Intramolecular mixed-valence state through silicon or germanium double bridges in rigid Bis(Tetrathiafulvalenes)

BIASO, Frédéric, et al.

Abstract
The synthesis and characterization of two ortho-dimethyltetrathiafulvalene (o-DMTTF)-based rigid dimers containing dimethylsilicon (Me(2)Si) or dimethylgermanium (Me(2)Ge) linkers are described. Single-crystal X-ray analysis reveals planar geometry for the central 1,4-disilicon or 1,4-digermanium six-membered rings. DFT calculations provide optimized conformations in agreement with the experimental ones, and also emphasize the role of the heteroatomic linkers in the conjugation between the two redox active units. Cyclic voltammetry measurements show sequential oxidation into radical cation, and then dication species. Solution EPR measurements on the radical-cation species indicate full delocalization of the unpaired electron over both electroactive TTF units, with an associated coupling of 0.42 G with twelve equivalent protons. DFT calculations afford fully planar geometry for the radical-cation species and confirm the experimental isotropic coupling constant. Single-crystal X-ray analyses of two charge-transfer compounds obtained upon chemical oxidation, formulated as [(Me(2)Si)(2)(o-DMTTF)(2)].1/2[TCNQ].1/2[TCNQF(4)] [...]
Intramolecular Mixed-Valence State Through Silicon or Germanium Double Bridges in Rigid Bis(Tetrathiafulvalenes)


Abstract: The synthesis and characterization of two ortho-dimethyltetraphiafulvalene (o-DMTTF)-based rigid dimers containing dimethylsilicon (Me₂Si) or dimethylgermanium (Me₂Ge) linkers are described. Single-crystal X-ray analysis reveals planar geometry for the central 1,4-disilicon or 1,4-digermanium six-membered rings. DFT calculations provide optimized conformations in agreement with the experimental ones, and also emphasize the role of the heteroatomic linkers in the conjugation between the two redox active units. Cyclic voltammetry measurements show sequential oxidation into radical cation, and then dication species. Solution EPR measurements on the radical-cation species indicate full delocalization of the unpaired electron over both electroactive TTF units, with an associated coupling of 0.42 G with twelve equivalent protons. DFT calculations afford fully planar geometry for the radical-cation species and confirm the experimental isotropic coupling constant. Single-crystal X-ray analyses of two charge-transfer compounds obtained upon chemical oxidation, formulated as [(Me₂Si)(o-

Keywords: conducting materials · EPR spectroscopy · main group elements · mixed-valent compounds · tetrathiafulvalenes

Introduction

The access to intramolecular mixed-valence states in a perfectly controlled manner is one of the main purposes of the efforts devoted to the synthesis of dimeric tetrathiafulvalenes (TTF),[1] because TTFs represent a class of precursors extensively studied in the quest for molecular conductors and superconductors.[2] In such multiredox compounds, the degree of electronic communication between the redox active units is governed by the magnitude of through-bond or through-space interactions, accounting for the occurrence and, ultimately, isolation, either in solution or solid state, of mixed-valence species. As a consequence, charge-transfer (CT) complexes or radical-cation salts derived from dimeric TTFs might exhibit unusual structures due to the enhancement of the dimensionality, with peculiar band-structure patterns and band fillings.[3] A straightforward strategy to link two TTF units in close vicinity relies on the utilization of heteroatom bridges, such as within the series of X(TTF)₂-type derivatives (X = S,[4] Se,[5] Te,[6] PPh,[6] SiMe₂,[6a] Hg[6b]).
Yet, single-crystal X-ray analyses of some of these compounds show that in the solid state the two TTF units are not coplanar, but are organized in a nearly perpendicular manner with respect to each other, thus completely hampering the possibility of extended conjugation.[4–7] In this respect, molecular rigidity has been achieved upon introduction of a second heteroatom bridge, within donors formulated as \( X_2 \) (TTF), in which two TTF units are linked either by two sulfur (\( X = S \))[6] or tellurium (\( X = Te \))[9] atoms, or, as described more recently, by two phenylphosphino groups (\( X = PPh \))[10] thus leading to the formation of a central six-membered ring.

\[ X_2 \text{(TTF)} \quad X = S, Te, PPh \]

Alternatively, two tetraselenafenulvalene (TSF) units have been connected through methylantimony groups to provide (MeSb)\(_2\) (TSF).[11] Nevertheless, within all the heteroatom-containing rigid dimeric bis(TTF) described so far, no clear evidence, such as EPR measurements, for the electron delocalization throughout both TTF units in the radical-cation species has been provided. Highly appealing heteroatom-based bridges consist of dialkylsilyl or dialkyldgermanium linkers. Indeed, the former has been successfully employed in the synthesis of rigid, doubly bridged metallocenes[12] with theoretical calculations, as well as on the preparation and properties of two crystalline conducting CT compounds of these new donors.

