Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 2997–3004
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and structure of a chiral dinuclear palladium(0) complex with a 30-membered hexaolefinic macrocyclic ligand

Anna Pla-Quintana [a], Anna Roglans [a,*], Teodor Parella [b], Jordi Benet-Buchholz [c]

[a] *Department of Chemistry, Universitat de Girona, Campus de Montilivi, E-17071 Girona, Spain*
[b] *Servei de RMN, Universitat Autònoma de Barcelona, Cerdanyola, E-08193 Barcelona, Spain*
[c] *X-Ray Diffraction Unit, Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans, 16, E-43007 Tarragona, Spain*

Received 20 February 2007; received in revised form 12 March 2007; accepted 12 March 2007
Available online 24 March 2007

Dedicated to Professor Miguel Yus on the occasion of his 60th birthday.

Abstract

Selective and efficient preparation of a new chiral dipalladium(0) complex with an olefinic macrocyclic ligand named (*E*,*E*,*E*,*E*,*E*,*E*)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazacyclotriaconta-3,8,13,18,23,28-hexaenedipalladium(0) (**5**) is reported. Dinuclear palladium(0) complex **5** has been fully characterized by means of NMR spectroscopy and X-ray diffraction analysis.

Keywords: Palladium; Dinuclear complexes; Alkene ligands; Macrocycles; Structural elucidation

1. Introduction

In the field of organometallic chemistry, many ligand systems have been developed in an attempt to find a way of locking two metals sufficiently close together as to provide new reactivity patterns [1]. In the particular case of organopalladium chemistry, a number of Pd(I)–Pd(I) dinuclear complexes, which have σ-bonds, have been isolated and characterized, but much less effort has been devoted to complexes with palladium in other electronic configurations [2]. Some d^{10}–d^{10} $Pd(0)_2$ complexes with a short Pd–Pd separation in which the dinuclear cluster is stabilized by two [3] or three bridging bisphosphines [4] have been structurally characterized. It is well known that olefins are also good ligands for the stabilization of palladium(0). An example of this is the catalytically active $Pd_2(dba)_3$ complex [5]. The molecular structure of $Pd_2(dba)_3$ was determined by X-ray diffraction analysis [6], which revealed that the two palladium atoms are bridged by the three dba ligands through the olefin bonds. However, in this case the two palladium(0) centres are separated by approximately 3 Å, a distance consistent with two non-interacting palladium atoms. Interestingly, the control of the Pd–Pd bond distance in dinuclear complexes can afford promising materials such as nano-structured palladium particles [2].

In recent years our group has been researching the synthesis of new polyolefinic nitrogen-containing macrocycles and their ability to coordinate palladium(0) metal [7]. Mononuclear palladium(0) complexes of types **1**–**4** (Fig. 1) have been prepared and fully characterized by means of NMR spectroscopy and X-ray diffraction [8]. These studies have demonstrated that the incorporation of a palladium atom into the cavity of a variety of sizeable polyunsaturated azamacrocyclic ligands forms stable tricoordinate complexes. The olefins in the preorganized macrocyclic ligands are ideally pre-positioned for palladium(0)-complex formation. Furthermore, palladium(0) complexes of type **1** showed excellent catalytic activity in certain carbon-carbon bond formation reactions [7,9].

* Corresponding author. Tel.: +34 972 418275; fax: +34 972 418150.
E-mail address: anna.roglans@udg.es (A. Roglans).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.03.025

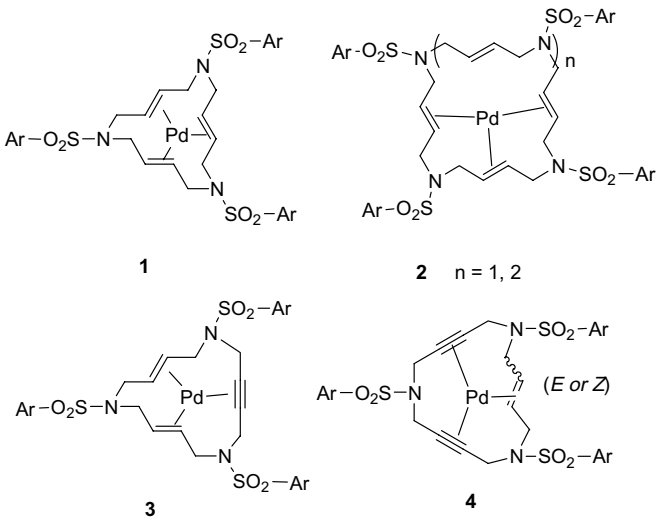


Fig. 1. General structure of monopalladium(0) complexes of polyunsaturated azamacrocyclic ligands.

Given that the 25-membered macrocycles of type **2** ($n = 2$) coordinate a single palladium(0) atom with three of its five olefins, we assumed that a 30-membered macrocyclic ligand could stabilize a dinuclear palladium–palladium motif inside the ring cavity bringing the two palladium atoms close to each other. As part of our ongoing research into the coordination properties of polyunsaturated macrocyclic ligands, and bearing in mind the scarcity of stable palladium complexes of polyolefinic macrocycles together with their potential use in catalysis and the design of new chiral topologies, we wish to report a highly efficient synthesis and the structural characterization of a dipalladium(0) complex of a 30-membered hexaazamacrocycle **5** (Fig. 2).

2. Results and discussion

The preparation of hexaazamacrocyclic ligand **13** [10] is shown in Scheme 1. The synthesis started with the condensation of butendiamine derivative **6** [7] with two equivalents of bromo compound **7** [7] in refluxing acetonitrile in the presence of K_2CO_3, which afforded a 94% yield of intermediate **8**. Compound **8** was deprotected with trifluoroacetic acid (TFAA) at room temperature and the resulting intermediate **9** was dialkylated again by treatment with two equivalents of **7** in the presence of K_2CO_3 as a base. A 76% yield of compound **10** was obtained from two steps. Deprotection of the BOC groups of derivative **10** was again achieved using trifluoroacetic acid in methylene chloride at room temperature. The desired macrocycle was obtained after a cyclisation reaction of an equimolar mixture of compound **11** with the commercially available (*E*)-1,4-dibromobutene **12** in refluxing acetonitrile and K_2CO_3 as a base. A 59% yield of hexaazamacrocycle **13** was obtained and an overall yield of 37% was achieved from the five-step synthesis.

