EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

FULL PAPER

DOI:10.1002/ejic.201300042

Mono- and Trinuclear Tripodal Platinum(II) Chelated Complexes Containing a Pyridine/Sulfoxide Based Anchoring Framework

Anna Barattucci,*[a] M. Rosaria Plutino,*[b] Cristina Faggi,[c] Paola Bonaccorsi,[a] Luigi Monsù Scolaro,[a] and Maria Chiara Aversa[a]

Keywords: Platinum(II) complexes / Tripodal ligands / S ligands / N ligands

New tripodal ligands 2,4,6-triethyl-1,3,5-tris{[1-(2-pyridinyl)-ethenyl]sulfinylmethyl}benzenes **6**, characterized by three pendant chains each containing both sulfoxide and pyridine moieties, were synthesized from the corresponding sulfenic acid and 2-ethynylpyridine. Two diastereomeric mixtures were obtained and separated, one racemic mixture **6a**, having a C_3 symmetry axis and the other **6b** with no symmetry. With the aim of studying the coordination ability of these chelating-κN,κS type ligands, monobranched racemic [1-(2-pyridinyl)ethenyl]sulfinylbenzene **9** was also synthesized. Upon addition of an equivalent amount of the monochelating ligand **9** or the tripodal species **6a** to a CD_3CN solution of a platinum(II) complex of the type *cis*-[$PtMe_2(Me_2SO)_2$] (**Pt1**) or *trans*-[$PtMeCl(Me_2SO)_2$] (**Pt2**), platinum(II) coordination and chelation occurred, as definitively indicated by a sharp change in the ^1H NMR spectrum towards the final corresponding chelated platinum(II) species and free dimethyl sulfoxide. The prepared platinum(II) species contain one or three fragments of the type {$PtMe_2$}(**10** or **12**) and {PtMeCl}(**11** or **13**) bound to the pyridinyl/sulfinyl skeleton in the coordinating ligands **9** and **6a**. All the prepared species were fully characterized by NMR spectroscopy from the connectivities in 2D-COSY, ^1H-^{13}C HSQC and phase-sensitive 2D-NOESY spectra which confirm the molecular mechanics calculation predictions.

Introduction

Polyfunctionalized flexible organic systems constitute a fascinating class of molecules owing to their general tendency to optimize their conformation to satisfy the host-guest interaction geometry and they may be employed as building blocks for the assembly of extended supramolecular architectures.[1] Hexafunctionalized 1,3,5-R-2,4,6-R′-substituted benzenes, where R is a linear aliphatic chain containing two or more carbon atoms, are known to adopt the most thermodynamically stable tripodal conformation, suitable for the interaction with host species such as anions and cations and small natural molecules.[2] Fascinating multibranched aromatic structures, where a sulfide moiety proximal to a trigonal nitrogen helps the coordination of a large variety of cations, have been recently synthesized. Depending on the kind of nitrogen, on the number of functionalized arms (from two to six) and the relative position of the two heteroatoms, they have found applications in ion-selective electrode construction, in the formation of multimetallic complexes and coordination polymers.[3]

As is evident from a large number of publications, the sulfinyl group has played a leading role as a ditopic organic labile ligand[4] and its corresponding transition metal complexes have been widely employed in catalysis.[5] More recently, organometallic systems derived from C_2 disulfoxides have been successfully used in enantioselective catalysis.[6] However, in comparison with the corresponding sulfides, very few articles deal with tri- or polysulfoxides and their metallorganic derivatives,[3f,7] possibly because of the difficulty in their synthesis and purification resulting from the stereogenicity of the sulfoxide sulfur and the subsequent obtainment of complex diastereomeric mixtures of enantiomers. Tripodal species containing three pyridine rings have been utilized in coordination chemistry and, depending on the stoichiometry of the reaction and coordination geome-

[a] Dipartimento di Scienze Chimiche, Università degli Studi di Messina,
Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina, Italy
Fax: +39-090-6765186
E-mail: abarattucci@unime.it
[b] Istituto per lo Studio dei Materiali Nanostrutturati, ISMN – CNR, Unità di Messina-Sezione di Palermo, Messina, Italy
c/o Dipartimento di Scienze Chimiche, Università degli Studi di Messina,
Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina, Italy
Fax: +39-090-3974108
E-mail: rosaria.plutino@pa.ismn.cnr.it
Homepage: http://www.pa.ismn.cnr.it/plutino.htm
[c] Centro Interdipartimentale di Cristallografia, Università degli Studi di Firenze,
Via della Lastruccia 3, 50019 Sesto Fiorentino, Firenze, Italy

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300042.

try of the metal ion, 1:3 or 1:1 complexes, the ones in which the metal is completely blocked inside the tripodal cavity, are formed.[8] However, to the best of our knowledge, nothing is known in the literature about tripodal N/S(O)[9] metal derivatives.

In this work we report the efficient synthesis of the tripodal system **6**, containing three functional chelating arms having both sulfoxide and pyridine moieties, and the easy separation of the corresponding C_3 and asymmetric diastereomers **6a** and **6b** as racemic mixtures. The synthesis can be accomplished by means of the regioselective addition of a transient sulfenic acid[10] to triple bonds. The first example of the application of a tripodal N/S(O) ligand as C_3 symmetric **6a** in the κN,κS coordination of the square planar platinum(II) complexes *cis*-[$PtMe_2(Me_2SO)_2$] (**Pt1**)[11] and *trans*-[$PtMeCl(Me_2SO)_2$] (**Pt2**)[12] is also reported.

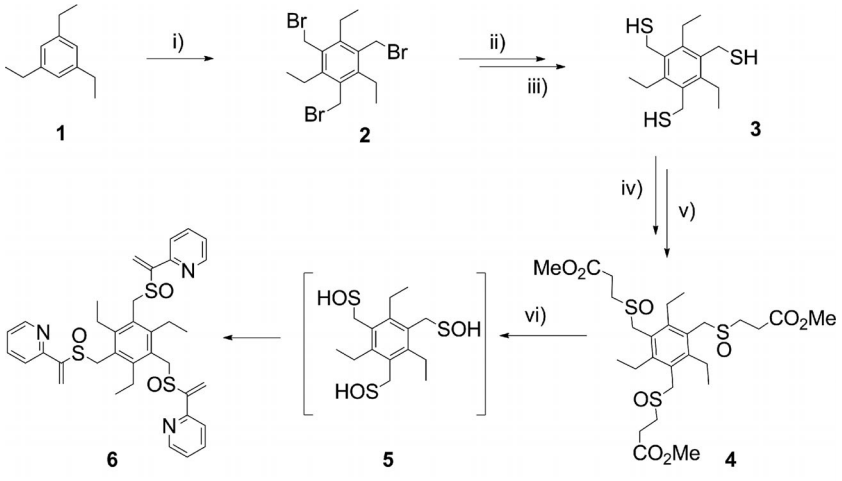
Results and Discussion

Synthetic Procedures

The synthetic pathway to the tripodal 2,4,6-triethyl-1,3,5-tris{[1-(2-pyridinyl)ethenyl] sulfinylmethyl}benzenes **6** is shown in Scheme 1. Starting from commercially available 1,3,5-triethylbenzene (**1**), the trithiol **3** was obtained following literature procedures[10c] from the tris(bromomethyl)-benzene **2** and was transformed, in three steps, into the trisulfoxides **6**, by the generation of the transient trisulfenic acid[10c,10f] **5** and its completely regioselective concerted addition to a suitable triple bond.[13] In particular, trisulfenic acid **5** has been generated in situ through the thermolysis of the racemic mixtures of the tripodal trisulfoxide **4** in 1,4-dioxane at reflux temperature for four hours and in the presence of a large excess of 2-ethynylpyridine (1:6).

Tripodal compounds **6** were obtained in 60% total yield, after column chromatography. The unreacted excess of 2-ethynylpyridine was almost quantitatively recovered from the head of the chromatographic column. After the intermediation of the achiral trisulfenic acid **5**, two new diastereomeric couples of enantiomers are formed: one having a C_3 symmetry axis (**6a**), where the three stereogenic sulfinyl centers have the same absolute stereochemistry, and the other where no symmetry is present (**6b**). The two diastereomeric mixtures were obtained, confirming the statistical prediction, in a 1:3 ratio and a simple flash column chromatographic process was needed to separate each of them as racemate.

