

A Xanthene-based Ligand with Two Adjacent Malonate Binding Sites

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Dedicated to Professor Gottfried Huttner on the occasion of his 70th birthday

The syntheses of two functionalized xanthenes are described which after deprotonation represent ligands for dinuclear metal complexes. For the previously prepared [^RXanthdim]H₂ – which after deprotonation leads to a ligand with two adjacent β-diiminato binding sites – a significantly improved synthetic procedure is described involving the Pd catalyzed coupling of two diethyl malonate moieties to the xanthene backbone. Deprotonation of the resulting compound [Xanthmal]H₂ provides a ligand with two adjacent diethyl malonate functions. To demonstrate this, [Xanthmal]H₂ was reacted exemplarily with two equivalents of LDA to obtain the lithium salt {Li₂[Xanthmal]}₂ (**4**) which can be treated with ZnBr₂ to yield the zinc complex [Xanthmal]₂Zn₂ (**5**). Alternatively, **5** can be obtained directly from [Xanthmal]H₂, when ZnEt₂ is chosen as the metal precursor. The crystal structures of **4** and **5** are discussed. In summary, the results show that [Xanthmal]²⁻ is a suitable ligand for the preparation of novel dinuclear metal complexes.

Key words: Zinc, Lithium, Ligand Synthesis, Xanthene, Malonate, Metalation

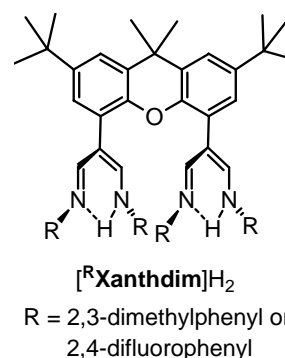
Introduction

There are numerous examples in the literature showing that the cooperation of metal centers in redox or hydrolytic reactions can lead to significant improvements [1], and in fact this concept is also utilized in many metalloenzymes [2]. It therefore seems rewarding to develop potential ligands that are preorganized for the complexation of two metal centers, thereby supporting their cooperation. In this context we have recently reported about the design of a novel ligand, [^RXanthdim]²⁻, with two adjacent diiminato binding sites [3, 4]. Here we first describe an optimized synthesis for its precursor [^RXanthdim]H₂, which gave rise to a new dinucleating ligand, the main subject of this contribution.

Results and Discussion

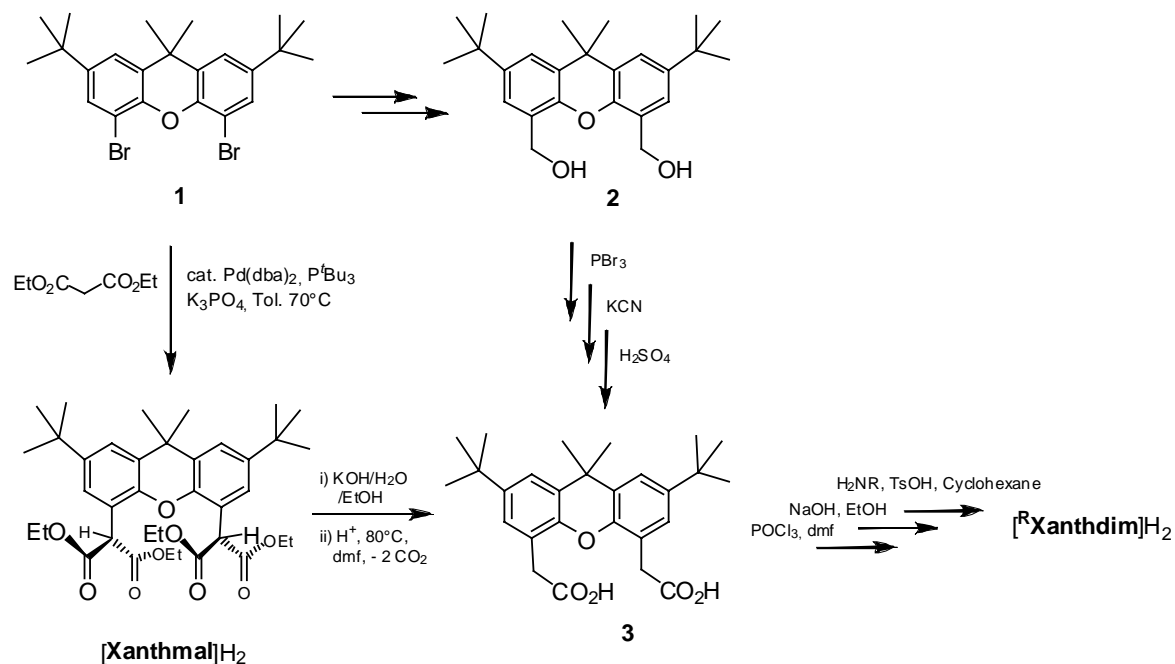
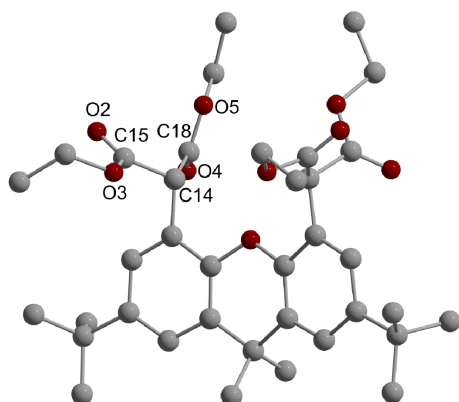
Ligand synthesis

