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Electrophilic C(2)-functionalization of nitronyl nitroxides: a reference to *N*-heterocyclic carbenes

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Abstract

In an attempt to generalize the recently introduced concept of 'auto-umpolung', nitronyl nitroxides are identified as precursors of a special class of electron-excess carbenes. The latter can be formally derived from nucleophilic carbenes of the Wanzlick–Arduengo type by replacing redox-inactive *N*-substituents by lone-pair donor functions. A first systematic access to this class of compounds is achieved by lithiating the nitronyl nitroxide **11a** at C(2), the central carbon position. The resulting radical anion equivalent **13** can be trapped in solution by various types of electrophiles to give C(2)-substituted nitronyl nitroxides **14**, much in the same way as are trapped nucleophilic carbenes of the Wanzlick–Arduengo type. Carboxylation, addition to an aldehyde as well as silylation at the C(2)-position lead to novel types of functional nitronyl nitroxides. Elemental sulfur and selenium yield new types of anionic nitronyl nitroxides. The first characterized C(2)-derived heavy-metal complex of a nitronyl nitroxide **14g** resulted, when $Hg(OAc)_2$ was used as a trapping agent. More conveniently this complex could also be obtained directly from **11a** and $Hg(OAc)_2$. The X-ray structure of **14g** is presented and analyzed in terms of cluster-forming secondary Hg–O interactions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrophiles; Nitronyl nitroxides; Heterocyclic carbenes

1. Introduction

Recently we have synthesized a novel type of nucleophilic carbene, in which the carbene center is conjugatively coupled to a 2,2′-bipyridine-based two-step redox system, as in **1** (Scheme 1) [1,2]. This system can be generated from its protonated precursor at −80°C in solution and spectroscopically characterized. It forms stable adducts with many electrophilic agents [1–3]. Depending on the electronic nature of the electrophile two types of adducts can be discerned:

- When attached to a lone pair donor (+M substituent) the former carbene center functions as an –M acceptor, as in **2**.
- When connected with an –M acceptor the former carbene center acts as an +M donor, as in **3**.

Thus, due to its integrated two-step redox system carbene **1** can function as an electronically extremely flexible unit, as evidenced by many synthesized systems of type **2** and **3**, as well as by accompanying calculations [1–3]. We have termed the underlying electronic principle 'auto-umpolung' [1] ('Selbstumpolung' in German). This particular quality is lacking in conventional Arduengo carbenes [4].

Obviously it would be highly desirable to generalize the concept of 'auto-umpolung' for carbenes beyond the singularity **1**. A formal approach to achieve this is shown in Scheme 2. Introducing lone-pair donor groups as *N*-substituents in Arduengo carbenes would lead to nucleophilic carbenes of type **4**.

Two directly connected lone-pair functions frequently form the basis of two-step redox systems [5]. In **4** two such systems are directly conjugated with the carbene center. Depending on the electronic nature of the *N*-attached donor group this will lead to a much higher population of the carbene's $2p_z$-orbital as compared to that of normal Arduengo carbenes. This is indicated in Scheme 3 for the singlet form **4** (S). A corresponding triplet form **4** (T) — interestingly a π-biradical — would also have to be considered. For both

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[1] X-ray analysis.

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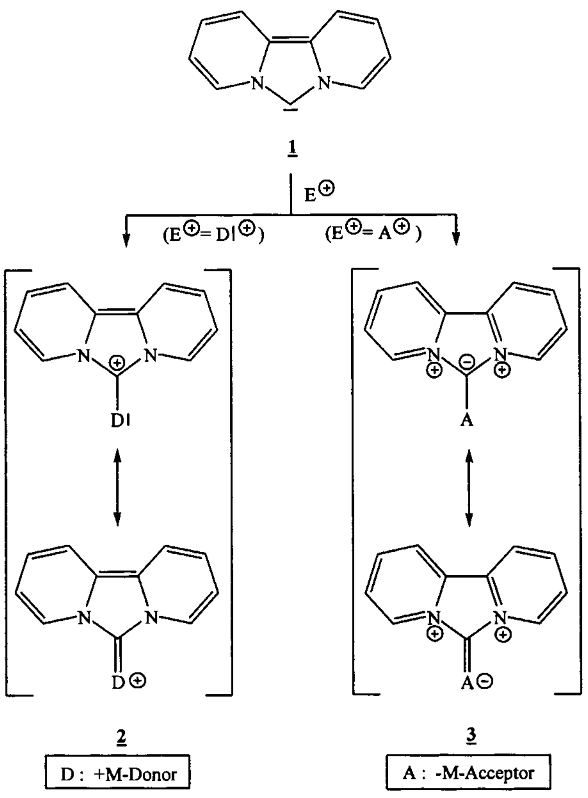
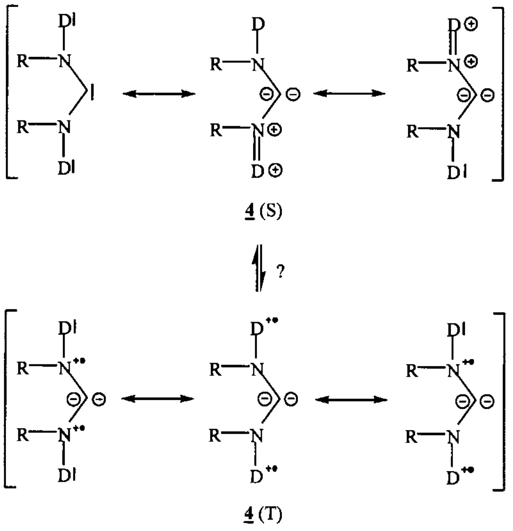


Scheme 1.



Scheme 2.

electronic configurations coordination of **4** to electron-demanding centers would massively umpole the former carbene center to an electron-surplus center, much beyond the stage of ‘auto-umpolung’ already present in the free carbene **4**.

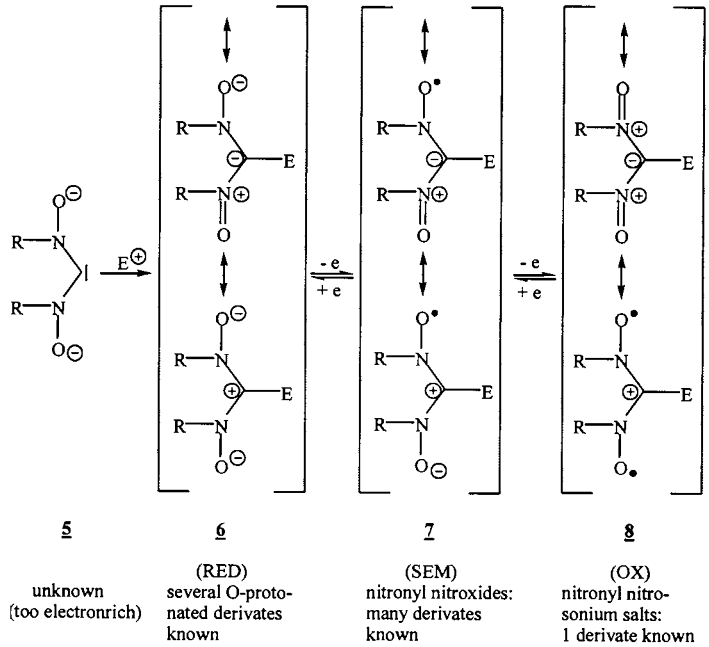
Can such systems be realized? For all practical purposes hydroxylamino- and hydrazino-derived carbenes **4** would be the obvious choice ($-D = -O^-$, $-OH$, $-OR$, $-NR_2$, etc.). Scanning the literature we found several feasible precursors for such compounds [6]. In this publication we approach this topic by looking at the situation for the simplest and simultaneously most powerful donor group $-D = -O^-$.