Results and Discussion

The synthesis of \((\text{Me}_2\text{E})_2(\text{o-DMTTF})\), \(E = \text{Si} \) (1) and Ge (2), is straightforward; that is, bis-lithiation of the ortho-dimethyltetraethiafulvalene (o-DMTTF) precursor followed by trapping the dianionic intermediate with \( \text{Me}_2\text{ECl}_2 \) in a one-pot procedure (Scheme 1).[13] The new donors were obtained as orange-yellow crystalline solids and were fully characterized.

Suitable single-crystals for X-ray analysis were successfully grown for both compounds. Even though they are not isostructural, their molecular conformation with respect to the planarity of the central six-membered ring is essentially the same; therefore, we discuss hereafter only the structure of the silicon compound 1.

![Scheme 1. Synthesis of (Me\(_2\text{Si}\))(o-DMTTF); (1) and (Me\(_2\text{Ge}\))(o-DMTTF); (2).](Image)

The most striking structural feature lies clearly in the full planarity of the central silicon-containing six-membered ring (Figure 1). This is in sharp contrast to the structures of Te-9 or P-[10] containing rigid TTF dimers, for which folding angles of 67.8° and 30.4°, respectively, for the central ring have been observed. Note also that various folding angles along the Si–Si hinge, leading to boat conformations, have been reported in the case of doubly silicon-bridged metallocenes.[12a,e,14] The overall geometry of 1 is bent within a chair-like conformation, mainly due to the folding along the S1–S2 hinges amounting to 20°. Bond lengths and angles are typical for a neutral TTF derivative, with the central C3–C4 double bond at 1.343(4) Å and the average of the central 15.3 Å. The planarity of the central ring might suggest some conjugation between the TTF moieties through the SiMe\(_2\) bridges, as pointed out within a series of bis(silicon)-bridged stilbene homologues, for which an orbital interaction between the SiMe\(_2\) o* orbital and the stilbene π* orbital has been evidenced, leading to a stabilization of the LUMO.[15] The same features are also present in the structure of the germanium compound 2 (Supporting Information). In order to estimate the extent of the communication between the symmetrical TTF units and to evidence the role of the SiMe\(_2\) and GeMe\(_2\) bridges, we performed theoretical calculations at the DFT level.[13] The optimized geometries are in good agreement with the experimental structures, reproducing the planarity of the central six-membered ring and the chair conformation of the molecule (Figure 2).

![Figure 1. ORTEP view of 1 (thermal ellipsoids set at 50% probability. H atoms omitted) (top) and side view of the molecule (bottom). Selected bond lengths [Å] and angles [°]: Si1–C1 1.870(3), Si1–C2* 1.869(3), C1–C2* 1.347(3), C3–C4 1.343(4), C1–Si1–C2 107.1(1). Folding angles [°]: Si1–Si1* 0.0(1), Si1–S2* 20.0(2), S3–S4 11.7(3). Symmetry operator for generating equivalent atoms (+): –x, 1–y, –z.](Image)
The analysis of the generated frontier orbitals is particularly interesting. First, an increase in degeneracy is observed at the HOMO level, thus providing a pair of π-type HOMOs, as an antisymmetric combination, and HOMO–1, as an symmetric combination, with an energy gap of 82 meV, indicative of a sizeable electronic communication between the TTF units. Secondly, the composition of the LUMO clearly evidences the role of the SiMe₂ bridge in the conjugation, as we observe favorable orbital overlaps between the SiMe₂ σ* orbitals and the vinylic π* orbitals (Figure 3).

