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From Triplesalen to Triplesalalen and Triplesalan – Strengthening the Aromatic Character of the Ligand Backbone in Extended Phloroglucinol Ligands by Prevention of Heteroradialene Formation

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The methyl-protected triplesalalen ligand $Me_3H_3talalen^{tBu_2}$ was synthesized from 2,4,6-tris(bromomethyl)-1,3,5-trimethoxybenzene and three equivalents of the secondary amine 4,6-di-*tert*-butyl-2-{[2-(methylamino)ethylimino]methyl}-phenol. A reduction with $NaBH_4$ afforded the methyl-protected triplesalan ligand $Me_3H_3talan^{tBu_2}$. Deprotection efforts of the methyl-protected $Me_3H_3talalen^{tBu_2}$ ligand with Lewis acids were unsuccessful. Using Cu^{II} ions as Lewis acid resulted in the formation of the methyl-protected triplesalalen complex $[(Me_3H_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$, which could be characterized by single-crystal X-ray diffraction. The bond-length analysis reveals the aromatic character of the central backbone without heteroradialene contribution, and this is corroborated by NMR spectra of the ligands, which exhibit a singlet assigned to the benzylic protons at δ = 3.50 ppm in the ^{1}H NMR and a resonance typical for an aromatic C^{Ar}–O group at δ = 160.0 ppm in the ^{13}C NMR spectroscopy. FTIR spectra of the ligands and of the complexes exhibit the typical features of a central aromatic unit and do not show the characteristic intense bands for vibrations of the exocyclic C=C and C=O double bonds of a heteroradialene. Additionally, the characteristic strong absorption bands for heteroradialenes in the 26000–35000 cm^{-1} region are absent in the UV/Vis/NIR spectra. The electrochemistry exhibits the reversible oxidation of the terminal phenolates of $[(Me_3H_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ at +0.72 V vs Fc^+/Fc, and the magnetic measurements reveal an uncoupled behavior due to the apical coordination of the central methoxy groups to the Cu^{II} ions.

Introduction

The discovery of the fascinating properties of single-molecule magnets (SMMs)[1] and their potential applications in memory devices, quantum computing, and molecular spintronics[2] has attracted much interest for new types of SMMs. To obtain a rational access to new types of SMMs, we developed the ligand system triplesalen.[3,4] The first generation of triplesalen ligands (e.g., $H_6talen^{tBu_2}$, Figure 1a, $R^1 = R^2 = t$Bu) is composed of a central 1,3,5-trihydroxybenzene (phloroglucinol) unit, which was chosen to enforce ferromagnetic interactions between the metal ions by the spin-polarization mechanism.[5,6] The salen-like coordination environment was chosen to induce a strong magnetic anisotropy through its strong axial ligand field.[7] Additionally, the C_3 symmetry of the ligand and hence of its complexes should reduce the rhombicity of the trinuclear complexes to minimize quantum-mechanical magnetization tunneling.[8] Indeed, the trinuclear Cu^{II} and V^{IV}=O complexes exhibit ferromagnetic interactions,[9–11] and by a supramolecular approach, we could assemble two trinuclear complexes $[(talen^{tBu_2})\{M^t(solv)_n\}_3]^{m+}$ serving as building blocks with a central hexacyanochromate $[M^c(CN)_6]^{3-}$ to heptanuclear complexes $[\{(talen^{tBu_2})M^t_3\}_2\{M^c(CN)_6\}]^{3+}$ subsequently abbreviated $[M^t_6M^c]^{n+}$: $[Mn^{III}_6Cr^{III}]^{3+}$,[12] $[Mn^{III}_6Fe^{III}]^{3+}$,[13] $[Mn^{III}_6Co^{III}]^{3+}$,[14] and $[Mn^{III}_6Mn^{III}]^{3+}$.[15] The complexes $[Mn^{III}_6Cr^{III}]^{3+}$ and $[Mn^{III}_6Mn^{III}]^{3+}$ were shown to be single-molecule magnets. However, the analysis of the magnetic properties in these heptanuclear complexes[12–14] and in trinuclear Mn^{III}_3[16] and Fe^{III}_3[17,18] complexes revealed that the interaction between the Mn^{III} (Fe^{III}) ions in the triplesalen subunits is not as expected ferromagnetic but weakly antiferromagnetic.

We identified a reason for this unexpected exchange coupling by extensive NMR spectroscopy on our ligands on the basis of the work of MacLachlan et al.[19] and later others.[20] The central phloroglucinol backbone is not in the usually assumed *O*-protonated tautomeric form (Figure 1d, **I** and **II**) but in the *N*-protonated form (Figure 1d, **III** and **IV**).[17,21–23] Furthermore, this *N*-protonated tautomer has the keto–enamine resonance structure **IV** as a main contribution to the resonance hybrid and not the enolate–iminium resonance structure **III**. This is in agreement with stud-

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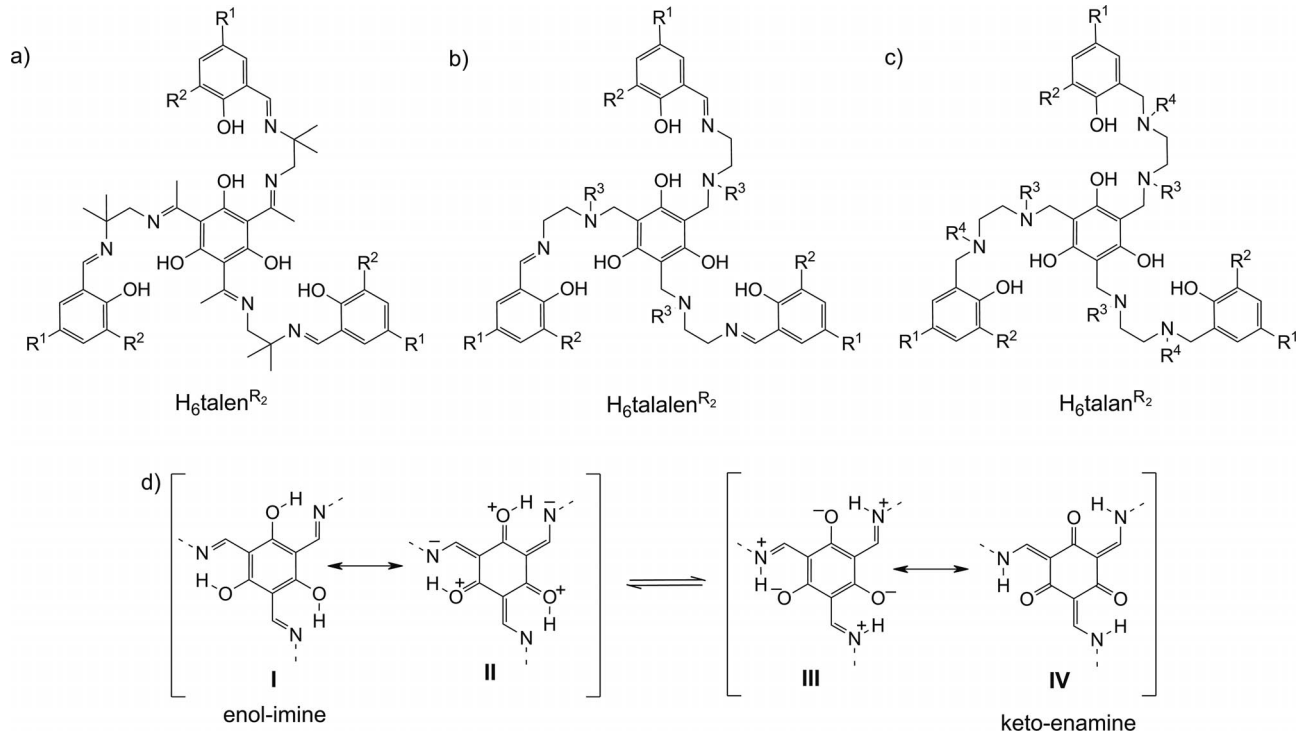