The synthesis of [^RXanthdim]H₂ reported previously [3] starts from the diol **2** which can be prepared from the dibromide **1** via two costly, low-yield steps (Scheme 1). **2** then has to be converted into the dicarboxylic acid **3** via initial OH/Br and Br/CN exchange followed by acidic hydrolysis.



We have now found a more facile synthesis for **3** starting also from **1**: in a Pd-catalyzed C–C coupling reaction adapted from Hartwig *et al.* [5] the two Br atoms are replaced by two diethyl malonate units to yield a compound that is designated [Xanthmal]H₂ throughout the rest of this paper (Scheme 1). After deprotonation the resulting [Xanthmal]²⁻ represents an interesting potential ligand in its own right. Hence, in addition to the usual characterization also the crystal structure of [Xanthmal]H₂ was investigated (see Fig. 1, Table 1).

It is clearly visible that the C atoms connected to the xanthene backbone (C14) are located above the

Scheme 1. Synthesis of [Xanthmal]H₂ and [^RXanthdim]H₂.Fig. 1. Molecular structure of [Xanthmal]H₂ (hydrogen atoms omitted for clarity).

planes defined by the surrounding “heavy” atoms thus indicating an *sp*³-hybridization and additional binding of hydrogen atoms, which, however, were not located. The presence of these hydrogen atoms was proved *via* ¹H NMR spectroscopy.

The saponification of [Xanthmal]H₂ with potassium hydroxide in ethanol/water leads to the corresponding dimalonic acid, which proved to be unstable in solution: it decomposes slowly under elimination of CO₂ to give **3**. It was found that this process can

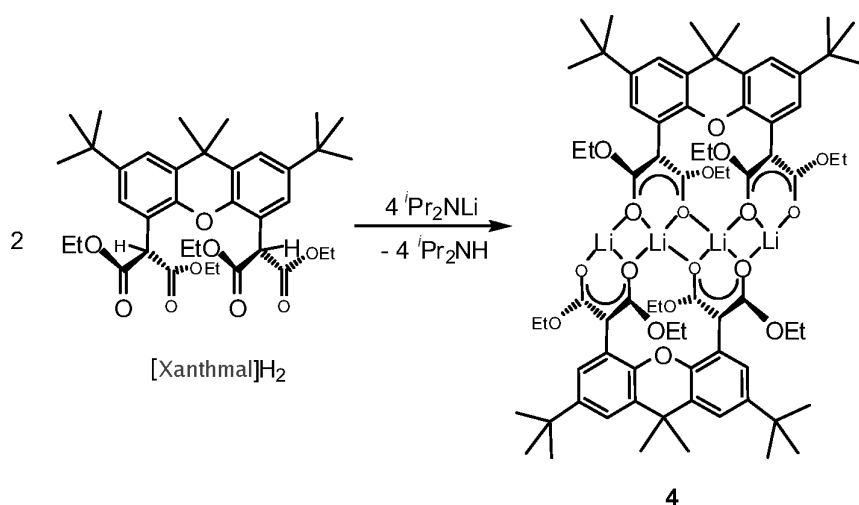
Table 1. Selected bond lengths (Å) and angles (deg) for [Xanthmal]H₂ with estimated standard deviations in parentheses.

Distances			
C15–O2	1.202(5)	C14–C15	1.524(5)
C18–O4	1.197(4)	C14–C18	1.529(4)
Angles			
C15–C14–C18	108.2(3)		