Analogous results are obtained in the case of the germanium compound 2,[13] with a HOMO/HOMO–1 gap of 60 meV and the HOMO level at −4.631 eV, suggesting an increased electron-donating character relative to the silicon compound 1 (HOMO at −4.653 eV). Cyclic voltammetry measurements on both donors show sequential reversible oxidations to radical cations (1⁺ and 2⁺) and then to the corresponding dication species, with associated potential differences in between of 120 mV for 1 and 110 mV for 2 (Figure 4), thus demonstrating sizeable electronic communication between the TTF units. Note the more facile oxidation of the germanium compound (E₁ = 0.225 V) relative to that of silicon (E₁ = 0.255 V).

It is thus clear that the selective generation of the mixed-valence radical-cation species from both donors, upon one-electron oxidation, should be feasible either electrochemically, or by chemical oxidation. This prompted us to undertake a solution EPR study in order to emphasize the formation of the corresponding radical cations and, more importantly, to have an ultimate proof about the electron delocalization within the molecule. Both compounds were thus oxidized in CH₂Cl₂ by one equivalent of NOSbF₆ and their EPR spectra recorded.

The hyperfine structure observed after oxidation of (Me₂Si)₂(o-DMTTF)₂ (Figure 5) is clearly consistent with the central part of a spectrum exhibiting a coupling of 0.42 G with 12 magnetically equivalent protons.[16] Moreover, a single hyperfine coupling constant (Aiso = 1.2 MHz) is
detected on the $^1$H ENDOR spectrum. The hyperfine structure is thus due to the coupling with four methyl groups, the corresponding constant amounting to half the value previously measured on a mono-TTF derivative containing two Me groups in lateral positions. This clearly demonstrates that in $1^+$ the unpaired electron is delocalized over both TTF units. Note that the same EPR spectrum is observed when the oxidation is carried out electrochemically at the appropriate potential value, in situ in the EPR cavity with an electrolytic cell allowing us to work at a controlled potential. The same EPR spectra were obtained with $(Me_2Ge)_2(o$-$DMTTF)$, to rationalize the EPR results, we performed unrestricted DFT calculations on the radical-cation species of $1$ and $2$. In both cases the optimized geometry is fully planar and the singly occupied molecular orbital (SOMO), consisting of the antisymmetrical combination of TTF $\pi$ orbitals, is delocalized on the two redox active units with a negligible contribution of Si or Ge atoms (Figure 6 for $1^+$, see Supporting Information for $2^+$).

Also, the calculated isotropic hyperfine coupling constant with the lateral methyl protons amounts to 0.49 G, in good agreement with the experimental value of 0.42 G (vide supra), while the coupling with the SiMe$_2$ protons is much weaker (−0.04 G), and thus, not surprisingly, it was not observed in the experimental EPR spectrum. With respect to the experimental and theoretical evidences, the new donors $1$ and $2$ can be regarded as Class III compounds if one refers to the Robin and Day classification of the mixed-valence systems, with strong coupling between the electroactive units, despite the saturated EMe$_2$ bridges. These results prompted us to attempt the preparation of mixed-valence salts derived from $1$ and $2$ in the solid state. Our rigid dimers indeed afforded, upon simple chemical oxidation with one equivalent of a 1:1 TCNQ (tetracyanoquinodimethane)/TCNQF$_4$ (tetrafluoro-tetracyanoquinodimethane) mixture in the case of $1$ or only TCNQ in the case of $2$, and subsequent slow evaporation of solvent, single crystals of two isostructural CT compounds formulated as [1]-1/2-[TCNQ]-1/2[TCNQF$_4$] and [2]-[TCNQ], respectively. The better electron-donating properties of $2$ relative to $1$ very likely allowed its oxidation by the TCNQ acceptor in solution, whereas TCNQF$_4$ was required to promote the oxidation of $1$, then both acceptors co-crystallized in a 1:1 ratio in their reduced form with the radical cation of the donor. The two isostructural mixed-valence CT compounds crystallize in the monoclinic system, space group $C2/m$, with the molecules of donors located in a special position, consisting of a mirror plane on the long axis of the molecule and a $C_2$ axis along the E–E hinge (E = Si, Ge), while the acceptor molecules are contained in a mirror plane and a $C_2$ axis passes through the middle of the central C–C double bonds. We detail hereafter only the structure of the mixed-valence salt of $1$.