Figure 1. Abbreviations of ligands (a–c). Tautomerism and mesomery in extended phloroglucinol ligands (d).

ies by Plass et al. on a comparable ligand system.[24] The resonance structure **IV** closely resembles [6]radialenes and has thus been named heteroradialene.[25] [6]Radialenes are cross-conjugated alicycles without a delocalized π system and thus have no aromatic character.[26,27] Moreover, we could show that also in our trinuclear complexes the main resonance structure is the heteroradialene **IV** but to a lower extend compared to the ligands.[17,21,22,28] As the spin-polarization mechanism is anticipated to be a π mechanism,[6,29] we identified the heteroradialene formation accompanied by the reduction of the aromaticity of the central ring as one major reason for the weak ferromagnetic interactions in the Cu^{II}_3 and $(V^{IV}{=}O)_3$ complexes and the weak antiferromagnetic interactions in the Mn^{III}_3 and Fe^{III}_3 complexes.[29]

In this contribution, we present an approach to preventing heteroradialene formation. As the heteroradialene formation is based on the conjugation of the sp^2-hybridized C=N groups, we intend to formally substitute the imine groups in the 2,4, and 6 position by amine groups ($H_6talalen^{R_2}$ and $H_6talan^{R_2}$, Figure 1b, c). We report our results for the reduction of the imine groups to amine functions and for the introduction of amine groups by a substitution approach.

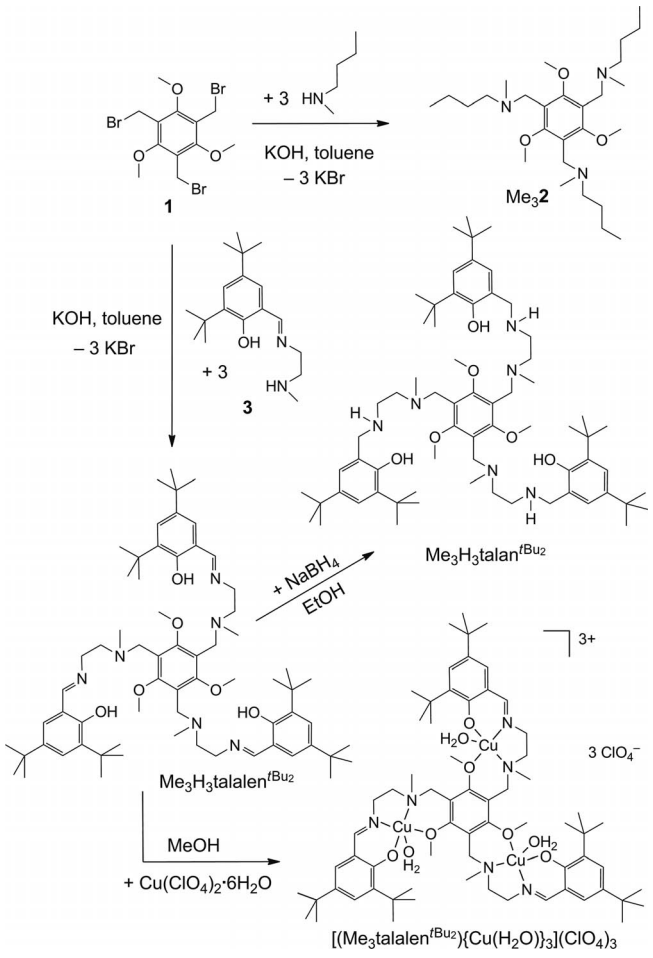
Results and Discussion

Synthesis

The most obvious route for the conversion of a triplesalen ligand to a triplesalan ligand is the reduction of the imine functions to amine functions. A problem that one faces with extended phloroglucinol ligands bearing central ketimine units as a starting material (like in $H_6talen^{R_2}$) is that the three reductions lead to the formation of three stereo centers and thus to diastereomeric mixtures. As we expect this to have severe consequences for the complex formation, we developed extended phloroglucinol ligands bearing central aldimine units for the reduction experiments.[21,22] We applied conventional reductive routines, using $NaBH_4$ and $LiAlH_4$, which easily convert salen ligands to salan ligands. However, despite extensive efforts, we could not obtain an experimental indication for the presence of three amine functions on a phloroglucinol backbone. The heteroradialene nature of the starting materials – the anticipated imine functions simply do not exist – provides an obvious explanation for the failure of this reductive route. Therefore, for the synthesis of triplesalen ligands that exhibit amine functions at the central phloroglucinol ring instead of imine units, that is, triplesalalen or triplesalan ligands (Figure 1b, c), we had to develop a new synthetic approach.

Another way to prepare asymmetrical salan (i.e., tetrahydrosalen) or salalen (i.e., dihydrosalen) ligands is to synthesize a half-unit that bears a secondary amine, which can be used in a nucleophilic substitution reaction, for example, with σ-(bromomethyl)phenols.[30,34] To follow this synthetic route for the preparation of triplesalalen ligands, the required synthon would be 2,4,6-tris(bromomethyl)-1,3,5-trihydroxybenzene. To the best of our knowledge, this has not yet been described in the literature. We used the methyl-protected derivative 2,4,6-tris(bromomethyl)-1,3,5-trimeth-

oxybenzene (**1**) for the preparation of the methyl-protected triplesalalen ligand $Me_3H_3talalen^{tBu_2}$ (Scheme 1), which should afford the free triplesalalen ligand $H_6talalen^{tBu_2}$ upon demethylation by Lewis acids.



Scheme 1.

To find suitable conditions for the substitution reaction, we first synthesized the model compound Me_3**2** by the reaction of **1** with *N*-methylbutylamine in toluene (Scheme 1). The presence of KOH leads to the precipitation of KBr, which is an additional driving force for the formation of Me_3**2**. In analogy, the protected triplesalalen ligand $Me_3H_3talalen^{tBu_2}$ was obtained by the reaction of **1** with half-unit **3**[44] and KOH in toluene (Scheme 1). The identity and purity of both compounds was confirmed by NMR spectroscopy, FTIR spectroscopy, mass spectrometry, and elemental analysis.

To obtain the deprotected ligand $H_6talalen^{tBu_2}$, we tried different approaches. Common routes for the demethylation of phenols use Lewis acids like BBr_3,[31] $BF_3{\cdot}SMe_2$,[32] or $AlCl_3$.[33] However, employing these reaction conditions for the deprotection of $Me_3H_3talalen^{tBu_2}$ yielded no pure products, but the cleavage of the terminal imine was frequently observed. Therefore, to enhance the stability of the protected ligand, we reduced the imine group with $NaBH_4$ to afford the protected triplesalan ligand precursor $Me_3H_3talan^{tBu_2}$. Unfortunately, this compound was also unstable under the harsh reaction conditions used in attempts to deprotect $Me_3H_3talalen^{tBu_2}$, and we were not able to isolate $H_6talan^{tBu_2}$.