It turns out that nucleophilic carbenes of type **5** are completely unknown — not surprisingly in view of their excessive electron-surplus character. Functionalization of **5** at the carbene center by an electrophile would lead to the reduced form (RED) **6** of a two-step redox system. The latter still possesses distinct electron-surplus character and the few representatives of this structural type are only known in protonated form [7h,11n]. However, monooxidation of **6** would lead to an electronically well-balanced neutral radical **7** (SEM), many stable derivates of which are known under the common term nitronyl nitroxides [7]. Surprisingly, only one representative of the corresponding OX-form **8** (nitronyl nitrosonium salts) has been synthesized and structurally characterized [8].

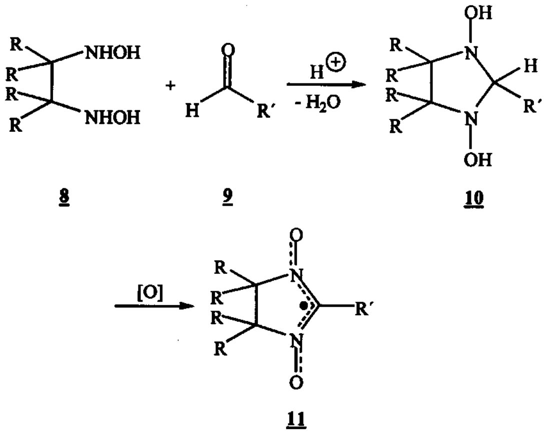
As can be inferred from resonance structures (a) and (b), the electron density at C(2) in **7** and **8** can still be flexibly modulated as a function of the substituent type E present at this position. This propensity is due to the electron reservoir present at the heteroatom functions and the structural consequences would be analogous to those discussed in Scheme 1. To exploit this potential it is of obvious interest to functionalize C(2) of these systems in quite general ways. This could probably be best achieved via generation of the underlying nucleophilic ‘carbenes’, followed by electrophilic derivatization. Subsequently we report on our endeavors to achieve this for nitronyl nitroxides. In a subsequent report [9] we shall deal with the corresponding chemistry of nitronyl nitrosonium salts **8**.

2. Nitronyl nitroxides: synthesis and significance

The first nitronyl nitroxides have been synthesized by Ullman in 1969 [10] and they now represent the most thoroughly investigated class of stable organic radicals known. Unlike other stable radicals they can act as mono- or bifunctional ligands in metal coordination chemistry via their Lewis basic oxygen centers [11]. Due to this, they have recently received a lot of attention in supramolecular magneto-structural investigations [12]. In spite of the ever-growing importance of nitronyl nitroxides the only systematic synthesis leading to them is still the one originally introduced by Ullman (Eq. (1)):



Scheme 3.



(1)

This synthesis has two principal limitations:

- The carbon centers of the two-carbon bridge have to be tertiary. This limitation arises from the synthesis of **8** [13]. For all known nitronyl nitroxides R=CH_3.
- As the condensation/oxidation sequence leading to **11** is limited to aldehydes **9**, nitronyl nitroxides with inorganic, elementorganic and metalorganic substituents at C(2) are virtually unknown.

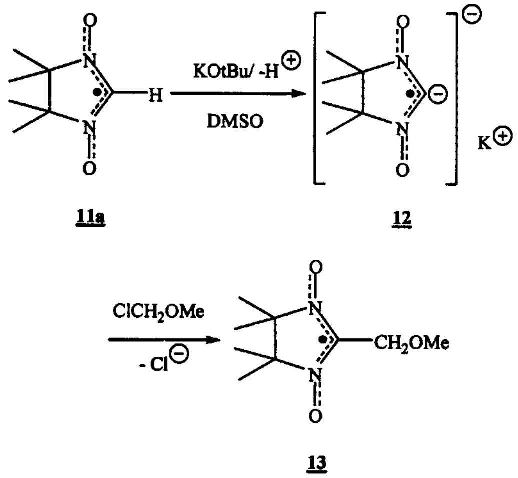
Although the first limitation certainly invites further study, the second one is much more serious from a general chemical point of view. Subsequently we turn to the question, how the latter limitation could be removed.

3. Experimental results

3.1. Deprotonation of a nitronyl nitroxide at C(2)

The starting point of further investigations was the nitronyl nitroxide **11a** ($R = CH_3$, $R' = H$), which is readily available according to the Ullman procedure (Eq. (1)). PM3 model calculations [14] on this radical show that its C(2) exhibits an unusually high degree of s-character ($sp^{1.34}$) in its bond to the ring proton. This is reminiscent of the bonding situation in the protonated precursor of **1** [1] and is a direct consequence both of ring strain in a planar five-membered ring and of the strong σ-withdrawing effect of the *N*-functional groups attached to C(2) (cf. 'Bent's rules') [15]. As a consequence, the calculated charge on the proton ($+0.20$) is comparable to the one found for typical precursors of Arduengo carbenes [16], although the latter are cationic. This points to a considerable CH-acidity of **11a**, for which also exists experimental support from the pioneering investigations of Ullman. The latter had already shown that **11a** undergoes H/D-exchange at C(2) in alkaline medium and can be methoxy-methylated according to Eq. (2):

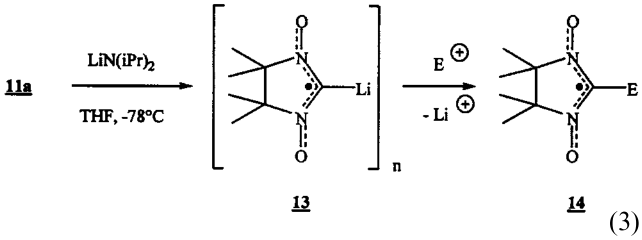
Thus, the C(2)-functionalized nitronyl nitroxide **13** was obtained, albeit in low yield (24%). Subsequently, no further C(2)-functionalizations of **11a** using this method were reported. This is not too surprising, because both



