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Xanthene-Based Ligand with Two Adjacent β-Diiminato Binding Sites

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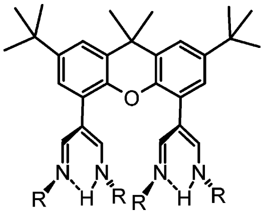
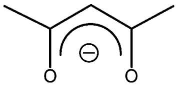


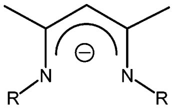
A novel potential ligand has been designed where two β-dialdimine units are linked by a xanthene backbone (H_2Xanthdim). The synthesis proceeds via a double vinamidinium salt and the products of its hydrolysis (containing eneamine/malonaldehyde units), which were converted into H_2Xanthdim via a reaction with 2,3-dimethylaniline. The reaction of H_2Xanthdim with *n*-butyllithium yields $((Et_2O)Li)_2$Xanthdim, which was isolated and crystallized. The crystal structures of both H_2Xanthdim and its lithium salt are discussed.

Introduction

For a given metal ion, the chemical and physical properties of its complexes are determined by the ligands, and consequently, in the past decades, a huge amount of research has been dedicated to ligand design: it has been recognized that the ligands are the key to new and improved functions and applications. This contribution describes the synthesis of a novel potential ligand providing two neighboring diiminato binding sites.



A



B

Deprotonation of acetylacetone yields the well-known acetylacetonato ligand **A** (abbreviation, acac), and the replacement of the keto functions in **A** by imino groups leads to the β-diketiminato ligand **B** (abbreviation, nacnac;[1] other names, diazapentadienide and β-iminatoaminat). Ligand **B** has proven to be a very versatile ligand in the past, both in main group and in transition metal chemistry:[2] it stabilizes high as well as low oxidation states, it can be used to prepare coordinatively unsaturated complexes, and often its complexes show interesting reactivities, like the catalysis of epoxide/CO_2 copolymerizations (Zn),[3] ring-opening polymerizations of lactides (Zn),[4] cyclopropanations (Cu),[5] olefin polymerizations (Cr),[6] or the activation of dinitrogen (Fe).[7]

There are many examples in coordination chemistry, proving that the cooperative behavior of *two* metal sites gives way to potentials that are not open to mononuclear complexes,[8] and the same principle is used by many dinuclear metalloenzymes.[9]

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[1] The designation [nacnac]$^-$ for the unsubstituted species [HC{C(Me)NH}$_2$]$^-$ was first proposed by Theopold and co-workers: Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541.

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Against this background it seemed rewarding to develop a potential ligand with two adjacent diiminato binding sites, especially because it has been shown that certain functions or reactions of mononuclear nacnac complexes likewise are enabled only by the cooperation of *two* molecules. Some ligands fulfilling this requirement have already been described; in most of these examples, the diiminato moieties are incorporated into a macrocyclic ring system,[10] in other cases two N atoms belonging to different diiminato units are linked,[11] and in all these compounds, the chelating functions are arranged vis-à-vis to each other. Here we report the synthesis of a potential ligand with a xanthene skeletal structure positioning two diiminato binding sites in parallel. Exemplarily, a lithium complex has been prepared, too.