All proton and carbon resonances belonging to compounds **6** were assigned through NMR spectroscopy in 2D-COSY and ^1H-^{13}C HSQC experiments, as also predicted by molecular mechanics calculation, and by phase-sensitive NOESY spectra. In particular, Figure 1 shows some 2D experiments performed on the racemic mixture of the C_3 symmetric compound **6a**. The "three-legged stool" most populated conformation in a solution of **6a**, with a mutual downwards disposition of the alternating three ethyl chains and three sulfinyl/pyridinyl anchoring fragments, is fully confirmed by strong interligand NOE cross-peaks between H^6 pyridine *ortho*-protons and methyl protons that lie close to them, on the vicinal ethyl substituents (blue square in Figure 1 on the left side). As expected for this kind of structure, the methylene protons of the ethyl groups are diastereotopic, as evidenced by the pair of multiplets at δ = 3.14 and 3.28 ppm (see Exp. Sect.), as well as those bound to the sulfinyl group, resonating as an AB system at δ = 4.45 and 4.12 ppm. Further evidence for the highly symmetric "three legged stool" conformation comes from the specific NOE contacts between the two different kinds of methylene protons, as shown in Figure 1 (right side), in particular between the three CH_ASO protons at 4.45 and the three methylenic protons CH_BCH_3 at δ = 3.14 ppm (green square) and between the other three CH_BSO protons at 4.12



i) $(CH_2O)_n$, HBr/HOAc, $ZnBr_2$, reflux, 20 h; ii) thiourea, EtOH, r.t., 20 h; iii) a. NaOH, H_2O, reflux, 4 h; b. HCl; iv) methyl acrylate, triton B, THF, –78 °C, 10 min; v) *m*CPBA, CH_2Cl_2, –78°C, 5 min; vi) 2-ethynylpyridyne, dioxane, reflux, 4 h.

Scheme 1. Synthetic pathway to 2,4,6-triethyl-1,3,5-tris{[1-(2-pyridinyl)ethenyl]sulfinylmethyl}benzenes **6**.

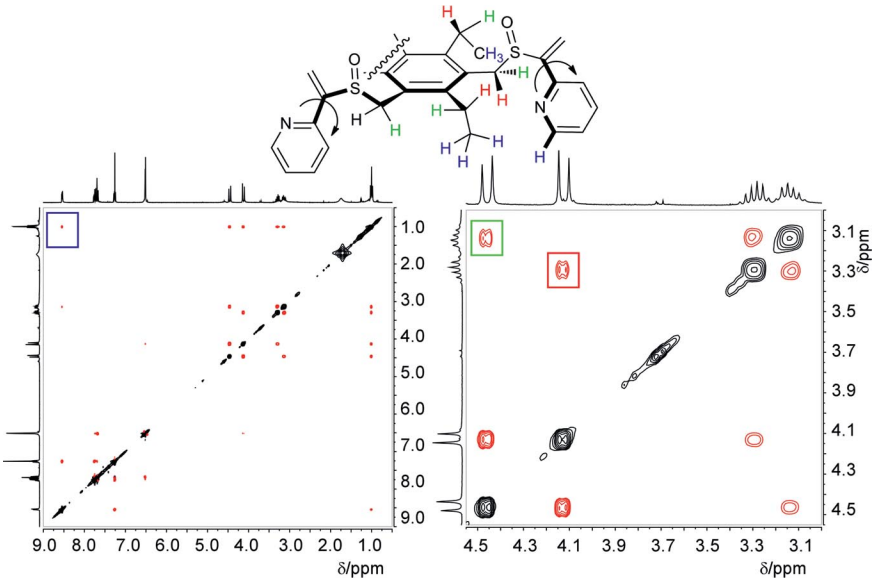


Figure 1. Phase-sensitive 2D-NOESY spectrum (*left*) and its aliphatic region (*right*) relative to a $CDCl_3$ solution of the **6a** conformer as assumed from the selective evidenced NOE peaks. The red cross-peaks arise from NOE (500 MHz, 298 K).

and the three methylenic protons CH_ACH_3 at δ = 3.28 ppm (red square).

Good crystals of the C_3 symmetric racemic mixture **6a** were obtained from a CH_2Cl_2/Et_2O mixture and the result of the X-ray diffractometry shows that the system crystallizes in the $P2_1/c$ space group in a more populated tripodal conformation. An ORTEP view of *rel*-2,4,6-triethyl-1,3,5-tris{[(*R*)-1-(2-pyridinyl)ethenyl]sulfinylmethyl}benzene (**6a**), together with the crystal packing in the unit cell is shown in Figure 2. When considering the above reported conformational analysis of **6a**, it would be logical to expect the highly symmetric "three legged stool" conformation in the crystalline state as well due to the reciprocal positions of substituents on the benzene ring. However, in the solid state, this symmetry is not exactly reflected, since the compound crystallizes in the monoclinic crystal system, within the $P2_1/c$ space group. This deviation from the expected highly symmetric preferred conformation is supported by the very different values found for the significant torsion angles and for the angles formed among the aromatic ring plane and the three planes of the heteroaromatic rings (see Supporting Information).

With the aim of studying the platinum(II) coordination ability towards the pyridine/sulfoxide functionalities that

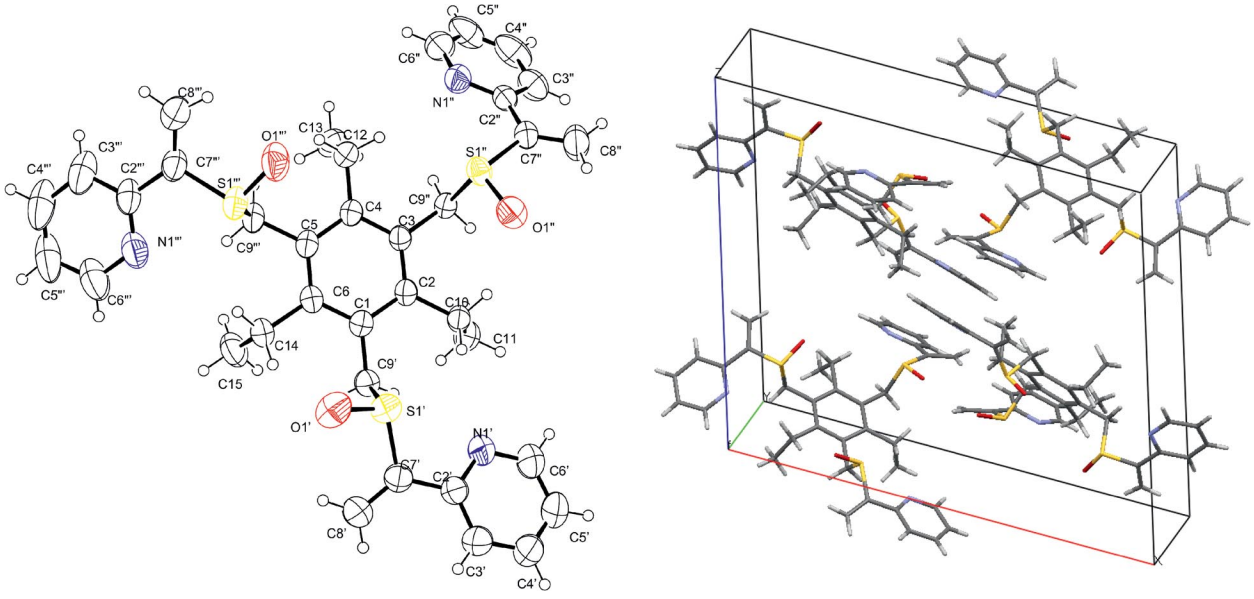
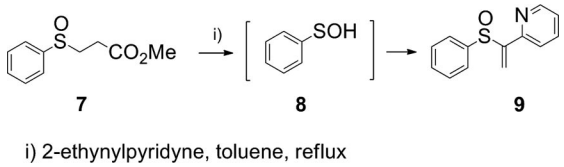


Figure 2. *Left*: Ortep view of *rel*-2,4,6-triethyl-1,3,5-tris{[(*R*)-1-(2-pyridinyl)ethenyl]sulfinylmethyl}benzene (**6a**) together with the structure numbering. Selected bond lengths [Å] and angles [°] for **6a**: S_1'–O_1' 1.495; S_1''–O_1'' 1.490; S_1'''–O_1''' 1.488; C_9'–S_1'–$C^{7'}$ 96.82; $C^{9''}$–S_1''–$C^{7''}$ 98.62; $C^{9'''}$–S_1'''–$C^{7'''}$ 96.10. *Right*: molecule crystal packing in the unit cell.

characterize the three N/S branches of the tripodal ligands **6**, we decided to start from a simple model molecule. For this reason we synthesized compound **9**, bearing only one sulfinyl and one pyridinyl anchoring moiety, in such a relative position that they could give the formation of a stable five-membered ring after chelation, with a phenyl moiety directly bound to the sulfoxide group for enhancing its steric requirements. Simple thermolysis of the already reported sulfoxide **7**[13] at the reflux temperature of toluene gave the intermediate benzenesulfenic acid (**8**) that was added in situ to the triple bond of commercial 2-ethynylpyridine, present in excess (Scheme 2). After easy and rapid column chromatography, a racemic mixture of the unique regioisomer **9** was obtained in almost quantitative yield and it was fully characterized.



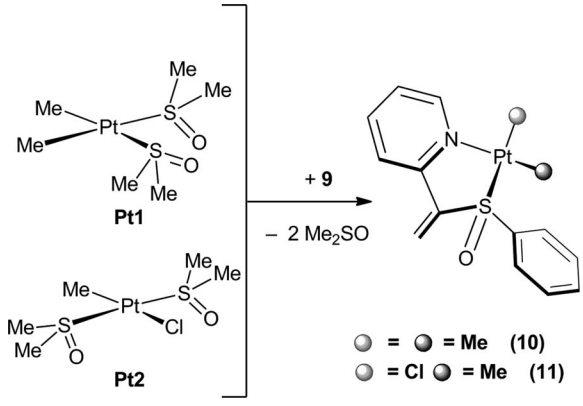
Scheme 2. Synthetic pathway to the racemic [1-(2-pyridinyl)ethenyl]sulfinylbenzene ligand **9**.