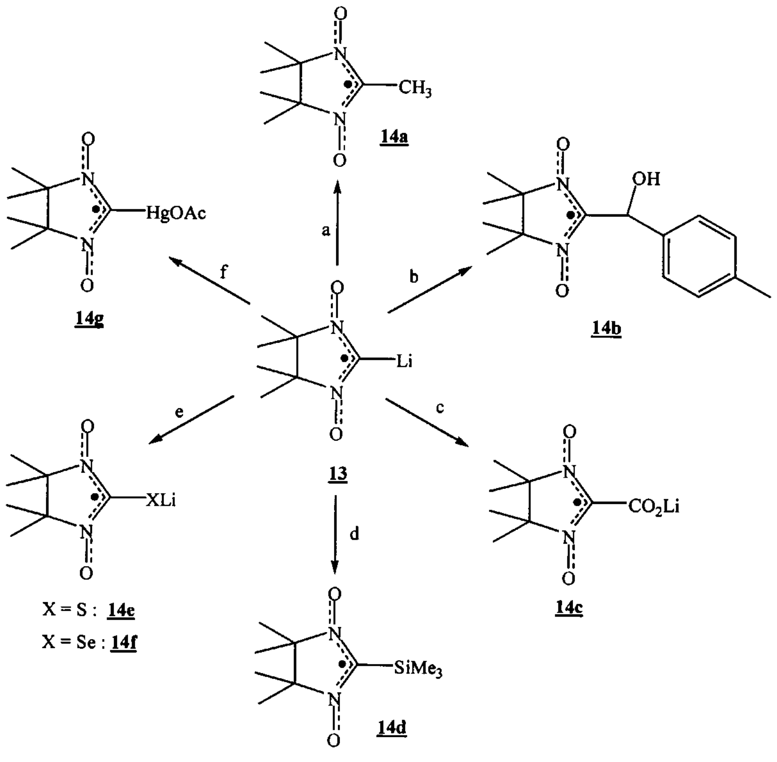
(2)

base and medium used by Ullman were unfortunate choices in view of the extremely electron-rich character of the deprotonated species — be it monomeric **12**, containing a 'naked' radical anion as assumed by Ullman (less likely), or a more highly clustered form thereof (much more likely). This is because DMSO possesses oxidizing character and may enter into redox reactions with **12** before an electrophile can attack at the desired position. Secondly, DMSO is also a nucleophile and it may compete for the electrophile employed. This is particularly true for the anion of DMSO, which is generated with KO^{t}Bu in this medium and might still co-exist with **11a** in an equilibrium. Thirdly, it is notoriously difficult to isolate neutral products from DMSO solution and this will be particularly true for a radical of limited stability like **13**. Having recognized this, we felt that lithiation of **11a** in THF would solve the above-mentioned problems of electrophilic C(2)-derivatization.

First, lithiation attempts using *n*-BuLi in THF failed completely. The characteristic red–blue color of the starting radical faded rapidly on addition of the base at − 78°C. This points to an irreversible destruction of the nitronyl nitroxide, possibly by reduction (*O*-transfer to *n*-BuLi?). Subsequent trapping attempts using various electrophiles gave no identifiable products. Success came then by replacing *n*-BuLi by the sterically hindered strong base Li–diisopropylamide, LDA. When this base was added to a solution of **11a** in THF at − 78°C a color change from red–blue to deep-red was observed. Subsequent addition of electrophiles gave the desired C(2)functionalized nitronyl nitroxides in satisfactory to good yields (45–70%), according to Eq. (3):



(3)



Scheme 4. Trapping of **13** by various electrophiles (a = MeOTf, b = *p*-tolylaldehyde, c = CO_2, d = TMSOTf, e = sulfur for **14e** and selenium for **14f**, f = $Hg(OAc)_2$).

In view of the general tendency of organyl–lithium compounds to form oligomeric clusters and taking into account results to be presented below one can safely assume that **13** exists as an *n*-mer ($n = 4$?, cf. below), due to stabilizing intermolecular Li–O contacts. This intermediate is sufficiently stable to be kept unchanged at low temperature for prolonged periods.

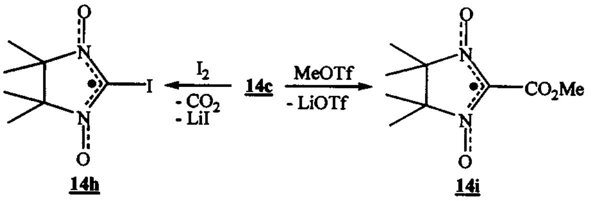
*3.2. Trapping of **13** by electrophiles*

The C(2)-lithiated nitronyl nitroxide was successfully trapped by various types of electrophiles. Scheme 4 gives an overview of functionalized nitronyl nitroxides **14** thus obtained. With one exception all of these systems are novel.

*3.2.1. C(2)-functionalization of **13** by carbon electrophiles*

In a first test run **13** was methylated by methyl triflate. After chromatographic workup the C(2)-methylated nitronyl nitroxide **14a** was obtained in analytically pure form. This compound was shown to be identical in all respects (analytical data, EIMS, UV, ESR, cf. Section 5) with an authentic sample, synthesized by Ullman according to Eq. (1) ($R' = CH_3$) [7h]. After this encouraging result other electrophiles were used to trap **13**. Under the same reaction conditions the first addition of **13** to a carbonyl group was achieved, using *p*-tolylaldehyde as an electrophile. After chromatographic work-up the carbinol derivate **14b** was obtained in pure form and good yield (43%) as a dark red radical. The UV spectrum was characteristic of a nitronyl nitroxide (absorption at 559, 530, 323 nm). Both EI-MS and FAB-MS exhibited the mole peak and characteristic degradation products (cf. Section 5).

Carboxylation of the lithiated nitronyl nitroxide also proved possible. Due to its salt-like structure the blue–violet radical **14c**, could not be chromatographically purified and the analytical data are therefore not yet entirely satisfactory. That carboxylation has indeed taken place can be seen from the IR (a new intense absorption at 1668 cm^{-1}, in addition to characteristic nitronyl nitroxide absorptions at 1446, 1372, 1171, 1141 cm^{-1}) and from the FAB mass spectrum, which exhibits a prominent MLi^+-peak. Furthermore, the carboxylate radical **14c** could be iododecarboxylated by iodine and methylated by methyl triflate, as shown in Eq. (4):



(4)

Both **14h** and **14i** proved to be identical with nitronyl nitroxides already synthesized by Ullman via a different route [7a,b].