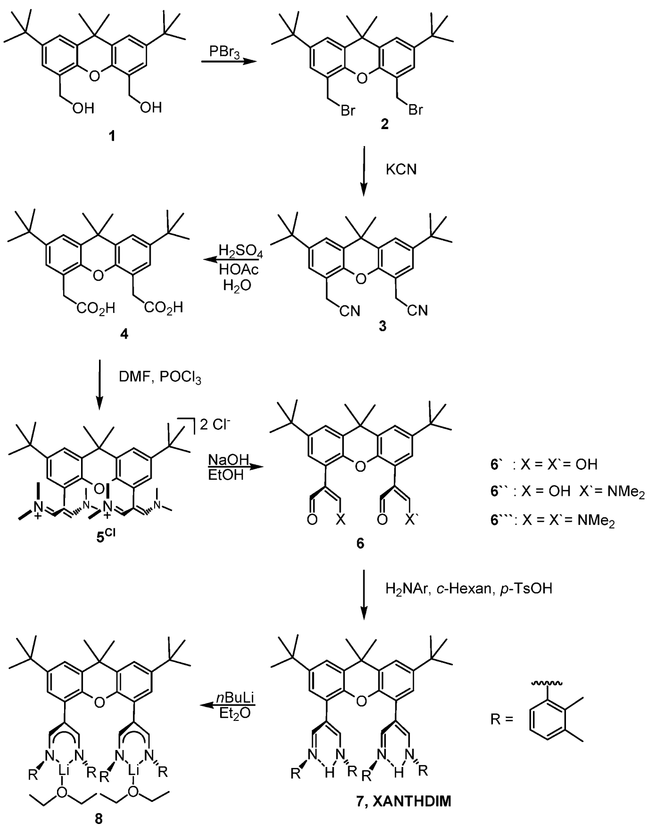
Results and Discussion

Xanthene was chosen as the backbone because it was anticipated to fix two diiminato units (once introduced in the 4,5 positions) in a distance that, after metal complexation, would allow *diatomic* units to be bound between these metals. At the same time, the xanthene spacer should permit the formation of dinuclear complexes with *monoatomic* bridging ligands, too, as the diiminato moiety is flexible enough in its binding properties to allow complexed metals a sufficient approach for that.[2] It was, therefore, envisaged to develop a synthesis in which two diiminato functions are (formally) linked to the 4 and 5 positions of xanthene via their meso carbon atoms.

It has been reported that $-CH_2-COOH$ groups can be converted into malonaldehyde functions, which in turn can be transformed into dialdiminato moieties: reaction of the corresponding carboxylic acid with DMF/$POCl_3$ leads in a complex Vilsmeier-type reaction, whose mechanism is not quite clear yet, to a vinamidinium salt;[12] after subsequent hydrolysis, the resulting malonaldehyde derivative can be transformed directly (in situ) into the corresponding dialdimine derivative through treatment with a chosen aniline.[13] To make use of this procedure for the preparation of the abovementioned potential ligand, first of all the synthesis of a doubly $-CH_2-COOH$ substituted xanthene derivative (**4** in Scheme 1) was pursued.

It was finally achieved starting from the diol **1**, which can be prepared via known procedures:[14] **1** was converted into the corresponding dibromide **2** via treatment with PBr_3, subsequent reaction with KCN then leads to the dicyanide **3**, and acidic hydrolysis of **3** yields the dicarboxylic acid **4**, whose crystal structure has been determined (as there are no peculiarities, a discussion is avoided here).

SCHEME 1



The proceedings of these three reactions can be nicely followed by ^1H NMR spectroscopy, studying the region between 4.8 and 3.7 ppm, where the methylene protons absorb, and this is important because, as a matter of course, it is essential for the successful preparation of the target ligand to make sure that in all steps the conversions nearly reach completion (as two functions have to be reacted, naturally each percent loss in conversion leads to two percent loss in yield); work up of the raw material then leads to isolated yields between 65 and 85%. Having prepared pure **4** in an acceptable overall yield, it was employed to obtain a double vinamidinium salt according to the abovementioned recipe for the parent compounds containing only one vinamidinium unit. Severe modifications of the published procedure[13] were necessary to apply it to the present problem (working under anhydrous conditions, longer reaction times, and with excessive $POCl_3$), but finally it indeed proved possible to prepare $\mathbf{5}^{Cl}$ (Scheme 1). Vinamidinium salts incorporating chloride counteranions as in $\mathbf{5}^{Cl}$ were reported to have undesirable thermal properties, and it has been recommended to avoid isolation; characterizations and also subsequent reactions were, thus, usually performed with the corresponding hexafluorophosphate or perchlorate salts.[12,13] In the present study, the dication of **5** was investigated in combination with chloride, hexafluorophosphate, and perchlorate anions. It was found that $\mathbf{5}^{Cl}$ is isolable and reasonably stable under anhydrous conditions; in this form it is ideally suited for subsequent reactions. The corresponding hexafluorophosphate and perchlo-

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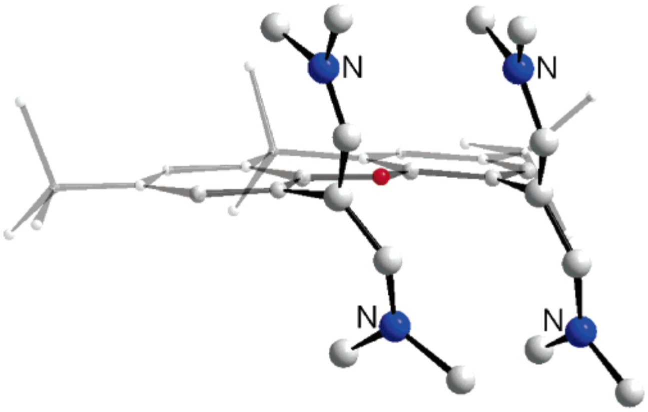


FIGURE 1. Structural representation of the dication in $\mathbf{5}^{ClO_4}$ (hydrogen atoms omitted for clarity).