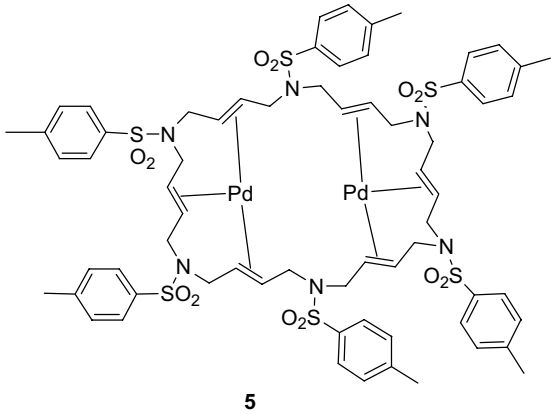


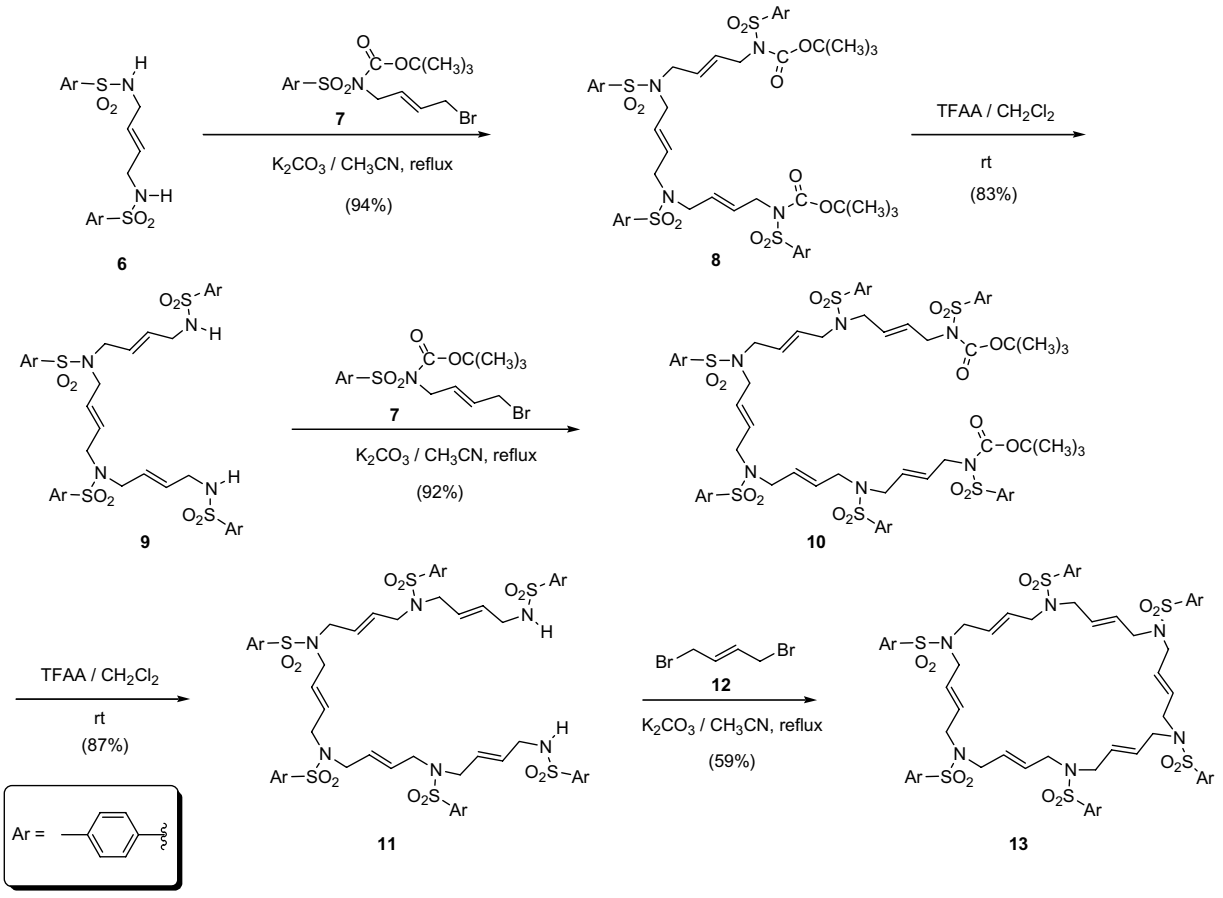
Fig. 2. Structure of the dipalladium(0) complex of a 30-membered hexaazamacrocyclic ligand.

Macrocycle **13** is a colourless solid which gives correct elemental analysis and presents simple ^1H and ^{13}C NMR spectra due to its high symmetry. The 12 methylene units in the ring appear at $\delta \approx 3.6$ ppm as a broad singlet and the 12 equivalent olefinic protons also give a broad singlet at $\delta \approx 5.4$ ppm. Finally, a singlet at $\delta \approx 2.4$ ppm ($CH_3C_6H_4$–) and aromatic protons at $\delta \approx 7.26$–7.67 ppm complete the expected resonances for the target compound. In the ^{13}C NMR spectrum, the chemical shift of the olefinic carbon atoms is observed at $\delta \approx 129.2$ ppm and the 12 CH_2 carbon atoms appear at $\delta \approx 48.8$ ppm. The ESI mass spectrum of compound **13** shows a peak at m/z 1339 corresponding to the molecular ion $[M+H]^+$ together with other cation adducts such as $[M+NH_4]^+$ at m/z 1356 and $[M+K]^+$ at m/z 1377.