*3.2.2. C(2)-functionalization of **13** by (derivates of) heavier main group elements*

Obviously, C(2)-silylated nitronyl nitroxides are of particular interest, since they could function as versatile precursors for various C(2)-derivatizations of nitronyl nitroxides. Due to the above mentioned limitations of the Ullman synthesis, this class of nitronyl nitroxides has remained inaccessible up to date. In view of the pronounced oxophilicity of silicon the site of electrophilic attack on **13** by a silylating agent is not a priori clear. Model calculations (PM3) predicted a 31.6 kcal mol^{-1} preference of C(2)-attack over *O*-attack for trimethylsilylation of **13**. This was confirmed by experiment. Under the reaction conditions specified above one single reaction product is obtained using trimethylsilyl triflate as an electrophile. After chromatographic purification a red–blue radical is obtained in 65% yield which analyzes correctly for **14d** (Scheme 4). This structure is confirmed by UV, IR and MS data (cf. Section 5). C(2)-silylation follows from the ESR spectrum, which proves coupling of the spin to two equivalent N centers ($a_N = 7.28$ G). Using tributyl tin triflate, an analogous tin compound was synthesized. The latter nitronyl nitroxide however proved extremely sensitive towards hydrolysis and could only be obtained in an impure form.

Finally, the lithiated nitronyl nitroxide **13** could also be trapped by elemental sulfur and selenium. Thus, radical salts **14e** and **14f** were obtained in reasonable yields as blue and green crystals, respectively. Although chromatographic purification was not possible due to the salt-like character of these products, the seleno derivate **14f** was obtained in pure form, in contrast to the sulfur analogue, which still contained some inorganic impurity. Structural confirmation for both compounds can be derived from the ESR spectra, which exhibit quintets in an intensity ratio of 1:3:5:3:1, as expected for two equivalent N centers (with $a_N = 7.96$ G for **14e** and $a_N = 8.20$ G for **14f**). The sulfur- and selenium-containing radical anions in these salts hold great promise as novel radical ligands in coordination chemistry.

3.2.3. Mercuration

Metal complexes of nitronyl nitroxides are of particular current interest in context with magneto-structural investigations [11]. A fair number of nitronyl nitroxide metal complexes is known, all of which have in common nitronyl nitroxide ligands bonded via the oxygen centers to the metal [11a–f]. By contrast, the corresponding C(2)-derived metalorganic chemistry is non-existent. The availability of **13** opens up a chance to develop this new research field.

In view of the known stability of Hg(II)-carbene complexes [17], C(2) mercuration of **13** appeared feasible.

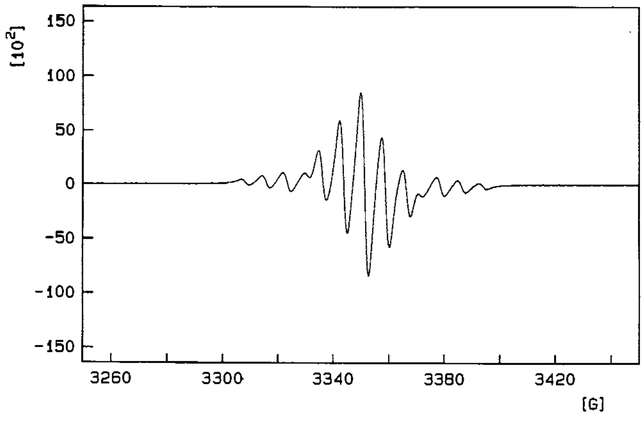


Fig. 1. ESR spectrum of **14g**.

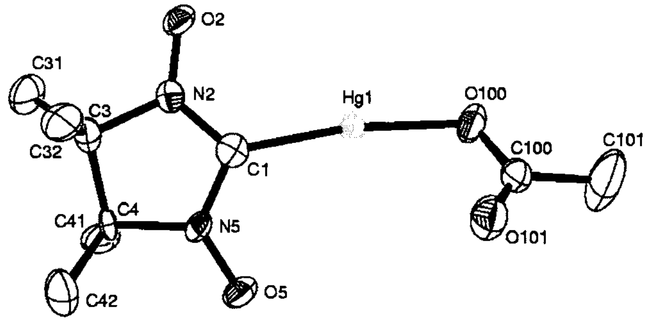


Fig. 2. X-ray structure of **14g**: monomeric unit (hydrogens omitted).

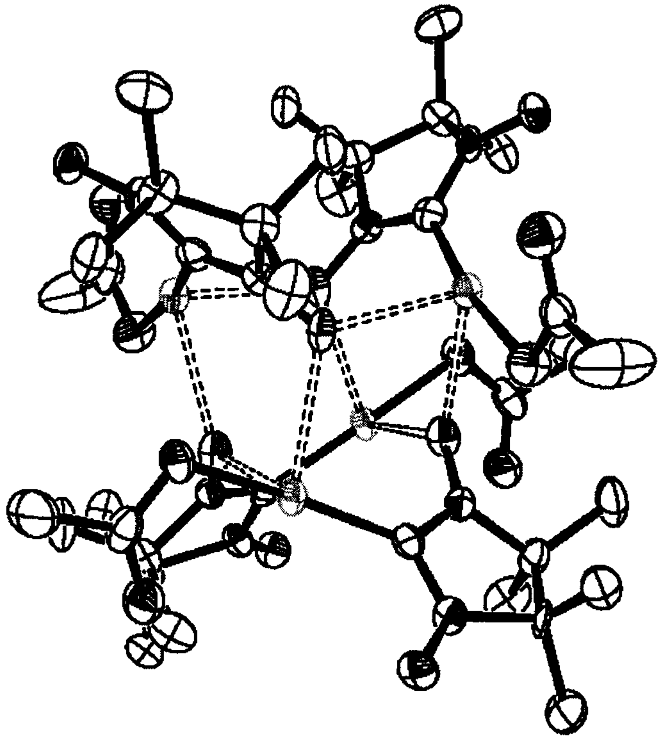


Fig. 3. X-ray structure of **14g**: tetrameric unit.

When $Hg(OAc)_2$ was reacted with 1 equivalent of **13** under the conditions shown in Scheme 4, the Hg(II)-nitronyl nitroxide complex **14g** was produced. According to MS analysis it is accompanied by the corresponding bis(nitronyl nitroxide)Hg(II) complex (the latter compound will be dealt with in a separate publication) [9]. This mixture proved difficult to separate. However, subsequently we found that the monosubstitution product **14g** could be prepared much more conveniently and quite selectively simply by reacting **11a** with 1 equivalent $Hg(OAc)_2$ in acetonitrile at room temperature.

Thus the first stable C(2)-metallated derivate of a nitronyl nitroxide was obtained in pure form and 77% yield [18]. **14g** was fully characterized spectroscopically. Both EI and FAB mass spectra exhibited a prominent mole peak at $m/z = 417$, accompanied by the characteristic isotope pattern of mercury. The latter element also has a characteristic influence on the corresponding ESR spectrum [19], which shows a somewhat more complex splitting pattern than the nitronyl nitroxides discussed above. This spectrum is shown in Fig. 1 and can be interpreted as follows.

