of Me→Br substitution in the solid solution is not homogeneous for all four sites inherent to the two independent complex molecules under discussion; the sites affected by substitutional disorder are occupied randomly by -Me and -Br ligands with no disturbance of the crystal lattice. Occurrence of this solid solution can be explained principally by an anion exchange between **2** and KBr, formed as a by-product, or by a Schlenk equilibrium between [^{Me_2C_6H_3}Xanthdim](MgMe(thf))$_2$ (**2**) and unreacted MeMgBr. However, a solution of **2** does not readily react to give [^{Me_2C_6H_3}Xanthdim](MgBr(thf))$_2$ (**3**) either on addition of KBr or MeMgBr as evidenced by NMR spectroscopy. We therefore assume that this transformation takes place very slowly during the crystallisation process, where obviously small amounts of bromide were present. However, we did not repeat crystallisation with rigorously purified **2** as the adequate treatment of the data collection revealed the complete structural information. The molecular structure of one of the independent molecules in the asymmetric unit of the solid solution is shown in Figure 2.

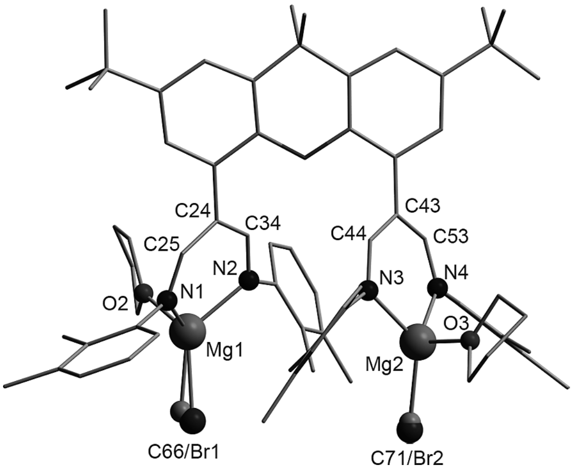


Figure 2. Molecular structure of one of the independent molecules in the asymmetric unit of the solid solution involving **2** co-crystallised with 0.5 molecules of thf and 0.25 molecules of hexane. All hydrogen atoms and solvent molecules were omitted for clarity. Selected bond lengths in Å and angles in deg: Mg1···Mg2 6.028(3), Mg1–C66 2.09(2), Mg2–C71 2.162(17), Mg1–Br1 2.33(4), Mg2–Br2 2.35(3), Mg1–O2 2.068(4), Mg2–O3 2.050(4), Mg1–N1 2.092(4), Mg1–N2 2.079(5), Mg2–N3 2.097(5), Mg2–N4 2.070(4), N1–C25 1.329(6), N2–C34 1.320(6), N3–C44 1.327(7), N4–C53 1.329(6), C24–C25 1.392(8), C24–C34 1.397(7), C43–C44 1.391(7), C43–C53 1.401(7), N1–Mg1–N2 92.72(18), N1–Mg1–C66 123.2(6), N1–Mg1–Br1 126.4(19), N1–Mg1–O2 104.75(18), N3–Mg2–N4 91.61(17), N3–Mg2–C71 140.9(8), N3–Mg2–O3 92.90 (17).

The two Mg–C bond lengths (Mg1–C66: 2.09(2) Å, Mg2–C71: 2.162(7) Å) are similar to those found for other nitrogen ligated methyl magnesium complexes.[35–40] The determined Mg–Br bond lengths of 2.33(4) Å and 2.35(3) Å, respectively, are somewhat shorter than those observed in similar systems ([L^{SiMe_3}Mg(Br)(thf)]: 2.4692(15) Å, L^{SiMe_3} = SiR{(C(2,6-Me$_2$C$_6$H$_3$)((R)N)}$_2$, R = SiMe$_3$,[41] [(thf)$_2$MgBr{(NtBu)$_2$-SMe}]: 2.4960(13) Å).[42] However, this might be a result of the substitutional disorder. The C–C, C–N and Mg–N bonds within the diiminato binding pockets pairwise have very similar lengths, that is, the diiminato-Mg units are highly symmetric. The distance between the two distorted tetrahedrally coordinated Mg^{2+} ions within one of the two independent molecules in the asymmetric unit cell amounts to 6.028(3) Å (6.351(3) Å for the second independent molecule), which is significantly shorter than the one found in [^{Me_2C_6H_3}Xanthdim](MgN(SiMe$_3$)$_2$(thf))$_2$ (8.003(3) Å).[31] This underlines again the strong dependence of the metal-to-metal distances in Xanthdim complexes on the steric bulk of the co-ligands[29] and the flexibility of the Xanthdim ligand in this respect.

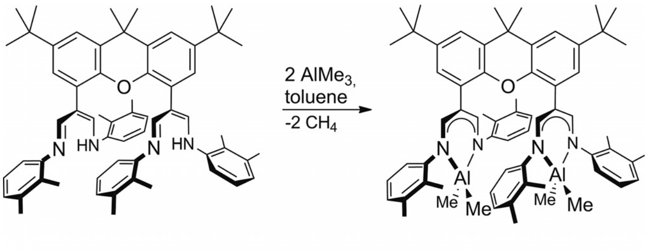
Selective synthesis of the pure bromido complex [^{Me_2C_6H_3}Xanthdim](MgBr(thf))$_2$ (**3**) can be achieved by reaction of MeMgBr directly with an excess of [^{Me_2C_6H_3}Xanthdim]H$_2$ in thf (Scheme 4). After workup **3** was accessible in 58 % yield, and its identity as well as purity was ensured with the aid of NMR spectroscopy. The ^{1}H NMR spectrum recorded for a [D$_2$]dichloromethane solution showed slightly different chemical shifts for the Xanthdim^{2-} signals as compared to those of **2**, especially in the aromatic region. However, as in case of **2** just one signal is observed for each of the methyl groups in the 2- and 3-positions at the nitrogen bound aryl residues. The main difference between the spectra of **2** and **3** obviously is the singlet at –1.54 ppm belonging to the magnesium bound methyl groups.

Group 13 Chemistry: Complexation of Two Dimethylaluminium Units in the Binding Pockets of Xanthdim^{2-}

In recent years poly(ε-caprolactone) and polylactides have emerged as being among the most promising sustainable polymers. Their production from renewable resources, their biodegradability and their versatile biomedical applications have spurred numerous studies in this field of research. A key step to obtain well defined materials with beneficial mechanical properties is rigid control of the polymer chain microstructure. Although there are reports on highly active and very selective *dinuclear* organoaluminium catalysts for ring opening polymerisations (ROP) of cyclic esters, structural studies and analyses concerning potential cooperative effects remain relativly scarce.[56–58] On the other hand, in the last twenty years numerous examples of *β*-diketiminato aluminium complexes have been published,[1,43,44,47–54] including a homoleptic tris-*β*-diketiminato aluminium complex,[55] an aluminium(I) complex[52] and a complex containing an Al–O–Al moiety, claimed to be the smallest MAO model conceivable.[54] The favourable properties of dinuclear organoaluminium compounds as polymerisation catalysts and the rich knowledge available on *β*-diketiminato aluminium complexes suggest attempts to prepare dinuclear diiminato diorgano aluminium compounds. Only few representatives (shown in Scheme 5) are known so far,[45,46] though, and corresponding Xanthdim complexes would add to the variety with a new structural motif based on a vis-à-vis arrangement of two diiminato AlMe$_2$ units. Hence, we have started a corresponding investigation.

