CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600061

Pyrimidinyl Nitronyl Nitroxides

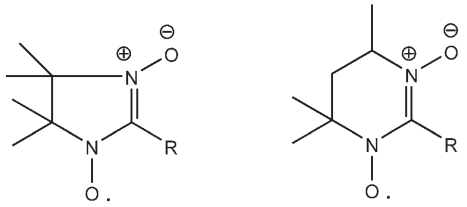
Peter Brough,[a] Jacques Pécaut,[a] André Rassat,[b] and Paul Rey*[a]

Abstract: The chemistry of 2,2,4,4-substituted pentane derivatives has been investigated with the aim of providing a flexible and versatile synthetic route to pyrimidinyl nitronyl nitroxides, in which the bis-*N*-oxy fragment is incorporated in a six-membered ring. The synthesis of 2,4-diamino-2,4-dimethylpentane and 2,4-bis(hydroxylamino)-2,4-dimethylpentane, convenient precursors of these nitroxides, is described and full characterization of a series of pyrimidinyl nitronyl nitroxides is reported, along with a preliminary study of their coordination properties.

Keywords: ESR spectroscopy · magnetic materials · nitronyl nitroxides · pyrimidines · stable free radicals

Introduction

Among stable nitroxide free radicals, imidazolyl nitronyl nitroxides **1** have found wide application as spin carriers for designing molecular magnetic materials.[1] They afforded the



1 **2**

first purely organic magnets,[2] and are the cornerstone of the so-called metal–radical approach, a strategy that has contributed significantly to the development of magnetochemistry.[3,4] Attractive properties of these free radicals include delocalized structures and two potentially coordinating sites carrying large spin density, two features well suited for obtaining strongly coupled multidimensional coordination compounds whose properties depend on the chemical structures of the free radical ligands.

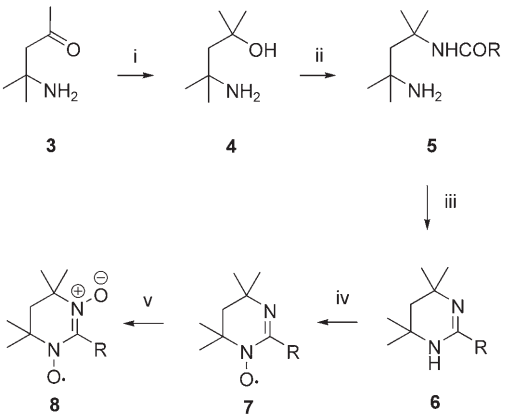
According to Ullman's pioneering work,[5,6] the structure of any aldehyde can be reflected in that of the corresponding free radical. This enables monitoring of steric and electronic factors and, in the metal–radical approach, gives opportunities to include extra coordination sites.[7] Although structural variations are almost infinite and are still the object of intense activity, needs for other structures corresponding to modification of other parts of the molecule have been suggested and have triggered studies in this field. As an example, imidazolinyl nitronyl nitroxides substituted in position(s) 4 and/or 5 with chiral centers introduced close to the *N*-oxy groups have been reported, opening a new route to enantiopure molecular magnetic materials.[8]

In relation to the usual imidazolinyl nitronyl nitroxides, pyrimidinyl analogues—in which the bis-*N*-oxyl fragment would be included in a six-membered ring—could exhibit new interesting features such as, for example, sterically different environments of the oxy groups, resulting in new binding geometries and new magnetic behavior in the corresponding metal complexes. Before this work, an attempt had been made to include the conjugated ONCNO fragment in a six-membered ring: 2,2,4-trimethylpyrimidinyl nitronyl nitroxides (**2**) had been prepared, but the substitution on the ring was insufficient to confer stability on the resulting free radicals.[9] Recently, however, we reported a synthesis of suitably substituted, stable, pyrimidinyl nitronyl nitroxides **8** (Scheme 1),[10] which is expeditious and uses common and

[a] Dr. P. Brough, Dr. J. Pécaut, Dr. P. Rey
CEA-Grenoble
Département de Recherche Fondamentale sur la Matière Condensée
Service de Chimie Inorganique et Biologique (UMR-E3, CEA-UJF)
17 rue des Martyrs, 38054 Grenoble Cedex 09 (France)
E-mail: prey@cea.fr

[b] Prof. A. Rassat[+]
l'Ecole Normale Supérieure
Département de Chimie
(UMR CNRS 8640, CNRS-ENS-Université Pierre-et-Marie-Curie)
24 rue Lhomond, 75231 Paris Cedex 05 (France)

[+] Deceased



Scheme 1. The nitrile route to pyrimidinyl nitronyl nitroxides. i) MeMgI/diethyl ether; ii) RCN/SO_4H_2; iii) $Ba(OH)_2/H_2O$, 100 °C; iv–v) *m*CPBA/THF, $NaIO_4$.

inexpensive reagents. By this synthetic pathway a variety of substituents R could in principle be introduced in position 2 of the pyrimidine ring.

A nitrile (RCN) supplied both the second nitrogen site and the substituent, through application of a Ritter reaction to **4**. However, high yields of amino amides **5** were obtained only in the presence of a large excess of nitrile, a possible limitation of this approach in view of the availability of specific nitrile compounds, which may also degrade in a medium as aggressive as concentrated sulfuric acid. Moreover, the yield of the last step, the oxidation of the tetrahydropyrimidine **6** through the intermediate imino nitroxide **7**, was frustratingly low, which is again a strong incentive to use another intermediate.

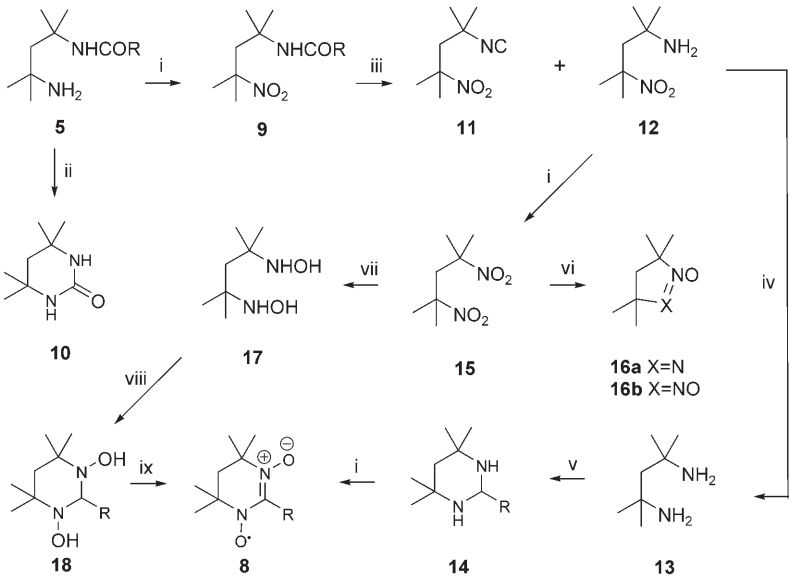
Here we describe a new and more flexible route to these nitroxides, which uses aldehydes instead of the less easily available nitriles and in which conventional oxidation procedures give more satisfactory yields. The synthesis of a series of pyrimidyl nitronyl nitroxides from the precursors 2,4-diamino-2,4-dimethylpentane (**13**) and 2,4-bis(hydroxylamino)-2,4-dimethylpentane (**17**, Scheme 2) is described, along with some of their properties.