We therefore envisioned deprotection by an internal Lewis acid like Cu^{II} or Fe^{III}, that is, a metal ion already coordinated in the NNO^{Ph} coordination pocket. This precoordination should also suppress the cleavage of the ligand backbone. Following this line of thought, we studied the reaction of $Me_3H_3talan^{tBu_2}$ with $Cu^{II}(ClO_4)_2{\cdot}6H_2O$, $Cu^{II}(BF_4)_2{\cdot}3H_2O$, $Cu^{II}Cl_2{\cdot}2H_2O$, $Fe^{II}(ClO_4)_2{\cdot}6H_2O$, and $Fe^{III}Cl_3{\cdot}6H_2O$, varying the solvent (MeOH, EtOH, dmf, ethylglycol), the temperature, and the reaction time, but we could not detect a deprotected product. However, the reaction of $Me_3H_3talalen^{tBu_2}$ with $Cu^{II}(ClO_4)_2{\cdot}6H_2O$ in methanol yielded green crystals, which were characterized by single-crystal X-ray diffraction analysis, elemental analysis, FTIR spectroscopy, and mass spectrometry and were identified as $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$.

NMR Spectroscopy

The ^1H NMR spectrum of the model compound Me_3**2** exhibits singlets at δ = 3.81, 3.44, and 2.14 ppm, triplets at δ = 2.37 and 0.85 ppm, and two multiplets at δ = 1.46 and 1.26 ppm. The multiplets between 2.37 and 0.85 ppm can be assigned to the butyl group, and the singlet at δ = 2.14 ppm can be assigned to the NCH_3 group, whereas the singlet at δ = 3.81 ppm belongs to the OCH_3 moiety, and the singlet at δ = 3.44 ppm belongs to the methylene group next to the central ring.

These spectral features are different from those of heteroradialene ligands,[17,21–23] which exhibit two multiplets at $\delta \approx$ 11.3 and 10.9 ppm. These signals are due to the NH protons, which couple with the vinylic CH proton (δ = 8.3–8.0 ppm) and the CH_2 protons (δ = 3.43 ppm) of the ethylene bridge. One set of signals can be assigned to the C_{3h} symmetric isomer, and three sets of signals can be assigned to the C_S symmetric isomer.

Also, the ^{13}C NMR spectrum of Me_3**2** is less complex than the ^{13}C NMR spectra of the heteroradialene ligands. Me_3**2** exhibits signals at δ = 159.9 and 122.4 ppm, which can be assigned to the $C^{Ar}OMe$ and the $C^{Ar}C^{CN}$ moiety of the central ring, respectively. In contrast, the $C^{Ar}O$ moieties of the heteroradialene ligands show signals between 188 and 183 ppm,[17,21–23] which are more characteristic for ketones (Figure 1, **IV**).[34] Also, the resonance of the $C^{Ar}C^{CN}$ carbon at $\delta \approx$ 105 ppm shows the strong distortion of the aromaticity of the central ring.

The ligands $Me_3H_3talalen^{tBu_2}$ and $Me_3H_3talan^{tBu_2}$ show almost identical NMR spectra. In the ^1H NMR spectra, singlets at δ = 3.77 and 3.56 ppm for $Me_3H_3talalen^{tBu_2}$ and at δ = 3.80 and 3.50 ppm for $Me_3H_3talan^{tBu_2}$ can be assigned to the OCH_3 and the $C^{Ar}CH_2$ moieties, respectively. The main difference between the ^1H NMR spectra of $Me_3H_3talalen^{tBu_2}$ and $Me_3H_3talan^{tBu_2}$ is a singlet at δ = 8.31 ppm for the terminal imine of $Me_3H_3talalen^{tBu_2}$, which

forms a new broad singlet at δ = 3.68 ppm for the benzylic unit upon reduction. The ^{13}C NMR spectra of Me_3H_3talalen^{tBu_2} and Me_3H_3talan^{tBu_2} show identical signals at δ = 160.0 and 122.1 ppm for the C^{Ar}OMe and $C^{Ar}C^{CN}$ units of the central ring, respectively. For Me_3H_3talan^{tBu_2}, an additional singlet can be detected at δ = 166.4 ppm, which is assigned to the *C*=N resonance of the terminal imine.

The comparison of the chemical shifts of the C^{Ar}O resonance of the central ring of Me_3**2**, Me_3H_3talalen^{tBu_2}, and Me_3H_3talan^{tBu_2} with aromatic phloroglucinol (δ = 158.8 ppm) or methoxybenzene (δ = 159.7 ppm) unambiguously demonstrates that the central ring is, in contrast to that of heteroradialene ligands, aromatic.

Structural Characterization

The crystal structure of the complex [(Me$_3$talalen^{tBu_2})-{Cu^{II}(H$_2$O)}$_3$](ClO$_4$)$_3$·4H$_2$O·CH$_3$OH was determined by single-crystal X-ray diffraction analysis, and the molecular structure is displayed in Figure 2. Selected interatomic distances and angles are summarized in Table 1. The structure contains three independent cations [(Me$_3$talalen^{tBu_2}){Cu^{II}-(H$_2$O)}$_3$]$^{3+}$, which all exhibit crystallographic C_3 symmetry. The deprotonated ligand (Me$_3$talalen^{tBu_2})$^{3-}$ acts as a triply tetradentate ligand for three Cu^{II} ions, which are in a distorted square-pyramidal coordination environment (τ values:[35] τ_{Cu1} = 0.32, τ_{Cu2} = 0.28, τ_{Cu3} = 0.35) and are coordinated by phenolate, amine, and imine donors of the ligand and by a water molecule in the basal plane. The ether function C^{Ar}–O–CH$_3$ of the central phloroglucinol is coordinated in the apical position. The Cu–O^{Ph} bond lengths are d_{Cu1} = 1.90 Å, d_{Cu2} = 1.89 Å, and d_{Cu3} = 1.89 Å, whereas the Cu–O^{CH_3} bond lengths are much longer (d_{Cu1} = 2.38 Å, d_{Cu2} = 2.40 Å, and d_{Cu3} = 2.36 Å). All Cu–N^{imine} bonds have the same length (d_{Cu} = 1.91 Å) and are shorter than the Cu–N^{amine} bond lengths (d_{Cu1} = 2.08 Å, d_{Cu2} = 2.09 Å, and d_{Cu3} = 2.10 Å).

The mean C–C bond length of the central ring is 1.40 Å for the molecule including Cu1 (molecule 1) and for the molecule including Cu3 (molecule 3), and it is 1.38 Å for the molecule including Cu2 (molecule 2). These values are significantly shorter than the mean bond lengths in a typical heteroradialene complex like [(talen^{tBu_2})Cu$^{II}_3$] with 1.43 Å[10] and are roughly the same as those of benzene (1.39 Å).[36] However, for an evaluation of the aromaticity, not only the mean C–C bond length has to be taken into account, but a complete delocalization of the C–C single bonds and the C=C double bonds is also required. These two criterions (bond lengths and their alternation) are considered in the HOMA value (harmonic oscillator model of aromaticity).[27,37] The HOMA value is 1 for benzene and 0 for the model nonaromatic benzene system with localized double and single bonds. The HOMA values for the three molecules in the crystal structure of [(Me$_3$talalen^{tBu_2})-{Cu^{II}(H$_2$O)}$_3$](ClO$_4$)$_3$·4H$_2$O·CH$_3$OH are 0.95 (molecule 1), 1.00 (molecule 2), and 0.96 (molecule 3), which clearly confirms the aromatic character of the central phloroglucinol backbone in the complexes.