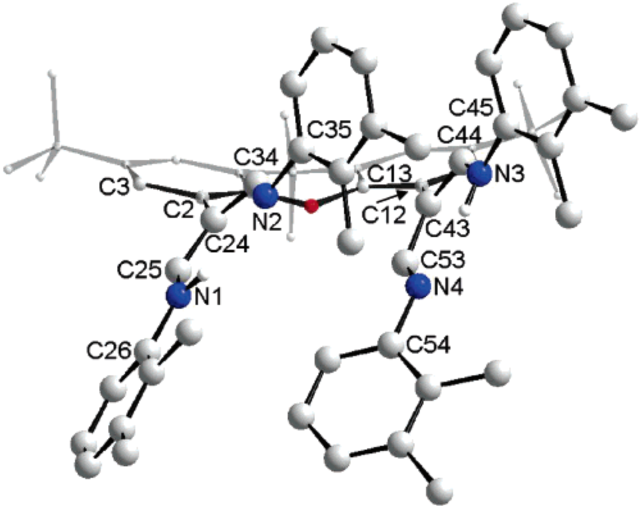


FIGURE 2. Structural representation of **7** (hydrogen atoms apart from those at the N atoms are omitted for clarity).

TABLE 1. Bond Lengths [Å] and Angles [°] of Compound 7

C(24)−C(25)	1.365(4)	C(43)−C(44)	1.380(4)
C(25)−N(1)	1.351(3)	C(44)−N(3)	1.339(3)
C(26)−N(1)	1.403(4)	C(45)−N(3)	1.409(4)
C(24)−C(34)	1.432(4)	C(43)−C(53)	1.411(4)
C(34)−N(2)	1.305(3)	C(53)−N(4)	1.320(3)
C(35)−N(2)	1.425(3)	C(54)−N(4)	1.419(4)
C(25)−C(24)−C(34)	123.7(2)	C(44)−C(43)−C(53)	122.0(2)
N(1)−C(25)−C(24)	126.5(3)	N(3)−C(44)−C(43)	125.2(3)
C(25)−N(1)−H(1N)	113.9(19)	C(44)−N(3)−H(3N)	114(2)
C(25)−N(1)−C(26)	126.0(2)	C(44)−N(3)−C(45)	122.5(3)
N(2)−C(34)−C(24)	123.6(3)	N(4)−C(53)−C(43)	123.5(3)
C(34)−N(2)−C(35)	116.8(2)	C(53)−N(4)−C(54)	120.3(2)
C(3)−C(2)−C(24)−C(34)	123.1(3)	C(24)−C(34)−N(2)−C(35)	170.4(2)
C(24)−C(25)−N(1)−C(26)	172.7(2)	C(43)−C(44)−N(3)−C(45)	171.3(2)
C(13)−C(12)−C(43)−C(44)	131.0(3)	C(43)−C(53)−N(4)−C(54)	177.2(2)

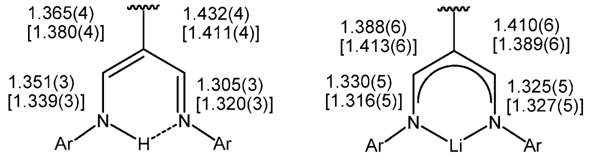
rate salts could also be isolated, but the hexafluorophosphate salt failed to react cleanly in subsequent reactions, while the perchlorate salt proved to be unreactive. However, the latter formed crystals that were suitable for a single-crystal X-ray analysis. As a result of severe disordering of the perchlorate anions, the solution did not reach a quality that would allow a detailed discussion of bond lengths and angles; nevertheless, the molecular structure of the dication in the solid, crystalline state, as shown in Figure 1, is beyond doubt. The structure exhibits planar, all-trans "W" configurations for the delocalized allyl cations, which are naturally oriented parallel. The aryl rings of the xanthene backbone are positioned almost perpendicular to the allyl chain.