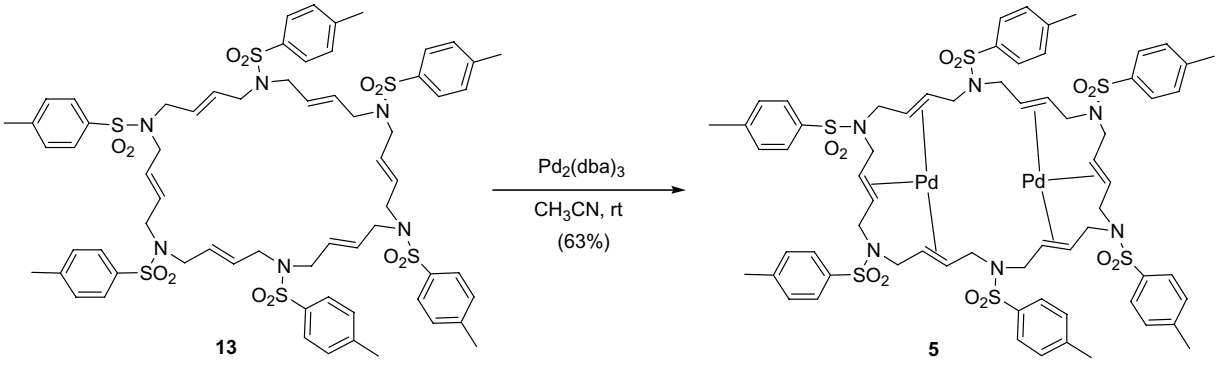
Dipalladium(0) complex **5** was easily prepared by ligand-exchange using $Pd_2(dba)_3$ as a source of palladium(0) in a solution of the 30-membered macrocycle **13** in acetonitrile (Scheme 2).

Compound **5** was purified by column chromatography on silica-gel. The compound was air and moisture-stable and gave a correct elemental analysis. The inclusion of two palladium atoms into the ring cavity was easily confirmed by ESI-MS analysis, which showed a peak at m/z 1575 consistent with the adduct of the dipalladium complex with sodium $[M+Na]^+$. Fig. 3 shows the ^1H and ^{13}C NMR chemical shift assignments for the dinuclear Pd-complex **5**. The simple ^1H and ^{13}C NMR spectra of complex **5** confirm the presence of a high symmetry in the molecule. The general conclusions regarding the structure of **5** in solution are in line with those reached after performing detailed NMR studies into similar 15-, 20- and 25-membered azamacrocylic complexes [8]. Each palladium atom coordinates independently with three olefin systems to form a highly rigid five-ring system consisting of consecutively fused three and six-membered rings, as shown in Fig. 3.

For each palladium metal six asymmetric carbon atoms are formed resulting from the coordination of the palladium to the two olefin faces of each double bond in the macrocycle [11]. However, since the three double bonds are of defined stereochemistry *trans,* three independent pairs of asymmetric centres must be considered. Therefore,



Scheme 1. Synthesis of hexaazamacrocycle **13**.



Scheme 2. Synthesis of dipalladium(0) complex **5**.

only eight stereoisomers grouped into four pairs of enantiomers should be possible. From NMR data all six-membered sub-structures present the same highly rigid *chair* conformation as deduced from the well characterized axial and equatorial position of the α-nitrogen methylene protons ($\Delta\delta$ about 3 ppm) and from clear NOE observed between the 1,3-diaxially positioned protons at 1.61 and 1.37 ppm. Therefore, it can be stated that stereoisomers containing palladacyclohexanic rings with a *twist* conformation are not formed, which leaves just four stereoisomers with overall *chair-chair* conformation. Obviously, all three cyclopropane moieties show a *trans* rearrangement. On the other hand, the central 12-membered ring shows a more flexible structure as seen from the smaller chemical shift difference in methylene groups ($\Delta\delta$ about 0.6 ppm between geminal protons). Fig. 4 shows the most stable stereoisomers expected for complex **5**, a *meso* form **A1/A2** and a pair of enantiomers **A3/A4**. In terms of molecular symmetry, the *meso* structure **A1/A2** has a symmetry plane intersecting the two nitrogen atoms N1/N16 and a C_2-axis crossing through the two palladium atoms. On the other hand, each enantiomer **A3/A4** presents three

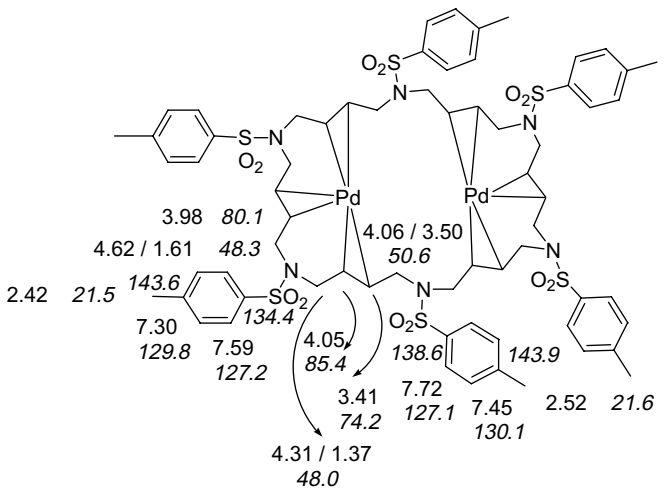


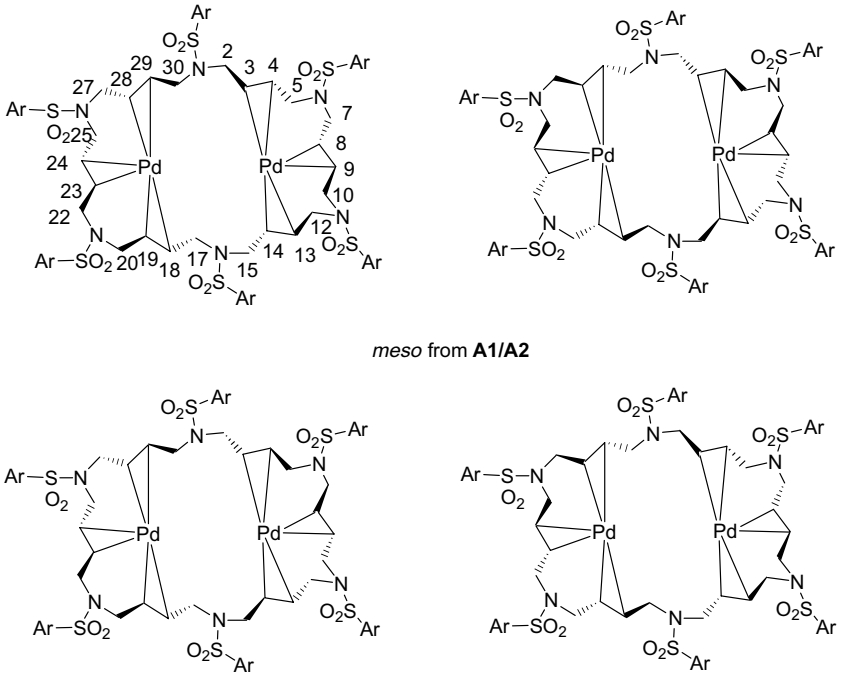
Fig. 3. ^{1}H and ^{13}C NMR (in italics) chemical shift assignments for dipalladium complex **5**.