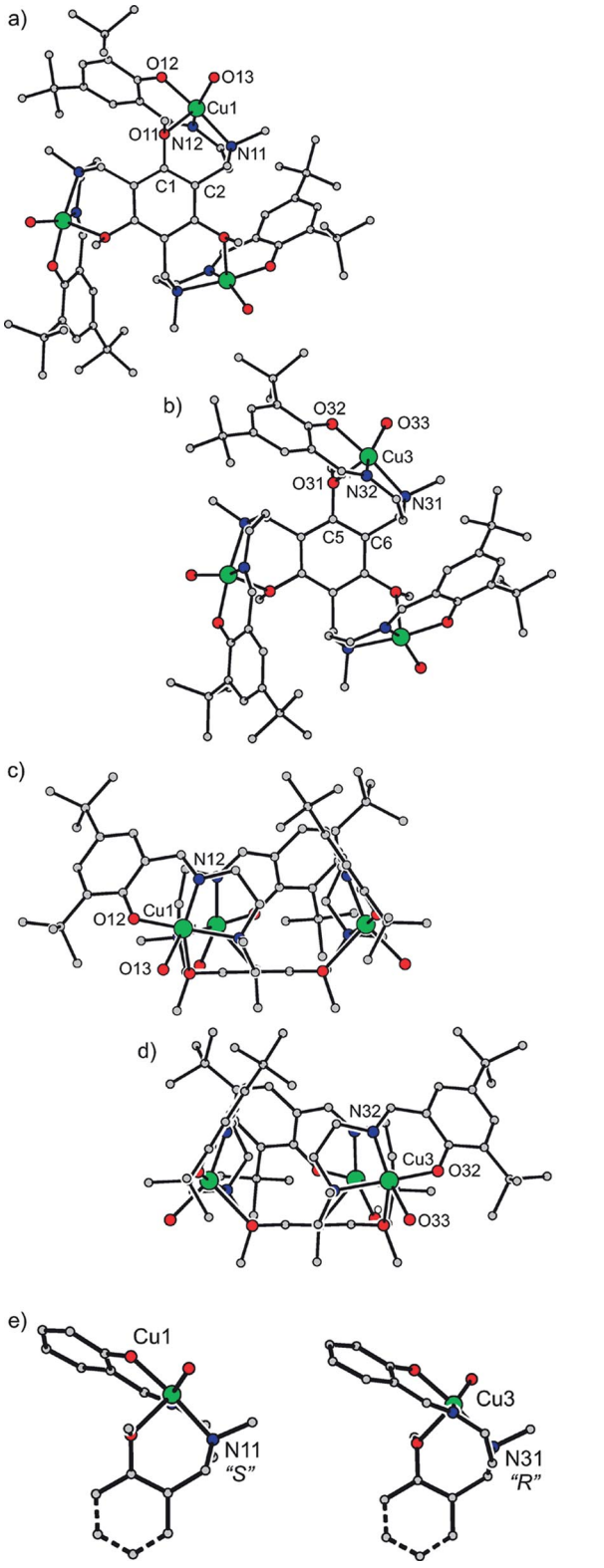


Figure 2. Molecular structure of [(Me$_3$talalen^{tBu_2}){Cu^{II}(H$_2$O)}$_3$]$^{3+}$ (molecule 1 and molecule 3) in crystals of [(Me$_3$talalen^{tBu_2}){Cu^{II}-(H$_2$O)}$_3$](ClO$_4$)$_3$·4H$_2$O·CH$_3$OH. Molecule 1 (a) and molecule 3 (b) drawn perpendicular to the central benzene ring of the phloroglucinol backbone. Molecule 1 (c) and molecule 3 (d) drawn parallel to the central benzene ring of the phloroglucinol backbone. Hydrogen atoms and counterions are omitted for clarity. The configuration of the tertiary amine results in different orientations of the terminal ring (e). *t*Bu groups are omitted for clarity.

Table 1. Selected interatomic distances [Å] and angles [°] for $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3{\cdot}4H_2O{\cdot}CH_3OH$.

Bond	[Å]	Angle	[°]
Cu1–O11	2.379(3)	N11–Cu1–O11	86.77(13)
Cu1–O12	1.895(3)	N12–Cu1–O11	117.71(13)
Cu1–O13	2.005(4)	O12–Cu1–O11	90.11(13)
Cu1–N11	2.083(4)	O13–Cu1–O11	87.11(15)
Cu1–N12	1.909(4)	N12–Cu1–N11	84.64(15)
O11–C1	1.377(5)	O12–Cu1–N11	174.53(14)
N11-C11	1.499(6)	O13–Cu1–N11	96.25(16)
C1–C2	1.404(6)	O12–Cu1–N12	92.85(15)
C1–C2#1	1.401(6)	N12–Cu1–O13	155.14(17)
C2–C11	1.507(6)	O12–Cu1–O13	88.07(15)
Cu2–O21	2.397(3)	N21–Cu2–O21	85.90(13)
Cu2–O22	1.893(3)	N22–Cu2–O21	116.28(14)
Cu2–O23	2.003(3)	O22–Cu2–O21	89.79(13)
Cu2–N21	2.086(4)	O23–Cu2–O21	87.17(13)
Cu2–N22	1.913(4)	N22–Cu2–N21	84.48(16)
O21–C3	1.397(5)	O22–Cu2–N22	93.05(16)
N21-C21	1.488(6)	O23–Cu2–N21	95.96(15)
C3–C4	1.383(6)	O22–Cu2–N21	173.46(14)
C3–C4#3	1.385(6)	N22–Cu2–O23	156.47(16)
C4–C21	1.528(6)	O22–Cu2–O23	88.73(15)
Cu3–O31	2.363(3)	N31–Cu3–O31	86.61(13)
Cu3–O32	1.890(3)	N32–Cu3–O31	118.30(13)
Cu3–O33	2.006(4)	O32–Cu3–O31	89.53(13)
Cu3–N31	2.097(3)	O33–Cu3–O31	88.26(15)
Cu3–N32	1.914(4)	N32–Cu3–N31	84.88(15)
O31–C5	1.382(5)	O32–Cu3–N32	93.07(16)
N31-C31	1.493(6)	O33–Cu3–N31	96.29(15)
C5–C6	1.401(6)	O32–Cu3–N31	107.3(3)
C5–C6#5	1.399(6)	N32–Cu3–O33	153.41(17)
C6–C31	1.496(6)	O32–Cu3–O33	88.01(15)

Trinuclear complexes of the triplesalen ligands exhibit overall bowl-shaped molecular structures, in which the NNOO planes are bent relative to the central phloroglucinol ring.[3,10] The different binding situation in $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3]^{3+}$ leads to a different ligand folding with an overall calix-like structure (Figure 2c and d) caused by the almost perpendicular orientation of the terminal salen subunits with respect to the central ring.

The complex $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3]^{3+}$ crystallizes in the chiral space group *P*3 and contains chiral molecules. Each molecule contains three centers of chirality, which are a result of the coordination of the asymmetrically substituted tertiary amines of the ligand to the Cu^{II} ions. The two coordinated enantiomeric amines may be named "*R*" and "*S*" and are defined in Figure 2e. As all starting materials are optically inactive, a spontaneous resolution of the racemic mixture must have occurred during the crystallization.

A molecule with three centers of chirality, which can either have *R* or *S* configuration, may exist in four different isomers, the enantiomeric pairs *RRR*–*SSS* and *RRS*–*SSR* (note that, e.g., *RRS*, *RSR*, and *SRR* are equivalent by symmetry), which are diasteromeric to each other. The C_3 symmetry of the molecules reduces the number of possible isomers from four to the two enantiomers *RRR* = ***R*** and *SSS* = ***S***.