[^{Me_2C_6H_3}Xanthdim](AlMe$_2$)$_2$ (4)

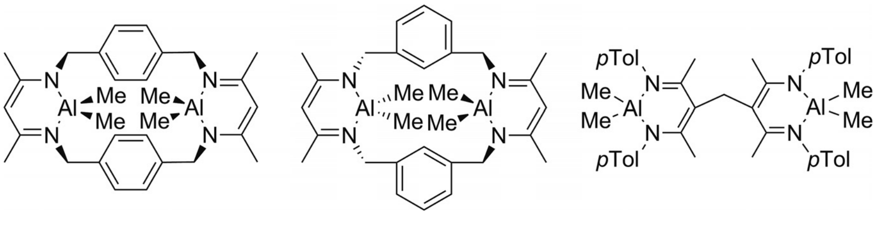
Treating a solution of [^{Me_2C_6H_3}Xanthdim]H$_2$ in toluene with a sixfold excess of trimethylaluminium in toluene caused a rapid colour change from intensively yellow to bright orange indicating deprotonation of [^{Me_2C_6H_3}Xanthdim]H$_2$, which did not occur, if thf was used as the solvent. After stirring at room temp. overnight and precipitation from hot toluene [^{Me_2C_6H_3}Xanthdim](AlMe$_2$)$_2$·tol (**4**·tol) was isolated in 51 % yield as a yellow powder (Scheme 6). Complete deprotonation of the ligand precursor was confirmed by the absence of the respective triplet resonance around 12 ppm in the ^{1}H NMR spectrum of a solution of **4** in [D$_6$]benzene. Instead a broad singlet ($\nu_{1/2}$ = 22 Hz) at –0.13 ppm was observed for the aluminium-bound methyl groups. Significant line broadening of this signal is attributed both to the coupling of the respective protons to the ^{27}Al nuclei and to a dynamic process that causes both methyl groups to be chemically equivalent on the NMR timescale. In a variable temperature NMR investigation performed for a solution of **4** in deuterated toluene decoalescence of the AlMe$_2$ resonance was observed below 273 K giving rise to two signals at 0.23 ($\nu_{1/2}$ = 14 Hz, 243 K) and –0.36 ppm ($\nu_{1/2}$ = 31 Hz, 243 K), respectively. Even after days solutions of **4** in dry and degassed toluene, benzene, thf or dichloromethane did not show any sign of decomposition.



4

Scheme 6. Synthesis of **4**.

Single crystals suitable for X-ray diffraction analysis were obtained by layering a concentrated solution of **4** in thf with hexane. The molecular structure is shown in Figure 3. It shows



Scheme 5. Known aluminium complexes of dinucleating β-diketiminato-based ligands.[45,46]

that as envisaged both of the diiminato binding sites are occupied by $AlMe_2$ groups. The aluminium atoms are coordinated in a distorted tetrahedral fashion by the nitrogen donor atoms of the diiminato pockets and the methyl groups. The relatively large metal-to-metal distance of 6.9354(12) Å reflects the increased steric bulk at the aluminium atoms in comparison to $[^{Me_2C_6H_3}Xanthdim](MgMe(thf))_2$, **2**, due to the additional covalently bound methyl groups (obviously, the coordinated thf ligands in **2** are more flexible). The aluminium–carbon distances (C62–Al1 1.943(4), C63–Al1 1.951(3), C64–Al2 1.954(3) and C65–Al2 1.951(3) Å) correspond well with those reported previously for $[^{Me}L^{pTol}](AlMe_2)$ (L = $CH\{(CMe)((pTol)N)\}_2$ 1.955(4) and 1.961(3) Å).[47] However, the aluminium–nitrogen bonds within **4** are slightly longer (Al1–N1 1.932(2), Al1–N2 1.932(2), Al2–N(4) 1.917(2) and Al2–N3 1.936(2) Å vs. 1.905(3) and 1.907(3) Å). In both of the binding units charge delocalisation is very effective as reflected by highly symmetric β-diiminato pockets exhibiting C–C and C–N distances, which pairwise are very similar.

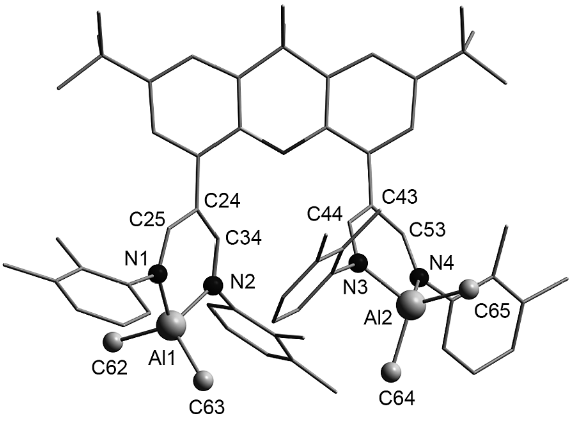
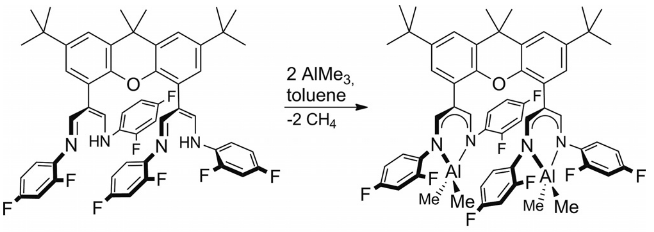


Figure 3. Molecular structure of **4**. All hydrogen atoms were omitted for clarity. Selected bond lengths in Å and angles in deg: Al1···Al2 6.9354(12), Al1–C62 1.943(4), Al1–C63 1.951(3), Al1–N1 1.932(2), Al1–N2 1.932(2), N1–C25 1.329(3), N2–C34 1.310(3), C25–C24 1.405(3), C34–C24 1.395(3), Al2–C64 1.954(3), Al2–C65 1.951(3), Al2–N3 1.936(2), Al2–N4 1.917(2), N3–C44 1.314(3), N4–C53 1.317(3), C43–C44 1.396(3), C43–C53 1.402(3), C63–Al1–C62 114.55(13), N1–Al1–N2 94.10(8), N1–Al1–C62 106.45(12), N1–Al1–C63 118.15(12), N3–Al2–N4 92.96(9), C64–Al2–C65 114.03(14), N3–Al2–C64 114.13(11), N3–Al2–C65 110.37(11).

$[^{F_2C_6H_3}Xanthdim](AlMe_2)_2$ (5)

In previous work we have investigated the catalytic activity displayed by zinc complexes of both, the methylated and the fluorinated $Xanthdim^{2-}$ ligand (Figure 1) in epoxide/ CO_2 copolymerisations.[27] Both complexes proved to be active, but the selectivity of $[^{Me_2C_6H_3}Xanthdim](ZnEt)_2$ was found to be distinctly different from the one of $[^{F_2C_6H_3}Xanthdim](ZnEt(thf))_2$, which mainly led to products of cyclohexene oxide homopolymerisation. This was ascribed to the increased Lewis acidity of the zinc ion in $[^{F_2C_6H_3}Xanthdim](ZnEt(thf))_2$ due to the electron withdrawing effect of the fluorine substituents. This effect should thus also increase the potential of $[Xanthdim](AlMe_2)_2$ complexes as ROP catalysts, which we intend to investigate in future work. Hence, the synthesis of the fluorinated derivative of **4**, $[^{F_2C_6H_3}Xanthdim](AlMe_2)_2$ (**5**) was pursued, too.