C_2-axis, one intersecting N1/N16 atoms, another centered in the middle of the molecule just perpendicular to the drawing and the other passing through the two palladium atoms. Both ^{1}H and ^{13}C NMR data are fully consistent with the three possible stereoisomers, but according to the X-ray structure (see below) we can suppose that the enantiomeric pair **A3**/**A4** is the only structure formed.

We performed PGSE studies [12] to confirm the inclusion of two palladium atoms inside the macrocylic cavity. Whereas the free ligand **13** presents a diffusion coefficient of 5.13×10^{-10} m^2/s, complex **5** shows a value of 4.84×10^{-10} m^2/s. These similar values agree with the fact that although the molecular weight increased by 15%, the contact surface and the overall molecular size of **5** with respect to **13** were not altered.

The structure of **5** was confirmed by X-ray diffraction study [13]. A perspective view of the molecule is shown in Fig. 5. Complex **5** crystallizes from dichloromethane as the main solvent in a centrosymmetrical space group with three disordered dichloromethane molecules in the crystal cell. In the crystal packing of compound **5**, a local C_2-symmetry is shown with the palladium atoms coordinated to three olefinic bonds. In agreement with the NMR results the four palladacyclohexanic rings observed in the crystal structure present a *chair* conformation. The only pair present in the solid state is the enatiomeric pair **A3**/**A4** (the observation of a stereoisomer in a centrosymmetrical space group implies the existence of its enantiomer in the structure). The olefinic *trans* double bonds are coordinated to the palladium(0) in a trigonal planar coordination geometry. The planes formed by the coordination sphere of Pd1 and Pd2 form an angle of 45°. The Pd1–Pd2 distance is of 7.3 Å similar to the intermolecular distances of the metallic atoms (Pd1(molecule A)–Pd1(molecule B) 8.1 Å and Pd2(molecule A)–Pd2(molecule B) 7.2 Å). In comparing distances between two externally located double bonds and their corresponding palladium atoms (Pd1/C23–C24 and Pd2/C10–C11) and Pd/double bond distances which are situated more internally, we find, taking into account standard deviations, that the former are slightly longer.

In summary, we have prepared a 30-membered hexaolefinic azamacrocyclic ligand **13** by a highly efficient synthesis in terms of yields and simplicity. Macrocycle **13** has shown a complexing ability towards palladium(0) and so generating a novel chiral dinuclear palladium complex.



A3 (3*R*, 4*R*, 8*S*, 9*S*, 13*R*, 14*R*, 18*R*, 19*R*, 23*S*, 24*S*, 28*R*, 28*R*) **A4** (3*S*, 4*S*, 8*R*, 9*R*, 13*S*, 14*S*, 18*S*, 19*S*, 23*R*, 24*R*, 28*S*, 28*S*)

Fig. 4. Expected stereoisomers for palladium(0) complex **5**, a *meso* form **A1**/**A2**, and a pair of enantiomers **A3**/**A4**.