Coordination of Ligands 6 and 9 with Square Planar Platinum(II) Complexes Pt1 and Pt2

Platinum(II) complexes of the type *cis*-[$PtMe_2(Me_2SO)_2$] (**Pt1**)[11] and *trans*-[$PtMeCl(Me_2SO)_2$] (**Pt2**)[12] have been employed as useful synthons for introducing the fragments {$PtMe_2$} and {PtMeCl}, respectively, into different monocoordinating or chelating heterocyclic systems.[12a,12c,14] We thought it worthwhile to extend this methodology to the coordination of the sulfinyl sulfur and pyridinyl nitrogen atoms of compound **9** and tripodal species **6**. In particular, we tested the reaction of the model monocoordinating [1-(2-pyridinyl)-ethenyl]sulfinylbenzene **9** with the two selected kinds of square planar platinum(II), complexes **Pt1** and **Pt2**.

The synthetic procedure for the platinum(II) derivatives **10** and **11** was first established in situ in a 5 mm NMR tube and then on a larger scale, at 298 K, in CD_3CN, since the starting compounds and products showed good solubility and no trace of decomposition in this solvent for up to one week. Upon addition of an equivalent amount of the ligand **9** to a solution of the appropriate platinum complex in CD_3CN, there is a sharp change in the NMR spectrum, from the signals belonging to the starting platinum(II) complexes and free ligand **9** to those that may be attributed to the final chelated platinum(II) species and free dimethyl sulfoxide.

The reaction of formation of complexes **10** and **11** takes place according to Scheme 3. The two platinum(II) species **10** and **11**, incorporating the chelated ligand **9** coordinated at the platinum(II) center through both the pyridine nitrogen (κN) and the sulfoxide sulfur (κS), were obtained quantitatively. A typical ^1H NMR spectroscopic comparison between the free species and the crude reaction product is reported in Figure 3 (spectra a and b). Taking as an example the reaction run in CD_3CN between *cis*-[$PtMe_2(Me_2SO)_2$] (**Pt1**) and ligand **9**, the downfield shift of ca. 0.5 ppm relative to the $H^{6'}$ *ortho*-proton of the pyridine ring (δ = 8.96 ppm) clearly indicates an established coordination which is further evidenced by the diagnostic hydrogen/platinum(II) coupling constant ($^3J_{Pt,H}$ = 22.0 Hz) for the same proton with the ^{195}Pt nucleus that gives rise to two typical satellite peaks. Otherwise, different methyl signals of the newly formed complex **10** are present, each with the two satellite peaks but each bearing different coupling constants with ^{195}Pt which are characteristic of a methyl group *trans* to a sulfoxide (δ = 0.85 ppm, $^2J_{Pt,H}$ = 77.9 Hz, $PtCH_3$ *trans* to S), and to a pyridine nitrogen (δ = 0.78 ppm, $^2J_{Pt,H}$ = 90.9 Hz, $PtCH_3$ *trans* to N). The presence of selective NOE cross peaks between (i) the signals relative to the *ortho*-pyridine proton at δ = 8.96 ppm ($H^{6'}$) and the methyl *trans* to sulfoxide at δ = 0.85 ppm (s with satellites, $^2J_{Pt,H}$ = 77.9 Hz, $PtCH_3$), and (ii) the peaks at δ = 7.90 ppm ($H^{2,6}$) of the *ortho*-phenyl protons and δ = 0.78 ppm (s with satellites, $^2J_{PtH}$ = 90.9 Hz) with the methyl protons $PtCH_3$ *trans* to pyridine (see Figure 3, left side), definitively confirm the results.



Scheme 3. Synthetic pathway of compound **9** towards platinum(II) complexes **10** and **11** (in CD_3CN at 298 K).

A brief comment should be devoted to compound **11**, the product of the reaction between **9** and *trans*-[$PtMeCl(Me_2SO)_2$] (**Pt2**). Besides the chemical shift of the heteroaromatic proton $H^{6'}$ that has moved to 9.49 ppm ($\Delta\delta$ ca. 1 ppm), a methyl signal with ^{195}Pt coupling constant (δ = 0.87 ppm, $^2J_{Pt,H}$ = 79.7 Hz, $PtCH_3$ *trans* to N) was noticed (Figure 3, c). This assignment was confirmed by a selective NOE cross peak between the signal relative to the methyl protons and the two *ortho*-protons of the phenyl ring (δ = 7.95 ppm $H^{2,6}$), while no NOE contact was found with the signal at δ = 9.49 ppm ($H^{6'}$) relative to the *ortho*-pyridine proton.

Taking into account the previous results, the racemic mixture of the tripodal sulfinyl/pyridinyl ligands **6a** was employed in complexation reactions with square planar plati-

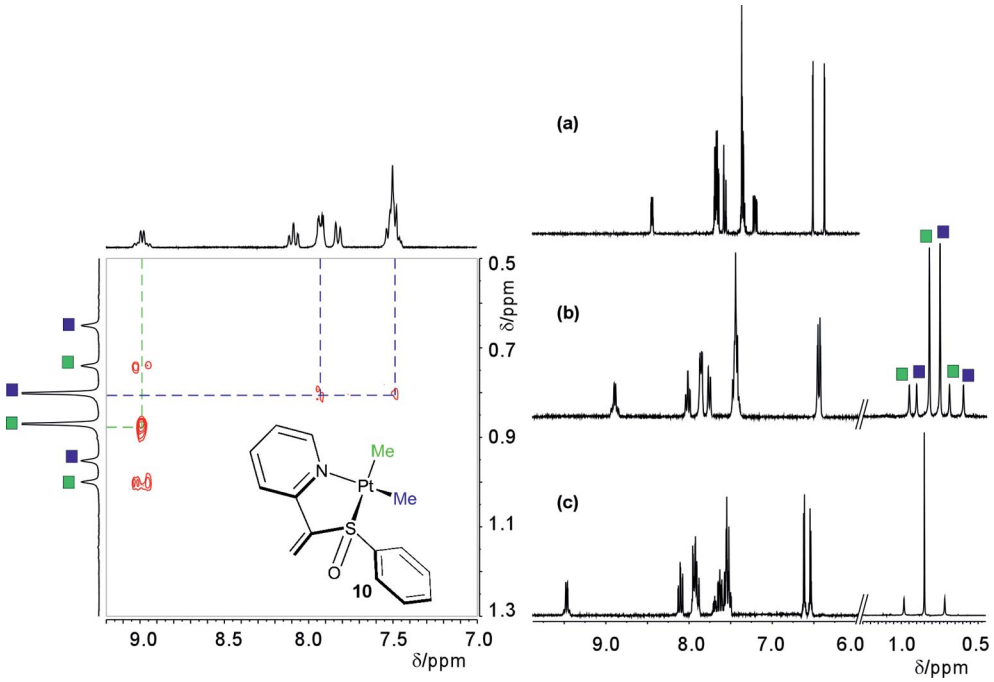
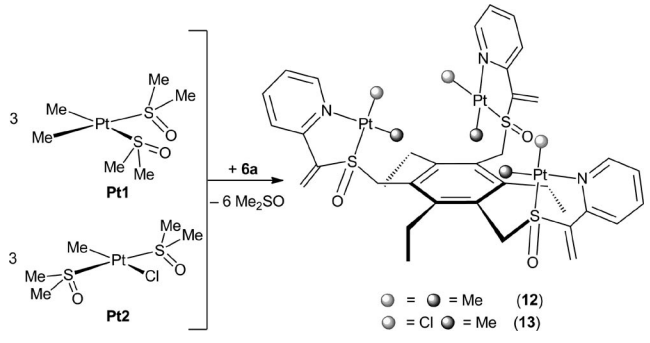


Figure 3. *Left:* aliphatic section of the 2D-NOESY spectrum showing selective NOE between $PtCH_3$ and the aromatic protons (300 MHz, 298 K). *Right:* ^{1}H NMR spectrum of (a) ligand **9** in CD_3CN (300 MHz, 298 K) and upon addition of one equiv. of (b) *cis*-[$PtMe_2(Me_2SO)_2$] or (c) *trans*-[$PtMeCl(Me_2SO)_2$].

num(II) complexes such as *cis*-[$PtMe_2(Me_2SO)_2$] (**Pt1**) and *trans*-[$PtMeCl(Me_2SO)_2$] (**Pt2**). As shown in Scheme 4, the syntheses of the trinuclear species of the type {[PtXY]$_3$(**6a**-κN,κS)} (X = Y = Me, **12**; X = Cl, Y = Me, **13**) were performed in situ by addition of three equiv. of the corresponding platinum(II) complexes to a CD_3CN solution of the tripodal ligand **6a**. Even in this case, the trinuclear platinum(II) derivatives and the free dimethyl sulfoxide are the only reaction products.



Scheme 4. Synthetic pathway towards the formation of the trinuclear platinum(II) complexes **12** and **13** (in CD_3CN at 298 K).