Treating a solution of $[^{F_2C_6H_3}Xanthdim]H_2$ in toluene with a sixfold excess of trimethylaluminium in toluene caused a rapid colour change from intensively yellow to bright orange due to deprotonation of the ligand precursor. After stirring at room temp. overnight and subsequent recrystallisation from hot toluene the product $[^{F_2C_6H_3}Xanthdim](AlMe_2)_2$·tol (**5**·tol) was isolated in a yield of 79 % as a microcrystalline solid (Scheme 7). Compound **5** is indefinitely stable in dry and degassed toluene, benzene, thf, dichloromethane or ethyl ether. As it is the case for **4**, also **5** shows a dynamic behaviour in solution, so that only one signal is observed for all aluminium bound methyl groups in the ^1H NMR spectrum. However, while this gives rise to a singlet in the case of **4**, a broad pseudo-triplet (J_{FH} = 2.85 Hz) at –0.39 ppm is found in the spectrum of a solution of **5** in deuterated toluene (Figure 4).



5

Scheme 7. Synthesis of **5**.

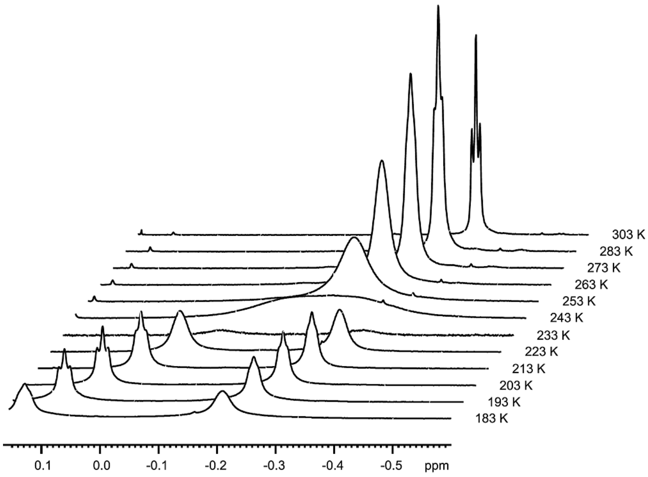


Figure 4. Decoalescence of the $AlMe_2$ resonance in a variable temperature ^1H NMR spectroscopic investigation of a solution of **5** in [D_8]toluene.

The splitting of this signal can be attributed to a coupling of the methyl-protons to the *ortho*-^{19}F nuclei of the two flanking aryl-substituents belonging to each diiminato unit as proved by a $^1H\{^{19}F\}$ NMR experiment. According to the molecular structure revealed for the solid state (see below and Figure 5), there are contacts between the protons of the exo AlMe groups and the aforementioned fluorine substituents (2.593(3), 2.564(2) Å), which are considerably smaller than the sum of the van-der-Waals radii of the respective atoms (F 1.47, H 1.20).[59] Therefore it seems reasonable that a "through space" coupling occurs,[60] and the same can be imagined for the endo AlMe groups. As due to the rotational fluxionality of the aryl residues each of the methyl groups is exposed to interactions with *two* fluorine substituents, and as further both methyl groups belonging to one $AlMe_2$ are equal on the NMR timescale only one pseudo-triplet resonance is observed. Decoalescence of this signal is observed below 243 K, giving rise to two distinctive pseudo triplet signals (–0.08 ppm and –0.24 ppm at 193 K, Figure 4). Both the lowering of the decoalescence temperature by 30 K and the reduction of the difference in the chemical shifts between the respective signals observed at 243 K indicate a significantly lower exchange barrier for the $AlMe_2$ groups of **5** as compared to those of **4**. Although it is possible to detect the signal of **5** in an ^{27}Al NMR experiment (188.9 ppm), application of this method is clearly limited due to the very large linewidth ($\nu_{1/2} \geq 2000$ Hz) and the very low intensity of the signal.

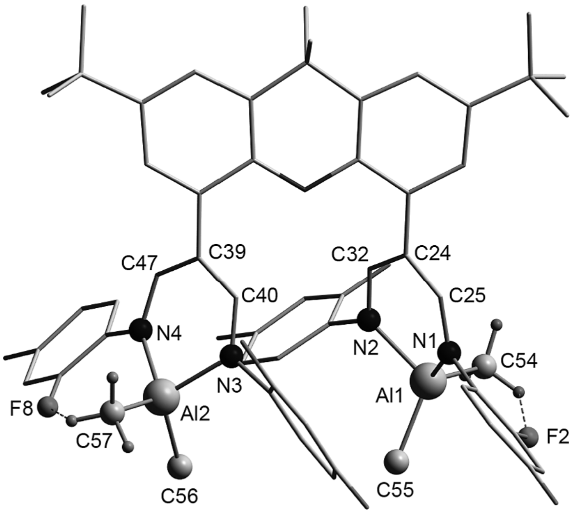


Figure 5. Molecular structure of **5**·thf. The non-coordinating thf molecule incorporated in the unit cell and all hydrogen atoms except for those of two of the AlMe groups were omitted for clarity. Selected bond lengths in Å and angles in deg: Al1···Al2 6.327(2), Al1–C54 1.953(5), Al1–C55 1.960(5), Al1–N1 1.933(3), Al1–N2 1.938(4), N1–C25 1.340(5), N2–C32 1.317(5), C25–C24 1.383(6), C24–C32 1.406(5), Al2–C56 1.961(5), Al2–C57 1.951(5), Al2–N3 1.954(4), Al2–N4 1.934(4), N3–C40 1.331(5), N4–C47 1.347(5), C39–C40 1.394(6), C39–C47 1.396(6) Å, C54–Al1–C55 115.3(2), N1–Al1–N2 91.66(15), N1–Al1–C54 117.80(19), N1–Al1–C55 110.57(19), C56–Al2–C57 115.5(2), N3–Al2–N4 92.06(16), N3–Al2–C56 114.4(2), N3–Al2–C57 104.40(18)°.

As in the case of **4**, single crystals suitable for X-ray diffraction analysis were obtained by layering a concentrated solution of **5** in thf with hexane. The molecular structure is shown in Figure 5. The metal-to-metal distance within **5**·thf is somewhat shorter than in **4**, amounting to 6.327(2) Å, which reflects the decrease of the steric crowding within the ligand binding pockets due to the lower steric demand of the fluorido substituents compared to the methyl groups. However, the aluminium–carbon distances are similar to those in **4** and excellently match previously reported data (C54–Al1 1.953(5), C55–Al1 1.960(5), C56–Al2 1.961(5), C57–Al2 1.951(5) Å).[47] The observed aluminium–nitrogen bond lengths are nearly similar to those in **4** (N1–Al1 1.934(4), N2–Al1 1.941(4), N3–Al2 1.954(4), N4–Al2 1.934(4) Å). Moreover, very similar C–C and N–C distances within the diiminato units again indicate effective charge distribution.