Results and Discussion

The main drawback of the previously reported synthetic pathway is the conversion of the imino moiety into the nitronyl nitroxide. The chemistry of imidazolines tells us that oxidation of imino nitroxides into nitronyl nitroxides is indeed difficult and proceeds with low yields;[5b] under the same conditions, however, *N*,*N*′-bis(hydroxylamino)imidazolidines and imidazolidines afford nitronyl nitroxides in fairly good yields.[5,6] We therefore searched for a more convenient synthetic pathway using precursors such as diamine **13** or bis(hydroxylamine) **17**, reacting stoichiometrically with an aldehyde acting as the substituent carrier to provide hexahydropyrimidines or *N*,*N*′-dihydroxyhexahydropyrimidines, which were expected to be more easily oxidized, as described for the imidazolinyl analogues.

Syntheses: We first tried to prepare the diamino precursor **13** (Scheme 2). At first glance, this compound seemed easy to obtain from the readily available amino amide **5a** (R = Me) or tetrahydropyrimidine **6a** (Scheme 1, R = Me).

As previously reported, however,[10,11] attempted hydrolysis of **5a** gave **6a**, which in turn could not be reduced: $NaBH_4$ or Na/EtOH were ineffective and neither diamine **13** nor hexahydropyrimidine **14a** (R = CH_3) were obtained. To avoid the intramolecular nucleophilic cyclization exhibited by amino amides **5**, the amino function was transformed into a nitro group: compound **5a** was easily converted into nitro amide **9a** (R = Me) in good yield by treatment with mCPBA, but attempts to hydrolyze this compound under various basic or



Scheme 2. The aldehyde route to pyrimidinyl nitronyl nitroxides. i) *m*CPBA, CH_2Cl_2; ii) $Ba(OH)_2$, H_2O, 100 °C (R = CCl_3); iii) $NaOH/H_2O$, (R = CCl_3); iv) Zn/AcOH; v) RCHO/diethyl ether; vi) $LiAlH_4$/diethyl ether; vii) Zn/NH_4Cl; viii) RCHO/PTSA; ix) $NaIO_4$ (R = aliphatic), *m*CPBA (R = aromatic).

acidic conditions ($Ba(OH)_2$, NaOH, HCl) produced intractable mixtures.

To enhance the ease of hydrolysis of the amide function, the methyl group was exchanged for CCl_3.[12] When amino amide **5b** (R = CCl_3) was heated at reflux in aqueous $Ba(OH)_2$, cyclic urethane **10** was obtained in good yield,[13] but could not be further hydrolyzed. Alternatively, **5b** was oxidized to nitro amide **9b** and easily converted into nitro amine **12** by treatment with aqueous sodium hydroxide. Although the chloroform produced in this reaction was eliminated through a Dean–Stark apparatus, some isonitrile **11** was also detected,[14] but acid treatment of the crude reaction mixture gave nitro amine **12** in 70% yield. The target nitronylnitroxides were then prepared by two reaction sequences:

Diamine path: Diamine **13** was obtained (>70%) by reduction of nitro amine **12** with zinc in acetic acid and was characterized by an X-ray diffraction study of the picrate. Condensation with aldehydes RCHO in chloroform at reflux with catalytic amounts of *p*-toluenesulfonic acid resulted in the corresponding hexahydropyrimidines **14**.

Oxidation to nitroxides with *m*CPBA was then expected to proceed readily. Under the conditions described for the five-membered ring analogues,[6] however, nitronyl nitroxides were detected by ESR but the major products of the reactions were the corresponding nitro amides **9**. The reasons for such behavior are not fully understood, but it was noted that the solvent had a crucial role: a 1:1 mixture of diethyl ether/acetonitrile as solvent gave better yields (10% for **8a** to 30% for **8d**) of nitronylnitroxides **8**. It therefore appeared that the diamine path had marginal preparative value in relation to the nitrile route.

Bis(hydroxylamino) path: The dinitro compound **15** was obtained in 90% yield from the corresponding nitro amine **12** by oxidation with *m*CPBA in dichloromethane at reflux. The bis(hydroxylamino) derivative **17** was then prepared in about 60% yield (NMR) by the procedure reported for the synthesis of 2,3-dimethyl-2,3-bis-(hydroxylamino)butane.[15] In this case, however, the reaction product always included variable amounts (5–20%) of cyclic azoxy and azodioxy compounds **16a** and **16b**. Note that these two compounds were also obtained by reduction of **15** by $LiAlH_4$, and neither gave **17**. Since bis(hydroxylamino) derivatives are poorly stable in solution when impure,[6] no attempt was made to obtain an analytical sample, and crude **17** was used in the following steps.

Condensation of precursor **17** with aldehydes proceeded satisfactorily with formaldehyde and acetaldehyde at room temperature and with other alkylaldehydes at higher temperature, to afford the corresponding *N,N'*-dihydroxy-hexahydropyrimidines **18**. As in the Ullman synthesis,[5b] aromatic aldehydes were less reactive: a higher temperature (60°C) and a catalyst (*p*-toluenesulfonic acid or pyridinium *p*-toluenesulfonate) were used to obtain the corresponding *N,N'*-dihydroxyhexahydropyrimidines (**18**) in good yields. When aldehydes were used in excess, the corresponding bis-nitrones were obtained as the major product.

Oxidation of alkyl-substituted bishydroxylamines such as **18a** or **18g** with sodium periodate proceeded smoothly, with 50–60% yields of radicals **8a** or **8g**. In the case of the aromatic analogues (**18c–f**), oxidation under the same conditions gave poor yields (<10%), and classical oxidants of hydroxylamines such as Ag_2O, PbO_2, and $NaWO_4/H_2O_2$ did not improve the yields. Finally, *m*CPBA was found to be the most efficient oxidant, affording aryl-substituted radicals **8c–f** in satisfactory (60–70%) yields.

These pyrimidyl nitronyl nitroxides are readily reduced to imino nitroxides by use of the conventional ice-cooled $NaNO_2$/HCl system.[16] For instance, conversion of **8d** into **7d** proceeded quantitatively (>95%).

Nitroxide properties: ESR spectra in solution show the usual five-line pattern resulting from coupling with two equivalent nitrogen nuclei ($I = 1$) and, on occasion, additional splittings when the substituent R carries hydrogen atoms at the position α to the pyrimidyl fragment. Values of the hyperfine couplings are displayed in Table 1, together with those of imidazolinyl analogues.[5] ^{14}N couplings are significantly weaker ($\Delta a_N \approx 0.2$ gauss) in pyrimidyl nitroxides than in their imidazolidinyl counterparts. Taking into account the structural differences, the spin densities for the phenyl-substituted radicals have been calculated in both cases.[17] These calculations afford weaker spin densities for the former than for the latter; even more interesting is the fact that their ratio (1.037 vs. 1.040) is almost the same as that of the experimental values.