The mercury isotopes ^{196}Hg, ^{198}Hg, ^{200}Hg, ^{202}Hg, ^{204}Hg with a total natural abundance of 69.8% and nuclear spin $I = 0$ are responsible for the five-line pattern characteristic of nitronyl nitroxides with equivalent nitrogen centers (here with $a(N) = 7.77$ G and $g = 2.01555$). Superimposed on this dominant feature is the splitting pattern of the corresponding ^{199}Hg compound. The ^{199}Hg isotope possesses $I = 1/2$ and therefore generates a doublet of quintets (with $a(^{199}Hg) = 52$ G). Due to the low natural abundance of this isotope (17%) the resulting ten line spectrum is much less intense than the aforementioned five-line

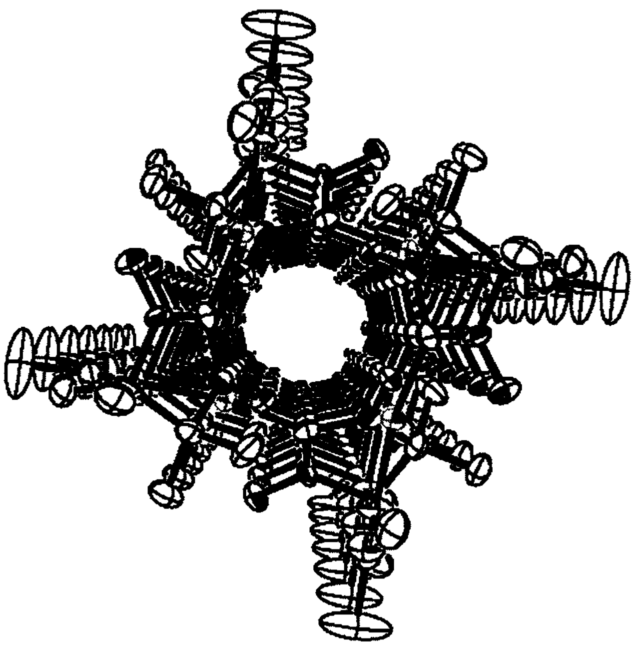


Fig. 4. X-ray structure of **14g**: view down the stacking axis of the tetrameric unit.

Table 1
Selected bond distances (Å) and angles (°) of compound **14g**

Hg1–C1	2.023(13)	N5–C1–Hg1	125.2(9)
Hg1–O100	2.041(10)	02–N2–C1	124.8(10)
Hg1–O2 # 1	2.597(8)	02–N3–C3	121.8(10)
Hg1–O2 # 2	2.597(10)	C1–N2–C3	112.9(10)
C1–N2	1.349(16)	N2–O2–Hg1 # 1	127.3(7)
C1–N5	1.369(16)	N2–O2–Hg1 # 3	119.3(6)
N2–O2	1.267(13)	Hg # 1–O2–Hg1 # 3	112.4(3)
N2–C3	1.497(15)	N2–C3–C32	106.3(10)
C3–C32	1.535(19)	N2–C3–C31	109.2(11)
C3–C31	1.535(19)	C32–0–01	111.4(12)
C3–C4	1.559(19)	N2–C3–C4	100.4(9)
C4–N5	1.500(14)	C32–C3–C4	114.8(11)
C4–C41	1.51(2)	C31–C3–C4	113.8(11)
C4–C42	1.55(2)	N5–C4–C41	106.5(11)
O5–N5	1.273(13)	N5–C4–C42	110.0(11)
C100–O101	1.21(2)	C41–C4–C42	110.6(13)
C100–O100	1.298(19)	N5–C4–C3	100.9(9)
C100–C101	1.49(2)	C41–C4–C3	115.2(12)
C1–Hg1–O100	169.7(5)	C42–C4–C3	113.7(13)
C1–Hg1–O2 # 1	104.5(4)	O5–N5–C1	123.7(10)
O100–Hg1–O2 # 1	85.4(4)	O5–N5–C4	123.0(10)
C1–Hg1–O(2) # 2	102.1(4)	C1–N5–C4	112.2(10)
O100–Hg1–O2 # 2	81.6(3)	O101–C100–O100	122.2(12)
O2 # 1–Hg1–O2 # 2	82.3(3)	O101–C100–O101	121.3(15)
N2–C1–N5	107.1(10)	O100–C100–C101	116.5(16)
N2–C1–Hg1	127.6(9)	C100–O100–Hg1	110.8(9)

spectrum. Eight out of these ten lines can be seen in Fig. 1, four on both the left- and right-hand sides of the quintet, which conceals two lines of the ^{199}Hg-induced splitting pattern.

In addition we succeeded in preparing crystals of **14g** suitable for X-ray analysis. Structural details are shown in Figs. 2–4 [20], characteristic bond lengths and angles are summarized in Table 1.

Fig. 2 shows the molecular structure of the C(2)-metallated nitronyl nitroxide. Bond lengths and angles do not differ significantly from the ones found for other nitronyl nitroxides. The two ligands form an angle of 169.7° with the Hg(II) center. This deviation from linearity is due to secondary interactions of the metal with several other Lewis basic oxygen centers in the vicinity. One such interaction takes place intramolecularly between the carbonyl–oxygen of the OAc ligand and the mercury(II) center, leading to a Hg–O distance of 2.813 Å and an *endo* arrangement of the ester carbonyl group with respect to the central atom (cf. Fig. 2).

In the crystal this Hg(II) complex forms discrete tetramers (Fig. 3). This specific association is brought about by two additional intermolecular Hg–O contacts with two neighboring molecules, involving the Lewis basic oxygen of the NO-functions. Only one such function per monomeric unit entertains two such interactions with the Hg(II) centers of two neighboring molecules, connecting four monomeric units via a boat-like cyclic array of symmetry-equivalent Hg–(N)O contacts, each of 2.597 Å in length. A bond length comparison shows that this intermolecular Hg–O coordination is definitely stronger than the above mentioned intramolecular one. These tetrameric subunits are stacked one on top of the other without any recognizable interaction between them. Looking down the stacking axis a tube-like arrangement of the tetramers becomes apparent, whose inner diameter approximates 3.7 Å (Fig. 4). The final crystal structure of **14g** is based on a parallel arrangement of identical tetramer tubes, in which any individual tube has four equidistant nearest neighbors. The space between these building blocks is filled by the methyl groups of the acetato ligands.

The solid state structure of the first stable C(2)-metallated nitronyl nitroxide **14g** contains a novel, highly ordered arrangement of molecular magnets. Investigation of its collective magnetic properties is clearly indicated.

4. Perspectives

Our investigations have made a radical anion equivalent of a nitronyl nitroxide readily accessible. Via the reactive intermediate **13** it will be possible to attach many more electrophiles — organic, inorganic and metalorganic — to the central carbon of the nitronyl nitroxide. Extensive research along these lines is being pursued in our laboratory. It is safe to predict that intermediates of type **13** will adopt a similar key position for structural variations of nitronyl nitroxides as do Wanzlick–Arduengo carbenes for the corresponding development of imidazolium chemistry [4].