The donor molecule is now completely planar (Figure 7), thus confirming the results of the theoretical calculations. Moreover, the bond lengths values are in good agreement with those for a mixed-valence species. Indeed, the central C2–C3 double bond lengths to 1.373(8) Å, to be compared with 1.343(4) Å in neutral $1$, while the average of the central C–S bonds decreases now to 1.737 Å (1.753 Å in neutral $1$). These geometrical characteristics for $1^+$, but also $2^+$, combined with the analysis of the geometrical parameters of TCNQ,$^{[15]}$ indicating a donor–acceptor charge transfer of 1, strongly support the assumption of mixed-valence charge-transfer compounds with a mean charge of +0.5 on each TTF unit. The donors are longitudinally shifted along the $c$ axis and interact along the $a$ axis in the $ac$ plane, through a favorable axial overlap (interaction I) between the external dithiol mieties, which is characterized by an
intermolecular S₂···S₂ contact at 3.726 Å, comparable with the sum of the van der Waals radii (3.70 Å) of two S atoms (Figure 7). Furthermore, additional S₂···S₂ intermolecular contacts at 4.030 Å (interaction II; Figure 8) are established in the ab plane, thus leading to the formation of a two-dimensional array containing channels in which acceptor molecules reside. These molecules are isolated with respect to each other and disposed perpendicularly to the donors and to the b axis, an original feature within this type of compounds (Figure 8).

Interesting insight was afforded by band structure calculations (Figure 10).

With the charge +1 per donor molecule, the upper band should be empty, and, moreover, because of the symmetry of the structure, the bands necessarily touch in the points X, Y, and M, thus avoiding the establishment of an energy gap at the Fermi level. Therefore, the semiconducting behavior must result from electron localization due to electron repulsions. Essentially, our system can be described as a series of intermolecular (TTF₂)⁺⁻ fragments (as highlighted in Figure 7, interaction I) that communicate through either the EMₑ₂ bridges or the S···S contact of interaction II. Calculation of the Fermi surface of the system assuming a metallic filling of the bands shows that, if the metallic state can be stabilized, our compounds should be pseudo-two-dimensional metals without any possibility for a Peierls transition to occur.

**Conclusion**

Original rigid TTF-based dimers containing SiMe₂ and GeMe₂ double bridges have been synthesized. The analysis of their solid-state structures, determined by single-crystal X-ray measurements, revealed fully planar central six-membered rings. The role of the Si and Ge bridges in the conjugation between the two redox active units has been emphasized upon theoretical calculations, and, accordingly, relies on favorable orbital overlaps between XMe₂ (X = Si, Ge) α* orbitals and vinylc π* orbitals. The full electron delocalization in the corresponding radical-cation species was clearly assessed upon solution EPR measurements, thus demonstrating sizeable electron communication through the heteroatomic linkers. Finally, conducting charge-transfer compounds, with a pseudo-two-dimensional electronic structure, were prepared by chemical oxidation of (Me₂Si)₂(α-DMTTF)₂ with a 1:1 mixture of TCNQ/TCNQF₄, and of (Me₂Ge)₂(α-DMTTF)₂ with TCNQ. Further attempts are under way to prepare new CT complexes and radical-cation salts derived from these new donors, and, also, variation of
the TTF substitution or the bridging heteroatoms is under investigation.

**Experimental Section**

**General:** Reactions were carried out under nitrogen, THF was distilled from NaN-benzophenone, and dry CH2Cl2 was obtained by distillation over P2O5. o-MeTF was prepared according to a literature method.[21] NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer operating at 500.04 MHz for 1H and 125.75 MHz for 13C. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: s, singlet. MALDI-TOF MS spectra were recorded on Bruker Biflex-IHTT apparatus, equipped with a 337 nm N2 laser. Elemental analyses were performed by the "Service d'Analyse du CNRS" at Gif/Yvette, France.

**Synthesis of (Me2Ge)2 (1):** Lithium diisopropylamide (8.25 mmol, 5.5 mL of a solution 1.5 M in cyclohexane) was added dropwise to a solution of o-DMTTF (0.928 g, 4 mmol) in THF (60 mL) at -78 °C, under magnetic stirring. After a period of 3 h, Me3SiCl (0.50 mL, 4.2 mmol) was added, then the temperature was allowed to rise slowly overnight up to room temperature. After partial evaporation of THF, addition of a large volume of hexane, filtration, addition of CHCl3 to the yellow precipitate in order to dissolve the target compound, filtration over P2O5. slow, providing brown, plate-shaped crystals of the charge-transfer compound. Elemental analyses were performed by the "Servic dMLGQAnalyse du CNRS" at Gif/Yvette, France.