Conclusions

A rubidium complex of $Xanthdim^{2-}$ with toluene co-ligands was synthesised by the reaction of $[^{Me2C6H3}Xanthdim]H_2$ with RbO*t*Bu in a toluene solution. The Rb^+ ions do not utilise the binding pockets offered by the ligand, but act as bridges between the two diiminato units, which adopt a W-conformation. The resulting structure can be viewed as intermediate between the structures of corresponding Cs^+ and K^+ compounds. Furthermore $[MgBr]^+$ and $[MgMe]^+$ complexes of $Xanthdim^{2-}$ have been prepared. They proved stable against ligand exchange in course of a Schlenk equilibrium in solution. Finally, dinuclear $[AlMe_2]^+$ complexes have been synthesised employing two electronically different variants of $Xanthdim^{2-}$. The $AlMe_2$ moieties proved to be fluxional within the binding pockets and for the fluorinated complex Al–CH_3···F-aryl interactions were revealed, both in the solid state and in solution. In future work the conversion of the aluminium compounds into complexes bearing two potentially cooperating Lewis acidic sites and their application in polymerisation catalysis will be investigated. The magnesium complexes will be tested in CO_2 activation studies.

Experimental Section

General Considerations: All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DPX 300 (^{1}H 300.1 MHz, ^{13}C 75.5 MHz, ^{19}F 282.4 MHz) or Bruker Avance III NMR spectrometer (^{1}H 400.1 MHz, ^{13}C 100.6 MHz, ^{27}Al 104.3 MHz) with [D_2]dichloromethane, [D_8]toluene or [D_6]benzene as the solvent at 20 °C. The ^{1}H NMR spectra were calibrated against the residual proton, the ^{13}C NMR spectra against natural abundance ^{13}C resonances of the deuterated solvents ([D_2]dichloromethane $\delta_H = 5.32$ ppm and $\delta_C = 53.5$ ppm, [D_6]benzene $\delta_H = 7.16$ ppm and $\delta_C = 128.0$ ppm and [D_8]toluene $\delta_H = 2.08$ ppm and $\delta_C = 20.4$ ppm, respectively). Calibration against $CFCl_3$ and $Al(H_2O)_6^{3+}$ as external standards was performed for ^{19}F and ^{27}Al NMR spectroscopy. Flame sealed tubes were used for low temperature NMR experiments. Microanalyses were performed with a Leco CHNS-932 or a HEKA Euro 3000 elemental analyser. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR-8400S-spectrometer.

Materials: Solvents were purified, dried, degassed and stored over molecular sieves prior to use. $[^{Me_2C_6H_3}Xanthdim]H_2$ and $[^{F_2C_6H_3}Xanthdim]H_2$ were prepared by published literature procedures.[26,27] RbO*t*Bu·0.81*t*BuOH was prepared by refluxing rubidium metal and an excess of *t*BuOH in thf for 20 h. A filtration, subsequent removal of the solvent and drying in vacuo gave a white solid, the purity of which was ensured by NMR spectroscopy. The composition of RbO*t*Bu·0.81*t*BuOH was determined by elemental analysis. Solu-

Table 1. Crystallographic data and structure refinement for **1**(tol)$_2$·2(tol), the solid solution **2**·0.5(thf)·0.25(hexane), **4** and **5**·thf.

	1(tol)$_2$·2(tol)	**2**·0.5(thf)·0.25(hexane)	**4**	**5**·thf
Formula	$C_{89}H_{100}N_4ORb_2$	$C_{148.79}H_{191.37}Br_{0.21}Mg_4N_8O_7$	$C_{65}H_{80}Al_2N_4O$	$C_{61}H_{64}Al_2F_8N_4O_2$
weight /g·mol^{-1}	1412.67	2317.97	987.29	1091.12
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a /Å	25.5865(7)	16.0882(5)	23.2697(19)	10.0758(3)
b /Å	13.7266(4)	18.1457(6)	21.0177(16)	13.2037(9)
c /Å	21.5311(8)	24.1793(8)	11.9568(9)	22.7600(12)
α /°	90	77.827(3)	90	104.753(8)
β /°	92.179(2)	76.905(2)	99.8530(15)	95.635(7)
γ /°	90	89.363(3)	90	98.494(9)
V /Å^3	7556.6(4)	6715.6(4)	5761.5(8)	2866.7(3)
Z	4	4	4	2
Density /g·cm^{-3}	1.242	1.146	1.138	1.264
μ(Mo-K_α) /mm^{-1}	1.344	0.148	0.095	0.122
F(000)	2976	2503	2128	1144
GoF	1.185	0.990	1.056	1.038
R_1	0.0490	0.0918	0.0497	0.0846
wR_2	0.0991	0.1874	0.0688	0.2004
R_1 (all data)	0.0649	0.1748	0.1148	0.1468
R_{ind} (all data) wR_2	0.1037	0.2227	0.0773	0.2285
$\Delta\rho_{\min}$ / $\Delta\rho_{\max}$ /e·Å^{-3}	–0.60 / 0.68	–0.82 / 0.63	0.22 / –0.24	0.94 / –0.59
CCDC	837208	837209	837210	837211

tions of $AlMe_3$ (2 M in toluene) and MeMgBr (1 M in thf) were obtained from Sigma–Aldrich.

Crystal Structure Determinations: Crystals of [^{Me_2C_6H_3}Xanthdim](Rb(tol))$_2$·2(tol) (**1**(tol)$_2$·2(tol)), suitable for single crystal analysis were obtained by slow evaporation of the solvent from a solution of **1** in toluene. Crystals of [^{Me_2C_6H_3}Xanthdim](MgMe(thf))$_2$ ·0.5(thf)·0.25(hexane) (**2**·0.5(thf)·0.25(hexane)), were obtained by slow evaporation of the solvent from a concentrated solution of **2** in a mixture of thf and hexane (1:2) at room temp. These crystals were twinned and represented a solid solution, in which the magnesium atoms bound methyl groups are partly replaced by bromide substituents. The ratio MgMe:MgBr within the solid solution amounts to 95:5 as determined by refining the population of the corresponding groups. For the refinement of the -Me vs. -Br disorder, Mg–Me and Mg–Br distances were freely refined. The components of the anisotropic displacement parameters for the related -Me and -Br substituents were constrained to be equal. Single crystals both of [^{Me_2C_6H_3}Xanthdim](AlMe$_2$)$_2$ (**4**) and [^{F_2C_6H_3}Xanthdim](AlMe$_2$)$_2$·thf (**5**·thf) were obtained by layering concentrated solutions of these complexes in thf with hexane. All data collections were performed at 100 K with a STOE IPDS 2T diffractometer except for **4**, for which data collection was performed at 180 K with a STOE IPDS I diffractometer. In all cases Mo-K_α radiation (λ = 0.71073 Å) was used; radiation source was a sealed tube generator with graphite monochromator. Multi-scan correction (PLATON)[61] was applied for complex **1**(tol)$_2$·2(tol). The structures were solved by direct methods (SHELXS-97)[62] and refined by full-matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97) (Table 1).[62] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their idealised positions and refined as riding.