However, there is a chemical dimension characteristic of nitronyl nitroxides that is not available to imidazolium. systems. As can be seen from Scheme 3 nitronyl nitroxides represent the SEM forms of a two-step redox system, and depending on the electrophile attached to the central carbon atom the corresponding RED and/or OX forms may also be accessible. Finally, as also indicated in Scheme 3 and discussed in the introduction of this publication, all three members of this two-step redox system have the structural prerequisites to induce an 'auto-umpolung' at the central carbon position, should this be required by the nature of substituent E. This view is fully confirmed by model calculations. The interplay of all these factors will open up a new research field.

5. Experimental

5.1. General comments

All reactions were carried out under a nitrogen atmosphere with anhydrous, N_2-saturated solvents (except ethyl acetate, which was not dried before use) in Schlenk vessels.

Mass spectra were recorded on a Varian MAT 311 A (EI) and micromass Zab Spec E (FAB) spectrometer. The ESR spectra were obtained on a Bruker 300 ESP (X Band), the UV spectra on a Shimadzu 3101 PC spectrometer. The IR spectra were recorded on a Bruker IFS 45 spectrometer.

5.2. Synthesis

5.2.1. 4,5-Dihydro-2,4,4,5,5-pentamethyl-1H-imidazole-1-oxyl-3-oxide ***14a***

227 mg (1.44 mmol) of 4,5-dihydro-4,4,5,5-tetramethyl-1*H*-imidazole-1-oxyl-3-oxide (**11a**) in 15 ml THF were cooled to -78°C and 0.79 ml of a 2 M LDA solution (1.58 mmol) were added. After stirring for 10 min 0.7 ml (1.58 mmol) methyltrifluoromethanesulfonate were added dropwise and the resulting solution was allowed to reach r.t. The solvent was removed under vacuum and the residue was chromatographed on silica gel with ethyl acetate as solvent. Yield 149 mg (60.5%).

Anal. Found: C, 56.08; H, 9.05; N, 16.26. Calc.: C, 56.12; H, 8.83; N, 16.36%. EI-MS (70 eV, 70°C) m/z: 171 $(M)^+$, 84 $(C_6H_{12})^+$, 69 $(C_5H_9)^+$, 55 $(C_4H_7)^+$. UV (hexane): λ (nm) 306.0, 317.5, 521.5, 555.5.

This compound proved to be identical to a sample prepared according to Ullman [7a].

5.2.2. 2-[1-Hydroxy-1-(4-methylphenyl)methyl]-4,5-dihydro-4,4,5,5-tetramethyl-1H-imidazole-1-oxyl-3-oxide ***14b***

200 mg (1.27 mmol) of 4,5-dihydro-4,4,5,5-tetramethyl-1*H*-imidazole-1-oxyl-3-oxide (**11a**) in 10 ml THF were cooled to -78°C and 0.7 ml of a 2 M LDA solution (1.4 mmol) were added. After stirring for 10 min 1.27 ml (1.27 mmol) *p*-tolylaldehyde were added dropwise and the resulting solution was allowed to reach r.t. The solvent was removed under vacuum and the residue was chromatographed on silica gel with ethylacetate as solvent. Yield 153 mg (43.4%).

Anal. Found: C, 65.18; H, 7.65; N, 9.97. Calc.: C, 64.96; H, 7.63; N, 10.10%. EI-MS (70 eV, 50°C) m/z: 277 $(M)^+$, 260 $(M-OH)^+$, 244 $(M-OH-O)^+$, 157 $(M-C_8H_8O)^+$, 119 $(C_8H_7O)^+$, 91 $(C_7H_7)^+$, 84 $(C_6H_{12})^+$, 69 $(C_5H_9)^+$, 55 $(C_4H_7)^+$. FAB-MS (NBA) m/z: 277 $(M)^+$. ESR (CH_2Cl_2): $g = 2.0000$, $a_N = 7.65$ G. UV (hexane): λ (ε) 261.0 (4643), 323.0 (25286), 530.0 (1000), 559.0 (1071). IR (KBr): ν (intensity) 3423 (s), 2987 (m), 2925 (m), 1606 (m), 1540 (w), 1513 (m), 1452 (s), 1410 (s), 1374 (ss), 1255 (m), 1213 (m), 1166 (m), 1138 (m), 1064 (w), 822 (w), 759 (w), 540 (m).

5.2.3. 4,5-Dihydro-4,4,5,5-tetramethyl-1H-imidazole-1-oxyl-3-oxide-2-carboxylate-lithium ***14c***

A solution of 315 mg (2 mmol) 4,5-dihydro-4,4,5,5-tetramethyl-1*H*-imidazole-1-oxyl-3-oxide (**11a**) in 20 ml THF was cooled to -78°C and 1.05 ml of a 2 M LDA solution (2.1 mmol) were added dropwise. After stirring for 10 min solid CO_2 was added; the color became deep purple. The solution was allowed to reach r.t. and concentrated under reduced pressure. A purple solid was then precipitated with Et_2O (40 ml), isolated by filtration, washed with Et_2O (10 ml) and dried under vacuum. Yield 282 mg (68%).

Anal. Found: C, 45.39; H, 6.09; N, 11.39. Calc.: C, 46.40; H, 5.84; N, 13.52%. EI-MS (70 eV, 200°C) m/z: 312 $(2M-2CO_2)^+$, 198 $(2M-2CO_2-C_6H_{12}NO)^+$, 182 $(2M-2CO_2-C_6H_{12}NO_2)^+$, 157 $(M-CO_2+1)^+$, 84 $(C_6H_{12})^+$, 69 $(C_5H_9)^+$. FAB-MS (NBA) m/z: 629 $(3M+Li+H)^+$, 421 $(2M+Li)^+$, 214 $(M+Li)^+$. ESR (THF): $g = 2.0007$, $a_N = 7.63$ G. UV (CH_2Cl_2): λ (ε) 325.5, 337.0, 540.0. IR (KBr): ν (intensity) 2991 (m), 1668 (s, b), 1537 (s), 1446 (s, b), 1372 (s), 1321 (s), 1218 (m), 1171 (s), 1142 (s), 902 (w), 872 (m), 819 (w), 784 (m), 740 (m), 618 (w), 545 (m).

5.2.4. 4,5-Dihydro-4,4,5,5-tetramethyl-2-(trimethylsilyl)-1-imidazole-1-oxyl-3-oxide ***14d***

203 mg (1.29 mmol) of 4,5-dihydro-4,4,5,5-tetramethyl-1*H*-imidazole-1-oxyl-3-oxide (in 10 ml THF were cooled to -78°C and 0.71 ml of a 2 M LDA solution (1.42 mmol) were added. After stirring for 10 min 0.26 ml (1.42 mmol) trimethylsilyltrifluormethansulfonate were added dropwise and the resulting solution was allowed to reach r.t. The solvent was removed under vacuum and the residue was chromatographed on silica gel with ethyl acetate as solvent. Yield 222 mg (75%).