The hydrolysis of $\mathbf{5}^{Cl}$, that was envisaged to lead to two malonaldehyde moieties, proceeds incompletely and yields a mixture of three compounds containing two malonaldehyde units **6′**, one malonaldehyde unit and one oxo eneamine unit, **6″**, or two oxo eneamine units, **6‴** (**6**, Scheme 1, with varying ratios **6′**/**6″**/**6‴**), as evidenced by ESI investigation. At first sight, the ^{1}H and ^{13}C NMR spectra of this mixture look surprisingly simple, as there are no obvious signals for the NMe_2 groups. This is due to the fact that incidentally the point of coalescence for the NMe_2 rotation is reached at 20 °C so that their signals are broadened into the baseline. However, on cooling to −20 °C, the sets of signals expected for the compounds **6** can nicely be observed. When the reactivity of the mixture **6′**, **6″**, and **6‴** was investigated, it turned out that the residual amino groups in **6″** and **6‴** do not prohibit the next step (the conversion to diiminato moieties). Hence, the raw material obtained after hydrolysis of **5** does not have to be worked up before the final conversion: the treatment with a chosen aniline derivative to obtain a bis(*β*-dialdiminato) ligand of type **7**. Commonly, acceptable yields in this type of condensation reaction are only observed, when the anilines employed are relatively electron rich, that is, it is helpful when the aryl rings are substituted by alkyl groups. For this reason and also for reasons of steric shielding, in many cases 2,6-diisopropylaniline or 2,6-di-*tert*-butylaniline have been employed in the past.[2] However, the *i*-propyl and *tert*-butyl groups appeared to be too bulky for the present system, considering that in the target ligand **7** four aryl residues are located in very close proximity. Hence, a more flat aryl residue being substituted only on one side seemed more appropriate, and accordingly, 2,3-dimethylaniline was chosen as the starting material. Heating **6** together with a 6-fold excess of 2,3-dimethylaniline in cyclohexane solution leads to **7** (XANTHDIM) with an isolated yield of 30%. After recrystallization from EtOH, single crystals could be obtained that were suitable for an X-ray crystal structure analysis, and the result is shown in Figure 2 (selected bond lengths and angles are listed in Table 1).

The diiminato moieties are almost planar, and as the vinamidinium units in **5** they are oriented in parallel. However, the torsion angles of the diiminato planes with respect to the xanthene backbone are wider than those observed in **5** (C13C12C43C44 and C3C2C24C34 torsion angles of 131.0(3) and 123.1(3)°). The H atoms of the N−H groups were located and refined: they were found to be bonded primarily to one of the two diimine nitrogen atoms, that is, at N3 and N1, respectively (N3−H, 0.88(2) Å; N1−H, 0.89(2) Å). Furthermore, each of those hydrogen atoms is located close to the plane formed by the two nitrogen atoms belonging to a respective dialdimine unit and their connecting carbon atoms, with the result that there are long N···H contacts to N2 (2.09(2) Å) and N4 (1.99(2) Å). In effect, N1 and N3 can be designated the amine nitrogen atoms, and this is supported by the pattern of N−C and C−C bond lengths in both units, as exemplified in Chart 1 (the numbers in brackets refer to the second diiminato function within **7**/**8**).

These distances indicate that localization of the N═C double bonds is far advanced, and a comparison with published structures containing diketiminato moieties with

CHART 1



7 **8**

localized N=C bonds[15] reveals a close similarity. Surprisingly, the bond localization in one of the units (brackets) is more pronounced than in the other one; the reasons for that are not clear.

The addition of *n*-BuLi to **7** in Et_2O solution and subsequent recrystallization of the raw material from diethyl ether afforded the lithium etherate **8** in the form of yellow crystals, which were examined by single-crystal X-ray crystallography, too. The crystal structure is shown in Figure 3, and relevant bond lengths and angles are summarized in Table 2.

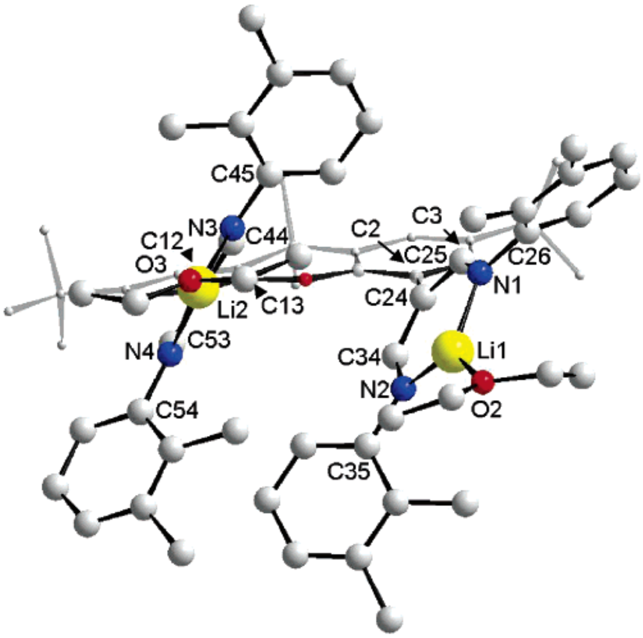


FIGURE 3. Structural representation of **8** (hydrogen atoms omitted for clarity, arrows point to covered atoms).