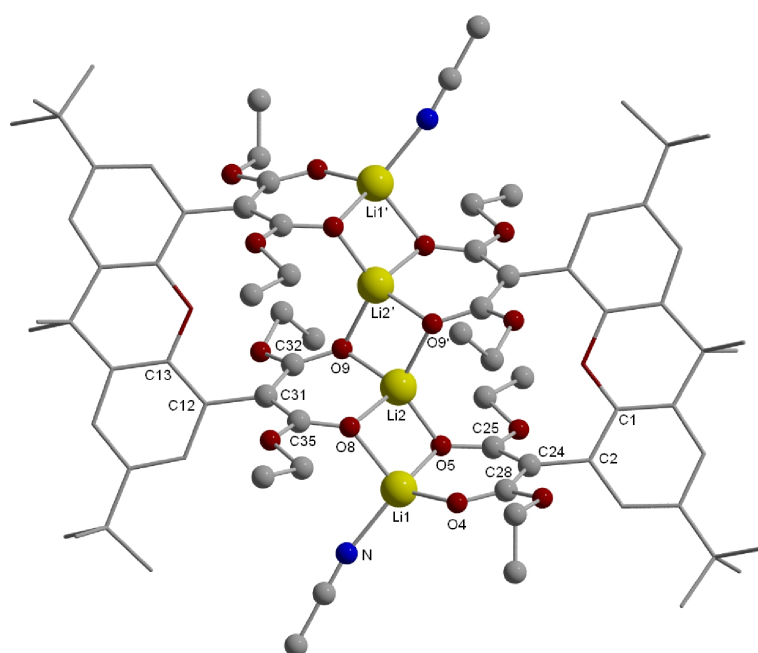
be accelerated by dissolution in diluted hydrochloric acid/dimethylformamide. Finally, **3** can be converted into [^RXanthdim]H₂ *via* the published procedure [3].

Turning the attention back onto [Xanthmal]H₂ and its dianion [Xanthmal]²⁻ as a potential ligand, two strategies can be envisioned for the preparation of transition metal complexes: first of all it should be possible to react [Xanthmal]H₂ directly with metal precursors containing sufficiently basic ligands to remove the protons at the C_α positions *in situ*. The second route starts with a lithiation of [Xanthmal]H₂ resulting in the lithium salt to be employed either *in situ* or after isolation in reactions with basically any metal halide compound. The results reported below show that both routes in principle are feasible.

For the abstraction of the C_α hydrogen atoms [Xanthmal]H₂ was reacted with lithium diisopropylamide in thf. After work-up a white solid was isolated,

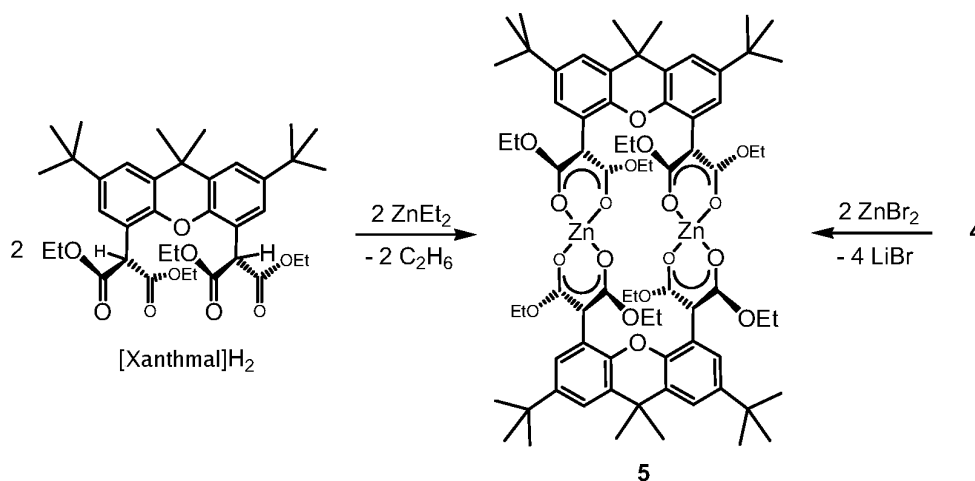


Scheme 2.

Fig. 2. Molecular structure of 4[CH₃CN]₂ (hydrogen atoms omitted for clarity).

whose characterization by NMR and IR spectroscopy indicated that the lithiation had proceeded successfully so that Li₂[Xanthmal] must have been formed initially. In principle, the residual coordination spheres of the Li cations could have been expected to be completed by thf solvent molecules, however, the analytical and spectroscopic data show that the system prefers a stabilization by dimerization yielding {Li₂[Xanthmal]}₂, **4** (Scheme 2). Recrystallization from acetonitrile yielded single crystals for an X-ray diffraction study (Fig. 2, Table 2) which confirmed that both C_α hydrogen atoms

belonging to [Xanthmal]H₂ had been removed, that the Li cations are coordinated to the terminal O atoms of the malonate units as intended, and that dimerization occurred subsequently. However, as the crystals were obtained from acetonitrile solution, two acetonitrile molecules can be found coordinating to the two outer Li cations which otherwise would only reach a coordination number of three and expose a Lewis acidic site. It can thus be assumed that in thf solutions **4** contains thf molecules at these sites; it is difficult to prove this, though, since on removing of all volatiles the com-



Scheme 3.

Table 2. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for $4[\text{MeCN}]_2$ with estimated standard deviations in parentheses.