Synthesis of [^{Me2C6H3}Xanthdim](Rb)$_2$ (1): After stirring of an orange solution of [^{Me_2C_6H_3}Xanthdim]H$_2$ (200 mg, 228 µmol) and RbO*t*Bu·0.81*t*BuOH (110 mg, 503 µmol, 2.2 equiv.) in thf (5 mL) for 15 h at room temp. all volatiles were removed in vacuo. The resulting orange solid was completely dissolved in toluene (5 mL), and the volume of the solution was concentrated under reduced pressure to 0.5 mL. Addition of hexane (5 mL) caused the formation of a yellow precipitate, which was filtered off. Drying of the residue under vacuum yielded 192 mg (184 µmol, 81 %) of **1**. Crystal samples of **1**(tol)$_2$ ·2(tol), which contained two molecules of coordinated as well as two molecules of co-crystallised toluene could be obtained by slow evaporation of the solvent from a concentrated solution of **1** in toluene at room temp. Extensive drying in vacuo led to the loss of all toluene molecules. The content of toluene in the samples submitted to elemental analysis was determined by ^{1}H NMR spectroscopy. Elemental analysis (%) calcd. for $C_{75}H_{84}N_4Rb_2O\cdot0.73(C_7H_8)$ (1295.69 g·mol^{-1}): C 74.26, H 6.99, N 4.32; found: C 74.27, H 7.08, N 4.24. **IR** (KBr): ṽ = 2962 (m), 2922 (m), 2860 (m), 1639 (w), 1586 (m), 1564 (m), 1517 (vs), 1458 (s), 1425 (s), 1369 (m), 1353 (m), 1261 (m), 1210 (s), 1159 (w), 1090 (w), 1052 (m), 1028 (w), 986 (w), 943 (w), 915 (w), 853 (w), 787 (m), 730 (m), 696 (m)cm^{-1}. **^{1}H NMR** (300.1 MHz, [D$_2$]dichloromethane): δ = 7.84 (s, 4 H, NC*H*), 7.54 (d, $^4J_{HH}$ = 2.3 Hz, 2 H, C*H*), 7.43 (d, $^4J_{HH}$ = 2.3 Hz, 2 H, C*H*), 7.00 (ps-t, 4 H, C*H*), 6.73 (d, $^3J_{HH}$ = 7.3 Hz, 4 H, C*H*), 6.42 (d, $^3J_{HH}$ = 7.9 Hz, 4 H, C*H*), 2.18 (s, 12 H, CC*H*$_3$), 2.03 (s, 12 H, CC*H*$_3$), 1.78 (s, 6 H, C(C*H*$_3$)$_2$), 1.40 (s, 18 H, C(C*H*$_3$)$_3$); **^{13}C{^{1}H} NMR** (75.5 MHz, [D$_2$]dichloromethane): δ = 163.6 (N*C*H), 154.8 (*C*), 146.7 (*C*), 144.3 (*C*), 137.5 (*C*), 132.7 (*C*H), 129.1 (*C*), 129.1 (*C*), 128.7 (*C*), 127.1 (*C*H), 122.8 (*C*H), 121.9 (*C*H), 116.6 (*C*H), 106.3 (*C*), 35.1 (C(*C*H$_3$)$_2$), 34.9(*C*(CH$_3$)$_2$), 34.9 (*C*(CH$_3$)$_3$), 31.9 (C(*C*H$_3$)$_3$), 20.5 (*C*H$_3$), 13.9 (*C*H$_3$).

Synthesis of [^{Me_2C_6H_3}Xanthdim](MgMe(thf))$_2$ (2): KH (20 mg, 499 µmol, 2.2 equiv.) was suspended in a solution of [^{Me_2C_6H_3}Xanthdim]H$_2$ (200 mg, 228 µmol) in thf (3 mL). After stirring the reaction mixture for 15 h at room temp. excessive KH was removed by filtration, and a MeMgBr solution (502 µL, 1 M in thf, 502 µmol, 2.2 equiv.) was added to the orange filtrate. After stirring of the resulting yellow suspension for additional 5 h, all volatiles were removed. The residue was redissolved in benzene (2 mL), and addition of hexane (10 mL) caused the precipitation of a pale yellow solid that was filtered off and washed with hexane (2 mL). Evaporation of the solvent from the combined filtrates and drying of the resulting orange residue yielded 176 mg (161 µmol, 71 %) **2**, which is pure by NMR spectroscopy. Crystallisation by slow evaporation of the volatiles from a concentrated thf/hexane solution yielded in crystals that represented a solid solution incorporating 5 % of MgBr units. Elemental analysis

(%) calcd. for $\mathrm{C_{69}H_{84}N_4Mg_2O_3(CH_3)_{1.7}Br_{0.3}}$ (1115.57 g·mol^{-1}): C 76.12, H 8.05, N 5.02, Br 2.1; found: C 76.01, H 8.39, N 4.89, Br 2.4. **IR** (KBr) ṽ = 2924 (m), 2862 (m), 1642 (m), 1588 (m), 1576 (m), 1550 (m), 1481 (s), 1461 (vs), 1458 (vs), 1441 (s), 1384 (w), 1363 (w), 1321 (vs), 1260 (m), 1241 (w), 1223 (m), 1093 (m), 1061 (m), 988 (w), 957 (w), 876 (w), 857 (w), 782 (m)cm^{-1}. **^{1}H NMR** (300.1 MHz, [D$_2$]dichloromethane): δ = 7.66 (s, 4 H, NC*H*), 7.24 (d, $^4J_\mathrm{HH}$ = 2.4 Hz, 2 H, C*H*), 7.14 (d, $^4J_\mathrm{HH}$ = 2.4 Hz, 2 H, C*H*), 6.85–6.98 (m, 8 H, C*H*), 6.42 (ps-t, J_HH = 7.5 Hz, 4 H, C*H*), 3.79 (m, 8 H, CH_2), 2.27 (s, 12 H, CH_3), 2.24 (s, 12 H, CH_3), 1.80 (m, 8 H, CH_2), 1.63 (s, 6 H, C(CH_3)$_2$), 1.34 (s, 18 H, C(CH_3)$_3$), –1.54 (s, 6 H, CH_3); **^{13}C{^{1}H} NMR** (75.5 MHz, [D$_2$]dichloromethane): δ = 163.8 (N*C*H), 152.1 (*C*), 145.1 (*C*), 144.5 (*C*), 137.9 (*C*), 130.4 (*C*), 129.6 (*C*), 129.1 (*C*), 126.9 (*C*H), 126.0 (*C*H), 125.6 (*C*H), 122.0 (*C*H), 120.4 (*C*H), 103.1 (*C*), 69.4 (*C*H$_2$), 34.9 (*C*(CH$_3$)$_3$), 34.2 (*C*(CH$_3$)$_2$), 33.7 (C(*C*H$_3$)$_2$), 31.4 (C(*C*H$_3$)$_3$), 25.3 (*C*H$_2$), 20.5 (C*C*H$_3$), 15.2 (C*C*H$_3$), –16.4 (Mg*C*H$_3$).