Table 1. ESR hyperfine splitting parameters (gauss) in pyrimidyl nitroxides, their imidazolinyl analogues (in parentheses, from reference [5]), and Weiss constants (θ, from magnetic measurements). For **8c** (R = Ph) the calculated spin densities on equivalent coupled nitrogen atoms (ρ_N) are reported.

R	A_{N1}[a]	A_{N1}[b]	A_{N2}[a]	A_{N2}[b]	A_H[a]	A_H[b]	Θ(K)
Me 8a	8.10	7.24			2.98	3.22	−0.4
	(8.25)	(7.4)				(3.3)	
Ph **8c** ρ_N	7.89	7.10					−2.5
	(8.18)	(7.43)					
	0.248						
	(0.258)						
p-$PhNO_2$ **8d**	7.89	7.12					−2.1
	(8.06)	(7.43)					
p-PhOMe **8e**	7.95	7.12					+3.9
3-Py **8f**	7.89	7.11					−3.7
Et **8g**	8.01	7.20			1.75	1.74	
	(8.21)	(7.42)				(2.0)	
H **8h**	7.86	6.88			3.53	3.76	−13.3
p-$PhNO_2$ **7d**	9.82	9.11	4.01	3.54			−3.5
	(9.90)		(4.35)				
mean	8.18	7.11					
	(8.52)	(7.42)					

[a] Measured in H_2O. [b] Measured in toluene.

Of the eight free radicals prepared in this study (see Table 2), one was an oil (**8g**, R = C_2H_5), whilst one was unstable (**8h**, R = H), but six were stable solids, the crystal structures of which were determined. As an example, the molecular structure of **8d** is displayed in Figure 1.

Table 2. Selected synthetic and conformational parameters in the solid state.

R	Yield [%]	M.p. [°C]	d_{N0} [Å]	⩛NCN [°]	α[a] [°]	β[b] [°]	Descriptor
Me **8a**	56	104	1.296	121.4	+6.7		
Ph **8c**	64	139	1.293	121.2	+12.5	−69.6	MP
p-PhNO$_2$ **8d**	47	191	1.283	122.2	+14.7	+56.7	PP
p-PhOMe **8e**[c]	58	116	1.288	120.6	+0.4	+64.7	PP
			1.287	120.7	−4.9	−61.6	MM
			1.286	119.5	−17.5	−54.8	MM
3-Py **8f**	81	151	1.289	121.2	+17.9	−64.8	MP
Et **8g**	35	liq.					
H **8h**	43	123					
p-PhNO$_2$[d] **7d**	93[e]	121	1.278	124.2	−11.6		
mean[f]	–	–	1.287(8)	121.4(7)	10.8(3.5)	62.0(7)	
mean[g]			1.281(10)	108.3(1.2)	25(4)	27.5(8.5)	

[a] N1-C2-C4-N2 dihedral angle. [b] Angle between the NCN fragment and the aromatic plane of the substituent. [c] Three independent molecules in the cell. [d] Imino nitroxide. [e] From the corresponding nitronyl nitroxide. [f] Absolute value. [g] For the imidazolinyl analogues.[18]

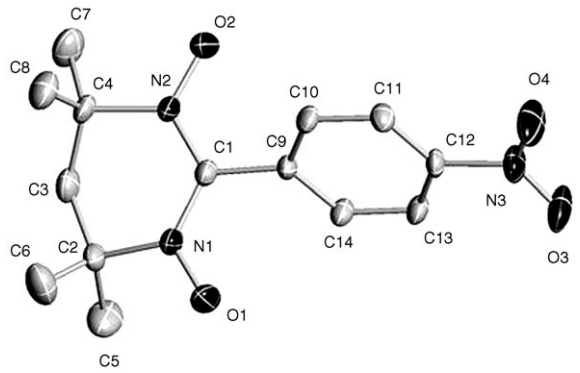


Figure 1. Molecular structure of **8d** showing the labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

In the solid state, a twisted flattened chair conformation in the pyrimidyl ring is observed in all compounds. Although all the compounds crystallize in centrosymmetric space groups, the crystals are racemates because of the chiral conformations of the molecules. As observed for the five-membered analogues,[18] chirality arises from a twisting of the pyrimidinyl ring, which can be gauged by the N1-C2-C4-N2 torsion angle (Table 2, α). For the aromatic substituted nitroxides, the conformation was also analyzed by taking the mean angle between the N1-C1-N2 plane and the aromatic plane into account (Table 2, β). Note that the signs of α and β reported in Table 2 refer to one enantiomer and are reversed for the other one; importantly, however, the relative signs of α and β for each compound determine the descriptors MP or PM and PP or MM, which correspond to a *pseudo-anti*, globular, and to a *pseudo-eclipsed*, planar conformation, respectively. Most of the radicals exhibit the *pseudo-eclipsed* conformation, as also observed for the imidazolinyl analogues.[18]

One observes that the α values are weaker than those in the imidazolinyl nitroxides, while the β values are much larger. This is easily understandable in the former case because the steric demand of the *gem*-dimethyl groups is better accommodated in a six-membered ring than in a five-membered ring, where they are located on adjacent carbons. In contrast, a larger β angle is the result of steric interaction between the oxyl oxygen atoms and the *ortho* hydrogen atoms of the aromatic ring. Note that the larger N(1)−C(1)−N(2) angle (≈120° vs. ≈110°) is the main cause of steric congestion in aromatic substituted pyrimidinyl nitroxides. Close examination of models shows that β angles of ca 30° in a imidazolinyl ring and 60° in a pyrimidyl ring result in a similar O···H(phenyl) distance of about 2.6 Å, close to the sum of the van der Waals radii (2.55 Å).[19]

In the solid state, the magnetic data point to Curie behavior down to low temperatures ($\chi T \approx 0.375\ cm^3\,K\,mol^{-1}$). Only at very low temperatures is a departure from this ideal behavior observed, modeled with negative Weiss parameters (Table 1, last entry), except in the case of **8f** (R = *p*-PhOMe), for which the Weiss constant is positive. Therefore, these new nitronyl nitroxides have magnetic properties similar to those of most organic free radicals, in which intermolecular interactions are weak and predominantly antiferromagnetic. No attempt was made to correlate the positive value of θ observed for **8f** with structural parameters since it has been shown that it would be highly speculative;[20] in that case, the presence of three independent molecules in the cell would make such a study even more complicated.