Distances			
Li1–O4	1.81(1)	Li2–O8	1.88(1)
Li1–O5	1.93(1)	Li2–O9	1.91(1)
Li1–O8	1.99(1)	C28–O4	1.243(7)
Li1–N	2.073(9)	C25–O5	1.280(6)
Li2–O5	1.87(1)		
Angles			
C25–C24–C28	118.1(5)	O8–Li1–N	105.1(5)
C32–C31–C35	118.9(5)	O5–Li2–O8	99.1(4)
O4–Li1–N	118.4(6)	O5–Li2–O9'	121.2(5)
O4–Li1–O5	94.0(4)	O8–Li2–O9	94.2(5)
O5–Li1–O8	93.3(4)	O9–Li2–O9'	96.2(4)
Dihedral angles			
C1–C2–C24–C25	–58.5(7)	C13–C12–C31–C32	–55.9(8)

plex loses these molecules completely and crystals could not be obtained from thf. In the solid state the $4[\text{CH}_3\text{CN}]_2$ molecules exhibit a crystallographic C_2 axis and the diethyl malonate moieties are twisted with respect to the xanthene backbone ($\text{C1–C2–C24–C25} = -58.5^\circ$ and $\text{C13–C12–C31–C32} = -55.9^\circ$). As indicated by the C–C–C angles and the C–O bond lengths belonging to the individual malonate binding pockets (exemplarily the C25–C24–C28 angle amounts to 118°) the negative charge is delocalized within the malonate backbones. The outer lithium ions are located in a distorted tetrahedral environment formed by three carbonyl–O atoms belonging to two Xanthmal entities and one acetonitrile ligand; the O–Li–O angles are in the range between 93.3° and 117.8° . The inner lithium ions also have a disordered tetrahedral coordination environment consisting of four O atoms belonging to three different diethyl malonate units. Both adjacent

diethyl malonate units of an individual Xanthmal ligand and are bridged by the inner lithium ions, and the corresponding Li–O distances are not significantly longer than those observed for the other Li–O bonds.

Deprotonation of $[\text{Xanthmal}]\text{H}_2$ can also be achieved by treatment with NaH, as evidenced by ^1H NMR spectroscopy. A full characterization of the sodium salt was not pursued as only *in situ* employment was envisaged for the future. However, a preliminary X-ray diffraction analysis of crystals obtained from diethyl ether confirmed that the solid state structure is comparable to the one displayed by $4[\text{CH}_3\text{CN}]_2$ with identical arrangements of the ligands around the cations and two terminal diethyl ether instead of acetonitrile ligands. The solution did not reach a quality that would allow any further discussion.

Complex formation with zinc

The feasibility of the above mentioned two strategies for the synthesis of complexes involving $[\text{Xanthmal}]^{2-}$ was demonstrated for the case of Zn^{2+} : in order to obtain dinculear complexes, (i) **4** was treated with ZnBr_2 , and (ii) $[\text{Xanthmal}]\text{H}_2$ was reacted with ZnEt_2 (Scheme 3).

Both routes led to $[\text{Xanthmal}]_2\text{Zn}_2$, **5**, in good yields, *i. e.* in the product two Zn ions are coordinated by two rather than only one ligand, and this observation was made independently of the molar ratio of the reactants employed. Hence, after complexation of a Zn–X unit (X = Br, Et) the intermediate is still sufficiently reactive to undergo further metathetic processes. Beside spectroscopic and analytical investigations a single crystal X-ray diffraction study was also performed,