TABLE 2. Bond Lengths [Å] and Angles [°] of 8

C(24)−C(25)	1.388(6)	C(43)−C(44)	1.413(6)
C(25)−N(1)	1.330(5)	C(44)−N(3)	1.316(5)
C(26)−N(1)	1.412(5)	C(45)−N(3)	1.426(6)
C(24)−C(34)	1.410(6)	C(43)−C(53)	1.389(6)
C(34)−N(2)	1.325(5)	C(53)−N(4)	1.327(5)
C(35)−N(2)	1.429(5)	C(54)−N(4)	1.422(6)
C(25)−C(24)−C(34)	125.4(4)	C(53)−C(43)−C(44)	125.0(4)
N(1)−C(25)−C(24)	128.5(4)	N(3)−C(44)−C(43)	127.6(4)
C(25)−N(1)−Li(1)	118.9(4)	C(44)−N(3)−Li(2)	119.7(4)
C(25)−N(1)−C(26)	113.4(4)	C(44)−N(3)−C(45)	115.8(4)
N(2)−C(34)−C(24)	127.6(4)	N(4)−C(53)−C(43)	127.5(4)
C(34)−N(2)−Li(1)	119.3(4)	C(53)−N(4)−Li(2)	119.1(4)
C(34)−N(2)−C(35)	115.0(3)	C(53)−N(4)−C(54)	116.0(4)
C(3)−C(2)−C(24)−C(34)	124.6(4)	C(43)−C(44)−N(3)−C(45)	178.3(5)
C(24)−C(25)−N(1)−Li(1)	176.8(7)	C(43)−C(44)−N(3)−Li(2)	170.7(7)
C(24)−C(25)−N(1)−C(26)	171.5(5)	C(43)−C(53)−N(4)−C(54)	176.8(5)
C(13)−C(12)−C(43)−C(53)	132.6(5)	C(43)−C(53)−N(4)−Li(2)	170.4(7)
C(24)−C(34)−N(2)−Li(1)	174.2(7)	N(1)−Li(1)−N(2)−C(34)	176.6(6)
C(24)−C(34)−N(2)−C(35)	178.1(4)	N(4)−Li(2)−N(3)−C(44)	178.9(6)

The replacement of hydrogen by lithium leaves the planarity of the C_3N_2 unit unaffected. However, it can be seen (Chart 1) that the two C−C and the two N−C distances within each of the C_3N_2Li rings equalize so that both units in **8** become even more symmetric than the more balanced unit within **7**. This indicates that the π bonding is now more delocalized for both units to the same degree. In effect, **8** may be described as a dinuclear diazapentadienide alkali metal complex; the Li−N bond lengths are all very similar and lie in the range of 1.95−1.92 Å. The Li ion has a trigonal planar coordination, with angles that are strongly distorted from idealized values, for example, N1−Li1−N2 and N3−Li2−N4 amount to only 100.1(4)° and 100.0(4)°, respectively. The Li−N and Li−O bond lengths are comparable to those previously described for lithium atoms coordinated by nacnac,[15] amide, and ether ligands.[16]

Conclusions

In conclusion, we have established a synthetic route to **7**, which after deprotonation should represent an interesting potential ligand for novel dinuclear complexes. The properties of these complexes can be anticipated to vary from analogous *mononuclear* compounds incorporating only *one* diiminato binding pocket; the cooperating effect of the two metal ions in complexes of **7** may even lead to advanced properties in applications, and especially in this respect it will be interesting to investigate the difference the parallel arrangement of the chelating function makes for the cooperativity of the metal ions in comparison to the "vis-à-vis" orientation.

Furthermore, **7** was lithiated to give **8**, which can be reacted with metal halides directly for the synthesis of corresponding metal complexes.

Experimental Section

All manipulations were carried out by means of Schlenk-type techniques involving the use of a dry argon atmosphere. Solvents were purified, dried, and degassed prior to use. Reagents were obtained commercially and used without further purification. Infrared (IR) spectra were recorded using samples prepared as KBr pellets. Melting points are uncorrected.

4,5-Dibromomethyl-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene, 2. 4,5-Dihydroxymethyl-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene, **1** (18.5 g (0.048 mol)), is placed into a 1 L three-necked flask in a dry atmosphere and dissolved in 600 mL of diethyl ether. Lithium bromide (2.0 g (0.023 mol)) is added, and the resulting suspension is treated at rt with 12 mL (0.126 mol) PBr_3 (dropwise within 10 min). After stirring overnight and subsequent cooling with ice, 20 mL of water is added to the suspension. The mixture is neutralized with $NaHCO_3$, the phases are separated, and the aqueous phase is extracted twice with 200 mL of diethyl ether. The two organic phases are combined and dried over $MgSO_4$. Evaporation of the solvent from the filtrate yields 21 g (0.041 mol, 85% yield) of **2**.