A preliminary investigation of the coordination properties of these free radicals showed that they behave as imino imidazolinyl analogues rather than as nitronyl nitroxides, in giving discrete complexes rather than 1D structures. Trinuclear complex **19** (Figure 2), in which—as an exception—ligand **8d** was characterized as bridging, was obtained from **8d** and [Cu(hfac)$_2$] in heptane under the experimental conditions described for imidazolinyl nitronyl nitroxides. However, **19** is also a discrete species in which each bidentate radical ligand is equatorially coordinated to a terminal pentacoordinated trigonal bipyramidal metal ion and axially to a central octahedral one. Salient features of this structure reflect the steric crowding of the oxyl coordination sites: the axial bond to the central metal center is long (2.476(6) Å) and the β angle between the phenyl ring and the bis-oxyl

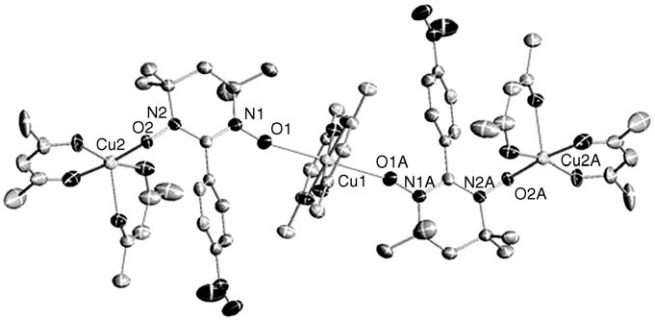


Figure 2. Molecular structure of **19** [((Cu(hfac)$_2$)$_3$·(**8d**)$_2$]. F and H atoms are not represented. Thermal ellipsoids are drawn at the 30% probability level.

fragment is also large (55°). In this respect, the structure is similar to that obtained with the phenyl-substituted imidazolinyl imino nitroxide, in which coordination of the imino nitrogen results in large steric constraints and precludes formation of an extended complex.[21] The magnetic properties of this complex are straightforward, since the equatorial ligation of the ligands to terminal metal ions results in spin pairing and the magnetic behavior of **19** is that of an isolated Cu^{II} center ($S = {}^1/_2$).

Conclusion

A reliable route to 2,2,4,4-substituted pentane derivatives, such as 2,4-dimethyl-2,4-dinitropentane and 2,4-diamino-2,4-dimethylpentane, precursors of pyrimidyl nitronyl and imino nitroxides, has been established. The synthesis of the pyrimidyl nucleus is more delicate than that of the imidazolinyl one, because condensation of these precursors with aldehydes is accompanied by side reactions. Moreover, oxidation of the diamagnetic precursors into nitroxides is also delicate: hexahydropyrimidines are overoxidized to open nitro derivatives, but, as also observed for the imidazolinyl analogues, the bis(hydroxylamine) route is more attractive, affording a series of pyrimidyl nitroxides in fairly good yield.

Most of the properties of these new free radicals are similar to those of the imidazolinyl analogues, except for the greater steric congestion of the oxyl groups. Indeed, a preliminary study of the coordination properties of these pyrimidyl nitronyl nitroxides showed that they do not function as bridging ligands except with [Cu(hfac)$_2$]. In that case a discrete complex was obtained, which suggests that these free radicals may, like imino imidazolinyl nitroxides, preferably function as monodentate terminal ligands. A thorough study of their behavior toward metal ions is underway.

Experimental Section

General procedures: Solvents were purified by standard literature methods. Reagents were used as received from Aldrich, except for 3-chloroperoxybenzoic acid (*m*CPBA), which was purified by washing with phosphate buffer (pH 7.5), dissolution in CH_2Cl_2, drying over Na_2SO_4, and concentration to dryness. ESR spectra were recorded in dilute solution and at ambient temperature with a Bruker EMX spectrometer operating at X-band frequency. ^{1}H and ^{13}C NMR spectra were determined at ambient temperature with a Bruker AC 200 (with the deuterated solvent as the lock and tetramethylsilane as the internal reference). Magnetic susceptibility data were recorded with a Quantum Design SQUID magnetometer operating at a field of 0.5 T. The mass spectra were acquired on a LCQ-ion trap (Thermofinnigan, San Jose, CA, USA), fitted with an electrospray source. Elemental analyses were determined by the CNRS Service Central d'Analyse Département Analyse Elémentaire. The UV/Vis spectra were obtained with a HP 8453 single-beam spectrometer. The X-ray crystal data were collected at room temperature on a Bruker Smart 1000 diffractometer (graphite-monochromated Mo Kα radiation; λ = 0.71073 Å) with crystals of approximate dimensions 0.15×0.15×0.15 mm. The structures were solved by direct methods with the aid of the SHELXS-97 program.[22] The H atoms were assigned with common isotropic displacement factors and were included in the final refinement by use of geometrical restraints.

CCDC-294866–CCDC-294884 contain the supplementary crystallographic data for this paper (compounds **4**, **5b**, **7d**, **8a**, **8d**, **8e**, **8f**, **9a**, **10**, **11**, **12**, **13**, **14a**, **14d**, **15**, **16a**, **16b**, **18c**, **19**, respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4-Amino-2,4-dimethylpentan-2-ol (4): 4-Amino-4-methylpentan-2-one (**3**) (10.4 g, 0.09 mol, freshly regenerated from 4-amino-4-methylpentan-2-one hydrogen oxalate (20 g) and 5 N NaOH (200 mL)) in diethyl ether (100 mL) was added dropwise to methylmagnesium iodide (0.4 mol) in dry diethyl ether (300 mL). When the addition was complete, the mixture was heated at reflux for 90 min and cooled in a ice bath, and water (30 mL) was then carefully added. The diethyl ether layer was discarded and the precipitate was extracted with CH_2Cl_2 over 28 h in a Soxhlet apparatus. Concentration of the solvent afforded white crystals of the hydroiodide (18.6 g, 78%). M.p. 139–140 °C; ^{1}H NMR (200 MHz, 20 °C, $CDCl_3$): δ = 1.44 (s, 6H; CH_3), 1.63 (s, 6H; CH_3), 1.99 (s, 2H; CH_2), 3.43 (brs, 3H; NH, OH) ppm; ^{13}C NMR (200 MHz, 20 °C, $CDCl_3$): δ = 32.45 (CH_3), 33.18 (CH_3), 51.55 (CH_2), 70.15 (C) ppm; elemental analysis (%) calcd for $C_7H_{18}NOI$: C 32.45, H 7.00, N 5.41; found: C 32.58, H 7.12, N 5.58.

NaOH pellets (40 g) were carefully added to a solution of the hydroiodide (10 g, 38.5 mmol) in water (100 mL), cooled in an ice bath. Extraction with diethyl ether gave, after conventional workup, **4** as a colorless liquid (5.0 g, 98%). M.p. −14±2 °C; ^{1}H NMR (200 MHz, 20 °C, $CDCl_3$): δ = 1.23 (s, 6H; CH_3), 1.24 (s, 6H; CH_3), 1.55 (s, 2H; CH_2), 3.12 (brs, 3H; NH_2, OH) ppm.