The ^{1}H spectrum of the dimethylplatinum(II) derivative **12** (lower side of Figure 4) shows a lower field shift in the pyridine proton signals in comparison with those of the corresponding starting tripodal species **6a**. The lower resolution can be attributed to the low solubility of the platinum(II) derivatives in CD_3CN. In particular, from the ^{1}H NMR spectra, it is possible to observe that: (i) the proton signals $H^{6',6'',6'''}$, $H^{5',5'',5'''}$, $H^{4',4'',4'''}$ and $H^{3',3'',3'''}$ of the pyridine are perfectly resolved and in particular the *ortho*-protons $H^{6',6'',6'''}$ show the characteristic ^{195}Pt coupling constants that demonstrates the chelation (δ = 9.00 ppm, $^3J_{Pt,H}$ = 27.4 Hz), (ii) below 1 ppm it is possible to observe the signals relative to the methyl protons *trans* to pyridine (δ = 0.90 ppm, $^2J_{Pt,H}$ = 91.2 Hz) and to sulfoxide (δ =

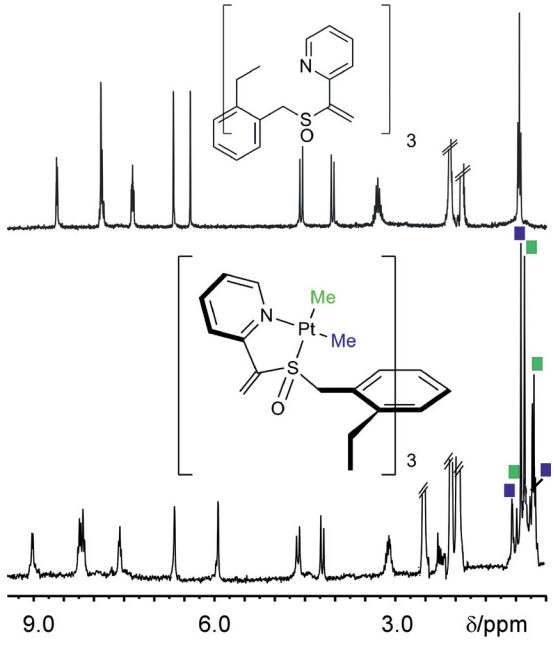


Figure 4. *Upper plot:* ^{1}H NMR spectrum of ligand **6a** in CD_3CN. *Lower plot:* ^{1}H NMR spectrum of the trinuclear derivative **12** as obtained in situ after the addition of three equiv. of *cis*-[$PtMe_2(Me_2SO)_2$] (300 MHz, 298 K).

0.84 ppm, $^2J_{Pt,H}$ = 78.7 Hz) directly linked to the platinum(II) center, (iii) the diastereotopic protons $-CH_2-S$ give a split AB system at δ = 4.20 and 4.59 ($^2J_{H,H}$ = 14.4 Hz), and the olefinic protons give two doublets at δ = 5.92 and 6.64 ppm ($^2J_{H,H}$ = 2.0 Hz), thus confirming the great symmetry of the newly-formed chelated system, and (iv) the methyl protons of each ethyl group resonate as a triplet at δ = 0.68 ppm (CH_2-CH_3), while the methylene protons give rise to two multiplets at δ = 2.25 and 3.09 ppm (CH_2-CH_3). The proton spectrum of the trinuclear species [{$PtMe_2$}$_3$(**6a**-κ*N*,κ*S*)] **12**, as well as that of the mononuclear complex [$PtMe_2$(**3**-κ*N*,κ*S*)] **10**, shows the expected inequivalence of the two halves of the molecule, especially concerning the two methyl groups directly bound to the platinum(II) center which exhibit two different singlets with typical ^{195}Pt satellites. The difference in the ^{195}Pt coupling constants is in agreement with the different *trans* influence of the pyridine and the sulfoxide moiety.[15] The pattern of the other signals shows a general down-field shift after platinum(II) coordination.

The ^{1}H NMR spectrum of compound **13**, relative to the chloromethylplatinum(II) derivatives with the tripodal ligand **6a**, shows similar features as far as the signals pattern of the coordinate organic moiety in **12** is concerned (see Figure S2 in Supporting Information). As already seen in the comparison between the two mononuclear species **10** and **11** (see Figure 3, spectra b and c), the *ortho*-pyridine proton of species **13** resonates at a higher frequency than that in the corresponding dimethylplatinum(II) species **12** (9.50 vs. 9.00 ppm). In the aliphatic region there is only one singlet at δ = 0.71 ppm ($^2J_{Pt,H}$ = 83.8 Hz) with typical platinum(II) satellites accounting for the unique methyl bound to the metal center. Phase-sensitive 2D-NOESY experiments confirmed the tripodal disposition of the substituents on the benzene platform of the chelated symmetric **12** and **13**.

Preliminary complexation experiments were also conducted between the non C_3 symmetric ligand **6b** and *cis*-[$PtMe_2(Me_2SO)_2$] (**Pt1**) or *trans*-[$PtMeCl(Me_2SO)_2$] (**Pt2**). ^{1}H NMR spectra were obtained in each case which were difficult to analyze and in which the broad signals of the pyridine protons lie in a lower field position with respect to those of the uncoordinated **6b** (see Experimental Section). As far as the diastereotopic $-CH_2-S$, the olefinic protons and the ethylic chains are concerned, complex and difficult to interpret multiplets between, respectively, δ = 7.00 and 5.00 ppm, δ = 5.00 and 4.00 ppm, and δ = 4.00 and 0.70 ppm were detected. The {PtMe} fragments show in each case up-field singlets with typical platinum(II) satellites with the expected ^{195}Pt coupling constants. Even if all data converge towards the formation of the two corresponding trinuclear platinum(II) derivatives, further studies are needed to completely clarify their structures.

The use of transition metal complexes containing sulfoxide ligands as precursors in synthetic procedures has been known and successfully employed for many years, especially in the chemistry of coordination and organometallic platinum(II) complexes.[17,18] The synthetic procedures exploit the fairly high lability of such weakly coordinating molecules. Of particular use would be a detailed knowledge of the mechanistic pathway of the dimethyl sulfoxide substitution process. As far as the formation of the chelated species is concerned, we suggest that the pyridinic nitrogen is the first coordinating group, followed by fast ring closure operated by the sulfur atom from the less nucleophilic sulfoxide.[19] However, the only species that can be detected in the reaction mixture in solution are, in any case, the starting platinum(II) complexes and free ligand (i.e. **6a** or **9**), together with the final chelated species and free dimethyl sulfoxide (diagnostic signal at 2.5 ppm). Any attempts to identify by ^{1}H NMR spectroscopy, even at low temperatures, the presence of other intermediate open-ring species or, in the case of the *trans*-platinum(II) complex **Pt2**, other coordination isomers were unsuccessful.[20] This means that the kinetic rate constant for the sulfoxide ring-closure is too high compared with that of the substitution process of the pyridine moiety, leading to the conclusions that the open-ring species once formed is rapidly converted into the corresponding chelated species.[20,21] The overall process is immediate in the case of complex **Pt1** and quite slow for the precursor complex **Pt2** (ca. 10 min reaction time). This is in agreement with the fast dissociative substitution process of the dimethyl sulfoxide for different nucleophiles already known for the complex **Pt1**, mainly due to the strong *trans* effect and *trans* influence exerted by the two *trans*-methyl groups.[22] On the other hand, the *trans*-chloromethyl species **Pt2** bears two less reactive dimethyl sulfoxides *trans* to each other, that, affected by the less dimethyl sulfoxide *trans*-influence, give rise to a slower substitution process. In this regard its observed high reactivity toward a variety of nucleophilic agents has to be ascribed to the corresponding aqua-species *trans*-[$PtMeCl(Me_2SO)(H_2O)$], due to multiple solvolysis and isomerization solution equilibria.[23]

Finally we must clarify the enhanced sulfinyl affinity shown in the chelate formation: by realizing the reaction in a 1:1 ratio, no open-ring species or any kind of equilibrium between reagents and the chelated product in solution could be detected. Several previous kinetic studies have been devoted to clarify the properties of dimethyl sulfoxide or other sulfoxides when acting as monocoordinating reagents in square-planar platinum(II) complexes that, in substitution reactions, can be regarded as a poor nucleophiles.[24] Interestingly, in our studied systems, the product formation appears to be favored by the "chelate effect" of the sulfoxide group, helped by the conformational rigidity of the chelating rigid N-S framework due to the presence of a rigid linking sp^2 carbon.

Conclusions

A new class of ligands, namely the 2,4,6-triethyl-1,3,5-tris{[1-(2-pyridinyl)ethenyl]sulfinylmethyl}benzenes **6** and [1-(2-pyridinyl)-ethenyl]sulfinylbenzene **9** has been efficiently prepared by a procedure based on the reactivity of the corresponding sulfenic acids. In particular, compounds

6, with the substituents distributed around a benzene platform in a tripodal fashion, have been separated into the diastereomeric couples of racemic trisulfoxides, the C_3 symmetric **6a** and the asymmetric **6b**, fully characterized by NMR spectroscopy and, in the case of **6a**, by single-crystal X-ray diffraction analysis. Additionally, as a first experiment in the study of the transition metal coordination ability of this type of organic ligand, we chose to treat them with platinum(II) synthons, such as *cis*-[$PtMe_2(Me_2SO)_2$] (**Pt1**) and *trans*-[$PtMeCl(Me_2SO)_2$] (**Pt2**), and so the corresponding mono- (**10** and **11**) and tris-chelated (**12** and **13**) species, each containing one *cis*-{$PtMe_2$} or *cis*-{PtMeCl} fragment for each bidentate anchoring κN,κS frame, were formed.