**Synthesis of [2]·1/2:** A solution of o-DMTTF (0.928 g, 4 mmol) in THF (60 mL) at -78 °C was recovered as a yellow crystal. Recrystallization from CH2Cl2 afforded brown, plate-shaped crystals of the charge-transfer compound. Elemental analyses were performed by the "Servic dMLGQAnalyse du CNRS" at Gif/Yvette, France.

**Synthesis of (Me2Ge)2 (2):** Lithium diisopropylamide (8.25 mmol, 5.5 mL of a solution 1.5 M in cyclohexane) was added dropwise to a solution of o-DMTTF (0.928 g, 4 mmol) in THF (60 mL) at -78 °C, under magnetic stirring. After a period of 3 h, Me3SiCl (0.50 mL, 4.15 mmol) was added, then the temperature was allowed to rise slowly overnight up to room temperature. After partial evaporation of THF, addition of a large volume of hexane, filtration, addition of CHCl3 to the yellow precipitate in order to dissolve the target compound, filtration and washing with MeOH to eliminate the lithium salts, washing with Et2O and drying, 2 was recovered as a yellow crystalline solid; yield 0.47 g (40%). Recrystallization from CH2Cl2 afforded yellow, plate-shaped, single crystals suitable for X-ray analysis. 1H NMR (CDCl3); δ = 0.39 (s, 12H; CH3 of SiMe3), 1.04 ppm (s, 12H; CH3 of TTF); 13C NMR (CDCl3); δ = 0.7 (s, CH3 of SiMe3), 12.7 (s, CH3 of TTF), 108.5–110.9 (s, C=C), 123.0 (s, C=CMe), 141.1 ppm (s, C=SiMe3); MS (MALDI-TOF); m/z: 576.9 [M]+; elemental analysis calcd (%) for C20H24Si2: C 36.06, H 3.63; found: C 35.74, H 3.51.

**Synthesis of (Me2Ge)2 (3):** A solution of LiHMDS (4.85 mg, 1.74 × 10-3 mmol) and TCNQ (3.5 mg, 1.74 × 10-3 mmol) in CH2Cl2 (10 mL) was added slowly to a solution of TTF (1.2 mmol) in cyclohexane) was added dropwise to a solution of o-DMTTF (0.928 g, 4 mmol) in THF (60 mL) at -78 °C, under magnetic stirring. After a period of 3 h, Me3SiCl (0.50 mL, 4.2 mmol) was added, then the temperature was allowed to rise slowly overnight up to room temperature. After partial evaporation of THF, addition of a large volume of hexane, filtration, addition of CHCl3 to the yellow precipitate in order to dissolve the target compound, filtration and washing with MeOH to eliminate the lithium salts, washing with Et2O and drying, 2 was recovered as a yellow crystalline solid; yield 0.47 g (40%). Slow evaporation from CH2Cl2 afforded yellow, plate-shaped, single crystals suitable for X-ray analysis. 1H NMR (CDCl3); δ = 0.56 (s, 12H; CH3 of GeMe3), 1.93 ppm (s, 12H; CH3 of TTF); 13C NMR (CDCl3); δ = 0.7 (s, CH3 of GeMe3), 13.7 (s, CH3 of TTF), 108.4–111.0 (s, C=C), 123.0 (s, C=CMe), 141.1 ppm (s, C=GeMe3); MS (MALDI-TOF); m/z: 657.6 [M]+; elemental analysis calcd (%) for C20H24Ge2: C 36.7, H 3.63; found: C 35.74, H 3.51.