There are four possible combinations for the composition of a crystal with three such independent molecules in a chiral space group: the "equal-enantiomeric" forms 3× ***R*** and 3× ***S*** and the "mixed-enantiomeric" forms (2× ***R*** + 1× ***S***) and (2× ***S*** + 1× ***R***). The examined single crystal exhibits molecule 2 and molecule 3 in the ***R*** configuration, whereas molecule 1 is in the ***S*** configuration (Figure 2e), therefore, the analyzed crystal is in the mixed-enantiomeric form 2× ***R*** + 1× ***S***.

Infrared Spectroscopy

The IR spectra of heteroradialene ligands exhibit characteristic bands at approximately 1610 cm^{-1}, which are assigned to a coupled vibration of the C=C and C–N stretches of the exocyclic double bonds of the heteroradialene backbone, and a broad band at approximately 1545 cm^{-1}, which is assigned to the C=O stretching vibrations of the keto functions.[38] Figure 3a exemplarily shows the IR spectrum of H_3felden[21], an extended phloroglucinol ligand with three 2-(dimethylamino)ethylimine groups. In contrast, in this region, Me_3**2** only exhibits a band at 1581 cm^{-1}, which is assigned to the ring stretching vibrations of the central phloroglucinol backbone. The li-

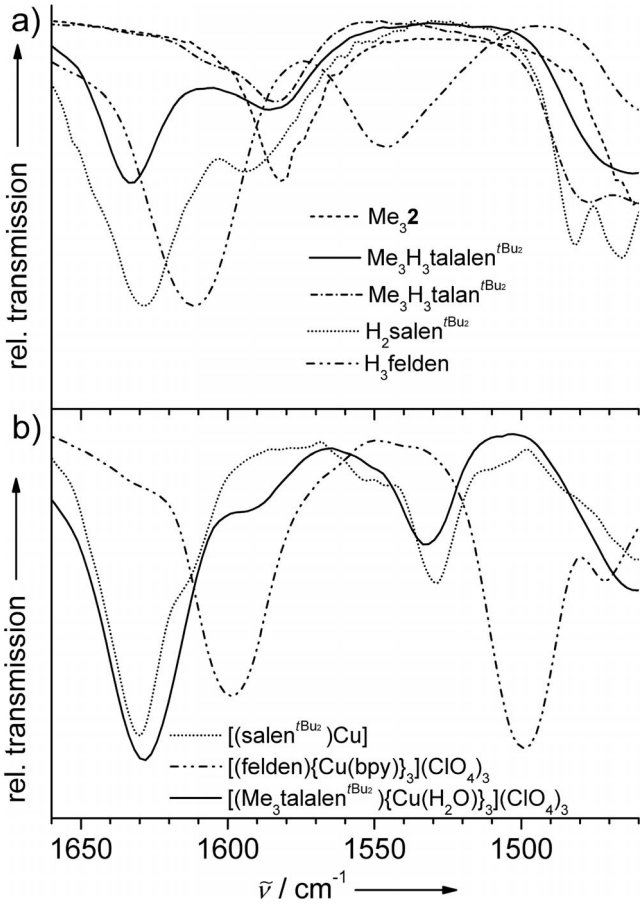


Figure 3. FTIR spectra of (a) Me_3**2**, $Me_3H_3talalen^{tBu_2}$, $Me_3H_3talan^{tBu_2}$, and H_3felden and (b) $H_2salen^{tBu_2}$, $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$, $[(felden)\{Cu^{II}(bpy)\}_3](ClO_4)_3$, and $[(salen^{tBu_2})Cu^{II}]$.

gands $H_2salen^{tBu_2}$, $Me_3H_3talalen^{tBu_2}$, and $Me_3H_3talan^{tBu_2}$ also show bands at 1594, 1586, and 1584 cm^{-1}, respectively, which correspond to these ring stretching vibrations. Additional bands in $Me_3H_3talalen^{tBu_2}$ at 1633 cm^{-1} and in $H_2salen^{tBu_2}$ at 1628 cm^{-1}, which are absent in $Me_3H_3talan^{tBu_2}$, may be assigned to the typical C=N stretching mode of the phenol–imine unit.

After coordination to Cu^{II} the bands of the phenol–imine unit shift only slightly in both $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ (1629 cm^{-1}) and $[(salen^{tBu_2})Cu^{II}]$ (1630 cm^{-1}). The ring stretches of the central backbone of $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ can be detected at 1593 cm^{-1}. A band at 1532 cm^{-1}, which is absent in the ligands, is also observed in $[(salen^{tBu_2})Cu^{II}]$ at 1530 cm^{-1} and was assigned to C–C ring stretches of the coordinating phenolate.[39] It may thus be assigned to the terminal phenolate in $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$. In comparison, the spectrum of the heteroradialene Cu^{II} complex $[(felden)\{Cu^{II}(bpy)\}_3](ClO_4)_3$ exhibits broad bands at 1598 and 1499 cm^{-1}, which can be assigned to the ligand backbone with strong contributions of the heteroradialene resonance structures. As these bands are absent in $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$, the heteroradialene formation was successfully precluded.

Electronic Absorption Spectroscopy

The electronic absorption spectra of the ligands $Me_3H_3talalen^{tBu_2}$ and $Me_3H_3talan^{tBu_2}$ and of the model Me_3**2** are displayed in Figure 4a. For comparison, the ligands $H_2salen^{tBu_2}$,[40] H_3felden,[21] and $H_6talen^{tBu_2}$[3] are included. In the inset, the d–d-transitions are displayed. The spectra of the heteroradialene ligands H_3felden and $H_6talen^{tBu_2}$ are dominated by two strong absorptions in the region 26000–35000 cm^{-1}, which are a typical signature of the central heteroradialene backbone.[17,22] The spectrum of the model Me_3**2** exhibits no absorptions of significant intensities between 10000 and 40000 cm^{-1}, whereas the spectrum of the ligand $Me_3H_3talalen^{tBu_2}$ almost coincides with the spectrum of $H_2salen^{tBu_2}$. Thus, the spectral features in $Me_3H_3talalen^{tBu_2}$ are assigned to the terminal phenol–imine chromophore. This assignment is confirmed by the spectrum of $Me_3H_3talan^{tBu_2}$, which possesses no terminal phenol–imine chromophore, and exhibits only one weaker band at 35000 cm^{-1}.

The spectra of the heteroradialene complexes $[(talen^{tBu_2})Cu^{II}_3]$ and $[(felden)\{Cu^{II}(bpy)\}_3](ClO_4)_3$ (Figure 4b) both exhibit strong absorption features in the region 27000–37000 cm^{-1}, which are absent in the spectra of the mononuclear complex $[(salen^{tBu_2})Cu^{II}]$ and are thus assigned to the heteroradialene backbone.[17,22,23] These intense absorptions are absent in the reduced triplesalen complex $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$, which indicates that the heteroradialene formation is successfully suppressed. As in $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$, absorptions at 36000 cm^{-1} are also observed in $[(salen^{tBu_2})Cu^{II}]$ and $[(talen^{tBu_2})Cu^{II}_3]$ and can therefore be mainly assigned to π–π* transitions of the terminal phenolate chromophore. The absorptions at 25500 cm^{-1} in $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ and $[(salen^{tBu_2})Cu^{II}]$ are the typical π–π* transitions of the conventional imine unit.