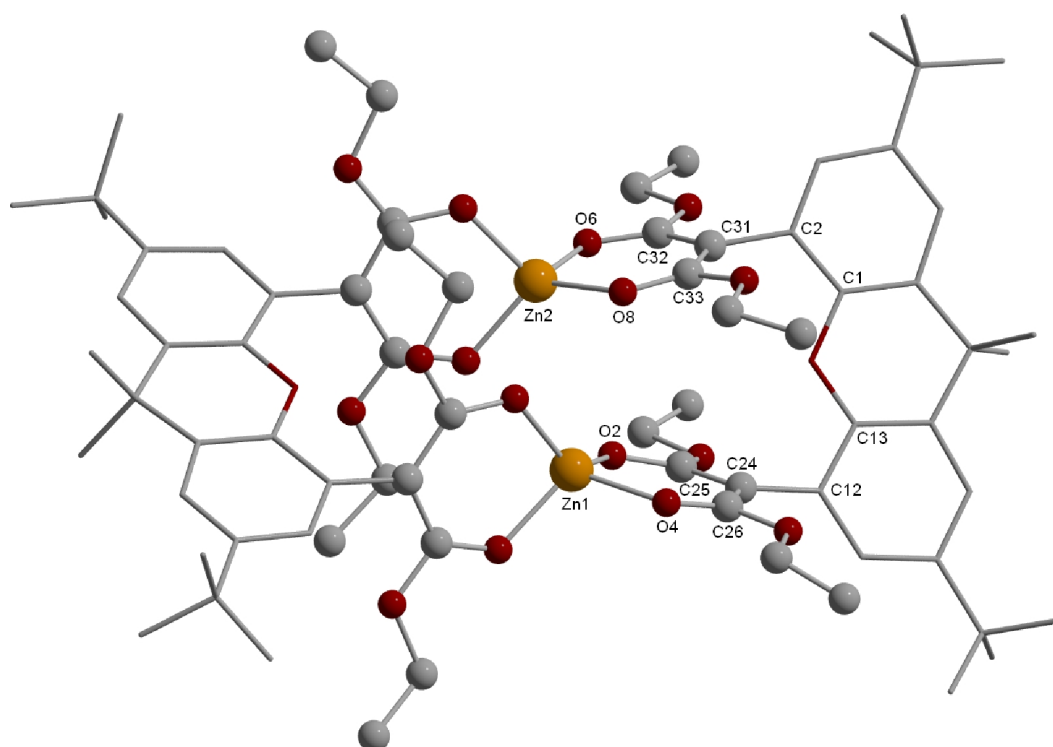


Fig. 3. Molecular structure of **5**. All hydrogen atoms have been omitted for clarity.

and the result is presented in Fig. 3 (Table 3 lists relevant bond lengths and angles).

The molecule shows a crystallographic S_4 axis and the coordination sphere around the zinc atoms can be described as being almost ideally tetrahedral. The planes defined by the diethyl malonate units are somewhat tilted in a way that brings the two Zn atoms closer together leading to a Zn–Zn distance of 3.766 Å. The Zn–Zn separation is thus significantly shorter than that reported for dinuclear bis- β -diiminato zinc complexes based on the xanthene backbone [4], presumably because the steric demand of the ethoxy groups is much smaller as compared to the aryl groups in the bis- β -diiminato zinc complexes. As in the case of the lithium salt the diethyl malonate moieties are twisted with respect to the xanthene backbone ($C13-C12-C24-C25 = 65.4^\circ$ and $C1-C2-C31-C33 = 65.7^\circ$) and the angles $C32-C31-C33$ of 121.6° and $C25-C24-C26$ of 119.7° point to an efficient delocalization of the π electrons.

As β -diketiminato zinc complexes have been shown to be efficient catalysts for CO_2 /epoxide copolymerizations [6], **5** was tested with respect to its activity under standard polymerization conditions. However, it proved to be inactive, probably as the ligands are

Table 3. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **5** with estimated standard deviations in parentheses.

Distances			
O2–Zn1	1.928(3)	O8–C33	1.273(5)
O4–Zn1	1.936(3)	O6–C32	1.270(6)
O6–Zn2	1.926(3)	Zn1–Zn2	3.766(1)
O8–Zn2	1.918(3)		
Angles			
C25–C24–C26	119.7(4)	C33–C31–C32	121.6(4)
Dihedral angles			
C13–C12–C24–C25	65.4(6)	C1–C2–C31–C33	65.7(6)

bound too tightly to the zinc centers, so that they cannot be replaced by CO_2 or epoxide. Certainly, complexes with a ligand to metal ratio of 1 : 2, *i. e.* compounds of the type $[Xanthmal]Zn_2X_2$ ($X = Et, Br$), would be more suitable, but these cannot be obtained *via* adjustment of the reactant ratios (*vide supra*). Accordingly, attempts were made to activate **5** by controlled addition of water and methanol, which was hoped to yield $[Xanthmal]Zn_2X_2$ ($X = OH, OMe$). However, treatment with two equivalents of water led quantitatively to $[Xanthmal]H_2$ and a white solid (presumably ZnO). In the presence of two equivalents of

methanol **5** is stable, but excessive methanol causes complete decomposition.

Conclusions

In conclusion we have established a synthetic route to [Xanthmal]H₂, a compound which after deprotonation provides an anionic ligand with interesting potential for novel dinuclear complexes. Such complexes can be obtained *via* reaction of [Xanthmal]H₂ with metal compounds whose ligands are capable of deprotonating it *in situ*, as illustrated by the reaction with ZnEt₂ leading to [Xanthmal]₂Zn₂ (**5**). Alternatively, [Xanthmal]H₂ can be lithiated and the resulting {Li₂[Xanthmal]}₂ (**4**), can be reacted with metal halides directly for the synthesis of corresponding metal complexes, as shown for ZnBr₂ whose reaction with **4** also provided **5**.

Furthermore it has been shown that [Xanthmal]H₂ can readily be converted into **3**, which in turn serves as starting material for the synthesis of another interesting dinucleating ligand: [R⁻Xanthdim]²⁻.