The synthesis of compounds **6** provides an efficient approach for obtaining a class of tripodal bidentate ligands: the coexistence of the two coordinating N,S sites in the suitable relative position and the tripodal conformation has been shown to be particularly efficient in platinum(II) coordination and may open the way to bind metals with an octahedral geometry.

Experimental Section

General Methods and Materials: All solvents (AR, LabScan Ltd., SpS, Romil Ltd.) used for synthetic procedures were obtained from commercial suppliers and used as received. All syntheses were carried out on the benchtop in atmospheric conditions unless otherwise stated. Reactions for the preparation of all the ethenylsulfinyl derivatives were monitored by TLC on commercially available Aldrich silica gel 60 F 254 precoated plates. Products were visualized by UV or vanillin [1 g dissolved in MeOH (60 mL) and conc. H_2SO_4 (0.6 mL)]. Column chromatography was performed on Aldrich 60 silica gel. $CDCl_3$ (D, 99.8%) and CD_3CN (D, 99.96%) for NMR measurements were purchased from Sigma–Aldrich Co. and used as received. All other reagents were of the highest purity grade commercially available and used without further purification. Infrared spectra were recorded with KBr cells in the range 4000–400 cm^{-1} using a Nicolet Impact 410 spectrometer. The samples for IR measurements were made up in nujol. NMR measurements were performed on a Bruker ARX-300 spectrometer equipped with a broad-band probe operating at 300.1 MHz (^1H) or on Varian Gemini-300 at 300.1 and 75.5 MHz and a Varian 500 spectrometer operating at 500.1 and 125.7 MHz. All chemical shifts (δ) are reported in parts per million (ppm) downfield of tetramethylsilane (Me_4Si) as an internal standard (δ = 0.0 ppm), or referenced to the proton resonance resulting from incomplete deuteration of the NMR solvents such as $CDCl_3$ (^1H NMR: 7.26 ppm and ^{13}C NMR: 77.0 ppm) and CD_3CN (^1H NMR: 1.94 ppm. ^{13}C NMR: 118.3, 1.3 ppm). Coupling constants *J* are given in Hertz. ^{13}C NMR spectra were acquired with the APT technique. NMR peak assignments at 298 K were performed by using homonuclear (COSY) and heteronuclear correlation (^1H-^{13}C) spectroscopy. Phase sensitive ^1H 2D-NOESY spectra were acquired by using a standard pulse sequence with mixing times of 500 (**9–11**), 800 (**12**, **13**) and 840 ms (**6**). ^1H-^{13}C HSQC correlation experiments were also performed for several compounds and were recorded in a *gradient*-selected phase-sensitive mode. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. The purity of all starting materials and reaction products was determined by ^1H NMR spectroscopy and clean spectra with correct integration were obtained in all cases. See Supporting Information for the adopted numbering of complexes **10**–**13**.

CCDC-868526 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthetic Procedures: The starting sulfoxides 3,3′,3′′-[(2,4,6-triethyl-1,3,5-benzenetriyl)tris(methylenesulfinyl)]trispropanoic acid 1,1′,1′′-trimethyl ester **4**[10a,10c] and 3-(phenylsulfinyl)propanoic acid methyl ester **7**[10b] were synthesized following already published methods.

[1-(2-Pyridinyl)ethenyl]sulfinylbenzene (9): A 1 mM solution of **1** in toluene was added to three equiv. of 2-ethynylpyridine and maintained at reflux temperature for 1 h until the disappearance of **7** by TLC. The reaction crude was then purified by column chromatography, m.p. 40 °C, 80% yield. TLC: R_f 0.35 (petrol/EtOAc, 60:40). $C_{13}H_{11}NOS$ (229.3): calcd. C 68.09, H 4.84, N 6.11; found C 68.00, H 4.88, N 6.20. IR (nujol): $\tilde{\nu}$ =1037 (S=O) cm^{-1}. ^1H NMR (300.1 MHz, $CDCl_3$, 298 K):δ = 8.51 (ddd, $^3J_{H,H}$ = 4.6, $^4J_{H,H}$ = 1.7, $^5J_{H,H}$ = 1.2 Hz, 1 H, $H^{6'}$), 7.71 (m, 2 H, H^2 + H^6), 7.62 (dt, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.7 Hz, 1 H, $H^{4'}$), 7.48 (ddd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.8, $^5J_{H,H}$ = 1.2 Hz, 1 H, $H^{3'}$), 7.34 (m, 3 H, $H^{3,5}$ + H^4), 7.17 (ddd, $^3J_{H,H}$ = 8.0, 4.6, $^4J_{H,H}$ = 1.8 Hz, 1 H, $H^{5'}$), 6.53 (d, $^2J_{H,H}$ = 1.2 Hz, 1 H, C=CH_A), 6.44 (d, $^2J_{H,H}$ = 1.2 Hz, 1 H, C=CH_B) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K):δ = 153.7 ($C^{2'}$), 152.3 (C=CH_2), 148.7 ($C^{6'}$), 144.1 (C^1), 136.6 ($C^{4'}$), 130.9 (C^4), 128.8 ($C^{3,5}$), 125.9 ($C^{2,6}$), 123.5 ($C^{5'}$), 120.7 ($C^{3'}$), 117.4 (C=CH_2) ppm. ^1H NMR (300.1 MHz, CD_3CN, 298 K):δ = 8.48 (ddd, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 1.8, $^5J_{H,H}$ = 1.1 Hz, 1 H, $H^{6'}$), 7.70 (m, 2 H, H^2 + H^6), 7.68 (dt, $^3J_{av}$ = 7.7, $^4J_{H,H}$ = 1.8 Hz, 1 H, $H^{4'}$), 7.60 (ddd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.2, $^5J_{H,H}$ = 1.0 Hz, 1 H, $H^{3'}$), 7.39 (m, 3 H, $H^{3,5}$ + H^4), 7.23 (ddd, $^3J_{H,H}$ = 7.5, 4.9, $^4J_{H,H}$ = 1.2 Hz, 1 H, $H^{5'}$), 6.54 (d, $^2J_{H,H}$ = 1.2 Hz, 1 H, C=CH_A), 6.40 (d, $^2J_{H,H}$ = 1.2 Hz, 1 H, C=CH_B) ppm. ^{13}C NMR (75.5 MHz, CD_3CN, 298 K):δ = 153.5 ($C^{2'}$), 152.1 (C=CH_2), 149.2 ($C^{6'}$), 144.2 (C^1), 137.6 ($C^{4'}$), 131.8 (C^4), 129.6 ($C^{3,5}$), 126.6 ($C^{2,6}$), 124.5 ($C^{5'}$), 121.5 ($C^{3'}$), 117.5 (C=CH_2) ppm.

2,4,6-Triethyl-1,3,5-tris{[1-(2-pyridinyl)ethenyl]sulfinylmethyl}benzenes (6): A 1 mM solution of **4** in 1,4-dioxane was added to six equiv. of 2-ethynylpyridine and maintained at reflux temperature for 4 h until the disappearance of the last –CO_2CH_3 signal by ^1H NMR spectroscopy. The crude reaction mixture was then purified by column chromatography and the two racemic mixtures of diastereoisomers separated. The first one to be eluted was ***rel*-2,4,6-Triethyl-1,3,5-tris{[(*R*)-1-(2-pyridinyl)ethenyl]sulfinylmethyl}benzene (6a)**. White solid, m.p. 197 °C, 15% yield. TLC: R_f 0.34 (acetone/petroleum ether, 65:35). $C_{36}H_{39}N_3O_3S_3$ (657.9): calcd. C 65.72, H 5.97, N 6.39; found C 65.59, H 6.06, N 6.34. IR (nujol): $\tilde{\nu}$ = 1039 (S=O) cm^{-1}. ^1H NMR (300.1 MHz, $CDCl_3$, 298 K): δ = 8.53 (ddd, $^3J_{H,H}$ = 4.5, $^4J_{H,H}$ = 1.8, $^5J_{H,H}$ = 1.0 Hz, 3 H, $H^{6',6'',6'''}$), 7.74 (dt, $^3J_{av}$ = 8.0, $^4J_{H,H}$ = 1.7 Hz, 3 H, $H^{4',4'',4'''}$), 7.68 (ddd, br, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.2, $^5J_{H,H}$ = 1.0 Hz, 3 H, $H^{3',3'',3'''}$), 7.25 (ddd, $^3J_{H,H}$ = 7.2, 4.5, $^4J_{H,H}$ = 1.8 Hz, 3 H, $H^{5',5'',5'''}$), 6.52 (d, $^2J_{H,H}$ = 1.4 Hz, 1 H, C=CH_A), 6.51 (d, $^2J_{H,H}$ = 1.4 Hz, 1 H, C=CH_B), 4.45 (AB system, $^2J_{A,B}$ = 13.4 Hz, 3 H, 3× CH_ASO), 4.12 (AB system, $^2J_{A,B}$ = 13.4 Hz, 3 H, 3× CH_BSO), 3.14 and 3.28 (2× m, 6 H, 3× CH_2CH_3), 1.0 (t, $^3J_{H,H}$ = 7.7 Hz, 9 H, 3× CH_2CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K):δ = 154.1 and 152.8 ($C^{2',2'',2'''}$ and 3× C=CH_2), 148.8 ($C^{6',6'',6'''}$), 146.0 ($C^{1,3,5}$), 137.0 ($C^{4',4'',4'''}$), 127.5 ($C^{2,4,6}$), 123.6 ($C^{5',5'',5'''}$), 120.6 ($C^{3',3'',3'''}$), 118.2 (3× C=CH_2), 56.3 (3× ArCH_2SO), 23.2 (3× CH_2CH_3), 13.9 (3× CH_2CH_3) ppm. ^1H NMR (300.1 MHz, CD_3CN, 298 K): δ = 8.65