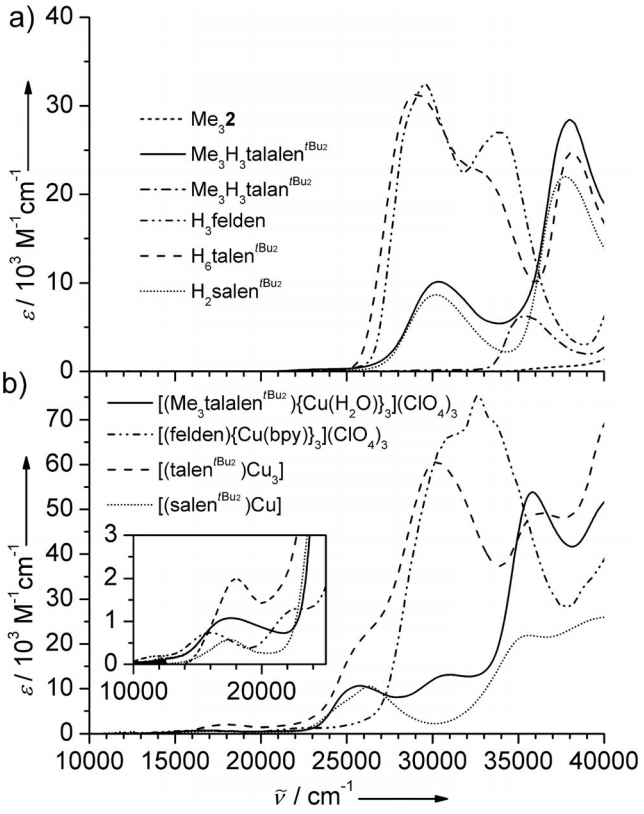


Figure 4. Electronic absorption (a) spectra of Me_3**2** (CH_3CN), $Me_3H_3talalen^{tBu_2}$ (CH_2Cl_2), $Me_3H_3talan^{tBu_2}$ (CH_2Cl_2), $H_2salen^{tBu_2}$ (CH_2Cl_2), H_3felden (CH_3CN), and $H_6talen^{tBu_2}$ (CH_2Cl_2). Electronic absorption spectra (b) of the Cu^{II} complexes $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ (CH_3CN), $[(salen^{tBu_2})Cu^{II}]$ (CH_2Cl_2), and $[(talen^{tBu_2})Cu^{II}_3]$ (CH_2Cl_2). The inset shows the d–d transitions.

Electrochemistry

The cyclic voltammogram of $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ (Figure 5) exhibits a reversible oxidation wave at $E_{1/2}$ = +0.72 V and two irreversible waves at E_p = –1.16 and –1.69 V with back currents at E_p = –0.65 and –0.50 V. Analogous reduction waves are also present in $[(talen)Cu^{II}_3]$[9,10] (H_6talen = Figure 1a, $R^1 = R^2 = H$)[4] at –1.84 V, whereas $[(talen^{tBu_2})Cu^{II}_3]$ shows no reductions, and they might be attributed to the Cu^{II}/Cu^{I} redox couple.[41] Interestingly, the voltammogram of $[(talen^{tBu_2})Cu^{II}_3]$[10] also reveals a reversible oxidation at +0.81 V, which is irreversible in $[(talen)Cu^{II}_3]$.[10] Although in the study of the trinuclear Cu^{II} triplesalen complexes a definitive assignment of this oxidation wave to an oxidation of the central phloroglucinol backbone or the terminal phenolates was not possible, the occurrence of almost the same oxidative wave in $[(talen^{tBu_2})Cu^{II}_3]$ and in $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}](ClO_4)_3$ precludes the assignment to the central ring system. The consequential assignment of the oxidation to the ter-

minal phenolates is corroborated by the well-known reversibility of the oxidation of coordinated 2,4-di-*tert*-butylphenolates to the corresponding phenoxyl radicals.[42]

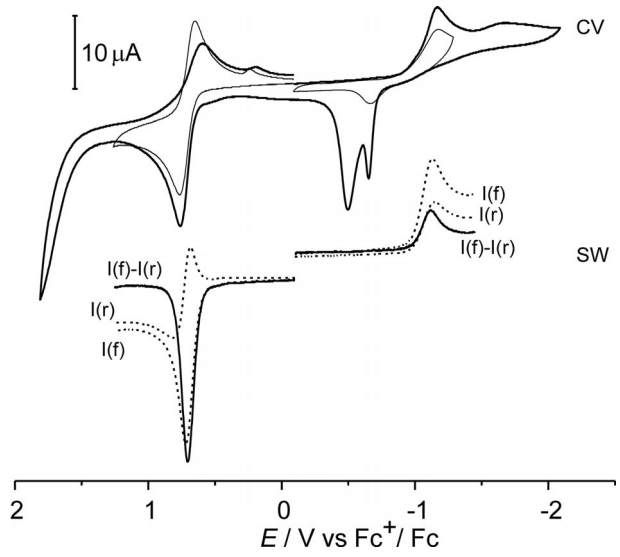


Figure 5. Electrochemical measurements of $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ in a CH_3CN solution [0.10 M $(NBu_4)PF_6$] at 20 °C, recorded with a Pt working electrode at a scan rate 200 mV s^{-1}.

Magnetochemistry

Temperature-dependent measurements of the magnetic susceptibility (SQUID, 2–290 K) at different magnetic fields of samples of $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ were performed (Figure 6). The effective magnetic moment μ_{eff} is 3.06 μ_B at 290 K, which is close to the expected μ_{eff} value of 3.17 μ_B for three non-interacting Cu^{II} ions (g = 2.11). When the temperature is lowered, μ_{eff} remains constant and exhibits a rapid drop below 10 K to a value of 1.92 μ_B at 2 K (Figure 5). This temperature behavior indicates that there is no significant interaction between the three Cu^{II} ions. We tried to simulate the temperature dependence of μ_{eff} with the appropriate spin Hamiltonian [Equation (1)] for an equilateral Cu^{II}_3 (S_i = 1/2) triangle, including a Heisenberg–Dirac–van Vleck (HDvV) exchange and Zeeman interactions, by using the program package JulX,[47] which also takes into account saturation effects. Fitted values of χ_{TIP} (TIP = temperature-independent paramagnetism) are subtracted from the simulated and experimental data.

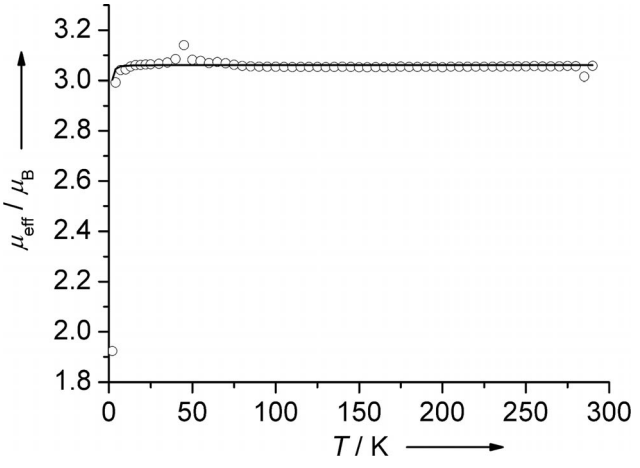


Figure 6. Temperature dependence of the effective magnetic moment μ_{eff} of $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$. The solid line corresponds to the best fits: J = –0.02 cm^{-1}, g = 2.04, and χ_{TIP} = 110 × 10^{-6} $cm^3 mol^{-1}$.

$$H = -2J(\mathbf{S_1S_2} + \mathbf{S_2S_3} + \mathbf{S_1S_3}) + \sum_{i=1}^{3} [g_i \mu_B S_i B] \quad (1)$$

The best agreement between the experimental and simulated data was obtained for J = –0.02 cm^{-1}, g = 2.04, and χ_{TIP} = 110 × 10^{-6} $cm^3 mol^{-1}$. The orthogonality of the $d_{x^2-y^2}$ magnetic orbital, which is of δ symmetry with respect to the Cu^{II}–O bond, and the O p-orbitals (none of δ symmetry) combined with the long and therefore weak Cu–O^{CH_3} bond precludes a significant delocalization of the spin from Cu^{II} to the oxygen atom. Therefore, this system is best described as consisting of three uncoupled Cu^{II} ions.