**Table 1. Crystallographic data, details of data collection and structure refinement parameters.**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>[1]-[2][TCNO]- [1/2][TCNO]-</th>
<th>[2][TCNO]-</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C2H4NS4Si</td>
<td>C2H4NS4Ge</td>
<td>C2H4F2NiNS4Si</td>
<td>C2H4GeNS4</td>
</tr>
<tr>
<td>M [g mol-1]</td>
<td>577.05</td>
<td>666.05</td>
<td>817.23</td>
<td>870.24</td>
</tr>
<tr>
<td>T [K]</td>
<td>293(2)</td>
<td>293(2)</td>
<td>293(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P21/n</td>
<td>P21</td>
<td>C2/m</td>
<td>C2/m</td>
</tr>
<tr>
<td>c [Å]</td>
<td>15.4492(16)</td>
<td>16.0675(19)</td>
<td>14.018</td>
<td>13.981(2)</td>
</tr>
<tr>
<td>α [%]</td>
<td>90</td>
<td>78.7</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β [%]</td>
<td>104.764(12)</td>
<td>114.959(17)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ρcalcd [g cm-3]</td>
<td>1.421</td>
<td>1.587</td>
<td>1.475</td>
<td>1.572</td>
</tr>
<tr>
<td>μ [mm]</td>
<td>0.759</td>
<td>2.763</td>
<td>0.591</td>
<td>2.119</td>
</tr>
<tr>
<td>GOF (σ)</td>
<td>1.003</td>
<td>0.849</td>
<td>0.980</td>
<td>0.897</td>
</tr>
<tr>
<td>R1lwR (I &gt; 2σ(I))</td>
<td>0.0395/0.0929</td>
<td>0.0632/0.0778</td>
<td>0.0612/0.1373</td>
<td>0.0339/0.0593</td>
</tr>
<tr>
<td>R1lwR (all data)</td>
<td>0.0582/0.0986</td>
<td>0.0638/0.0589</td>
<td>0.0943/0.1486</td>
<td>0.0620/0.0653</td>
</tr>
</tbody>
</table>

**Electrochemical studies:** Cyclic voltammetry measurements were performed by using a three-electrode cell equipped with a platinum milli-electrode of 0.126 cm2 area, an Ag/Ag+ pseudo-reference and a platinum wire counter electrode. The potential values were then re-adjusted with respect to the saturated calomel electrode (SCE), using the ferrocene as internal reference. The electrolytic media involved a 0.1 M 1 solution of (n-Bu4N)PF6 in CH2Cl2. All experiments have been performed at room temperature at 0.1 Vs-1. Experiments were carried out with an EG & G PAR 273 A potentiostat with positive feedback compensation.

**Computational details:** Geometry optimizations of 1, 2, and 2 + were performed using the Turbomole program package (version 5.8) by using the B-P86 exchange-correlation functional[20] and SV (P) [21] standard basis sets. This basis set had the following contractions: (5s,1p)/ (4s,1p)/ (3s,1p)/ (2s,1p) for Ge. Molecular orbitals were represented by using the GaussView program.[28]
Single-crystal conductivity measurements: Electrical resistivity was measured on plate-like shaped crystals of [1][TCNQ][1][TCNQ][1] and [2][TCNQ]. Four gold contacts were evaporated on the crystals and gold wires were glued with silver paste on those contacts. Resistivity measurements were performed with a four-point method. A low-frequency (< 100 Hz) lock-in technique with measuring current I = 1 μA was used for resistance values lower than 20 kOhm, while higher resistances were measured with a dc current ranging from 100 to 1 nA.

Band-structure calculations: The tight-binding band-structure calculations were of the extended Hückel type[29a] with a modified Wollfsberg-Helmholtz formula to calculate the nondiagonal H values.[29b] The basis set consisted of double-ζ Slater-type orbitals for C, Ge, Si, and S and single-ζ Slater-type orbitals for H.

EPR measurements: EPR and ENDOR spectra were recorded on a Bruker ESP 300 spectrometer (X-band) equipped with a variable temperature attachment. Electrochemical oxidations at a controlled potential were performed by using a quartz electrocyclic cell that was present in situ in the EPR cavity. A silver wire electrode was used as a pseudoreference. The working electrode and the counter electrode were platinum. Chemical oxidations were performed under a nitrogen atmosphere in a glove box.

Acknowledgements

Financial support from the French Ministry of Foreign Affairs, Germaine de Staël project, 2006–2007 (PAI 10613RJ) is gratefully acknowledged. This work was also supported by the CNRS (France), the Swiss National Science Foundation (Switzerland) and by MEC-Spain (Project FIS2006-12117-C04-01) and Generalitat de Catalunya (Project 2005-SGR-683).

[13] Details are provided in the Supporting Information.
[16] Nine of the thirteen expected lines are observed in the spectrum. As shown in Supporting Information, the intensity distribution is in good accordance with the simulated spectrum.

Received: February 9, 2007
Published online: April 17, 2007