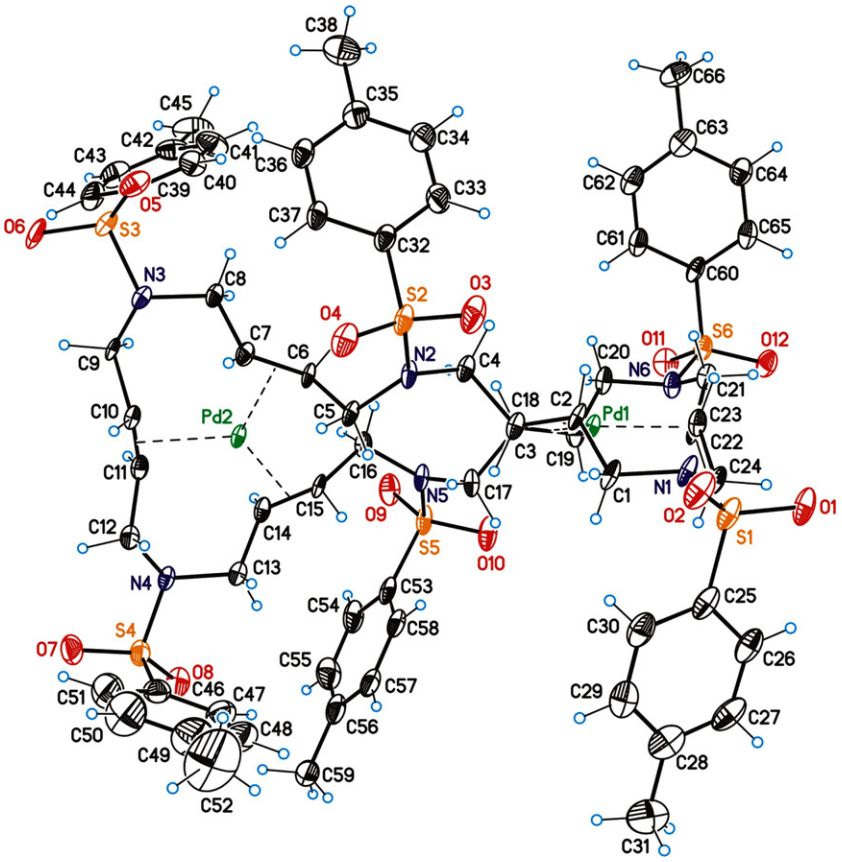


Fig. 5. ORTEP plot (50%) obtained from single crystal X-ray structure analysis of **5**. Selected bond distances (Å): C(2)–C(3): 1.383(5); C(6)–C(7): 1.362(6); C(10)–C(11): 1.384(6); C(14)–C(15): 1.397(5); C(18)–C(19): 1.391(7); C(22)–C(23): 1.376(6); Pd(1)–C(2): 2.187(4); Pd(1)–C(3): 2.177(4); Pd(1)–C(18): 2.185(4); Pd(1)–C(19): 2.190(4); Pd(1)–C(22): 2.202(4); Pd(1)–C(23): 2.213(4); Pd(2)–C(6): 2.197(4); Pd(2)–C(7): 2.178(4); Pd(2)–C(10): 2.225(5); Pd(2)–C(11): 2.217(4); Pd(2)–C(14): 2.188(4); Pd(2)–C(15): 2.172(5).

The dipalladium complex was characterized by NMR and X-ray diffraction analysis. The rigid conformation of the two triolefin–palladium moieties in the macrocyclic ring separates the two metal atoms to a distance of approx. 7 Å and prevents their interaction. Applications of **5** in catalysis are now under investigation.

3. Experimental

3.1. General methods

IR spectra were recorded with a FT-IR using a single reflection ATR system as a sampling accessory. ^{1}H NMR (^{13}C NMR) spectra were recorded at 200 MHz and 500 MHz (50 MHz and 125 MHz) using Me_4Si as the internal standard. Chemical shifts are given in δ units. NMR experiments were recorded at 298 K on an AVANCE500 Bruker spectrometer equipped with a cryogenically cooled probe. Full ^{1}H and ^{13}C NMR resonance assignments were confirmed from 2D COSY and HSQC methods. Self-diffusion coefficient measurements were made under routine conditions using the BPLED pulse scheme with a diffusion time of 150 ms and with sample rotation of 20 Hz to avoid undesired convection effects [14]. ESI mass spectra were acquired using a Navigator quadrupole instrument (Finnigan AQA ThermoQuest) equipped with an electrospray ion source. Elemental analyses were determined by the Chemical Analysis Service of the University of Girona.

1,4-Dibromobutene (**12**), is commercially available and was used without further purification. Butendiamine derivative **6** and bromo compound **7** were prepared as previously reported [7].

3.2. Preparation of (*E,E,E*)-1,16-bis(tert-butyloxicarbonyl)-1,6,11,16-tetrakis[(4-methylphenyl)sulfonyl]-1,6,11,16-tetraazahexadeca-3,8,13-triene (*8*)

A mixture of (*E*)-*N*,*N*′-bis[(4-methylphenyl)sulfonyl]-2-buten-1,4-diamine (**6**) (1.20 g, 3.0 mmol), and anhydrous potassium carbonate (2.84 g, 20.5 mmol) in acetonitrile (70 mL) was heated at 70 °C for 30 min in a 250 mL round-bottomed flask equipped with magnetic stirring and a condenser. Then, a solution of *N*-[(*E*)-4-bromo-2-butenyl]-*N*-(*tert*-butyloxicarbonyl)-(4-methylphenyl)sulfonamide, (**7**), (2.48 g, 6.1 mmol) in acetonitrile (80 mL) was added and the mixture was refluxed for 6 h (TLC monitoring). After cooling to room temperature, the salts were filtered off and the filtrate was evaporated. The residue was

purified by column chromatography through silica gel with mixtures of hexane–dichloromethane–ethyl acetate of increasing polarity as the eluent (from 8:1:1 to 6:2:2) to afford (*E*,*E*,*E*)-1,16-bis(*tert*-butyloxicarbonyl)-1,6,11,16-tetrakis[(4-methylphenyl)sulfonyl]-1,6,11,16-tetraazahexadeca-3,8,13-triene (**8**), as a colourless solid (2.97 g, 94% yield); m.p. 138–139 °C (hexane–dichloromethane–ethyl acetate); IR (ATR) 2923, 1713, 1331, 1133 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.32 (s, 18H), 2.42 (s, 12H), 3.68–3.78 (m, 8H), 4.32–4.37 (m, 4H), 5.37–5.77 (br abs, 6H), 7.30 (m, 8H), 7.67 (BB′ part of the AA′BB′ system, $J = 8.2$ Hz, 4H), 7.76 (BB′ part of the AA′BB′ system, $J = 8.4$ Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 21.4, 21.5, 27.8, 47.5, 48.0, 48.2, 84.3, 127.1, 127.9, 128.3, 128.8, 129.2, 129.7, 137.0, 137.1, 143.3, 144.2, 150.6; ESI-MS (*m*/*z*) 1041 $[M+H]^+$, 1058 $[M+NH_4]^+$, 1063 $[M+Na]^+$. Anal. Calc. for $C_{50}H_{64}N_4O_{12}S_4$ (1041.3): C, 57.67; H, 6.19; N, 5.38; S, 12.32. Found: C, 57.64; H, 6.51; N, 5.40; S, 12.14%.