(ddd, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 1.8, $^5J_{H,H}$ = 1.0, 3H, $H^{6',6'',6'''}$), 7.93 (ddd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.0, $^5J_{H,H}$ = 1.0, 3H, $H^{4',4'',4'''}$), 7.90 (dt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.8, 3H, $H^{3',3'',3'''}$), 7.40 (ddd, $^3J_{H,H}$ = 7.2, 4.9, $^4J_{H,H}$ = 2.0, 3H, $H^{5',5'',5'''}$), 6.72 (d, $^2J_{H,H}$ = 1.1, 3H, C=CH_A), 6.44 (d, $^2J_{H,H}$ = 1.1, 3H, C=CH_B), 4.61 (AB system, $^2J_{A,B}$ = 13.6, 3H, 3× CH_ASO), 4.07 (AB system, $^2J_{A,B}$ = 13.6, 3H, 3× CH_BSO), 3.33 (m, 6H, 3× CH_2CH$_3$), 0.98 (t, $^3J_{H,H}$ = 7.7, 9H, 3× CH$_2$CH_3) ppm. The second one to be eluted was ***rel*-2,4,6-triethyl-1,3-bis{[(*R*)-1-(2-pyridinyl)ethenyl]sulfinylmethyl}-5-{[(*S*)-1-(2-pyridinyl)ethenyl]sulfinylmethyl}benzene (6b)**. Yellow solid, m.p. 120 °C, 45% yield TLC: R_f 0.32 (acetone/petroleum ether, 65:35). $C_{36}H_{39}N_3O_3S_3$ (657.9): calcd. C 65.72, H 5.97, N 6.39; found C 65.56, H 6.07, N 6.50. IR (nujol): $\tilde{\nu}$ = 1038 (S=O) cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 K):δ = 8.55 (m, 3 H, $H^{6',6'',6'''}$), 7.72 (m, 6 H, $H^{3',4',3'',4'',3''',4'''}$), 7.27 (m, 3 H, $H^{5',5'',5'''}$), 6.51 (m, 6 H, 3× CH_2=C), 4.53 (AB system, $^2J_{A,B}$ = 13.2 Hz, 3 H, 3× CH_ASO), 4.13 (AB system, $^2J_{A,B}$ = 13.2 Hz, 3 H, 3× CH_BSO), 3.18 (m, 6 H, 3× CH_2CH$_3$), 1.0 (t, 9 H, 3× CH$_2$CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K):δ = 153.9 and 153.7 ($C^{2',2'',2'''}$), 152.5 and 152.3 (3× C=CH$_2$), 148.8 and 148.7 ($C^{6',6'',6'''}$), 146.1 ($C^{1,3,5}$), 137.0 ($C^{4',4'',4'''}$), 127.5 and 127.2 ($C^{2,4,6}$), 123.7 and 123.6 ($C^{5',5'',5'''}$), 120.3 ($C^{3',3'',3'''}$), 118.1 (3× C=CH$_2$), 56.1 and 55.9 (3× ArCH$_2$SO), 23.5 and 23.1 (3× CH$_2$CH$_3$), 14.2 and 13.9 (3× CH$_2$CH$_3$) ppm. ^{1}H NMR (300.1 MHz, CD_3CN, 298 K):δ = 8.67 (d, $^3J_{H,H}$ = 4.9 Hz, 3 H, $H^{6',6'',6'''}$), 7.92 (m, 3 H, $H^{3',3'',3'''}$), 7.90 (m, 3 H, $H^{4',4'',4'''}$), 7.41 (m, 3 H, $H^{5',5'',5'''}$), 6.72 (d, $^2J_{H,H}$ = 1.1 Hz, 1 H, C=CH_A), 6.43 (d, $^2J_{H,H}$ = 1.1 Hz, 1 H, C=CH_B), 4.63 (AB system, $^2J_{A,B}$ = 13.4 Hz, 3 H, 3× CH_ASO), 4.06 (AB system, $^2J_{A,B}$ = 13.4 Hz, 3 H, 3× CH_BSO), 3.31 (br. m, 6 H, 3× CH_2CH$_3$), 0.99 (t, br, 9 H, 3× CH$_2$CH_3) ppm.

Platinum(II) Complexes Derivatives: The platinum(II) compounds *cis*-[PtMe$_2$(Me$_2$SO)$_2$] (**Pt1**)[19] and *trans*-[PtMeCl(Me$_2$SO)$_2$] (**Pt2**)[20] were prepared according to already published methods and were purified by several crystallizations from a 1:1 CH_2Cl_2/Et_2O mixture (v/v).

Mononuclear Platinum(II) Species [PtXY(9-κ*N*,κ*S*)], 10 and 11: Compound **9** (2.3 mg, 0.01 mmol) was initially dissolved in CD_3CN (0.5 mL) and afterwards added of an equivalent amount (0.01 mm) of the appropriate platinum(II) complex, *cis*-[PtMe$_2$(Me$_2$SO)$_2$] (**Pt1**) or *trans*-[PtMeCl(Me$_2$SO)$_2$] (**Pt2**). The colorless solutions almost instantly turned to light yellow. The two synthetic procedures to obtain **10** and **11** were conducted on a larger scale too by using the same molar ratio as above, in CH_3CN as solvent, and almost quantitative yields were obtained.

[PtMe$_2$(9-κ*N*,κ*S*)] (10): M.p. 58 °C. $C_{15}H_{17}NOPtS$ (454.5): calcd. C 39.64, H 3.77, N 3.08; found C 39.81, H 3.69, N 3.01. IR (nujol): $\tilde{\nu}$ = 1146 (S=O) cm^{-1}. ^{1}H NMR (300.1, CD_3CN, 298 K):δ = 8.96 (d, $^3J_{Pt,H}$ = 22.0, $^3J_{H,H}$ = 5.7 Hz, 1 H, $H^{6'}$), 8.06 (td, $^3J_{av}$ = 7.9, $^4J_{H,H}$ = 1.4 Hz, 1 H, $H^{4'}$), 7.90 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.6 Hz, 2 H, $H^{2,6}$), 7.80 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, $H^{3'}$), 7.49 (ddd, $^3J_{H,H}$ = 5.7, 7.8, $^4J_{H,H}$ = 1.4 Hz, 1 H, $H^{5'}$), 7.48 (m, 2 H, $H^{3,5}$), 7.42 (m, 1 H, H^4), 6.47 (AB system, $^4J_{Pt,H}$ = 7.0, $^2J_{A,B}$ = 2.1 Hz, 1 H, C=CH_A), 6.44 (AB system, $^4J_{Pt,H}$ = 5.8, $^2J_{A,B}$ = 2.1 Hz, 1 H, C=CH_B), 0.85 (s with satellites, $^2J_{Pt,H}$ = 77.9 Hz, 3 H, PtCH_3 *trans* to S), 0.78 (s with satellites, $^2J_{Pt,H}$ = 90.9 Hz, 3 H, Pt-CH_3 *trans* to N) ppm. ^{13}C NMR (75.5 MHz, CD_3CN, 298 K):δ = 156.0 and 152.2 ($C^{2'}$ and C=CH$_2$), 148.9 ($C^{6'}$), 144.9 (C^1), 140.0 ($C^{4'}$), 133.2 (C^4), 130.3 (C^3 + C^5), 126.6 ($C^{5'}$), 126.6 (C^2 + C^6), 119.8 (C=CH$_2$), 123.8 ($C^{3'}$), 0.85 (s, $^1J_{PtC}$ = 797 Hz, Pt-C *trans* to S), –22.0 (s with satellites, $^1J_{PtC}$ = 940 Hz, PtC *trans* to N) ppm.