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Mp 212−213 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 18H), 1.63 (s, 6H), 4.80 (s, 4H), 7.25 (d, J = 2.26 Hz, 2H), 7.38 (d, J = 2.26 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.6, 31.5, 32.7, 34.5, 34.5, 123.8, 124.3, 125.7, 129.4, 145.6, 145.9. IR (KBr): $\tilde{\nu}$ 2963, 2904, 2869, 1457, 1363, 1280, 1229, 881, 758 cm^{-1}. HRMS (EI; m/z): calcd for $C_{25}H_{32}Br_2O$, 506.0819; found, 506.0819. MS (EI; m/z): 508 [M$^+$], 493 [M$^+$ − CH_3], 429 [M$^+$ − Br], 415 [M$^+$ − CH_2Br], 414 [M$^+$ − Br − CH_3], 349, 333, 330, 319, 271. Anal. Calcd for $C_{25}H_{32}Br_2O$ (508.3): C, 59.07; H, 6.35. Found: C, 59.20; H, 6.37.

4,5-Dicyanomethyl-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene, 3. Compound **2** (20.5 g (0.04 mol)) is dissolved in 600 mL ethanol, and 21 g (0.32 mol) of KCN, dissolved in 40 mL water, is added. After heating under reflux for 4 h, most of the ethanol is removed under vacuum, and the residue is extracted several times with diethyl ether. The combined organic phases are dried over $MgSO_4$. Evaporation of the solvent from the filtrate yields a brownish solid, which is recrystallized from ethanol. After drying under vacuum, 12.6 g (0.031 mol, 78% yield) of white **3** is isolated.

Mp 181−183 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 18H), 1.64 (s, 6H), 3.87 (s, 4H), 7.20 (d, J = 2.38 Hz, 2H), 7.39 (d, J = 2.38 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 31.4, 32.9, 34.4, 34.6, 116.7, 117.9, 123.2, 125.0, 129.3, 145.1, 146.3. IR (KBr): $\tilde{\nu}$ 2966, 2910, 2873, 2247 (ν(CN)), 1460, 1417, 1365, 1333, 1277, 1224, 877, 848, 754 cm^{-1}. HRMS (ESI; m/z): calcd for $C_{27}H_{32}N_2O$ + Na$^+$, 423.2407; found, 423.2407. HRMS (ESI; m/z): calcd for $C_{27}H_{32}N_2O$ + K$^+$, 439.2146; found, 439.2148. MS (ESI; m/z): 839 [2M + K$^+$], 823 [2M + Na$^+$], 447, 439 [M + K$^+$], 423 [M + Na$^+$], 418 [M + NH_4^+]. Anal. Calcd for $C_{27}H_{32}N_2O$ (400.5): C, 80.96; H, 8.05; N, 6.99. Found: C, 80.02; H, 8.10; N, 6.46.

4,5-Diethylcarboxy-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene, 4. Compound **3** (12.6 g (31.5 mmol)) is placed into a 1 L flask, and 150 mL of water and 150 mL of glacial acetic acid, as well as 150 mL of concentrated sulfuric acid, are added. After refluxing for 6 h, the resulting mixture is extracted three times with 100 mL of diethyl ether. The combined ether phases are dried with $MgSO_4$, and, after filtration, the solvent is removed. The resulting beige solid is washed with acetone. This leads to 8.9 g (20.3 mmol, 65% yield) of white **4**. Colorless crystals could be obtained by the slow evaporation of a THF solution of **4**.

Mp 291 °C. ^{1}H NMR (400 MHz, THF-d_8): δ 1.32 (s, 18H), 1.62 (s, 6H), 3.72 (s, 4H), 7.18 (d, J = 2.38 Hz, 2H), 7.37 (d, J = 2.38 Hz, 2H), 10.78 (b, 2H). ^{13}C NMR (100 MHz, THF-d_8): δ 31.9, 32.7, 35.0, 35.4, 36.2, 122.1, 123.2, 126.7, 129.9, 145.4, 147.4, 172.7. IR (KBr): $\tilde{\nu}$ 2963, 2907, 2872, 1715 (ν(CO)), 1458, 1278, 1225 cm^{-1}. HRMS (EI; m/z): calcd for $C_{27}H_{34}O_5$, 438.2406; found, 438.2406. MS (EI; m/z): 438 [M$^+$], 423 [M$^+$ − CH_3], 281 [M$^+$ − CH_3 − H_2O]. Anal. Calcd for $C_{27}H_{34}O_5$ (438.5): C, 73.94; H, 7.81. Found: C, 73.54; H, 7.78.