2-Acetamido-4-amino-2,4-dimethylpentane (5a; R = CH_3): Amino alcohol **4** (2 g, 15 mmol) was added dropwise to an ice-cooled mixture of acetonitrile (5 mL) and sulfuric acid (96%, 5 mL). Stirring was continued at room temperature for 2 h. Then, with cooling, NaOH (10 M, 30 mL) was carefully added and the solution was extracted with diethyl ether. After drying and concentration, **5a** was obtained as an oil (2.93 g, 95%), which crystallized slowly at room temperature. M.p. 28–32 °C); ^{1}H NMR (200 MHz, 20 °C, $CDCl_3$): δ = 1.21 (s, 6H; CH_3), 1.44 (s, 6H; CH_3), 1.49 (s, 2H; CH_2), 1.85 (brs, 3H) ppm. The phenyl thiourea was obtained by mixing equimolar quantities of **5a** and phenyl isothiocyanate in diethyl ether (77%). M.p. 168 °C; elemental analysis (%) calcd for $C_{16}H_{25}N_3OS$: C 62.51, H 8.2, N 13.67; found: C 62.75, H 8.19, N 13.73.

2-Acetamido-2,4-dimethyl-4-nitropentane (9a; R = CH_3): *m*-Chloroperoxybenzoic acid (2.1 g, 12 mmol) in diethyl ether (10 mL) was added to **5a** (R = CH_3; 500 mg, 3.3 mmol) in diethyl ether (50 mL). The solution turned yellow, then blue and on standing became colorless. Stirring was continued for 3 h and the solution was washed with NaOH (0.5 N, 2× 50 mL) and H_2O. After drying (Na_2SO_4) and evaporation of the solvent the crude solid was chromatographed (Al_2O_3, diethyl ether) to yield the nitroacetamido compound **9a** (478 mg, 73%). M.p. 74 °C; ^{1}H NMR (200 MHz, 20 °C, $CDCl_3$): δ = 1.26 (s, 6H; CH_3), 1.55 (s, 2H; CH_2), 1.61 (s, 6H; CH_3), 1.91 (s, 3H; CH_3) ppm; elemental analysis (%) calcd for $C_9H_{18}N_2O_3$: C 53.45, H 8.97, N 13.85; found: C 53.29, H 9.01, N 13.92.

2-Amino-2,4-dimethyl-4-trichloroacetamidopentane (5b; R = CCl_3): Sulfuric acid (96%, 50 mL) was added dropwise to an ice-cooled mixture of trichloroacetonitrile (50 mL) and 4-amino-2,4-dimethylpentan-2-ol (**4**, 5.2 g, 0.04 mol). The reaction mixture was brought to ambient temperature and stirred for 14 h. The viscous yellow oil was cooled with an ice-bath during dropwise addition of water (100 mL) and the solution was then extracted with diethyl ether (2×200 mL) to remove trichloroacetamide. The acid aqueous phase was cooled in ice and basified by careful addition of sodium hydroxide (75 g NaOH in 250 mL H_2O). The solution was extracted with diethyl ether (4×100 mL) and the ethereal layer was filtered through anhydrous Na_2SO_4. 4-Amino-2,4-dimethyl-2-trichloroacetamidopentane (**5b**; R = CCl_3) was obtained in 70% yield (7.6 g, 0.028 mol); ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 1.24 (s, 6H; CH_3), 1.49 (s, 6H; CH_3), 1.60 (s, 2H; CH_2) ppm.

Recrystallization from *n*-hexane gave an analytical sample. M.p. 92–94°C; elemental analysis (%) calcd for $C_9H_{17}N_2OCl_3$: C 39.20, H 6.17, N 10.16, Cl 38.66; found: C 39.46, H 6.39, N 10.16, Cl 38.37. Single crystals suitable for a X-ray diffraction analysis were obtained.

2,4-Dimethyl-4-nitro-2-trichloroacetamidopentane (9b): *m*-Chloroperoxybenzoic acid (13.5 g, 0.079 mol) was added portionwise to 4-amino-2,4-dimethyl-2-trichloroacetamidopentane (**5b**; R = CCl_3; 5.4 g, 0.019 mol) in CH_2Cl_2 (100 mL). The solution was heated at reflux for 2 h and, after cooling, washed with a basic solution (NaOH, 3N, 3×50 mL). Filtration through anhydrous Na_2SO_4 and concentration gave 2,4-dimethyl-4-nitro-2-trichloroacetamidopentane (**9b**) as a yellow oil that slowly crystallized on standing (5.0 g, 0.016 mol, 84%); ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 1.34 (s, 6H; CH_3), 1.62 (s, 6H; CH_3), 2.69 (s, 2H; CH_2) ppm.

Recrystallization from *n*-hexane gave an analytical sample. M.p. 95–96°C; elemental analysis (%) calcd for $C_9H_{17}N_2O_3Cl_3$: C 35.35, H 4.91, N 9.17; found: C 35.54, H 4.94, N 8.88.

4,4,6,6-Tetramethyl-1,3-diazacyclohexan-2-one (10): 4-Amino-2,4-dimethyl-2-trichloroacetamidopentane (**5b**, 0.20 g, 0.73 mmol) was heated at reflux for 5 h in a solution of $Ba(OH)_2$ (3 g) in H_2O (40 mL). The suspension was filtered, extracted with dichloromethane and then dried over anhydrous Na_2SO_4. Removal of the solvent gave an off-white solid of cyclic urethane (0.07 g, 61%). An analytical sample was obtained by crystallization from Et_2O/hexane: M.p. 200°C (dec.) (lit.[13] 219–220.5°C, with onset of decomposition at approximately 170°C); ^{1}H NMR (200 MHz, 20°C, DMSO-d_6): δ = 1.28 (s, 12H; CH_3), 1.71 (s, 2H; CH_2) ppm; elemental analysis (%) calcd for $C_8H_{16}N_2O$: C 61.54, H 10.26, N 17.95; found: C 61.73, H 9.98, N 18.03. The structure was confirmed by X-ray diffraction.

4-Amino-2,4-dimethyl-2-nitropentane (12): 2,4-Dimethyl-4-nitro-2-trichloroacetamidopentane (**9b**, 4.60 g, 0.0143 mol) was added to a solution of sodium hydroxide (10 g) in H_2O (100 mL); the reaction was conducted with use of a Dean–Stark apparatus to remove $CHCl_3$, with heating at 80–85°C for 14 h. The solution was combined with the residues from the Dean–Stark apparatus and extracted with diethyl ether (2×200 mL). The solvent was removed under vacuum to give a yellow semi-solid, consisting of a mixture of 4-amino-2,4-dimethyl-2-nitropentane (**12**), isonitrile **11** (10–15%), and unreacted starting material (<10%). This mixture was heated at reflux in acidic medium (HCl, 2N, 180 mL) for 2 h. The solution was then extracted with diethyl ether (2×100 mL) to remove unreacted **9b** and basified with sodium hydroxide (22 g) in H_2O (200 mL). The basic solution was extracted with diethyl ether (4×200 mL) and dried (Na_2SO_4), and after evaporation one obtained **12** as a pale yellow liquid (1.60 g, 0.0106 mol, 70%); ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 1.11 (s, 6H; CH_3), 1.63 (s, 6H; CH_3), 2.13(s, 2H; CH_2) ppm.