Anal. Found: C, 52.66; H, 9.37; N, 12.32. Calc.: C, 52.36; H, 9.23; N, 12.21%. EI-MS (70 eV, 60°C) m/z: 303 $(M+TMS+H)^+$, 230 $(M+H)^+$, 98 $(TMSCN-H)^+$, 84 $(C_6H_{12})^+$, 73 $(TMS)^+$, 69 $(C_5H_9)^+$. ESR (THF): $g = 2.0527$, $a_N = 7.28$ G. UV (pentane): λ (ε) 315.5 (7869), 327.5 (10061), 549.0 (615), 591 (471). IR (KBr): ν (intensity) 2957 (s), 1635 (m), 1466 (m), 1452 (m), 1418 (s), 1367 (s), 1342 (m), 1250 (s), 1213 (w), 1170 (m), 1138 (m), 947 (m), 935 (m), 922 (m), 872 (s), 846 (s), 754 (m), 537 (w).

5.2.5. 4,5-Dihydro-4,4,5,5-tetramethyl-1H-imidazole-1-oxyl-3-oxide-2-mercapto-lithium ***14e***

225 mg (1.43 mmol) of 4,5-dihydro-4,4,5,5-tetramethyl-1*H*-imidazole-1-oxyl-3-oxide (**11a**) in 15 ml THF were cooled to -78°C and 0.71 ml of a 2 M LDA solution (1.43 mmol) were added dropwise. After stirring for 10 min 46 mg (1.43 mg) sulfur were added and the resulting solution was allowed to reach r.t.; the pale red color became blue. Filtration over Celite, concentration under reduced pressure and addition of petrolether yielded a blue solid, isolated by filtration and dried under vacuum. Yield 208 mg (80%).

Anal. Found: C, 41.05; H, 6.48; N, 11.93; S, 16.35. Calc.: C, 43.07; H, 6.20; N, 14.35; S, 16.42%. FAB-MS (NBA) *m*/*z*: 397 $(2M+Li)^+$, 202 $(M+Li)^+$. ESR (THF): $g = 1.9932$, $a_N = 8.2$ G. IR (KBr): ν (intensity) 2982 (s), 2934 (m), 1677 (s), 1627 (m), 1537 (s), 1483 (m), 1459 (s), 1371 (s), 1343 (s), 1273 (s, b), 1215 (s, b), 1154 (s), 1139 (s), 1053 (m), 1000 (m), 950 (m), 890 (m), 866 (m), 768 (m), 739 (w), 624 (m), 541 (s).

5.2.6. *4,5-Dihydro-4,4,5,5-tetramethyl-1H-imidazole-1-oxyl-3-oxide-2-seleno-lithium* ***14f***

184 mg (1.17 mmol) 4,5-dihydro-4,4,5,5-tetramethyl-1*H*-imidazole-1-oxyl-3-oxide (**11a**) in 20 ml THF were cooled to −78°C and 0.58 ml of a 2 M LDA solution (1.17 mmol) were added dropwise. After stirring for 10 min 92 mg (1.17 mmol) selenium were added and the resulting solution was allowed to reach r.t.; the pale red color became green. Filtration over Celite, concentration under reduced pressure and addition of Et_2O yielded a green solid, isolated by filtration and dried under vacuum. Yield 157 mg (55%).

Anal. Found: C, 35.28; H, 5.49; N, 10.82. Calc.: C, 34.73; H, 5.00; N, 11.57%. ESR (THF): $g = 2.0096$, $a_N = 7.96$ G. IR (KBr): 2984 (s), 2933 (s), 1676 (s), 1620 (s), 1576 (s), 1537 (s), 1449 (s), 1367 (s), 1283 (s), 1213 (s), 1153 (s), 1136 (s), 1041 (s), 992 (m), 957 (w), 894 (w), 875 (w), 854 (m), 839 (m), 777 (m), 660 (m), 542 (s).

Table 2
Crystal data and structure refinement

Empirical formula	$C_9H_{15}HgN_2O_4$
Formula weight	415.82
Temperature (K)	173
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	*I*-4
Unit cell dimensions	
a (Å)	15.1008(6)
b (Å)	15.1008(6)
c (Å)	10.9154(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	2489.08(16)
Z	8
Absorption coefficient (mm^{-1})	12.368
Crystal color, habit	Deep purple, block
Crystal size (mm)	$0.250\times0.1\times0.1$
θ-Range for data collection (°)	1.91–29.50
Reflections collected	2706
Independent reflections	2701 [$R_{int} = 0.0461$]
Reflections	2412
Absorption correction method	Ψ-scans
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2701/0/145
Goodness-of-fit on F^2	1.059
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.441$, $wR_2 = 0.10423$
R indices (all data)	$R_1 = 0.0544$, $wR_2 = 0.\ 1110$
Absolute structure parameter	0.52(3)
Largest difference peak and hole (e Å^{-3})	1.299 and −2.079

5.2.7. *(Acetato-μ-O)-(4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1-oxy-1H-imidazole-2-yl)mercury* ***14g***

To a solution of 185 mg (1.18 mmol) 4,5-dihydro-4,4,5,5-tetramethyl-1*H*-imidazole-1-oxyl-3-oxide (**11a**) in 10 ml acetonitrile 375 mg (1.18 mmol) of $Hg(OAc)_2$ were added and stirred for 24 h. The purple product was precipitated with Et_2O, isolated by filtration, washed with Et_2O and dried under vacuum. Yield 377 mg (77%).

Anal. Found: C, 25.96; H, 3.54; N, 6.50. Calc.: C, 25.99; H, 3.63; N, 6.74%. EI-MS (70 eV, 120°C) *m*/*z*: 417 $(M)^+$, 358 $(M-C_2H_3O_2)^+$, 202 $(Hg)^+$, 84 $(C_6H_{12})^+$, 69 $(C_5H_9)^+$. FABMS (NBA) *m*/*z*: 417 $(M)^+$, 358 $(M-C_2H_3O_2)^+$. ESR (CH_2Cl_2): $g = 2.0000$, $a_N = 7.52$ G, $a_{Hg} = 55.52$ G. UV (CH_2Cl_2): λ (ε) 347.0 (6146), 527 (613), 560.5 (719). IR (KBr): ν (intensity) 2991 (w), 1632 (m), 1612 (m), 1574 (s), 1452 (w), 1404 (m), 1344 (m, b), 1262 (w), 1211 (w), 1160 (w), 1137 (w), 1020 (w), 921 (w), 841 (w), 802 (w), 648 (m).

5.3. *Crystallographic studies*

Crystals suitable for X-ray structure analysis were obtained by solvent diffusion of Et_2O in a saturated solution of compound **14j** in CH_2Cl_2. The measurements were carried out on a Nonius Mach3 single-crystal diffractometer with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The hydrogen atoms were fixed in idealized positions with a riding model. Table 2 lists details of unit cell data, intensity data collection and structure refinement.