3.3. Preparation of (*E*,*E*,*E*)-1,6,11,16-tetrakis[(4-methylphenyl)sulfonyl]-1,6,11,16-tetraazahexadeca-3,8,13-triene (**9**)

Trifluoroacetic acid (6 mL, 77.9 mmol) was added dropwise to a solution of (*E*,*E*,*E*)-1,16-bis(*tert*-butyloxicarbonyl)-1,6,11,16-tetrakis[(4-methylphenyl)sulfonyl]-1,6,11,16-tetraazahexadeca-3,8,13-triene (**8**), (2.63 g, 2.5 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature for 9 h (TLC monitoring). Then, the solution was evaporated and the excess of trifluoroacetic acid was eliminated by means of a nitrogen gas flow. The white residue was purified by column chromatography through silica gel with mixtures of dichloromethane–ethyl acetate of increasing polarity as the eluent (from 20:0 to 20:2) to afford (*E*,*E*,*E*)-1,6,11,16-tetrakis[(4-methylphenyl)sulfonyl]-1,6,11,16- tetraazahexadeca-3,8,13-triene (**9**), as a colourless solid (1.75 g, 83% yield); m.p. 158–160 °C (dichloromethane–ethyl acetate); IR (ATR) 3268, 2923, 1322, 1155 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 2.41 (s, 6H), 2.44 (s, 6H), 3.44–3.48 (m, 4H), 3.64–3.69 (m, 8H), 5.12–5.14 (m, 2H), 5.38–5.64 (br. abs, 6H), 7.25–7.34 (m, 8H), 7.67 (BB′ part of the AA′BB′ system, $J = 8.4$ Hz, 4H), 7.71 (BB′ part of the AA′BB′ system, $J = 8.4$ Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 21.5, 44.3, 48.8, 49.3, 127.1, 127.2, 127.9, 129.2, 129.7, 129.8, 130.0, 136.5, 136.8, 143.4, 143.6; ESI-MS (*m*/*z*) 841 $[M+H]^+$. Anal. Calc. for $C_{40}H_{48}N_4O_8S_4$ (841.1): C, 57.12; H, 5.75; N, 6.66; S, 15.25. Found: C, 56.70; H, 5.95; N, 6.43; S, 14.87%.

3.4. Preparation of (*E*,*E*,*E*,*E*,*E*)-1,26-bis(tert-butyloxi carbonyl)-1,6,11,16,21,26-hexakis[(4-methylphenyl)-sulfonyl]-1,6,11,16,21,26-hexaazahexacosa-3,8,13,18,23-pentaene (**10**)

A mixture of (*E*,*E*,*E*)-1,6,11,16-tetrakis[(4-methylphenyl)sulfonyl]-1,6,11,16-tetraazahexadeca-3,8,13-triene (**9**), (1.51 g, 1.8 mmol) and anhydrous potassium carbonate (1.91 g, 13.8 mmol) in acetonitrile (65 mL) was heated at 70 °C for 30 min in a 250 mL round-bottomed flask equipped with magnetic stirring and a condenser. Then, a solution of *N*-[(*E*)-4-bromo-2-butenyl]-*N*-(*tert*-butyloxicarbonyl)-(4-methylphenyl)sulfonamide (**7**), (1.46 g, 3.6 mmol) in acetonitrile (80 mL) was added and the mixture was refluxed for 20 h (TLC monitoring). After cooling to room temperature, the salts were filtered off and the filtrate was evaporated. The residue was purified by column chromatography through silica gel with mixtures of dichloromethane-ethyl acetate of increasing polarity as the eluent (from 20:0 to 20:2) to afford (*E*,*E*,*E*,*E*,*E*)-1,26-bis(*tert*-butyloxicarbonyl)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazahexacosa-3,8,13,18,23-pentaene (**10**), as a colourless solid (2.67 g, 92% yield); m.p. 133–135 °C (dichloromethane–diethyl ether–hexanes); IR (ATR) 2927, 1716, 1355, 1335, 1145, 1177 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.31 (s, 18H), 2.42 (s, 18H), 3.64–3.76 (m, 16H), 4.30–4.36 (m, 4H), 5.40–5.69 (br abs, 10H), 7.24–7.32 (m, 12H), 7.65 (BB′ part of the AA′BB′ system, $J = 8.4$ Hz, 4H), 7.66 (BB′ part of the AA′BB′ system, $J = 8.4$ Hz, 4H), 7.75 (BB′ part of the AA′BB′ system, $J = 8.4$ Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 21.5, 27.8, 47.5, 48.2, 48.4, 84.4, 127.2, 127.9, 128.2, 128.7, 128.9, 129.1, 129.3, 129.8, 136.9, 137.2, 143.4, 144.3, 150.6; ESI-MS (*m*/*z*) 1487 $[M+H]^+$, 1504 $[M+NH_4]^+$, 1509 $[M+Na]^+$, 1525 $[M+K]^+$. Anal. Calc. for $C_{72}H_{90}N_6O_{16}S_6$ (1487.9): C, 58.12; H, 6.10; N, 5.65; S, 12.93. Found: C, 58.23; H, 6.38; N, 5.64; S, 12.85%.

3.5. Preparation of (*E*,*E*,*E*,*E*,*E*)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazahexacosa-3,8,13,18,23-pentaene (**11**)

Trifluoroacetic acid (5 mL, 64.9 mmol) was added dropwise to a solution of (*E*,*E*,*E*,*E*,*E*)-1,26-bis(*tert*-butyloxicarbonyl)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazahexacosa-3,8,13,18,23-pentaene (**10**), (2.35 g, 1.6 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature for 6 h (TLC monitoring). Then, the solution was evaporated and the excess of trifluoroacetic acid was eliminated by means of a nitrogen gas flow. The white residue was purified by column chromatography through silica gel with mixtures of dichloromethane–ethyl acetate of increasing polarity as the eluent (from 25:0 to 23:2) to afford (*E*,*E*,*E*,*E*,*E*)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazahexacosa-3,8,13,18,23-pentaene (**11**), as a colourless solid (1.77 g, 87% yield); m.p. 151–153 °C (ethyl acetate–dichloromethane); IR (ATR) 3271, 2924, 1716, 1334, 1156 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 2.40 (s, 6H), 2.42 (s, 12H), 3.41–3.45 (m, 4H), 3.62–3.66 (m, 16H), 5.13–5.15 (m, 2H), 5.29–5.56 (br abs, 10H), 7.22–7.35 (m, 12H), 7.64 (BB′ part of the AA′BB′ system, $J = 8.2$ Hz, 4H), 7.67 (BB′ part of the AA′BB′ system, $J = 8.2$ Hz, 4H), 7.69 (BB′ part of the AA′BB′ system,

$J = 8.2$ Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 21.4, 44.3, 48.5, 48.6, 48.8, 127.0, 127.1, 127.7, 128.9, 129.2, 129.6, 129.7, 129.8, 136.4, 136.6, 136.8, 143.3, 143.5, 143.6; ESI-MS (m/z) 1287 $[M+H]^+$, 1304 $[M+NH_4]^+$, 1309 $[M+Na]^+$, 1325 $[M+K]^+$. Anal. Calc. for $C_{62}H_{74}N_6O_{12}S_6$ (1287.7): C, 57.83; H, 5.79; N, 6.53; S, 14.91. Found: C, 57.68; H, 5.96; N, 6.49; S, 14.65%.