An analytical sample of the picrate was obtained by mixing **12** (80 mg, 0.5 mmol) and picric acid (115 mg, 0.5 mmol) in ethanol. One obtained the salt (138 mg, 73%). M.p. 203°C (dec.); elemental analysis (%) calcd for $C_{13}H_{19}N_5O_9$: C 40.10, H 4.88, N 17.99; found: C 40.17, H 5.02, N 17.87.

When the hydrolysis reaction was conducted with a regular condenser, isonitrile **11** sublimed and could be obtained directly as single crystals by scraping the condenser (85 mg, 3%). M.p. 73°C; ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 1.38 (t, 6H; CH_3), 1.70 (s, 6H; CH_3), 2.36 (t, 2H; CH_2) ppm. The structure was determined by X-ray diffraction.

2,4-Diamino-2,4-dimethylpentane (13): Powdered zinc (3.27 g, 5 mmol) was added portionwise, with vigorous stirring, to **12** (1.0 g, 0.0063 mol) in a mixture of water (15 mL) and acetic acid (15 mL). An exothermic reaction was observed during the addition. The gray suspension was heated at reflux at 100°C for 4 h and was then cooled to ambient temperature. Water (30 mL) was then added, followed by diethyl ether and by the careful addition of sodium hydroxide pellets (20 g). A gray emulsion was observed during the basification but during the final stages the aqueous and ethereal phases were well separated. The aqueous layer was re-extracted with ether (4×100 mL) and the combined organic solutions were carefully concentrated under vacuum at ambient temperature, giving 2,4-diamino-2,4-dimethylpentane (**13**) as a colorless liquid (0.70 g, 86%, 0.0054 mol). ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 0.68 (s, 12H; CH_3), 0.85 (s, 2H; CH_2) ppm.

A crystalline picrate was obtained as described for **12** (68%). M.p. >200°C (dec.); elemental analysis (%) calcd for $C_{19}H_{24}N_8O_{14}$: C 38.78, H 4.08, N 19.08; found: C 39.00, H 4.19, N 18.76. Single crystals suitable for a X-ray diffraction analysis were obtained.

Hexahydropyrimidines 14: These were obtained by condensation of diamine **13** with aldehydes in $CHCl_3$. As an example, **14c** was prepared as follows: diamine **13** (494 mg, 3.8 mmol), benzaldehyde (420 mg, 3.9 mmol), and *p*-toluenesulfonic acid (20 mg) were mixed in $CHCl_3$ (20 mL) and the solution was stirred at room temperature overnight. The solvent was then evaporated under vacuum and the semi-solid residue was chromatographed on alumina (Et_2O/EtOAc). Compound **14d** was obtained as a white solid (530 mg, 65%). M.p. 124–126°C; ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 0.85 (s, 6H; CH_3), 1.13 (s, 6H; CH_3), 1.32 (s, 2H; CH_2), 4.96 (s, 1H; CH), 7.48–7.52 (m, 3H; aromatic), 7.70–7.75 (m, 2H; aromatic) ppm; elemental analysis (%) calcd for $C_{14}H_{22}N_2$: C 77.06, H 10.10, N 12.85; found: C 76.93, H 9.97, N 13.05.

Compound **14a** (76%) was obtained as an oil, from which a crystalline picrate was prepared. M.p. 183°C; elemental analysis (%) calcd for $C_{15}H_{23}N_5O_7$: C 46.75, H 5.97, N 18.18; found: C 47.01, H 5.87, N 17.97.

2,4-Dimethyl-2,4-dinitropentane (15): *m*-Chloroperoxybenzoic acid (25 g, 0.15 mol) was added portionwise to 4-amino-2,4-dimethyl-2-nitropentane (**12**, 6 g, 0.0375 mol) in dichloromethane (400 mL). The solution was heated at reflux for 2 h and was then washed with basic solution (NaOH, 3N, 3×100 mL); drying (Na_2SO_4) and concentration under vacuum gave a pale yellow crystalline solid. The crude product was purified by chromatography on alumina with hexane/dichloromethane (2:1) as eluent. 2,4-Dimethyl-2,4-dinitropentane (**15**) was obtained as a colorless crystalline solid in 84% yield (6 g). M.p. 79°C, 81–82°C; ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 1.50 (s, 12H; CH_3), 2.85 (s, 2H; CH_2) ppm; ^{13}C NMR (200 MHz, 20°C, $CDCl_3$): δ = 25.29 (CH_3), 47.49 (CH_2) 86.18 (C) ppm; IR (KBr disk): $\tilde{\nu}$ = 1540(s; NO_2), 2968(m; CH) cm^{-1}; elemental analysis (%) calcd for $C_7H_{14}N_2O_4$: C 44.21, H 7.37, N 14.74; found: C 44.17, H 7.45, N 14.65. Single crystals were grown from *n*-hexane and an X-ray diffraction study was performed.

Reduction of 2,4-dimethyl-2,4-dinitropentane with $LiAlH_4$: Lithium aluminium hydride (0.40 g, 10.5 mmol) was added portionwise to a solution of 2,4-dimethyl-2,4-dinitropentane **15** (0.20 g, 1.05 mmol) in dry THF (20 mL). Once the addition was complete, the suspension was heated at a gentle reflux for 1 hour. After the mixture had cooled back to ambient temperature, cold water was added carefully (10 mL). Diethyl ether (50 mL) was added to aid extraction of the organic phase. After drying over Na_2SO_4, the mixture was separated by chromatography on alumina ($CHCl_3$/EtOAc). Two products were identified:

3,3,5,5-Tetramethyl-1,2-diazacyclopentene *N,N'*-dioxide (16b): Yield 28%; m.p. 228–231 (dec.); ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 1.55 (s, 12H; CH_3), 2.31 (s, 2H; CH_2) ppm; elemental analysis (%)calcd for $C_7H_{14}N_2O_2$: C 53.16, H 8.86, N 17.72; found C 53.17, H 8.65, N 17.69.

3,3,5,5-Tetramethyl-1,2-diazacyclopentene N-oxide (16b): Yield 62%; m.p. 78°C; ^{1}H NMR (200 MHz, 20°C, $CDCl_3$): δ = 1.35 (s, 6H; CH_3), 1.52 (s, 6H; CH_3), 2.09 (s, 2H; CH_2) ppm; elemental analysis (%) calcd for $C_7H_{14}N_2O$: C 59.16, H 9.87, N 19.71; found: C 59.27, H 9.95, N 19.63.

In both of the above cases crystals were grown from ethyl acetate solutions and X-ray diffraction studies were performed.