2,7-Bis(1,1-dimethylethyl)-9,9-dimethylxanthene-4,5-bis(1,3-bis(dimethylamino)trimethinium Chloride), 5^{Cl}, and Its Hydrolysis Products, 6. Compound **4** (1.5 g (3.4 mmol)) is dissolved in 15 mL of dry DMF. After cooling to 0°C, 3.4 mL (37 mmol) of phosphoryl chloride is added slowly via a syringe. Subsequently, the solution is allowed to warm to rt (during this process it turns yellow). The reaction vessel is equipped with a reflux condenser wearing a drying tube on top, and the mixture is heated to 84 °C for 17 h. A beige suspension is formed from which the solution is removed via cannula. The beige solid residue mainly consists of **5**^{Cl} (by redissolution and addition of $NaClO_4$, it can be converted into **5**^{ClO_4}, which can be crystallized (see Figure 1)), and for the preparation of **6**, it is treated directly without further purification with a solution of 4 g (0.1 mol) of NaOH in 40 mL of a 1:1 EtOH/water mixture. After heating for 1 h under reflux, the solution is buffered with $NaHCO_3$ and diluted hydrochloric acid, the EtOH is removed under vacuum, and the resulting dispersion is extracted several times with a mixture of diethyl ether and tetrahydrofuran in a ratio of 2:1. After drying over magnesium sulfate and filtering, the solvent is removed, leaving behind 1.5 g of an orange solid that mainly contains **6** (1.5 g/3.0 mmol, 85%). This raw material can be employed directly in the synthesis of **7** without further purification.

As pointed out in Results and Discussion, the dimethylamino groups are coalescent at rt so that averaged spectra are observed. Exemplarily, the NMR data for **6‴** are: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.33 (s, 18H), 1.67 (s, 6H), 2.3−3.3 (b, 6H), 6.79 (s, 2H), 7.04 (d, J = 2.4 Hz, 2H), 7.37 (d, J = 2.4 Hz, 2H), 9.03 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 31.6, 33.1, 34.6, 34.8, 37−40 (b), 45−48 (b), 110.9, 122.1, 122.2, 128.6, 128.9, 144.8, 145.9, 159.5, 188.3. Only lowering the temperature to −20 °C allows the observation of resolved signals for the NMe_2 groups: ^{1}H NMR (400 MHz, CD_2Cl_2, −20 °C): δ 1.29 (s, 18H), 1.65 (s, 6H), 2.40 (s, 6H), 3.06 (s, 6H), 6.80 (s, 2H), 7.01 (d, J = 2.2 Hz, 2H), 7.33 (d, J = 2.2 Hz, 2H), 8.98 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 31.3, 33.3, 34.3, 34.3, 37.9, 47.0, 109.9, 121.6, 122.1, 128.1, 128.3, 144.3, 144.9, 159.5, 188.1. The ^{1}H NMR spectrum at 40 °C shows only one broad peak for the NMe_2 groups: ^{1}H NMR (300 MHz, CD_2Cl_2, 40 °C): δ 1.34 (s, 18H), 1.67 (s, 6H), 2.60−2.85 (b, 6H), 6.70−6.86 (b, 2H), 7.04 (d, J = 2.4 Hz, 2H), 7.38 (d, J = 2.4 Hz, 2H), 9.04 (s, 2H).

6: HRMS (ESI; m/z): calcd for $C_{33}H_{45}N_2O_3$ + Na$^+$ (**6‴**), 539.3244; found, 539.3243. HRMS (ESI; m/z): calcd for $C_{33}H_{45}N_2O_3$, 517.3425; found, 517.3424. HRMS (neg. ESI; m/z): calcd for $C_{31}H_{38}NO_4$ (**6″**), 488.2795; found, 488.2795. MS (ESI; m/z): 461 [M$^-$ − H$^+$] (**6′**); 488 [M$^-$ − H$^+$] (**6″**); 516 [M$^+$] (**6‴**).

2,7-Bis(1,1-dimethylethyl)-9,9-dimethyl-4,5-bis(1-(2,3-dimethylphenylamino)-3-(2,3-dimethylphenylimino)isopropenyl)-xanthene, 7. Raw material obtained in the synthesis of **6** (1.5 g) is dissolved in 150 mL of cyclohexane and 5 mL (41 mmol) of 2,3-dimethylaniline, and 1.5 g (7.9 mmol) of *p*-toluenesulfuric acid is added. The flask is equipped with a Dean Stark apparatus and a reflux condenser wearing a drying tube on top, and the mixture is heated for 3 days under reflux. The resulting solution is neutralized with a saturated solution of $NaHCO_3$, and the aqueous phase is extracted with a mixture of diethyl ether and tetrahydrofuran in a ratio of 2:1. After drying the combined organic phases with $MgSO_4$, all volatile compounds are removed from the filtrate under vacuum. The resulting amber oil is recrystallized several times from absolute ethanol and dried sufficiently under vacuum so that 820 mg (0.94 mmol) of pure **7** is obtained as a yellow solid (27% starting from the acid).