3.6. Preparation of (*E,E,E,E,E,E*)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazacyclotriaconta-3,8,13,18,23,28-hexaene (**13**)

A mixture of (*E,E,E,E,E*)-1,6,11,16,21,26-hexakis [(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazahexacosa-3,8,13,18,23-pentaene (**11**), (1.51 g, 1.2 mmol), (*E*)-1,4-dibromobutene (**12**), (0.26 g, 1.2 mmol), and anhydrous potassium carbonate (1.09 g, 7.9 mmol) in acetonitrile (130 mL) was refluxed for 21 h (TLC monitoring) in a 250 mL round-bottomed flask equipped with magnetic stirring and a condenser. After cooling to room temperature, the salts were filtered off and the filtrate was evaporated. The residue was purified first by column chromatography through silica gel with mixtures of hexanes–dichloromethane–ethyl acetate of increasing polarity as the eluent (from 7:2:1 to 2:5:3) and secondly by crystallization from mixtures of hexanes–dichloromethane–ethyl acetate to afford (*E,E,E,E,E,E*)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazacyclotriaconta-3,8,13,18,23,28-hexaene (**13**), as a colourless solid (0.92 g, 59% yield); m.p. 182–185 °C; IR (ATR) 2920, 1332, 1157 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 2.43 (s, 18H), 3.64 (broad s, 24H), 5.45 (broad s, 12H), 7.30 (AA′ part of the AA′BB′ system, $J = 8.2$ Hz, 12H), 7.64 (BB′ part of the AA′BB′ system, $J = 8.2$ Hz, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) 21.5, 48.8, 127.2, 129.2, 129.8, 136.3, 143.5; ESI-MS (m/z) 1339 $[M+H]^+$, 1356 $[M+NH_4]^+$, 1377 $[M+K]^+$. Anal. Calc. for $C_{66}H_{78}N_6O_{12}S_6$ (1339.7): C, 59.17; H, 5.87; N, 6.27; S, 14.36. Found: C, 59.02; H, 6.20; N, 6.20; S, 14.10.

3.7. Preparation of (*E,E,E,E,E,E*)-1,6,11,16,21,26-hexakis-[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaaza-cyclotriaconta-3,8,13,18,23,28-hexaenedipalladium(0) (**5**)

A mixture of (*E,E,E,E,E,E*)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazacyclotriaconta-3,8,13,18,23,28-hexaene (**13**), (0.15 g, 0.1 mmol) and bis (dibenzylideneacetone)palladium(0) (0.13 g, 0.2 mmol) in acetonitrile (8 mL) was stirred at room temperature for 8 h (TLC monitoring). After removing the solvent, the residue was purified first by column chromatography through silica gel with mixtures of hexanes–dichloromethane–ethyl acetate of increasing polarity as the eluent (from 7:2:1 to 0:3:7) and secondly by crystallization from mixtures of hexanes–dichloromethane–ethyl acetate to afford (*E,E,E,E,E,E*)-1,6,11,16,21,26-hexakis[(4-methylphenyl)sulfonyl]-1,6,11,16,21,26-hexaazacyclotriaconta-3,8,13,18,23,28-hexaenedipalladium(0) (**5**), as a colourless solid (0.11 g, 63% yield); m.p. 190–191 °C (dec); IR (ATR) 2921, 1331, 1158 cm^{-1}; ^{1}H NMR (500.13 MHz, $CDCl_3$): 1.37 (dd, $J = 10.8$ and 14.1 Hz, 4H), 1.61 (m, 4H), 2.42 (s, 12H), 2.52 (s, 6H), 3.41 (t, $J = 11.2$ Hz, 4H), 3.50 (dd, $J = 10.8$ and 14.3 Hz, 4H), 3.98 (m, 4H), 4.05 (m, 4H), 4.06 (m, 4H), 4.31 (d, $J = 14.1$ Hz, 4H), 4.62 (d, $J = 13.8$ Hz, 4H), 7.30 (AA′ part of the AA′BB′ system, $J = 8.2$ Hz, 8H), 7.45 (AA′ part of the AA′BB′ system, $J = 8.2$ Hz, 4H), 7.59 (BB′ part of the AA′BB′ system, $J = 8.2$ Hz, 8H), 7.72 (BB′ part of the AA′BB′ system, $J = 8.2$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 21.5, 21.6, 48.0, 48.3, 50.6, 74.2, 80.1, 85.4, 127.1, 127.2, 129.8, 130.1, 134.4, 138.6, 143.6, 143.9; ESI-MS (m/z) 1575 $[M+Na]^+$. Anal. Calc. for $C_{66}H_{78}N_6O_{12}S_6$ (1552.5): C, 51.06; H, 5.06; N, 5.41. Found: C, 50.95; H, 5.43; N, 5.22%.

Crystal structure determination: Colourless crystals of **5** were grown by slow evaporation at room temperature in dichloromethane. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection: Measurements were made on a Bruker–Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, an FR591 rotating anode with Mo Kα radiation, Montel mirrors as monochromator and a Kryoflex low temperature device ($T = 100$ K). Full-sphere data collection was used with ω and φ scans. Programs used: data collection APEX2 V. 1.0-22 (Bruker–Nonius 2004), data reduction SAINT+ Version 6.22 (Bruker–Nonius 2001) and absorption correction SADABS V. 2.10 (2003).

Structure solution and refinement: SHELXTL Version 6.10 (Sheldrick, 2000) was used.

Acknowledgements

The financial support from Ministry of Education and Science (MEC) of Spain (Projects CTQ2005-04968 and BQU2003-01677) and Generalitat de Catalunya (Project 2005SGR00305) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 637301 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.03.025.