2,4-Bis(hydroxylamino)-2,4-dimethylpentane (17): Dinitro compound **15** (5 g, 26 mmol) was dissolved in THF (100 mL). Zn powder (3.5 g) was added to this solution and the mixture was cooled to ca 10 °C in a ice bath. NH_4Cl (10 g) in H_2O (40 mL) was then added dropwise, with stirring, at such a rate that the temperature did not exceeded 15 °C. The reaction mixture was stirred 3 h more at room temperature and filtered, the THF was evaporated under vacuum, and the resulting semi-solid compound was extracted with CH_2Cl_2 (3×100 mL). The organic phase was dried over Na_2SO_4 and concentrated to give a white powder (3.2 g, 76 %). M.p. 108–117 °C; ^{1}H NMR (200 MHz, 20 °C, $CDCl_3$): δ = 1.16 (s, 12H; CH_3), 1.52 (s, 2H; CH_2) ppm. Indirect characterization of **17** was provided by the *N*,*N*′-dihydroxyhexahydropyrimidine derivatives.

***N*,*N*′-Dihydroxy-hexahydropyrimidines 18**: Crude bis(hydroxylamine) **17** (0.40 g, 2.5 mmol) and *p*-toluenesulfonic acid (PTSA; 0.1 g, 0.53 mmol) were dissolved in chloroform (20 mL), and benzaldehyde (0.27 g, 2.5 mmol) was added in five portions over a period of 5 h at reflux and with stirring. The pale yellow solution was cooled to room temperature, diluted with diethyl ether (100 mL), washed with saturated Na_2CO_3 (3× 20 mL), and then dried over Na_2SO_4. Concentration gave a crude yellow liquid (600 mg) that was purified by chromatography on silica (Et_2O/petroleum ether 1:1), giving the condensed bis(hydroxylamine) **18c** as a white, powder-like solid (473 mg, 77 %). M.p. 83 °C; ^{1}H NMR (200 MHz, 20 °C, $CDCl_3$): δ = 1.12 (s, 6H; CH_3), 1.17 (s, 6H; CH_3), 1.52 (s, 2H; CH_2), 4.58 (s, 1H; CH); elemental analysis (%) calcd for $C_{14}H_{22}N_2O_2$: C 67.23, H 8.80, N 11.21, O 12.78; found: C 67.36, H 8.72, N 11.28. Crystals suitable for X-ray analysis were obtained by slow evaporation from Et_2O/CH_2Cl_2.

Compounds **18a** (73 %, M.p. 89 °C), **18d** (83 %, M.p. 142 °C), **18e** (75 %, M.p. 177 °C), **18f** (79 %, M.p. 178 °C), **18g** (67 %, M.p. 108 °C), and **18h** (87 %, M.p. 125 °C) were prepared similarly.

If the aldehyde was added in one portion, a large proportion of the product was a bis-nitrone, arising from the addition of two molecules of aldehyde to one molecule of bis(hydroxylamine). Portionwise addition of the aldehyde minimizes this unwanted byproduct.

Nitronyl Nitroxides (8)

Alkyl-substituted: Solid $NaIO_4$ (230 mg, 2.1 mmol) was added to **18a** (100 mg, O.53 mmol) in a ice-cooled mixture of CH_2Cl_2 (20 mL) and saturated $NaHCO_3$ (20 mL). Stirring was continued for 30 minutes, and the deeply colored organic phase was dried over Na_2SO_4 and evaporated under vacuum. The solid was chromatographed on Al_2O_3 (CH_2Cl_2/diethyl ether) to give **8a** (55 mg, 56 %). M.p. 104 °C; elemental analysis (%) calcd for $C_9H_{17}N_2O_2$: C 58.38, H 9.19, N 15.14, O 17.30; found: C 58.24, H 9.23, N 15.08.

Aromatic-substituted: Dropwise addition of mCPBA (140 mg, 0.81 mmol) in CH_2Cl_2 (10 mL) to **18c** (100 mg, 0.4 mmol) in a mixture of CH_2Cl_2 (20 mL) and saturated $NaHCO_3$ (20 mL) gave a dark blue solution. After a further 15 minutes of stirring at room temperature the organic phase was washed again with saturated Na_2CO_3 (2×20 mL) and then dried over Na_2SO_4. Concentration and chromatography on alumina (diethyl ether) gave nitroxide **8c** as a blue solid (64 %). M.p. 139–140 °C; elemental analysis (%) calcd for $C_{14}H_{19}N_2O_2$: C 68.02, H 7.69, N 11.34; found: C 67.90, H 7.84, N 11.09.

All the other pyrimidyl nitroxides—**8g**/**8h** and **8d**–**f**—were prepared by these two procedures. Their properties are reported in Table 1 and Table 2; satisfactory analyses were obtained and their crystal structures (except for **8g**/**8h**) can be found in the Supporting Information.

4,4,6,6-Tetramethyl-2-(*p*-nitrophenyl)pyrimidinyl-1-oxyl (7d): Diluted HCl (0.1 N) was added dropwise to a solution of $NaNO_2$ (4 g) in H_2O (50 mL). The resulting NO gas was bubbled through a solution of nitronyl nitroxide **8d** (100 mg, 0.34 mmol) in CH_2Cl_2 (30 mL) until TLC showed the disappearance of the purple starting material. The solution was dried over Na_2SO_4 and concentrated under vacuum. The resulting solid was chromatographed on Al_2O_3 (diethyl ether/petroleum ether 1:1) to give imino nitroxide **7d** (90 mg, 96 %). M.p. 121 °C; elemental analysis (%) calcd for $C_{14}H_{18}N_3O_3$: C 60.87, H 6.52, N 15.22, O 17.40; found: C 60.69, H 6.61, N 15.29.

Tris[copper(II)-bis(hexafluoroacetylacetonato)]-bis[(μ-1,3)-2-*p*-nitrophenyl-4,4,6,6-pyrimidinyl-3-oxide-1-oxyl] (19): Anhydrous $[Cu(hfac)_2]$ (456 mg, 1 mmol) was dissolved in *n*-heptane and the mixture was warmed to 50 °C. Solid **8d** (266 mg, 1 mmol) was added to this solution and stirring was continued for 15 min at 50 °C. The blue solution was filtered and allowed to stand in the dark for two days. The dark green crystals that formed (443 mg, 67 %) were collected, washed with cold heptane (10 mL), and dried. M.p. 124–125 °C; elemental analysis (%) calcd for $C_{58}H_{42}F_{36}N_6O_{20}Cu_3$: C 34.51, H 2.08, F 33.92, N 4.17, O 15.87, Cu 9.45; found: C 34.38, H 1.97, N 4.23, Cu 9.61. The structure was confirmed by X-ray diffraction.

Acknowledgements

P. B. thanks the Région Rhône-Alpes-Direction de l'Economie, du Tourisme, de la Recherche et de la Technologie for financial support.