5.4. *Supplementary material*

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. CCDC 147580 for compound **14g**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] R. Weiss, S. Reichel, M. Handke, F. Hampel, Angew. Chem. 110 (1998) 352; Angew. Chem. Int. Ed. Engl. 37 (1998) 344.
[2] R. Weiss, S. Reichel, Eur. J. Inorg. Chem. (2000) 1935.
[3] Ph.D. Thesis, S. Reichel, University of Erlangen-Nürnberg, 1998.
[4] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39.

[5] K. Deuchert, S. Hünig, Angew. Chem. 12 (1978) 927.
[6] (a) H. Link, W. Klötzer, M. Karpitschka, M. Montavon, R. Müssner, N. Singewald, Angew. Chem. 102 (1990) 559. (b) W. Klötzer, H. Baldinger, E.M. Karpitschka, J. Knoflach, Synthesis (1982) 592. (c) G. Laus, W. Klötzer, Synthesis (1989) 269 (d) G. Laus, J. Stadlwieser, W. Klötzer, Synthesis (1989) 773. (e) G. Laus, J. Stadelwieser, W. Klötzer, Synthesis (1990) 795. (f) V. Bock, W. Klötzer, N. Singewald, G. Strieder, Synthesis (1987) 1058.
[7] (a) D.G.B. Boocock, R. Darcy, E.F. Ullman, J. Am. Chem. Soc. 21 (1968) 5945. (b) D.G.B. Boocock, E.F. Ulman, J. Am. Chem. Soc. 24 (1968) 6874. (c) E.F. Ullman, D.G.B. Boocock, Chem. Commun. 20 (1969) 1161. (d) P.W. Kopf, R. Kreilich, D.G.B. Boocock, E.F. Ullman, J. Am. Chem. Soc. (1970) 4531. (e) E.F. Ullman, L. Call, J.H. Osieckie, J. Org. Chem. 35 (1970) 3623. (f) E.F. Ullman, L. Call, J. Am. Chem. Soc. 92 (1970) 7210. (g) L. Call, E.F. Ullman, Tetrahedron Lett. (1973) 961. (h) E.F. Ullman, J.H. Osieckie, D.G.B. Boocock, R. Darcy, J. Am. Chem. Soc. 94 (1972) 7049. (i) E.F. Ullman, L. Call, S.S. Tseng, J. Am. Chem. Soc. 95 (1973) 1677. (j) M. Deumal J. Cirujed, J. Vaciena, J.J. Novoa, Chem. Eur. J. 5 (1999) 1631.
[8] A. Caneschi, J. Laugier, P. Rey, J. Chem. Soc. Perkin Trans. 1 (1987) 1077.
[9] R. Weiss, N. Kraut, in preparation.
[10] E.F. Ullman, J.H. Osieckie, J. Am. Chem. Soc. 90 (1968) 1078.
[11] (a) A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, Acc. Chem. Res. 22 (1989) 392. (b) A. Caneschi, P. Chiesi, L. David, F. Ferraro, D. Gatteschi, R. Sessoli, Inorg. Chem. 32 (1993) 1445. (c) A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey, R. Sessoli, Inorg. Chem. 29 (1990) 4217. (d) A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey, R. Sessoli, Inorg. Chem. 30 (1991) 3126. (e) C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, P. Rey, Inorg. Chem. 29 (1990) 4223. (f) A. Caneschi, D. Gatteschi, M.C. Melandri, P. Rey, R. Sessoli, Inorg. Chem. 29 (1990) 4228. (g) G. Ulrich, R. Ziessel, Tetrahedron Lett. (1993) 1211. (h) G. Ulrich, R. Ziessel, Tetrahedron Lett. 35 (1993) 1215.
[12] (a) R. Kumai, M.M. Matsushita, A. Izuoka, T. Sugawara, J. Am. Chem. Soc. 116 (1994) 4523. (b) N. Yoshioka, M. Irisawa, Y. Mochizuki, T. Kato, H. Inoue, S. Ohba, Chem. Lett. (1997) 251. (c) A. Izuoka, M. Hiraishi, T. Abe, T. Sugawara, J. Am. Chem. Soc. 122 (2000) 3234. (d) J.P. Sutter, M.L. Kahn, O. Kahn, Adv. Mater. 11 (1999) 863. (e) O. Felix, M.W. Hosseini, A.D. Cian, J. Fischer, L. Catala, P. Turek, Tetrahedron Lett. 40 (1999) 2943. (f) T. Mitsumori, K. Inoue, N. Koga, H. Iwamura, J. Am. Chem. Soc. 117 (1995) 2467. (g) L. Dulog, J.S. Kim, Angew. Chem. 102 (1990) 403. (h) C. Batz, P. Amann, H.-J. Deiseroth, L. Dulog, Liebigs Ann. Chem. (1994) 739. (i) T. Akita, Y. Mazaki, K. Kobayashi, J. Org. Chem. 60 (1995) 2092. (j) T. Akita, K. Kobayashi, Tetrahedron Lett. 52 (1996) 6893. (k) T. Akita, Y. Mazaki, K. Kobayashi, Tetrahedron Lett. 36 (1995) 5543. (l) M.M. Matsushita, A. lzuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, M. Ishikawa, J. Am. Chem. Soc. 119 (1997) 4369. (m) M. Tanaka, K. Matsuda, T. Itoh, H. Iwamura, J. Am. Chem. Soc. 120 (1998) 7168. (n) G. Ulrich, P. Turek, R. Ziessel, Tetrahedron Lett. 37 (1996) 8755. (o) F.M. Romero, R. Ziessel, Tetrahedron Lett. 40 (1999) 1895. (p) C. Stroh, R. Ziessel, Tetrahedron Lett. 40 (1999) 4543. (q) C. Stroh, P. Turek, R. Ziessel, Chem. Commun. (1998) 2337.
[13] (a) M. Lammchen, T.W. Mittag, J. Chem. Soc. C (1966) 2300. (b) R. Sayre, J. Am. Chem. Soc. 77 (1955) 6689.
[14] (a) J.P. Foster, F. Weinhold, J. Chem. Soc. 102 (1980) 7211. (b) A.E. Reed, F. Weinhold, Chem. Rev. 88 (1988) 899.
[15] H.A. Bent, Chem. Rev. 61 (1961) 275.
[16] A.J. Arduengo, Acc. Chem. Res. 32 (1999) 913.
[17] (a) H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. 80 (1968) 154. (b) A.J. Arduengo, R.L. Harlow, W.J. Marshall, T.K. Prakasha, Heteroat. Chem. 7 (1996) 421.
[18] After completion of this work we discovered that **14g** is mentioned in an early patent claim by R.K. Leute, E.F. Ullman, US Patent 3,697,535, 1969. Only the analytical composition of an otherwise structurally uncharacterized compound of unknown purity is cited in support of this claim.
[19] By courtesy of Professor Dr. U. Zenneck and Dipl. Chem. M. Zeller, Institut für Anorganische Chemie der Universität Erlangen-Nürnberg.
[20] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.