Experimental Section

General informations

Apart from the ligand synthesis all manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques in a dry argon atmosphere. The ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 NMR spectrometer (¹H 400.13 MHz; ¹³C 100.63 MHz) with CDCl₃ or CD₃CN as solvents at 20 °C. The spectra were calibrated against the residual proton and natural abundance ¹³C resonances of the deuterated solvent (CDCl₃, δ_H = 7.26 ppm, CD₃CN, δ_H = 1.94 ppm). Microanalyses were performed on a Leco CHNS-932 elemental analyzer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Digilab Excalibur FTS 4000 FTIR-spectrometer. High-resolution mass spectra were recorded with a Varian MAT311A/AMD instrument with electron spray ionization.

Materials

Solvents were dried using a Braun Solvent Purification System and degassed by vacuum-freezing cycles. Diethyl malonate was freshly distilled and degassed; K₃PO₄ was heated at 150 °C and dried in vacuum. Lithium diisopropylamide was prepared at –78 °C in diethyl ether from diisopropylamine and *n*-butyllithium.

4,5-Bis(1'3'-ethoxy-1',3'-propanedionyl)-2,7-di-^tbutyl-9,9-dimethylxanthen, [Xanthmal]H₂

7.9 mL of diethyl malonate (52 mmol) were added to a suspension of 11.3 g **1** (23.5 mmol), 25.1 g K₃PO₄

(118 mmol), 350 mg Pd(dba)₂ (0.608 mmol), and 250 mg P^tBu₃ (1.24 mmol) in 100 mL toluene under an argon atmosphere and exclusion of light at r. t. The resulting suspension was heated for 15 h at 70 °C. Subsequently the insoluble residue was removed *via* filtration over celite. After removal of all volatiles from the filtrate *in vacuo* the residual yellow solid was recrystallized from 60 mL diethyl ether. The precipitated product was extracted with 20 mL dichloromethane and the solution filtered from the remaining black solid. After removal of all volatiles from the filtrate 12.5 g of [Xanthmal]H₂ (19.6 mmol, 83.4%) was obtained in form of a white solid. – IR: ν = 2969 (s), 2940 (m), 2907 (m), 2873 (m), 1754 (vs), 1732 (vs), 1460 (s), 1416 (vw), 1391 (w), 1366 (s), 1305 (s), 1284 (s), 1258 (w), 1225 (s), 1199 (m), 1152 (s), 1115 (w), 1093 (w), 881 (m), 859 (w) cm⁻¹. – ¹H NMR (CDCl₃): δ = 1.28 (t, *J* = 7.1 Hz, 12H, OCH₂–CH₃), 1.32 (s, 18H, C(CH₃)₃), 1.63 (s, 6H, (CH₃)₂), 4.26 (q, *J* = 7.2 Hz, 8H, OCH₂–CH₃), 5.26 (s, 2H, CH–(C(O)OEt)₂), 7.26 (d, *J* = 2.4 Hz, 2H, CH_{ar}), 7.38 (d, *J* = 2.3 Hz, 2H, CH_{ar}). – ¹³C{¹H} NMR (CDCl₃): δ = 14.0 (OCH₂–CH₃), 31.4 (C(CH₃)₃), 32.2 (methyl-(CH₃)₂), 34.5 (C_{quart}), 34.8 (C_{quart}), 51.4 (CH–(C(O)OEt)₂), 61.6 (OCH₂–CH₃), 119.8 (C_{ar}), 122.5 (CH_{ar}), 124.5 (CH_{ar}), 129.2 (C_{ar}), 145.3 (C_{ar}), 145.6 (C_{ar}), 168.4 (C=O). – HRMS ((+)-ESI): *m/z* = 661.3341 (calcd. 661.3347 for C₃₇H₅₀ONa), 677.3081 (calcd. 677.3086 for C₃₇H₅₀OK). – C₃₇H₅₀O₉ (638.79): calcd. C 69.57, H 7.89; found C 69.73, H 7.79.

4,5-Diethylcarboxy-2,7-di-^tbutyl-9,9-dimethylxanthen, (**3**)

1.00 g [Xanthmal]H₂ (1.57 mmol) and 614 mg KOH (11.0 mmol) were suspended in 15 mL EtOH/H₂O in the ratio 2 : 1 and heated at 80 °C for 5.5 h. After removal of all volatile components *in vacuo* the residual solid was dissolved in 30 mL diethyl ether and the tetracarboxylate was extracted with water (15 mL) four times. The combined water phases were washed with diethyl ether and then acidified with diluted hydrochloric acid to pH 3–4. The resulting pale yellow precipitate was filtered off and dried *in vacuo*; it represents a mixture of xanthenes with malonic acid and acetic acid functions. Complete decarboxylation (yielding **3**) can be achieved either by dissolution in 5 mL dmsO and stirring for 6 h or by dissolution in a mixture of 5 mL dmf and 1 mL diluted hydrochloric acid followed by heating for 6 h. In both cases subsequently all volatile components have to be removed *in vacuo* to obtain **3** in yields of 69 and 72%, respectively. The spectroscopic and analytic data of **3** are identical to those in ref. [3].