Synthesis of [$^{\mathrm{Me_2C_6H_3}}$Xanthdim](MgBr(thf)))$_2$ (3): A solution of MeMgBr (95 µL, 1 M in thf, 285 µmol) was added to [$^{\mathrm{Me_2C_6H_3}}$Xanthdim]H$_2$ (300 mg, 343 µmol, 1.2 equiv.) dissolved in thf (5 mL), and the resulting clear yellow reaction mixture was stirred for 17 h at room temp. Subsequently all volatiles were removed in vacuo and the residue was dissolved in thf (1 mL). Addition of hexane (10 mL) and storage of the solution at 4 °C for 14 h led to the formation of a yellow precipitate, which was filtered off. Drying of the residue in vacuo yielded 101 mg (82 µmol, 58 %) **3**, which was pure according to NMR spectroscopy. **IR** (KBr): ṽ = 2923 (m), 2864 (m), 1637 (vs), 1587 (m), 1545 (s), 1471 (s), 1461 (m), 1442 (m), 1386 (w), 1363 (w), 1321 (vs), 1288 (s), 1266 (m), 1242 (m), 1224 (m), 1096 (m), 1051 (m), 1017 (m), 877 (w), 857 (w)cm^{-1}. **^{1}H NMR** (300.1 MHz, [D$_2$]dichloromethane): δ = 7.70 (s, 4 H, NC*H*), 7.24 (d, $^4J_\mathrm{HH}$ = 2.4 Hz, 2 H, C*H*), 7.11 (d, $^4J_\mathrm{HH}$ = 2.4 Hz, 2 H, C*H*), 7.03 (d, $^3J_\mathrm{HH}$ = 7.5 Hz, 4 H, C*H*), 6.91 (d, $^3J_\mathrm{HH}$ = 7.2 Hz, 4 H, C*H*), 6.42 (ps-t, J_HH = 7.7 Hz, 4 H, C*H*), 3.86 (m, 8 H, CH_2), 2.28 (s, 12 H, CCH_3), 2.27 (s, 12 H, CCH_3), 1.85 (m, 8 H, CH_2), 1.63 (s, 6 H, C(CH_3)$_2$), 1.34 (s, 18 H, C(CH_3)$_3$); **^{13}C{^{1}H} NMR** (75.5 MHz, [D$_2$]dichloromethane): δ = 165.4 (N*C*H), 151.5 (*C*), 145.1 (*C*), 144.9 (*C*), 138.6 (*C*), 130.1 (*C*), 129.8 (*C*), 129.4 (*C*), 126.8 (*C*H), 126.4 (*C*H), 126.4 (*C*H), 122.7 (*C*H), 121.1 (*C*H), 103.2 (*C*), 70.1 (*C*H$_2$), 35.1 (*C*(CH$_3$)$_3$), 34.6 (*C*(CH$_3$)$_2$), 34.1 (C(*C*H$_3$)$_2$), 31.7 (C(*C*H$_3$)$_3$), 25.6 (*C*H$_2$), 20.9 (C*C*H$_3$), 15.7 (C*C*H$_3$).

Synthesis of [$^{\mathrm{Me_2C_6H_3}}$Xanthdim](AlMe$_2$)$_2$·tol (4·tol): [$^{\mathrm{Me_2C_6H_3}}$Xanthdim]H$_2$ (400 mg, 457 µmol) was dissolved in toluene (15 mL) giving an intensively yellow solution. Trimethylaluminium (1.4 mL, 2 M in toluene, 2.8 mmol, 6 equiv.) was added afterwards, which led to an orange solution. After stirring at room temp. for 24 h, all volatiles were removed in vacuo (50 °C, overnight) and after dissolution of the yellow residue in hot toluene (3 mL) cooling led to the precipitation of 251 mg (233 µmol, 51 %) of [$^{\mathrm{Me_2C_6H_3}}$Xanthdim](AlMe$_2$)$_2$·tol (**4**·tol). The content of toluene was determined by ^{1}H NMR spectroscopy. Elemental analysis (%) calcd. for $\mathrm{C_{65}H_{80}Al_2N_4O{\cdot}C_7H_8}$: C 80.11, H 8.22, N 5.19; found: C 79.85, H 7.96, N 5.59. **IR** (KBr): ṽ = 2962 (vs), 2928 (s), 2865 (w), 1650 (s), 1639 (vs), 1622 (m), 1612 (w), 1602 (w), 1580 (m), 1575 (m), 1556 (vs), 1544 (vs), 1527 (m), 1511 (w), 1507 (w), 1472 (vs), 1461 (vs), 1442 (vs), 1424 (w), 1382 (w), 1302 (vs), 1263 (vs), 1225 (m), 1187 (vw), 1096 (s), 1076 (s), 1044 (s), 875 (vw), 857 (w), 801 (vs), 771 (w), 703 (w), 683 (w), 672 (w)cm^{-1}. **^{1}H NMR** (400.1 MHz, [D$_6$]benzene): δ = 7.79 (s, 4 H, C*H*N), 7.55 (d, J_HH = 7.9 Hz, 4 H, C*H*), 7.37 (d, $^4J_\mathrm{HH}$ = 2.3 Hz, 2 H, C*H*), 7.33 (d, $^4J_\mathrm{HH}$ = 2.3 Hz, 2 H, C*H*), 6.91 (t, $^3J_\mathrm{HH}$ = 7.7 Hz, 4 H, C*H*), 6.81 (d, $^3J_\mathrm{HH}$ = 7.4 Hz, 4 H, C*H*), 2.30 (s, 12 H, CCH_3), 1.92 (s, 12 H, CCH_3), 1.57 (s, 6 H, C(CH_3)$_2$), 1.29 (s, 18 H, C(CH_3)$_3$), –0.13 (br. s, 12 H, Al(CH_3)$_2$); **^{1}H NMR** (400.1 MHz, [D$_8$]toluene): δ = 7.75 (s, 4 H, C*H*N), 7.49 (d, J_HH = 7.7 Hz, 4 H, C*H*), 7.37 (d, $^4J_\mathrm{HH}$ = 2.4 Hz, 2 H, C*H*), 7.31 (d, $^4J_\mathrm{HH}$ = 2.4 Hz, 2 H, C*H*), 6.89 (t, $^3J_\mathrm{HH}$ = 7.7 Hz, 4 H, C*H*), 6.79 (d, $^3J_\mathrm{HH}$ = 7.4 Hz, 4 H, C*H*), 2.30 (s, 12 H, CCH_3), 1.95 (s, 12 H, CCH_3), 1.59 (s, 6 H, C(CH_3)$_2$), 1.29 (s, 18 H, C(CH_3)$_3$), –0.22 (br. s, 12 H, Al(CH_3)$_2$); **^{13}C{1H} NMR** (100.1 MHz, [D$_6$]benzene): δ = 164.3 (*C*HN), 147.6 (C_q), 145.8 (C_q), 145.5 (C_q), 138.9 (C_q), 131.0 (C_q), 130.7 (C_q), 128.3 (*C*H), 128.1 (*C*H), 127.4 (*C*H), 126.3 (*C*H), 124.3 (*C*H), 121.6 (*C*H), 104.1 (C_qCHN), 35.3 (*C*(CH$_3$)$_2$), 34.3 (*C*(CH$_3$)$_3$), 33.4 (C(*C*H$_3$)$_2$), 31.5 (C(*C*H$_3$)$_3$), 20.6 (*C*CH$_3$), 15.5 (*C*CH$_3$), –7.54 (Al(*C*H$_3$)$_2$.