[1] For reviews, see: a) V. I. Ovcharenko, R. Z. Sagdeev, *Uspekhi Khimii* **1999**, *68*, 381–400; *Russ. Chem. Rev.* **1999**, *68*, 345–363; b) *Magnetism: A Supramolecular Function* (Ed.: O. Kahn), Kluwer Academic, Dordrecht, **1996**; c) *Mol. Cryst. Liq. Cryst.* (Eds.: K. Itoh, J. S. Miller, T. Takui), **1997**, *305/306*, 1–586/1—520; d) *Mol. Cryst. Liq. Cryst.* (Ed.: O. Kahn), **1999**, *334/335*, 1–712/1–706; e) *Magnetic Properties of Organic Materials* (Ed.: P. M. Lahti), Marcel Dekker, New York, **1999**; f) *Molecular Magnetism* (Eds.: K. Itoh, M. Kinoshita), Gordon and Breach, Amsterdam, **2000**; g) D. B. Amabilino, J. Veciana in *Magnetism: Molecules to Materials II*, (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinhein, **2000**, p. 1; h) P. Rey, V. I. Ovcharenko in *Magnetism: Molecules to Materials IV*, (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinhein, **2003**, p. 41.

[2] a) M. Takahashi, P. Turek, Y. Nakazawa, M. Tamura, K. Nozowa, D. Shiomi, M. Ishikawa, M. Kinoshita, *Phys. Rev. Lett.* **1991**, *67*, 746–748; b) K. Awaga, Y. Maruyama, *J. Chem. Phys.* **1989**, *91*, 2743–2747; c) J. Cirujeda, M. Mas, E. Molins, F. Lanfranc de Panthou, J. Laugier, J. Park, C. Paulsen, P. Rey, C. Rovira, J. Veciana, *J. Chem. Soc. Chem. Commun.* **1995**, 709–710; d) J. A. Crayston, J. N. Devine, J. C. Walton, *Tetrahedron* **2000**, *56*, 7829–7857.

[3] a) A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, *Acc. Chem. Res.* **1989**, *22*, 392–398; b) A. Caneschi, D. Gatteschi, P. Rey, *Progr. Inorg. Chem.* **1991**, *39*, 331–429.

[4] Molecular magnetic complexes involving other organic spin carriers: a) K. Inoue, H. Iwamura, *J. Am. Chem. Soc.* **1994**, *116*, 3173–3174; b) K. Inoue, T. Hayamizu, H. Iwamura, D. Hashizume, Y. Ohashi, *J. Am. Chem. Soc.* **1996**, *118*, 1803–1804; c) R. G. Hicks, M. T. Lemaire, L. K. Thompson, T. M. Barclay, *J. Am. Chem. Soc.* **2000**, *122*, 8077–8078; d) J. M. Rawson, G. D. McManus, *Coord. Chem. Rev.* **1999**, *189*, 135–168; e) W. Fujita, K. Awaga, *J. Am. Chem. Soc.* **2001**, *123*, 3601–3602.

[5] a) J. H. Osiecki, E. F. Ullman, *J. Am. Chem. Soc.* **1968**, *90*, 1078–1079; b) E. F. Ullman, L. Call, J. H. Osiecki, *J. Org. Chem.* **1970**, *35*, 3623–3631; c) E. F. Ullman, J. H. Osiecki, D. G. B. Boocock, R. Darcy, *J. Am. Chem. Soc.* **1972**, *94*, 7049–7059.

[6] C. Hirel, K. E. Vostrikova, V. I. Ovcharenko, J. Pécaut, P. Rey, *Chem. Eur. J.* **2001**, *7*, 2007–2014.

[7] a) A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey, R. Sessoli, *Inorg. Chem.* **1991**, *30*, 3162–3166; b) D. Luneau, G. Rissoan, P. Rey, A. Grand, A. Caneschi, D. Gatteschi, J. Laugier, *Inorg. Chem.* **1993**, *32*, 5616–5622; c) F. Lanfranc de Panthou, E. Belorizky, R. Calemzuk, D. Luneau, C. Marcenat, E. Ressouche, P. Turek, P. Rey, *J. Am. Chem. Soc.* **1995**, *117*, 11247–11253; d) K. Fegy, D. Luneau, T. Holm, C. Paulsen, P. Rey, *Angew. Chem.* **1998**, *110*, 1331–1335; *Angew. Chem. Int. Ed.* **1998**, *37*, 1270–1273.

[8] C. Hirel, J. Pécaut, S. Choua, Ph. Turek, D. B. Amabilino, J. Veciana, P. Rey, *Eur. J. Org. Chem.* **2005**, 348–359.

[9] S. N. Ghriofa, R. Darcy, M. Conlon, *J. Chem. Soc. Perkin Trans. 1* **1977**, 651–653.
[10] P. Brough, R. Chiarelli, J. Pécaut, A. Rassat, P. Rey, *Chem. Commun.* **2003**, 2722–2723.
[11] D. J. Brown in *The Chemistry of Heterocyclic Compounds: the Pyrimidines, vol. 16*, Interscience, the Netherlands, **1962**, chapt. II.
[12] T. W. Greene, P. G. M. Wuts in *Protective Groups in Organic Chemistry*, Wiley, New York, **1999**, pp. 550–556.
[13] C. A. Renner, F. D. Greene, *J. Org. Chem.* **1976**, *41*, 2813–2819.
[14] a) P. A. S. Smith in *The Chemistry of Open-Chain Organic Nitrogen Compounds, Vol. I*, W. A. Benjamin, Inc., New York, **1965**, pp. 46; b) P. A. S. Smith, N. Kalenda, *J. Org. Chem.* **1958**, *23*, 1599–1603.
[15] R. Sayre, *J. Am. Chem. Soc.* **1955**, ***77***, 6689–6690.
[16] "Supramolecular and Engineering of Synthetic Metallic Materials: Conductors and Magnets": P. Rey, D. Luneau, *Nato ASI Ser. Ser. C* **1999**, *518*, 145.
[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Kamaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Kaith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98, Gaussian, Inc.: Pittsburgh, PA, **1998**.
[18] M. Minguet, D. B. Amabilino, J. Cirujeda, K. Wurst, I. Mata, E. Molins, J. J. Novoa, J. Veciana, *Chem. Eur. J.* **2000**, *6*, 2350–2361.
[19] T. Steiner, W. Saenger, *J. Am. Chem. Soc.* **1993**, *115*, 4540–4547.
[20] a) M. Deumal, J. Cirujeda, J. Veciana, J. J. Novoa, *Chem. Eur. J.* **1999**, *5*, 1631–1642; b) D. B. Amabilino, J. Cirujeda, J. Veciana, *Philos. Trans. R. Soc. London Ser. A* **1999**, *357*, 2873–2877.
[21] D. Luneau, P. Rey, J. Laugier, P. Fries, A. Caneschi, D. Gatteschi, R. Sessoli, *J. Am. Chem. Soc.* **1991**, *113*, 1245–1251.
[22] G. M. Sheldrick, SHELXTL-Plus, Göttingen, Germany, **1994**.

Received: January 16, 2006
Published online: April 27, 2006