References

[1] A.L. Gavrilova, B. Bosnich, Chem. Rev. 104 (2004) 349–383; B. Chaudret, B. Delavaux, R. Poilblanc, Coord. Chem. Rev. 86 (1988) 191–243.

[2] For a review on organopalladium complexes containing Pd–Pd bonds, see: T. Murahashi, H. Kurosawa, Coord. Chem. Rev. 231 (2002) 207–228, and references cited therein.
[3] Y. Pan, J.T. Mague, M.J. Fink, J. Am. Chem. Soc. 115 (1993) 3842–3843;
S.M. Reid, J.T. Mague, M.J. Fink, J. Am. Chem. Soc. 123 (2001) 4081–4082.
[4] P.D. Harvey, H.B. Gray, J. Am. Chem. Soc. 110 (1988) 2145–2147;
R.U. Kirss, R. Eisenberg, Inorg. Chem. 28 (1989) 3372–3378.
[5] E. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, John Wiley & Sons, New York, 2002.
[6] K. Selvakumar, M. Valentini, M. Wörle, P.S. Pregosin, A. Albinati, Organometallics 18 (1999) 1207–1215;
C.G. Pierpont, M.C. Mazza, Inorg. Chem. 13 (1974) 1891–1895;
T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet, J.A. Ibers, J. Organomet. Chem. 65 (1974) 253–266.
[7] M. Moreno-Mañas, R. Pleixats, A. Roglans, R.M. Sebastián, A. Vallribera, Arkivoc 109 (2004) 109–129. http://www.arkat-usa.org;
M. Moreno-Mañas, R. Pleixats, R.M. Sebastián, A. Vallribera, A. Roglans, J. Organomet. Chem. 689 (2004) 3669–3684.
[8] A. Pla-Quintana, A. Roglans, J. Vicente de Julián-Ortiz, M. Moreno-Mañas, T. Parella, J. Benet-Buchholz, X. Solans, Chem. Eur. J. 11 (2005) 2689–2697;
A. Pla-Quintana, A. Torrent, A. Dachs, A. Roglans, R. Pleixats, M. Moreno-Mañas, T. Parella, J. Benet-Buchholz, Organometallics 25 (2006) 5612–5620.
[9] J. Cortés, M. Moreno-Mañas, R. Pleixats, Eur. J. Org. Chem. (2000) 239–243;
B. Estrine, B. Blanco, S. Bouquillon, F. Hénin, M. Moreno-Mañas, J. Muzart, C. Pena, R. Pleixats, Tetrahedron Lett. 42 (2001) 7055–7057;
S. Cacchi, G. Fabrizi, A. Goggiamani, M. Moreno-Mañas, A. Vallribera, Tetrahedron Lett. 43 (2002) 5537–5540;
A. Llobet, E. Masllorens, M. Moreno-Mañas, A. Pla-Quintana, M. Rodríguez, A. Roglans, Tetrahedron Lett. 43 (2002) 1425–1428;
J. Masllorens, M. Moreno-Mañas, A. Pla-Quintana, A. Roglans, Org. Lett. 5 (2003) 1559–1561.
M. Moreno-Mañas, R. Pleixats, J. Spengler, C. Chevrin, B. Estrine, S. Bouquillon, F. Hénin, J. Muzart, A. Pla-Quintana, A. Roglans, Eur. J. Org. Chem. (2003) 274–283;
A. Llobet, E. Masllorens, M. Rodríguez, A. Roglans, J. Benet-Buchholz, Eur. J. Org. Chem. (2004) 1601–1610;
J. Masllorens, S. Bouquillon, A. Roglans, F. Hénin, J. Muzart, J. Organomet. Chem. 690 (2005) 3822–3826;
J. Masllorens, I. González, A. Roglans, Eur. J. Org. Chem. (2007) 158–166.
[10] Low yields of an analogous 30-membered azamacrocycle containing six 4-fluorophenylsulfonyl units instead of six 4-methylphenylsulfonyl units were obtained mixed together with the corresponding 15-membered azamacrocycle and polymeric materials by Moreno-Mañas: M. Moreno-Mañas, J. Spengler, Tetrahedron 58 (2002) 7769–7774.
[11] An olefinic compound without substituent asymmetric groups, and without symmetry planes perpendicular to the plane of the double bond, becomes asymmetric upon coordination. See: G. Paiaro, Organomet. Chem. Rev. Sect. A 6 (1970) 319–335.
[12] P.S. Pregosin, P.G.A. Kumar, I. Fernandez, Chem. Rev. 105 (2005) 2977–2998;
M. Valentini, P.S. Pregosin, H. Ruegger, Organometallics 19 (2000) 2551–2555.
[13] Crystal data for **5** at 100 K:$C_{66}H_{78}N_6O_{12}Pd_2S_6$, 1552.50 g mol^{-1}, monoclinic, $P2_1/c$, $a = 13.9703(15)$ Å, $b = 29.077(3)$ Å, $c = 20.402(2)$ Å, $\beta = 99.852(3)°$, $V = 8165.5(15)$ Å^3, $Z = 4$, $\rho_{calc} = 1.539$ Mg/m^3 (taking into account three disordered dichloromethane molecules), $R_1 = 0.0785$ (0.1052), $wR_2 = 0.1959$ (0.2098), for 16,467 reflections with $I > 2\sigma(I)$ (for 23,871 reflections [R_{int}: 0.0876] with a total measured of 107,896 reflections), goodness-of-fit on $F^2 = 1.015$, largest difference peak (hole) = 3.779(−2.851) e Å^{-3}. The measured crystal contains three highly disordered dichloromethane molecules which were treated with the program Squeeze included in the multipurpose crystallographic tool Platon (A.L. Spek, Acta Crystallogr. A 46 (1990) C34). For details see the CIF-file. The R_1-value could be improved, using this program, from 0.12 to 0.078.
[14] N. Esturau, F. Sánchez-Ferrando, J.A. Gavin, C. Roumestand, M.A. Delsuc, T. Parella, J. Magn. Reson. 153 (2001) 48–55;
D. Wu, A. Chen, C.S. Johnson Jr, J. Magn. Reson. A 115 (1995) 260–264.