Mp 247 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 18H), 1.73 (s, 6H), 2.01 (s, 12H), 2.12 (s, 12H), 6.65 (d, J = 7.2 Hz, 4H), 6.73 (d, J = 7.2 Hz, 4H), 6.79 (*ps*-t, J = 7.6 Hz, 4H), 7.12 (d, J = 2.4 Hz, 2H), 7.35 (d, J = 2.4 Hz, 2H), 7.92 (d, J = 5.2 Hz, 1H), 12.16 (*ps*-t, J = 5.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 13.9, 20.3, 31.6, 33.2, 34.7, 34.8, 106.4, 114.3, 121.0, 124.8, 125.7, 126.0, 126.5, 127.7, 129.4, 136.8, 145.2, 145.3, 145.8, 150.9. IR (KBr): $\tilde{\nu}$ 3434 (NH), 2962, 2864, 1640, 1542, 1286, 1266 cm^{-1}. HRMS (EI; m/z): calcd for $C_{61}H_{70}N_4O_1$, 874.5549; found, 874.5549. MS (EI; m/z): 874.6 [M$^+$], 753.5 [M$^+$ − $C_8H_{10}N$ − H], 633.4 [M$^+$ − 2 $C_8H_{10}N$ − H], 121 [$C_8H_9NH_2^+$]. Anal. Calcd for $C_{61}H_{70}N_4O$ (875.2): C, 83.71; H, 8.06; N, 6.40. Found: C, 83.17; H, 8.56; N, 6.28.

Dilithium 2,7-Bis(1,1-dimethylethyl)-9,9-dimethyl-4,5-bis(1-(2,3-dimethylphenylamido)-3-(2,3-dimethylphenylimino)isopropenyl)-xanthene, 8. Compound **7** (200 mg (0.230 mmol)) is dissolved in 10 mL diethyl ether, and the solution is cooled to −78 °C. *n*-Butyllithium (0.18 mL (0.46 mmol)) is added via a syringe, and after further 10 min of stirring, the solution is warmed to rt. It is subsequently concentrated to a volume of about 2 mL, and storing at rt for 3 days finally leads to the precipitation of 152 mg (0.121 mmol, 53%) of yellow crystals of **8**.

^{1}H NMR (400 MHz, THF-d_8): δ 1.34 (s, 18H), 1.63 (s, 6H), 2.14 (s, 24H), 6.57 (d, J = 7.6 Hz, 4H), 6.70 (*ps*-t, J = 8.0 Hz, 4H), 6.90 (d, J = 8.0 Hz, 4H), 7.09 (*ps*-dd, J = 2.4, 9.00 Hz, 8H), 7.94 (s, 4H). ^{13}C NMR (100 MHz, THF-d_8): δ 14.9, 20.8, 32.1, 34.8, 35.0, 35.5, 105.2, 119.2, 121.2, 123.6, 127.0, 127.2, 128.7, 129.4, 134.2, 136.4, 144.0, 145.7, 157.4, 161.1. IR (KBr): $\tilde{\upsilon}$ 2958, 2867, 1641, 1571, 1458, 1374, 1323, 1244, 1216, 1052, 778 cm^{-1}. Anal. Calcd for $C_{61}H_{68}Li_2N_4O{\cdot}(C_4H_{10}O)_2$ (1035.3): C, 80.04; H, 8.56; N, 5.41. Found: C, 80.13; H, 8.31; N, 5.74.

X-ray Diffraction Data Collection for 4, 7, and 8. Single crystals of the compounds were selected in a cold stream of nitrogen. They were then mounted on top of a fiber and quickly frozen to −93 °C. Centered reflections were refined by least-squares calculations to indicate the unit cells. Unit cell and collection parameters for the complexes are listed in Table S1 in the Supporting Information section. Diffraction data were collected in the appropriate hemispheres and under the conditions specified also in Table S1.

Solution and Refinement of the Structures of 4, 7, and 8. The structures were solved by direct methods (program, SHELXS-97)[17] and refined versus $F2$ (program, SHELXL-97)[18] with anisotropic temperature factors for all nonhydrogen atoms. The hydrogen atoms of **7** were found and refined isotropically, while all hydrogen atoms of **8** were added geometrically and refined by using a riding model.

The final residuals are indicated in Table S1. The crystallographic data (apart from structure factors) of **4**, **7**, and **8** were deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-298178, CCDC-298176, and CCDC-298177. Copies of the data can be ordered free of charge from the following address in Great Britain: CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Table S1 and crystallographic information files for **4**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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