Synthesis of [$^{\mathrm{F_2C_6H_3}}$Xanthdim](AlMe$_2$)$_2$·tol (5·tol): [$^{\mathrm{F_2C_6H_3}}$Xanthdim]H$_2$ (400 mg, 441 µmol) was dissolved in toluene (15 mL) giving a yellow solution. A solution of trimethylaluminium (1.4 mL, 2 M in toluene, 2.8 mmol, 6 equiv.) was added, which led to an orange solution. After stirring at room temp. for 24 h, all volatiles were removed in vacuo (50 °C, overnight) and the yellow residue was recrystallised from toluene (8 mL) giving 252 mg (227 µmol, 51 %) of [$^{\mathrm{F_2C_6H_3}}$Xanthdim](AlMe$_2$)$_2$·tol (**5**·tol). Cooling of the filtrate to –30 °C for several days yielded another 135 mg (122 µmol, 28 %) of the desired product. The content of toluene was determined by ^{1}H NMR spectroscopy. Elemental analysis (%) calcd. for $\mathrm{C_{57}H_{56}Al_2F_8N_4O{\cdot}C_7H_8}$: C 69.18, H 5.81, N 5.04; found: C 68.85, H 5.79, N 4.90. **IR** (KBr): ṽ = 2962 (w), 2937 (w), 2927 (w), 2904 (vw), 2869 (vw), 1597 (m), 1506 (s), 1473 (vs), 1445 (s), 1433 (m), 1420 (w), 1387 (w), 1363 (m), 1316 (vs), 1282 (m), 1264 (s), 1230 (m), 1198 (m), 1141 (m), 1099 (m), 1078 (w), 977 (w), 967 (m), 957 (w), 850 (w), 811 (w), 789 (vw), 733 (w), 706 (w), 683 (w), 602 (vw), 556 (w), 526 (vw)cm^{-1}. **^{1}H NMR** (400.1 MHz, [D$_6$]benzene): δ = 7.65 (d, J_FH = 1.0 Hz, 4 H, C*H*N), 7.52 (d, $^4J_\mathrm{HH}$ = 2.4 Hz, 2 H, C*H*), 7.30 (d, $^4J_\mathrm{HH}$ = 2.4 Hz, 2 H, C*H*), 6.61 (m, 4 H, C*H*), 6.36 (m, 4 H, C*H*), 6.30–6.22 (m, 4 H, C*H*), 1.72 (s, 6 H, C(CH_3)$_2$), 1.25 (s, 18 H, C(CH_3)$_3$), –0.30 (ps-t, *J*(F,H) = 2.9 Hz, 12 H, Al(CH_3)$_2$); **^{1}H NMR** (400.1 MHz, [D$_8$]toluene): δ = 7.71 (d, J_FH = 1.0 Hz, 4 H, C*H*N), 7.51 (d, J_HH = 2.4 Hz, 2 H, C*H*), 7.29 (d, J_HH = 2.4 Hz, 2 H, C*H*), 6.69 (m, 4 H, C*H*), 6.39–6.33 (m, 4 H, C*H*), 6.29–6.22 (m, 4 H, C*H*), 1.74 (s, 6 H, C(CH_3)$_2$), 1.28 (s, 18 H, C(CH_3)$_3$), –0.39 (ps-t, J_FH = 2.9 Hz, 12 H, Al(CH_3)$_2$); **^{19}F{^{1}H} NMR** (282.4 MHz, [D$_6$]benzene): δ = –112.67 (d, $^4J_\mathrm{FF}$ = 5.5 Hz), –117.62 (d, $^4J_\mathrm{FF}$ = 6.0 Hz). **^{13}C{^{1}H} NMR** (100.1 MHz, [D$_6$]benzene): δ = 162.7 (C_q), 160.4 (dd, $^1J_\mathrm{CF}$ = 248.0, $^3J_\mathrm{CF}$ = 11.4 Hz, *C*F), 155.9 (dd, $^1J_\mathrm{CF}$ = 250.0, $^3J_\mathrm{CF}$ = 12.2 Hz, *C*F), 146.5 (C_q), 145.7 (C_q), 132.5 (dd, $^2J_\mathrm{CF}$ = 11.3, $^4J_\mathrm{CF}$ = 3.6 Hz, C_q), 130.3 (C_q), 128.3 (*C*H), 126.8 (*C*H), 125.5 (dd, $^3J_\mathrm{CF}$ = 9.4, $^5J_\mathrm{CF}$ = 2.2 Hz, *C*H), 122.4 (*C*H), 112.0 (dd, $^2J_\mathrm{CF}$ = 22.3, $^4J_\mathrm{CF}$ = 3.6 Hz, *C*H), 108.1 (C_q), 104.9 (ps-t, $^2J_\mathrm{CF}$ = 25.4 Hz, *C*H), 35.1 (C_q), 34.4 (C_q), 33.6 (C(*C*H$_3$)$_2$), 31.4 (C(*C*H$_3$)$_3$), –9.4 (br. m, Al(*C*H$_3$)$_2$); **^{27}Al NMR** (104.3 MHz, [D$_6$]benzene): δ = 188.9 (br., m, *Al*(CH$_3$)$_2$).

Acknowledgement

We are grateful to the *Fonds der Chemischen Industrie*, the *Bundesministerium für Bildung und Forschung*, as well as to *Bayer Services GmbH & Co. OHG*, *BASF AG*, and *Sasol GmbH* for the supply of chemicals. Furthermore we thank the Cluster of excellence "*Unifying concepts in catalysis*" for valuable discussions.

References

[1] L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3066.

[2] E. Hevia, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2011**, DOI:10.1002/anie.201102978.

[3] S. Harder, J. Spielmann, J. Intemann, H. Bandmann, *Angew. Chem.* **2011**, *123*, 4242–4246; *Angew. Chem. Int. Ed.* **2011**, *50*, 4156–4160.

[4] J. Spielmann, D. F.-J. Piesik, S. Harder, *Chem. Eur. J.* **2010**, *16*, 8307–8318.

[5] J. Spielmann, S. Harder, *J. Am. Chem. Soc.* **2009**, *131*, 5064–5065.

[6] D. F.-J. Piesik, S. Range, S. Harder, *Organometallics* **2008**, *27*, 6178–6187.

[7] J. Spielmann, S. Harder, *Chem. Eur. J.* **2007**, *13*, 8928–8938.

[8] C. Ruspic, S. Nembenna, A. Hofmeister, J. Magull, S. Harder, H. W. Roesky, *J. Am. Chem. Soc.* **2006**, *128*, 15000–15004.

[9] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754–1757.

[10] P. B. Hitchcock, M. F. Lappert, D.-S. Liu, R. Sablong, *Chem. Commun.* **2002**, 1920–1921.

[11] B. Horn, S. Pfirrmann, C. Limberg, C. Herwig, B. Braun, S. Mebs, R. Metzinger, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1169–1174.

[12] S. Pfirrmann, C. Limberg, C. Herwig, C. Knispel, B. Braun, E. Bill, R. Stößer, *J. Am. Chem. Soc.* **2010**, *132*, 13684–13691.

[13] S. Pfirrmann, C. Limberg, C. Herwig, R. Stößer, B. Ziemer, *Angew. Chem.* **2009**, *121*, 3407–3411; *Angew. Chem. Int. Ed.* **2009**, *48*, 3357–3361.