[PtMeCl(9-κ*N*,κ*S*)] (11): m.p. 125 °C. $C_{14}H_{14}ClNOPtS$ (474,9): calcd. C 35.41, H 2.97, N 2.95; found C 35.35, H 3.05, N 2.99. IR (nujol): $\tilde{\nu}$ = 1147 (S=O) cm^{-1}. ^{1}H NMR (300.1, CD_3CN, 298 K):δ = 9.49 (ddd, $^3J_{Pt,H}$ = 14.3, $^3J_{H,H}$ = 5.6, $^4J_{H,H}$ = 1.6, $^5J_{H,H}$ = 0.8 Hz, 1 H, $H^{6'}$), 8.12 (td, $^3J_{av}$ = 7.8, $^4J_{H,H}$ = 1.6 Hz, 1 H, $H^{4'}$), 7.95 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.4 Hz, 2 H, $H^{2,6}$), 7.91 (ddd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.4, $^5J_{H,H}$ = 0.8 Hz, 1 H, $H^{3'}$), 7.64 (ddd, $^3J_{H,H}$ = 5.6, 7.8, $^4J_{H,H}$ = 1.4 Hz, 1 H, $H^{5'}$), 7.56 (m, $^3J_{av}$ = 7.9 Hz, 2 H, $H^{3,5}$), 7.53 (m, $^3J_{HH}$ = 7.3 Hz, 1 H, H^4), 6.62 (AB system, $^4J_{Pt,H}$ = 9.6, $^2J_{A,B}$ = 3.1 Hz, 1 H, C=CH_A), 6.55 (AB system, $^4J_{Pt,H}$ = 11.2, $^2J_{A,B}$ = 3.1 Hz, 1 H, C=CH_B), 0.87 (s with satellites, $^2J_{Pt,H}$ = 79.7 Hz, 3 H, PtCH_3 *trans* to N) ppm. ^{13}C NMR (75.5 MHz, CD_3CN, 298 K):δ = 155.5 and 152.5 ($C^{2'}$ and C=CH$_2$), 148.9 ($C^{6'}$), 146.8 (C^1), 141.1 ($C^{4'}$), 134.4 (C^4), 130.7 (C^3 + C^5), 127.7 ($C^{5'}$), 126.9 (C^2 + C^6), 123.7 (C=CH$_2$), 123.6 ($C^{3'}$), –18.3 (s with satellites, $^1J_{PtC}$ = 726 Hz, 3 H, Pt-C) ppm.

Trinuclear Platinum(II) Complex [PtXY]$_3$(6a-κ*N*,κ*S*): A solution of **6a** (1 mg, 0.0015 mmol) in CD_3CN (ca. 500 μL), hold into a 5 mm NMR tube, was mixed with three equivalent amount of complexes **Pt1** or **Pt2** (0.0045 mmol). Immediately after platinum(II) addition, the color solution changes from colorless to light-yellow.

[(PtMe$_2$)$_3$(6a-κ*N*,κ*S*)] (12): M.p. 175 °C. $C_{42}H_{57}N_3O_3Pt_3S_3$ (1333.4): calcd. C 37.83, H 4.31, N 3.15; found C 37.78, H 4.27, N 3.19. IR (nujol): $\tilde{\nu}$ = 1154 (S=O) cm^{-1}. ^{1}H NMR (300.1, CD_3CN, 298 K):δ = 9.00 (d, $^3J_{Pt,H}$ = 27.4, $^3J_{H,H}$ = 5.9 Hz, 3 H, $H^{6',6'',6'''}$), 8.25 (td, $^3J_{av}$ = 7.9 Hz, 3 H, $H^{4',4'',4'''}$), 8.15 (d, $^3J_{av}$ = 7.9 Hz, 3 H, $H^{3',3'',3'''}$), 7.55 (dd, $^3J_{H,H}$ = 5.9, 7.2 Hz, 3 H, $H^{5',5'',5'''}$), 6.64 (d, $^2J_{H,H}$ = 2.0 Hz, 3 H, 3× C=CH_A), 5.92 (d, $^2J_{H,H}$ = 2.0 Hz, 3 H, 3× C=CH_B), 4.59 (AB system, $^2J_{A,B}$ = 14.4 Hz, 3 H, 3× CH_ASO), 4.20 (AB system, $^2J_{A,B}$ = 14.4 Hz, 3 H, 3× CH_BSO), 3.09 (m, $^3J_{H,H}$ = 7.6 Hz, 1 H, 3× CH_a–CH$_3$), 2.25 (m, $^3J_{H,H}$ = 7.6 Hz, 3 H, 3× CH_b–CH$_3$), 0.90 (s with satellites, $^2J_{Pt,H}$ = 91.2 Hz, 9 H, PtCH$_3$ *trans* to N), 0.84 (s with satellites, $^2J_{Pt,H}$ = 78.7 Hz, 3 H, Pt-CH$_3$ *trans* to S), 0.68 (t, $^3J_{H,H}$ = 7.6 Hz, 9 H, CH$_2$–CH_3) ppm.

[(PtMeCl)$_3$(6a- κ*N*,κ*S*)] (13): M.p. > 220 °C. $C_{39}H_{48}Cl_3N_3O_3Pt_3S_3$ (1394.6): calcd. C 33.59, H 3.47, N 3.01; found C 33.65, H 3.40, N 3.05. IR (nujol): $\tilde{\nu}$ = 1142 (S=O) cm^{-1}. ^{1}H NMR (300.1, CD_3CN, 298 K):δ = 9.50 (ddd, $^3J_{Pt,H}$ = 20.2, $^3J_{H,H}$ = 5.6, $^4J_{H,H}$ = 1.6, $^5J_{H,H}$ = 0.8 Hz, 3 H, $H^{6',6'',6'''}$), 8.26 (td, $^3J_{av}$ = 7.8, $^4J_{H,H}$ = 1.6 Hz, 3 H, $H^{4',4'',4'''}$), 8.20 (ddd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.6, $^5J_{H,H}$ = 0.8 Hz, 3 H, $H^{3',3'',3'''}$), 7.70 (ddd, $^3J_{H,H}$ = 5.6, 7.6, $^4J_{H,H}$ = 1.6 Hz, 3 H, $H^{5',5'',5'''}$), 6.84 (d, $^2J_{H,H}$ = 2.8 Hz, 1 H, C=CH_A), 5.94 (d, $^2J_{H,H}$ = 2.8 Hz, 1 H, C=CH_B), 4.93 (AB system, $^2J_{A,B}$ = 15.0 Hz, 3 H, 3× CH_ASO), 4.57 (AB system, $^2J_{A,B}$ = 15.0 Hz, 3 H, 3× CH_BSO), 3.03 (m, $^3J_{H,H}$ = 7.6 Hz, 3 H, 3× CH_a–CH$_3$), 2.29 (m, $^3J_{H,H}$ = 7.6 Hz, 3 H, 3× CH_b–CH$_3$), 0.71 (s with satellites, $^2J_{Pt,H}$ = 83.8 Hz, 9 H, PtCH$_3$ *trans* to N), 0.70 (t, $^3J_{H,H}$ = 7.6 Hz, 9 H, 3× CH$_2$CH_3) ppm.

Computational Details: Molecular mechanics calculations were performed on a Pentium® IV personal computer using the Spartan package version '02.[16] A modified version of the MMFF94 force field implemented for transition metal parameters was used in the minimization on calculations. The X-ray structure of *rel*-2,4,6-triethyl-1,3,5-tris{[(*R*)-1-(2-pyridinyl)ethenyl]sulfinyl}methylbenzene (**6a**) was properly modified and used as an input for the calculations to gauge the performance of the MMFF calculations. Lowest-energy conformations of the trinuclear complexes **12**–**13**, as well as the monomeric species **10**–**11**, were generated. Full geometry optimization for each structure to a gradient convergence limit of less than 10^{-5} was carried out before a final single point energy calculation. During the minimization, no symmetry restriction was imposed but the positions of all atoms in both of the square coordination planes, that is, Pt–S–N–CA–CB, were kept frozen.

Supporting Information (see footnote on the first page of this article): Structural formulae of the platinum(II) derivatives **10** and **11**, as well as the trinuclear species **12** and **13**, with the adopted numbering (Charts S1–S2); crystallographic data and figure (Tables S1–S3 and Figure S1); ^{1}H NMR spectrum of the trinuclear derivative **13** (Figure S2).

Acknowledgments

This work was financially supported by Ministero dell'Istruzione, Università e Ricerca (MIUR) (PRIN 2008, prot. 200859234J and 2008A9C4HZ) and by the Italian Consiglio Nazionale delle Ricerche (CNR). M. R. P. thanks Mr. G. Irrera (ISMN-CNR) for technical assistance.