Bis(κ²-O,O-4,5)-bis(1'3'-ethoxy-1',3'-propanedionyl)-2,7-di-^tbutyl-9,9-dimethyl-xanthenato)dilithium(I), {Li₂[Xanthmal]}₂, (**4**)

670 mg lithium diisopropylamide (6.25 mmol) was added to a solution of 2.00 g [Xanthmal]H₂ (3.13 mmol) in thf,

	[Xanthmal]H ₂	4[MeCN] ₂	5
Formula	C ₃₇ H ₅₀ O ₉	C ₇₈ H ₁₀₂ Li ₄ N ₂ O ₁₈	C ₃₇ H ₄₈ O ₉ Zn
<i>M_r</i>	638.77	1383.38	702.12
Cryst. size, mm ³	0.4 × 0.2 × 0.12	0.24 × 0.1 × 0.08	1 × 0.16 × 0.12
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	<i>Pnma</i>	<i>P</i> $\bar{1}$	<i>Pccn</i>
<i>a</i> , Å	15.334(2)	11.964(4)	15.586(2)
<i>b</i> , Å	25.308(2)	12.187(3)	27.882(5)
<i>c</i> , Å	9.2913(7)	14.142(4)	18.728(2)
α , deg	90	82.13(3)	90
β , deg	90	77.19(4)	90
γ , deg	90	78.96(4)	90
<i>V</i> , Å ³	3605.6(5)	1964(1)	8139(2)
<i>Z</i>	4	1	8
<i>D</i> _{calcd} , g cm ⁻³	1.177	1.170	1.146
μ (MoK α), mm ⁻¹	0.083	0.081	0.650
<i>F</i> (000), e	1376	740	2976
<i>hkl</i> range	±18, ±31, ±11	±14, ±14, ±16	±17, ±31, ±20
Refl. measured	25123	13216	42206
Refl. unique	3620	6671	6348
<i>R</i> _{int}	0.137	0.107	0.074
Data/restr./params.	3620/0/215	6671/2/473	6348/0/426
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²) (all refl.)	0.076/0.192	0.082/0.236	0.064/0.193
GoF (<i>F</i> ²)	0.997	0.804	0.986
$\Delta\rho_{\text{min}}$ (max/min), e Å ⁻³	0.73/−0.30	0.41/−0.46	1.27/−0.39

Table 4. Crystal structure data for [Xanthmal]H₂, 4[MeCN]₂ and 5.

and the mixture was stirred for 8 h. After removal of all volatile components *in vacuo* the residual yellow solid was washed twice with 30 mL diethyl ether. The remaining white powder was dried *in vacuo* to obtain 1.76 g **4** (2.70 mmol, 86.4%). – IR: $\nu = 2963$ (s), 2906, 2868 (m), 1622, 1617, 1609, 1602 (vs), 1284, 1464, 1458, 1447, 1438, 1431, 1419, 1375 (s), 1362 (m), 1334 (s), 1293, 1274, 1243, 1168 (m), 1106 (vs), 1034 (vw), 877 (m), 860 (w), 793 (m), 741 (w) cm⁻¹. – ¹H NMR (CD₃CN): $\delta = 1.00$ (t, *J* = 7.1 Hz, 12H, OCH₂–CH₃), 1.34 (s, 18H, C(CH₃)₃), 1.65 (s, 6H, (CH₃)₂), 3.79 (dq, *J* = 7.2, 3.6 Hz, 4H, OCH₂–CH₃), 4.13 (dq, *J* = 7.1, 3.6 Hz, 4H, OCH₂–CH₃), 7.12 (d, *J* = 2.5 Hz, 2H, CH_{ar}), 7.24 (d, *J* = 2.5 Hz, 2H, CH_{ar}). – ¹³C{¹H} NMR (CD₃CN): $\delta = 15.2$ (OCH₂–CH₃), 31.8 ((C(CH₃)₃), 34.5 (methyl-(CH₃)₂), 34.7 (C_{quart}), 35.3 (C_{quart}), 59.1 (OCH₂–CH₃), 78.0 (C–(C(O)OEt)₂), 120.4 (C_{ar}), 126.8 (C_{ar}), 128.0 (C_{ar}), 131.5 (C_{ar}), 143.0 (C_{ar}), 146.9 (C_{ar}), 173.6 (C=O). – C₃₇H₄₈O₉Li₂ (650.65): calcd. C 68.30, H 7.44; found C 66.89, H 7.46.