[14] S. Pfirrmann, S. Yao, B. Ziemer, R. Stößer, M. Driess, C. Limberg, *Organometallics* **2009**, *28*, 6855–6860.

[15] S. Yao, C. Herwig, Y. Xiong, A. Company, E. Bill, C. Limberg, M. Driess, *Angew. Chem.* **2010**, *122*, 7208–7212; *Angew. Chem. Int. Ed.* **2010**, *49*, 7054–7058.

[16] S. Yao, Y. Xiong, M. Vogt, H. Grützmacher, C. Herwig, C. Limberg, M. Driess, *Angew. Chem.* **2009**, *121*, 8251–8251; *Angew. Chem. Int. Ed.* **2009**, *48*, 8107–8110.

[17] K. Ding, W. W. Brennessel, P. L. Holland, *J. Am. Chem. Soc.* **2009**, *131*, 10804–10805.

[18] J. M. Smith, R. L. Lachicotte, K. A. Pittard, T. R. Cundari, G. Lukat-Rodgers, K. R. Rodgers, P. L. Holland, *J. Am. Chem. Soc.* **2001**, *123*, 9222–9223.

[19] S. Hong, A. K. Gupta, W. B. Tolman, *Inorg. Chem.* **2009**, *48*, 6323–6325.

[20] N. W. Aboelella, S. V. Kryatov, B. F. Gherman, W. W. Brennessel, V. G. Young Jr., R. Sarangi, E. V. Rybak-Akimova, K. O. Hodgson, B. Hedman, E. I. Solomon, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2004**, *126*, 16896–16911.

[21] N. W. Aboelella, E. A. Lewis, A. M. Reynolds, W. W. Brennessel, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 10660–10661.

[22] D. J. E. Spencer, N. W. Aboelella, A. M. Reynolds, P. L. Holland, W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 2108–2109.

[23] W. H. Monillas, G. P. A. Yap, L. A. MacAdams, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 8090–8091.

[24] Y.-C. Tsai, P.-Y. Wang, S.-A. Chen, J.-M. Chen, *J. Am. Chem. Soc.* **2007**, *129*, 8066–8067.

[25] D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911–11924.

[26] M. F. Pilz, C. Limberg, B. Ziemer, *J. Org. Chem.* **2006**, *71*, 4559–4564.

[27] M. F. Pilz, C. Limberg, B. B. Lazarov, K. C. Hultzsch, B. Ziemer, *Organometallics* **2007**, *26*, 3668–3676.

[28] M. F. Pilz, C. Limberg, S. Demeshko, F. Meyer, B. Ziemer, *Dalton Trans.* **2008**, 1917–1923.

[29] P. Haack, C. Limberg, K. Ray, B. Braun, U. Kuhlmann, P. Hildebrandt, C. Herwig, *Inorg. Chem.* **2011**, *50*, 2133–2142.

[30] P. Haack, C. Limberg, T. Tietz, R. Metzinger, *Chem. Commun.* **2011**, *47*, 6374–6376.

[31] D. F.-J. Piesik, P. Haack, S. Harder, C. Limberg, *Inorg. Chem.* **2009**, *48*, 11259–11264.

[32] M. H. Chisholm, J. Gallucci, K. Phomphrai, *Inorg. Chem.* **2004**, *43*, 6717–6725.

[33] C. Ruspic, S. Harder, *Inorg. Chem.* **2007**, *46*, 10426–10433.

[34] S. Harder, J. Brettar, *Angew. Chem.* **2006**, *118*, 3554–3558; *Angew. Chem. Int. Ed.* **2006**, *45*, 3474–3478.

[35] V. C. Gibson, J. A. Segal, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 7120–7121.

[36] P. J. Bailey, C. M. E. Dick, S. Fabre, S. Parsons, *J. Chem. Soc., Dalton Trans.* **2000**, 1655–1661.

[37] T. Greiser, J. Kopf, D. Thoennes, E. Weiss, *J. Organomet. Chem.* **1980**, *191*, 1–6.

[38] V. R. Magnuson, G. D. Stucky, *Inorg. Chem.* **1969**, *8*, 1427–1433.

[39] J. Toney, G. D. Stucky, *J. Organomet. Chem.* **1970**, *22*, 241–249.

[40] R. Han, G. Parkin, *Organometallics* **1991**, *10*, 1010–1020.

[41] J. D. Farwell, P. B. Hitchcock, M. F. Lappert, A. V. Protchenko, *Chem. Commun.* **2005**, 2271–2273.

[42] T. Schulz, S. Deuerlein, D. Stalke, *Eur. J. Inorg. Chem.* **2010**, 2178–2184.

[43] N. Kuhn, A. Kuhn, J. Lewandowski, M. Speis, *Chem. Ber.* **1991**, *124*, 2197–2201.

[44] H. Gornitzka, D. Stalke, *Organometallics* **1994**, *13*, 4398–4405.

[45] L. Bourget-Merle, P. B. Hitchcock, M. F. Lappert, *J. Organomet. Chem.* **2004**, *689*, 4357–4365.

[46] J. Vela, L. Zhu, C. Flaschenriem, W. W. Brennessel, R. Lachicotte, P. L. Holland, *Organometallics* **2007**, *26*, 3416–3423.

[47] B. Qian, D. L. Ward, M. R. Smith III, *Organometallics* **1998**, *17*, 3070–3076.

[48] Y.-L. Huang, B.-H. Huang, B.-T. Ko, C.-C. Lin, *J. Chem. Soc., Dalton Trans.* **2001**, 1359–1365.

[49] C. E. Radzewich, I. A. Guzei, R. F. Jordan, *J. Am. Chem. Soc.* **1999**, *121*, 8673–8674.

[50] S. de Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Inorg. Chem.* **1992**, *31*, 2520–2527.

[51] J. C. Cannadine, W. Errington, P. Moore, M. G. H. Wallbridge, E. Nield, D. Fenn, *J. Organomet. Chem.* **1995**, *486*, 237–242, and literature cited therein.

[52] C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem.* **2000**, *112*, 4444–4446; *Angew. Chem. Int. Ed.* **2000**, *39*, 4274–4276.

[53] F. Coslédan, P. B. Hitchcock, M. F. Lappert, *Chem. Commun.* **1999**, 705–706.

[54] D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, B. Walfort, D. Stalke, *Angew. Chem.* **2002**, *114*, 4470–4472; *Angew. Chem. Int. Ed.* **2002**, *41*, 4294–4296.

[55] N. Kuhn, S. Fuchs, C. Maichle-Mössmer, E. Niquet, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2248–2250.

[56] M.-H. Thibault, F.-G. Fontaine, *Dalton Trans.* **2010**, 5688–5697.

[57] A. Arbaoui, C. Redshaw, D. L. Hughes, *Chem. Commun.* **2008**, 4717–4719, and literature cited therein.

[58] J. Wu, T.-L. Yu, C.-T. Chen, C.-C. Lin, *Coord. Chem. Rev.* **2006**, *250*, 602–626.

[59] J. Bondi, *J. Phys. Chem.* **1964**, *63*, 441–451.

[60] D. Noveski, T. Braun, B. Neumann, A. Stammler, H.-G. Stammler, *Dalton Trans.* **2004**, 4106–4119, and literature cited therein.

[61] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

[62] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

Received: August 1, 2011