[1] a) J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*; Wiley-VCH, Weinheim, Germany, **1995**; b) L. Zhao, B. H. Northrop, P. J. Stang, *J. Am. Chem. Soc.* **2008**, *130*, 11886–11888.
[2] G. Hennrich, E. V. Anslyn, *Chem. Eur. J.* **2002**, *8*, 2218–2224, and references cited therein.
[3] a) N. Kaur, N. Singh, D. Cairns, J. F. Callan, *Org. Lett.* **2009**, *11*, 2229–2232; b) G. Tresoldi, S. Lanza, S. Di Pietro, D. Drommi, *Eur. J. Inorg. Chem.* **2008**, 4807–4815, and references cited therein; c) V. K. Bhardwaj, M. S. Hundal, G. Hundal, *Tetrahedron* **2009**, *65*, 8556–8562; d) D. B. Cordes, L. R. Hanton, *Inorg. Chem. Commun.* **2005**, *8*, 967–970; e) D. A. McMorran, C. M. Hartshorn, P. J. Steel, *Polyhedron* **2004**, *23*, 1055–1061; f) C. Yang, Q. H. Zhou, C. Yang, X.-M. Chen, X.-Q. Lu, Q.-H. Zhou, Y.-S. Yang, *Chem. Commun.* **1997**, 2041–2042.
[4] M. Calligaris, *Coord. Chem. Rev.* **2004**, *248*, 351–375; M. Calligaris, O. Carugo, *Coord. Chem. Rev.* **1996**, *153*, 83–154.
[5] E. Alessio, *Chem. Rev.* **2004**, *104*, 4203–4242; I. Fernandez, N. Khiar, *Chem. Rev.* **2003**, *103*, 3651–3705.
[6] J. Chen, J. Chen, F. Lang, X. Zhang, L. Cun, J. Zhu, J. Deng, J. Liao, *J. Am. Chem. Soc.* **2010**, *132*, 4552–4553; R. Martinez Mallorquin, S. Chelli, F. Brebion, L. Fensterbank, J.-P. Goddard, M. Malacria, *Tetrahedron: Asymmetry* **2010**, *21*, 1695–1700 and refs therein.
[7] J.-R. Li, X.-H. Bu, R.-H. Zhang, *Eur. J. Inorg. Chem.* **2004**, 1701–1704; C. Yang, W.-T. Wong, *J. Mater. Chem.* **2001**, *11*, 2898–2900.
[8] V. Amendola, M. Boiocchi, B. Colasson, L. Fabbrizzi, E. Monzani, M. J. Douton-Rodriguez, C. Spadini, *Inorg. Chem.* **2008**, *47*, 4808–4816; C. Walsdorff, S. Park, J. Kim, J. Heo, K.-M. Park, J. Oh, K. Kim, *J. Chem. Soc., Dalton Trans.* **1999**, 923–929.
[9] T. Schaub, U. Radius, Y. Diskin-Posner, G. Leitus, L. J. W. Shimon, D. Milstein, *Organometallics* **2008**, *27*, 1892–1901; E. C. Carson, S. J. Lippard, *Inorg. Chem.* **2005**, *44*, 837–848; L. Cattalini, G. Chessa, G. Marangoni, B. Pitteri, M. L. Tobe, *J. Chem. Soc., Dalton Trans.* **1985**, 2091–2094.
[10] a) P. Bonaccorsi, F. Marino-Merlo, A. Barattucci, G. Battaglia, E. Papaianni, T. Papalia, M. C. Aversa, A. Mastino, *Bioorg. Med. Chem.* **2012**, *20*, 3186–3195; b) M. C. Aversa, A. Barattucci, P. Bonaccorsi, A. Temperini, *Eur. J. Org. Chem.* **2011**, 5668–5673; c) M. C. Aversa, A. Barattucci, P. Bonaccorsi, *Synlett* **2011**, 254–258, and references cited therein; d) M. C. Aversa, A. Barattucci, P. Bonaccorsi, F. Marino-Merlo, A. Mastino, M. T. Sciortino, *Bioorg. Med. Chem.* **2009**, *17*, 1456–1463; e) M. C. Aversa, A. Barattucci, P. Bonaccorsi, P. Giannetto, *Curr. Org. Chem.* **2007**, *11*, 1034–1052; f) M. C. Aversa, A. Barattucci, P. Bonaccorsi, C. Faggi, T. Papalia, *J. Org. Chem.* **2007**, *72*, 4486–4496; g) M. C. Aversa, A. Barattucci, P. Bonaccorsi, P. Giannetto, *Curr. Org. Chem.* **2007**, *11*, 1034–1052; h) M. C. Aversa, A. Barattucci, M. C. Bilardo, P. Bonaccorsi, P. Giannetto, P. Rollin, A. Tatibouët, *J. Org. Chem.* **2005**, *70*, 7389–7396; i) M. C. Aversa, A. Barattucci, P. Bonaccorsi, P. Giannetto, *J. Org. Chem.* **2005**, *70*, 1986–1992.
[11] R. Romeo, L. Monsù Scolaro, *Inorg. Synth.* **1998**, *32*, 153–158.
[12] a) L. Monsù Scolaro, M. R. Plutino, A. Romeo, R. Romeo, G. Ricciardi, S. Belviso, A. Albinati, *Dalton Trans.* **2006**, 2551–2559; b) R. Romeo, L. Monsù Scolaro, M. R. Plutino, F. Fabrizi de Biani, G. Bottari, A. Romeo, *Inorg. Chim. Acta* **2003**, *350*, 143–151; c) R. Romeo, S. Carnabuci, L. Fenech, M. R. Plutino, A. Albinati, *Angew. Chem.* **2006**, *118*, 4606; *Angew. Chem. Int. Ed.* **2006**, *45*, 4494–4498.
[13] M. C. Aversa, A. Barattucci, P. Bonaccorsi, A. Contini, *J. Phys. Org. Chem.* **2009**, *22*, 1048–1057.
[14] a) M. R. Plutino, L. Fenech, S. Stoccoro, S. Rizzato, C. Castellano, A. Albinati, *Inorg. Chem.* **2010**, *49*, 407–418; b) R. Romeo, M. R. Plutino, A. Romeo, *Helv. Chim. Acta* **2005**, *88*, 507–522.
[15] M. L. Tobe, J. Burgess, *Inorganic Reaction Mechanism*; Addison Wesley Longman Ltd., Essex, UK, **1999**, and references cited therein; L. Monsù Scolaro, A. Mazzaglia, A. Romeo, M. R. Plutino, M. Castriciano, R. Romeo, *Inorg. Chim. Acta* **2002**, *330*, 189–196.
[16] Wavefunction Inc., *Spartan*, *'02, Molecular Modeling and Computational Chemistry Application*, **1991**–**2002**.
[17] a) M. R. Plutino, L. Fenech, S. Stoccoro, S. Rizzato, C. Castellano, A. Albinati, *Inorg. Chem.* **2010**, *49*, 407–418; b) R. Romeo, M. R. Plutino, A. Romeo, *Helv. Chim. Acta* **2005**, *88*, 507–522.
[18] a) M. R. Plutino, M. A. Castriciano, A. Mazzaglia, M. Saporita, A. Romeo, L. Monsù Scolaro, *J. Porphyrins Phthalocyanines* **2011**, *15*, 1052–1061; b) L. Alexandrova, O. G. D'Yachenko, G. M. Kazankov, V. A. Polyakov, P. V. Samuleev, E. Sansores, A. D. Ryabov, *J. Am. Chem. Soc.* **2000**, *122*, 5189–5200; c) J. A. Davies, C. M. Hockensmith, V. Y. Kukushkin, Y. N. S. C. C. Kukushkin, *Synthetic Coordination Chemistry: Theory and Practice*, World Scientific Publishing Co., **1996**; d) R. Romeo, L. Monsù Scolaro, *Inorg. Synth.* **1998**, *32*, 153–158.
[19] a) M. L. Tobe, J. Burgess, *Inorganic Reaction Mechanism*, Addison Wesley Longman Ltd., Essex, UK, **1999**, and references cited therein; b) L. Monsù Scolaro, A. Mazzaglia, A. Romeo, M. R. Plutino, M. Castriciano, R. Romeo, *Inorg. Chim. Acta* **2002**, *330*, 189–196.
[20] R. Romeo, L. Monsù Scolaro, M. R. Plutino, A. Romeo, F. Nicoló, A. Del Zotto, *Eur. J. Inorg. Chem.* **2002**, 629–638.
[21] a) R. Romeo, G. Alibrandi, G. Arena, L. Monsù Scolaro, M. R. Plutino, *Inorg. Chim. Acta* **1995**, *235*, 281–290; b) R. Romeo, L. Monsù Scolaro, M. R. Plutino, A. Del Zotto, *Trans. Met. Chem.* **1998**, *23*, 789–793.
[22] a) M. R. Plutino, L. Monsù Scolaro, R. Romeo, A. Grassi, *Inorg. Chem.* **2000**, *39*, 2712–2720; b) R. Romeo, L. M. Scolaro, in: *Perspectives, in: Organometallic Chemistry* (Eds.: C. G. Screttas, B. R. Steele), The Royal Society of Chemistry (RSC), **2003**, p. 208–221, and references cited therein; c) M. R. Plutino, L. Monsù Scolaro, A. Albinati, R. Romeo, *J. Am. Chem. Soc.* **2004**, *126*, 6470–6484.
[23] R. Romeo, L. Monsù Scolaro, N. Nastasi, B. E. Mann, G. Bruno, F. Nicolò, *Inorg. Chem.* **1996**, *35*, 7691–7698.
[24] a) L. I. Elding, A. B. Gröning, *Inorg. Chim. Acta* **1978**, *31*, 243–250; b) G. Annibale, L. Cattalini, L. Canovese, G. Michelon, G. Marangoni, M. L. Tobe, *Inorg. Chem.* **1983**, *22*, 975–978; c) F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, G. Uccello-Barretta, *Inorg. Chem.* **1990**, *29*, 29–33.

Received: January 14, 2013
Published Online: May 24, 2013