Bis(κ²-*O,O*-4,5)-*bis*(1'³'-ethoxy-1',3'-propanedionyl)-2,7-di-¹butyl-9,9-dimethyl-xanthenato)dizinc(II), [Xanthmal]₂Zn₂, (**5**)

(i) 100 mg diethylzinc (0.809 mmol) was added to a solution of 517 mg [Xanthmal]H₂ (0.801 mmol) in 15 mL diethyl ether. After stirring for 2 h at r.t. the volatiles were removed *in vacuo*. In order to remove residual traces of diethylzinc the resulting brown solid was redissolved in hexane, and again all volatiles were removed. The pale brown residue was suspended in 15 mL hexane and the solution was filtered off.

The remaining white powder was dried *in vacuo* to obtain 262 mg **5** (0.187 mmol, 46.2%).

(ii) 173 mg ZnBr₂ (0.768 mmol) was added to a solution of 500 mg **4** (0.768 mmol) in 30 mL thf. After stirring for 36 h at r.t. the pale yellow suspension was filtered off and the white precipitate was washed twice with 10 mL thf. The white powder was dried *in vacuo* to obtain 301 mg **5** (0.21 mmol, 55.8%). – IR (cm⁻¹): $\nu = 2963$ (s), 2906, 2868 (m), 1622, 1617, 1609, 1602 (vs), 1482, 1464, 1458, 1447, 1438, 1431, 1419, 1375 (s), 1362 (m), 1334 (s), 1293, 1274, 1243, 1168 (m), 1106 (vs), 1034 (w), 877 (m), 860 (w), 793 (s), 741 (w) cm⁻¹. – ¹H NMR (CDCl₃): $\delta = 1.07$ (t, *J* = 7.0 Hz, 24H, OCH₂–CH₃), 1.34 (s, 36H, C(CH₃)₃), 1.64 (s, 12H, (CH₃)₂), 3.88 (dq, *J* = 7.1, 3.5 Hz, 8H, OCH₂–CH₃), 4.27 (dq, *J* = 7.2, 3.4 Hz, 8H, OCH₂–CH₃), 7.13 (d, *J* = 1.7 Hz, 4H, CH_{ar}), 7.26 (s br., 4H, CH_{ar}). – ¹³C{¹H} NMR (CDCl₃): $\delta = 14.6$ (OCH₂–CH₃), 31.5 (methyl-(CH₃)₂), 31.7 C(CH₃)₃, 34.3 (C_{quart}), 35.0 (C_{quart}), 60.2 (OCH₂–CH₃), 78.5 (C–(C(O)OEt)₂), 119.4 (CH_{ar}), 123.3 (C_{ar}), 128.6 (C_{ar}), 128.7 (CH_{ar}), 142.8 (C_{ar}), 147.1 (C_{ar}), 174.2 (C=O). – C₇₄H₉₆O₁₈Zn₂ (1404.32): calcd. C 63.29, H 6.89; found C 62.95, H 7.05.

X-Ray structure determination

Suitable crystals of [Xanthmal]H₂ and **5** were obtained by slow evaporation of the solvent from saturated diethyl ether solutions. Single crystals of **4** were obtained by slow evaporation of the solvent from a saturated acetonitrile solution. The crystals were mounted on a glass fiber and then

transferred into the cold nitrogen gas stream of the diffractometer (Stoe IPDS (4, 5), Stoe IPDS2T ([Xanthmal]H₂), both using MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$). The structures were solved by Direct Methods (SHELXS-97 [7]), refined versus F^2 (SHELXL-97 [8]) with anisotropic temperature factors for all non-hydrogen atoms (Table 4). All hydrogen atoms were added geometrically and refined by using a riding model.

CCDC 643951 (4[MeCN]₂), 643949 (5) and 643950 ([Xanthmal]H₂) contain the supplementary crystallographic

data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] B. Bosnich, A. Gavrilova, *Chem. Rev.* **2004**, *104*, 349.
- [2] *Comprehensive Coordination Chemistry II*, Vol. 8 (Eds.: J. A. McCleverty, T. J. Meyer; vol. eds.: L. Que Jr., W. B. Tolman), Elsevier, Oxford, **2004**, chs. 8.1, 8.10, 8.13, 8.15, 8.19, 8.24.
- [3] M. F. Pilz, C. Limberg, B. Ziemer, *J. Org. Chem.* **2006**, *71*, 4559.
- [4] M. F. Pilz, C. Limberg, B. B. Lazarov, K. C. Hultzsich, B. Ziemer, *Organometallics* **2007**, *26*, 3668.
- [5] N. A. Beare, J. F. Hartwig, *J. Org. Chem.* **2002**, *67*, 541
- [6] a) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738; b) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *Angew. Chem.* **2002**, *114*, 2711; *Angew. Chem. Int. Ed.* **2002**, *41*, 2599; c) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 14284; M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018; M. Cheng, N. A. Darling, E. B. Lobkovsky, G. W. Coates, *J. Chem. Soc., Chem. Commun.* **2000**, 2007.
- [7] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
- [8] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.