Conclusions

To overcome the heteroradialene formation in extended phloroglucinol ligands, we intended to formally substitute the three imine groups by amine groups. Herein, we could show that a simple reduction of the imine groups to amine groups is not feasible, as no real imine groups are present in heteroradialene ligands. As an alternative synthetic pathway, we investigated the triple nucleophilic substitution of 2,4,6-tris(bromomethyl)-1,3,5-trimethoxybenzene (**1**) with secondary amines, which resulted in Me_3**2** and $Me_3H_3talalen^{tBu_2}$. Interestingly, in contrast to our efforts to reduce the triplesalen ligands, the remaining terminal imine in this triplesalalen ligand could easily be reduced to afford $Me_3H_3talan^{tBu_2}$. In analogy to literature reports, we tried to deprotect $Me_3H_3talalen^{tBu_2}$ by reacting it with Lewis acids, which was not successful. Even the use of transition metal ions did not result in a demethylation, but we could obtain the trinuclear complex $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$.

The characterization of the newly synthesized compounds by FTIR, UV/Vis, and NMR spectroscopy and in the case of $[(Me_3talalen^{tBu_2})\{Cu^{II}(H_2O)\}_3](ClO_4)_3$ by X-ray diffraction and electrochemistry clearly demonstrates the suppression of heteroradialene formation. This arises from the substitution of imine by amine groups and from the methyl protection of the phenolate. As this reaction pathway does not afford the methyl deprotected triplesalalen and triplesalan ligands and complexes, we are currently investigating other synthetic pathways to the anticipated ligands and complexes.

Experimental Section

General: Solvents and starting materials were of the highest commercially available purity and used as received. 2,4,6-Tris(bromo-

methyl)-1,3,5-trimethoxybenzene (**1**)[43] and the half-unit **3**[44] were prepared according to reported procedures.

2,4,6-Trimethoxy-1,3,5-tris[(methylbutylamino)methyl]benzene ($Me_3$2): 2,4,6-Tris(bromomethyl)-1,3,5-trimethoxybenzene (**1**) (82 mg, 0.183 mmol), *N*-methylbutylamine (56 mg, 0.642 mmol), and KOH (56 mg) were dissolved in toluene (20 mL) and stirred for 2 h at 80 °C. The mixture was filtered, and the volatiles were removed in vacuo, which yielded the product as a colorless oil (yield: 75 mg, 0.161 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.81 (s, 9 H, OCH_3), 3.44 (s, 6 H, Ar-CH_2), 2.37 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, NCH_2CH_2), 2.14 (s, 9 H, NCH_3), 1.46 (m, 6 H, NCH_2CH_2), 1.26 (sextet, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH_2CH_3), 0.85 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, $CDCl_3$, 25 °C): δ = 159.9 (s, *C*OMe), 122.4 (s, C^{Ar}C), 63.0 (s, OCH_3), 57.6 (s, NCH_2CH_2), 50.8 (s, $C^{Ar}CH_2$), 41.9 (s, NCH_3), 29.8 (s, NCH_2CH_2), 20.8 (s, CH_2CH_3), 14.2 (s, CH_2CH_3) ppm. ESI-MS: *m*/*z* = 466.4 [M + H]$^+$, 488.3 [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 2957 (s), 2934 (s), 2872 (s), 2861 (s), 2843 (s), 2789 (s), 1582 (s), 1462 (s), 1452 (s), 1410 (s), 1366 (m), 1306 (m), 1283 (m), 1261 (w), 1244 (w), 1204 (m), 1169 (m), 1103 (s), 1063 (w), 1034 (m), 1015 (m), 997 (m), 972 (m), 891 (w), 858 (w), 816 (w), 733 (w) cm^{-1}. Me_3**2** ($C_{27}H_{51}N_3O_3$): calcd. C 69.63, H 11.04, N 9.02; found C 69.86, H 11.17, N 8.63.

Me_3H_3talalen^{tBu_2}: 2,4,6-Tris(bromomethyl)-1,3,5-trimethoxybenzene (**1**) (47 mg, 0.105 mmol), half-unit **3** (90 mg, 0.310 mmol), and KOH (45 mg) were suspended in toluene (6 mL) and stirred for 10 h at 80 °C. The mixture was filtered, and the volatiles were removed in vacuo, which yielded the product as a yellow oil, which was redissolved in CH_2Cl_2, the solvent was evaporated in vacuo, and the process was repeated two times to yield the product as a yellow powder (yield: 81 mg, 0.075 mmol, 72%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 13.9 (s, 3 H, O*H*), 8.31 (s, 3 H, N=C*H*), 7.36 (d, $^4J_{H,H}$ = 2.3 Hz, 3 H, $C^{Ar}H$), 7.04 (d, $^4J_{H,H}$ = 2.3 Hz, 3 H, $C^{Ar}H$), 3.77 (s, 9 H, OCH_3), 3.70 (m, 6 H, CH_2N=C), 3.56 (s, 6 H, $C^{Ar}CH_2$), 2.77 (t, $^3J_{H,H}$ = 6.7 Hz, 6 H, 6H, CH_2NMe), 2.28 (s, 9 H, NCH_3), 1.45 (s, 27 H, *t*Bu), 1.31 (s, 27 H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, $CDCl_3$, 25 °C): δ = 166.4 (s, C=N), 160.0 (s, C^{Ar}OMe), 158.3 (s, C^{Ar}OH), 139.8 (s, C^{Ar}–*t*Bu), 136.6 (s, C^{Ar}–*t*Bu), 126.7 (s, C^{Ar}H), 125.8 (s, C^{Ar}H), 122.1 (s,$C^{Ar}CH_2$), 118.0 (s, $C^{Ar}CH_2$), 63.3 (s, OCH_3), 57.8 (s, CH_2NMe), 57.4 (s, CH_2N=C), 50.8 (s, $C^{Ar}CH_2$), 42.1 (s, NCH_3), 35.1 (s, CMe_3), 34.2 (s, CMe_3), 31.6 [s, C(CH_3)$_3$], 29.5 [s, C(CH_3)$_3$] ppm. ESI-MS: *m*/*z* = 1075.7 [M + H]$^+$, 1097.7 [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 2955 (s), 2909 (m), 2868 (m), 2793 (m), 1636 (s), 1584 (m), 1460 (m), 1441 (s), 1412 (w), 1391 (w), 1362 (m), 1341 (w), 1275 (m), 1252 (m), 1202 (m), 1175 (m), 1130 (w), 1101 (m), 1036 (w), 999 (w), 970 (w), 878 (w), 827 (w), 773 (w), 729 (w), 644 (w) cm^{-1}. Me_3H_3talalen^{tBu_2} ($C_{66}H_{102}N_6O_6$): calcd. C 73.70, H 9.56, N 7.81; found C 73.54, H 9.60, N 7.58.

Me_3H_3talan^{tBu_2}: Me_3H_3talalen^{tBu_2} (110 mg, 0.102 mmol) was dissolved in EtOH (10 mL) and cooled to 0 °C. To this solution, $NaBH_4$ (140 mg, 3.700 mmol) was added in small portions, and the reaction mixture was warmed up to room temperature overnight. The volume of the resulting colorless solution was reduced in vacuo until a colorless solid precipitated, and then water (20 mL) was added. After extraction with CH_2Cl_2, the organic layers were collected, dried with Na_2SO_4, and the volatiles were evaporated in vacuo, which yielded the ligand precursor Me_3H_3talan^{tBu_2} as a colorless solid (yield: 80 mg, 0.074 mmol, 73%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.21 (d, $^4J_{H,H}$ = 2.0 Hz, 3 H, $C^{Ar}H$), 6.81 (d, $^4J_{H,H}$ = 2.0 Hz, 3 H, $C^{Ar}H$), 3.68 (s, 6 H, CH_2NH), 3.80 (s, 9 H, OCH_3), 3.50 (s, 6 H, CH_2NMe), 2.74 (m, 6 H, CH_2NH), 2.59 (m, 6 H, CH_2NMe), 2.17 (s, 9 H, NCH_3), 1.42 (s, 27 H, *t*Bu), 1.29 (s, 27 H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, $CDCl_3$, 25 °C): δ = 160.0 (s, C^{Ar}OMe), 155.0 (s, C^{Ar}OH), 140.2 (s, C^{Ar}*t*Bu), 135.7 (s, C^{Ar}*t*Bu), 123.1 (s, C^{Ar}H), 122.8 (s, C^{Ar}H), 122.1 (s, $C^{Ar}CH_2$NMe), 63.1 (s, OCH_3), 56.1 (s, CH_2NMe), 53.4 (s, $C^{Ar}CH_2$NH), 50.7 (s, CH_2NMe), 46.0 (s, CH_2CH_2NH), 41.9 (s, NCH_3), 35.0 (s, CMe_3), 34.2 (s, CMe_3), 31.8 [s, C(CH_3)$_3$], 29.7 [s, C(CH_3)$_3$] ppm. ESI-MS: *m*/*z* = 1081.7 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 3304 (w), 2955 (s), 2907 (s), 2868 (s), 2799 (s), 1584 (m), 1479 (s), 1458 (s), 1412 (m), 1391 (m), 1362 (m), 1302 (m), 1238 (m), 1202 (m), 1165 (m), 1126 (m), 1101 (s), 1057 (w), 1036 (w), 1013 (w), 972 (w), 910 (w), 878 (w), 822 (w), 799 (w), 762 (w), 733 (m) cm^{-1}. Me_3H_3talan^{tBu_2}·2.5H_2O ($C_{66}H_{113}N_6O_{8.5}$): calcd. C 70.36, H 10.11, N 7.46; found C 70.46, H 9.84, N 7.13.

[(Me_3talalen^{tBu_2}){$Cu^{II}(H_2O)$}$_3$](ClO_4)$_3$: To a suspension of Me_3H_3-talalen^{tBu_2} (263 mg, 0.244 mmol) in methanol (25 mL) was added a solution of $Cu^{II}(ClO_4)_2$·6H_2O (285 mg, 0.769 mmol) in methanol (10 mL), and the resulting mixture was stirred for 16 h at 50 °C. The green solution was filtered, and slow evaporation of the solvent yielded green crystal needles, which were washed with ethyl ether and dried in vacuo to yield the product as a green solid (yield: 144 mg, 0.089 mmol, 36%). ESI-MS: *m*/*z* = 420.8 [M – 3ClO_4 – 3H_2O]$^{3+}$, 638.7 [M – 3ClO_4 – 2H_2O – H]$^{2+}$. IR (KBr): $\tilde{\nu}$ = 2959 (s), 2907 (m), 2870 (w), 1630 (s), 1533 (m), 1460 (w), 1437 (w), 1414 (w), 1389 (w), 1364 (w), 1323 (w), 1273 (w), 1256 (w), 1231 (w), 1200 (w), 1169 (mm), 1121 (s), 1094 (s), 970 (m), 837 (w), 787 (w), 746 (w), 623 (w) cm^{-1}. [(Me_3talalen^{tBu_2}){$Cu^{II}(H_2O)$}$_3$](ClO_4)$_3$·3.5H_2O·0.5MeOH ($C_{66.5}H_{114}N_6O_{25}Cu_3Cl_3$): calcd. C 47.13, H 6.78, N 4.96; found C 47.13, H 6.59, N 5.05.

X-ray Crystallography: Crystal data for [(Me_3talalen^{tBu_2}){Cu^{II}-(H_2O)}$_3$](ClO_4)$_3$·4H_2O·1MeOH: M = 1719.64 g mol^{-1}, $C_{67}H_{117}N_6$-$O_{26}Cu_3Cl_3$, trigonal, space group $P3$, a = 28.3863(12) Å, c = 9.8085(5) Å, V = 6844.6(5) Å^3, Z = 3, ρ = 1.252 g cm^{-3}, μ = 2.199 mm^{-1}, F(000) = 2721, Crystal size: 0.25 × 0.08 × 0.06 mm^3, Flack parameter: 0.036(19). Crystals of [(Me_3talalen^{tBu_2}){Cu^{II}-(H_2O)}$_3$](ClO_4)$_3$·4H_2O·1MeOH were removed from the mother liquor and immediately cooled to 100(2) K on a Bruker X8 Prospector Ultra diffractometer (three circle goniometer with 4K CCD detector, Cu-K_α radiation, IμS microfocus tube, multilayer optics). A total of 90422 reflections (3.11° < Θ < 69.96°) were collected, of which 15149 reflections were unique [R(int) = 0.0437]. An empirical absorption correction based on equivalent reflections was performed with the program SADABS 2008/1.[45] The structure was solved with the program SHELXS-97[46] and refined by using SHELXL-97[33] to R = 0.0582 for 13557 reflections with $I > 2\sigma(I)$, R = 0.0640 for all reflections; the maximal and minimal residual electron density is 1.086 and –1.126 e Å^{-3}, respectively.

During the early stages of structure completion one MeOH and four H_2O molecules were found in the asymmetric unit, but except for 0.5 MeOH molecules, they did not refine properly, which was due to severe disorder, and they were therefore removed from the coordinate set. The resulting void was then treated with the SQUEEZE routine to account for the now missing scattering power. The removed molecules, however, are included in the given formula and thus contribute to derived quantities.

CCDC-897942 contains 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.

Other Physical Measurements: Infrared spectra (400–4000 cm^{-1}) of solid samples were recorded with a Shimadzu FTIR-8400S spectrometer and KBr-disk samples. UV/Vis/NIR absorption spectra of

the solutions were measured with a Shimadzu UV-3101PC spectrophotometer in the range 200–1200 nm at ambient temperatures. ESI mass spectra were recorded with a Bruker Esquire 3000 ion trap mass spectrometer equipped with a standard ESI source. ^{1}H and ^{13}C NMR spectra were measured either with a Bruker DRX500 or a Bruker AV300 spectrometer by using the solvent as an internal standard. The electrochemical experiments were performed with Ar-flushed CH_3CN solutions containing 0.1 M $[NBu_4]PF_6$ in a classical three-electrode cell. The working electrode was a platinum electrode, the counter electrode was a platinum wire, and the reference electrode was Ag/0.01 M $AgNO_3/CH_3CN$. All potentials are referenced with respect to the ferrocenium/ferrocene (Fc^+/Fc) couple used as an internal standard. The electrochemical cell was connected to an EG&G potentiostat–galvanostat (model 273 A). Temperature-dependent magnetic susceptibilities were measured by using a SQUID magnetometer (MPMS-7, Quantum Design) at 1 T (0.2–300 K). To calculate the molar magnetic susceptibilities, χ_m, the measured susceptibilities were corrected for the underlying diamagnetism of the sample holder and the sample by using tabulated Pascal constants. The JulX program package was used for simulations of the spin Hamiltonian and for the fitting of the data by a full-matrix diagonalization approach.[47]

Acknowledgments

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