The First Transition Metal Complexes of 15-Membered Triolefinic Macrocycles: (*E,E,E*)-1,6,11-Tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene Complexes of Palladium(0), Platinum(0), and Silver(I)

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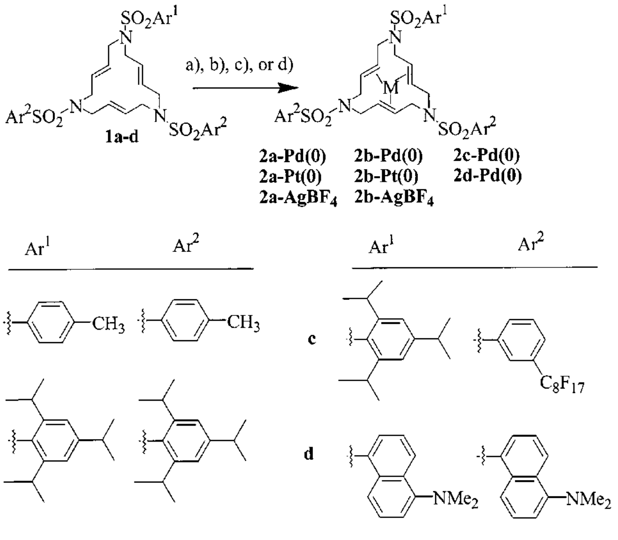
(*E,E,E*)-1,6,11-Tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes (**1**) form very stable complexes with Pd^0 and Pt^0, and moderately stable complexes with Ag^I. The three olefins in the macrocycle are responsible for the complexation. The X-ray structures of two complexes of Pd^0 and Pt^0 are presented; both complexes are planar trigonal.

Introduction

Nitrogen-containing 15-membered macrocycles are commonplace.[1,2] However, nitrogen-containing 15-membered macrocycles featuring internal olefinic double bonds are exceptional. The few known examples contain only one double bond, and metathesis is the key step for their preparation.[3] In 1998 we described the serendipitous formation of (*E,E,E*)-1,6,11-tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes (**1**) and the complex **2b-Pd^0** (Scheme 1) by nonselective palladium(0)-catalyzed Tsuji−Trost allylation of arenesulfonamides with *cis*-2-butene-1,4-diol dicarbonate.[4] The macrocycle **1b** affords the complex **2b-Pd^0** by treatment with sources of Pd^0. This complex is very stable, catalyses certain Suzuki-type cross-coupling reactions, and is easily recovered after catalysis.[5] Later we published the optimized preparations of macrocycles **1** featuring a vast array of substituents at the arenesulfonyl moieties.[6]

The complexes Pd$_2$(dba)$_3$-solvent and Pd$_2$(dba)$_4$ [7] are very well-known and their catalytic effect has been recognized. Many other complexes of olefins with palladium(0) and platinum(0) have been described.[8−10] However, only a few complexes of transition metals with triolefinic macrocycles are known. Thus, the diverse configurational isomers of the 12-membered carbocycle cyclododeca-1,5,9-triene have a rich coordination chemistry, and their Ni^0 complexes have played a fundamental role in catalysis and in organonickel chemistry.[11] X-ray diffraction data of the (*E*,*E*,E) isomer show that the complex is planar trigonal.[11b] Other metals form complexes with cyclododecatrienes: Cu^I,[12] Pd^{II},[13] Ag^I,[14] Rh^{III},[15] and Ru^{II}.[16] Related 12-membered carbocycles also form nickel(0) complexes.[17] At the upper limit of ring size, 13-membered (*Z,E,Z*)-cyclotrideca-1,5,9-triene forms a complex with Ag^I.[18] A special case is the complexation of Ag^I by [2.2.2]paracyclophanes, which occurs in an η^2 manner at each of the three benzene rings.[19] The related [2$_6$](1,2,4,5)cyclophane (deltaphane) presents the same behavior.[19b] In contrast, (*Z,Z,Z*)-tribenz[12]annulene, the triunsaturated analogue of [2.2.2]orthocyclophane coordinates Ag^I through the three olefins.[20] Metal complexes of macrocyclic triolefins higher than 13-membered are unknown.



Scheme 1. Preparation of complexes **2**: a) Pd(PPh$_3$)$_4$ in THF for **2a-Pd^0** and **2b-Pd^0**; b) Pd(dba)$_2$ in THF for **2c-Pd^0** and **2d-Pd^0**; c) Pt(PPh$_3$)$_4$ in THF for **2a-Pt^0** and in DMF for **2b-Pt^0**; d) AgBF$_4$ in acetone for **2a-Ag^{I}BF$_4$** and **2b-Ag^{I}BF$_4$**

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Spurred on by these findings we decided to study the complexing ability of macrocycles **1** towards transition metals.

Results and Discussion

Complexes **2** were very easily prepared by the reaction of macrocycles **1** with familiar sources of the corresponding metals. Both tetrakis(triphenylphosphane)palladium(0) and Pd(dba)$_2$ gave excellent results as Pd sources, whereas only tetrakis(triphenylphosphane)platinum(0) was tested for platinum (Scheme 1). Silver tetrafluoroborate was used for the formation of the silver complexes. These complexes are much less stable than those of Pd^0 and Pt^0. Strong evidence for the structures was secured by X-ray diffraction for **2a-Pd^0** (Figure 1 and 2) and **2a-Pt^0** (Figure 3 and 4) and in all cases by MALDI-TOF mass spectrometry.

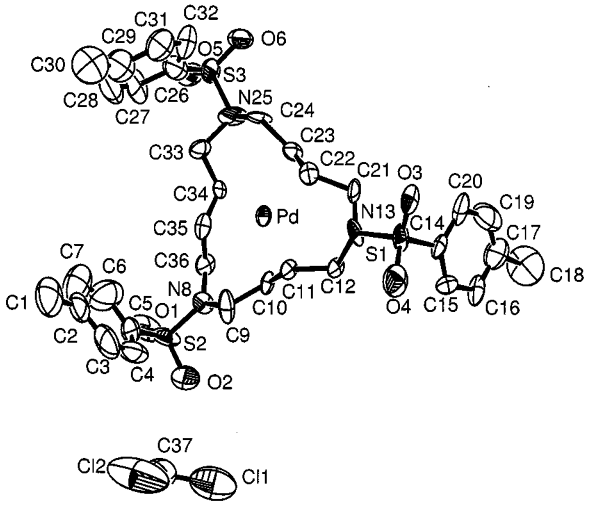


Figure 1. Perspective view of the **2a-Pd^0** molecule with the crystallographic atom numbering; atoms are represented as their thermal vibration ellipsoids (50% probability)

Complexes **2a-Pd^0** and **2a-Pt^0** are planar trigonal, with the distances from the metal atoms to the plane defined by the central points of the three olefin bonds being 0.018 and 0.015 Å, respectively. The complexes crystallize with one molecule of dichloromethane. They are not symmetrical, and in particular they lack a C_3 axis of symmetry. Two C=C bonds are longer than in the corresponding free ligand **1a**[6] (see Table 1). However, the third C=C bond is shorter than the other two in both complexes, and is close to the distance in the free ligand. These facts suggest that complexation by one olefin is weaker than complexation by the other two, a feature that is also evident in solution from NMR spectroscopic data.

The ^{13}C NMR spectrum of **2a-Pd^0** shows three signals of about the same intensity for three different types of CH$_2$ groups at δ = 45.1, 48.2, and 49.5 (Table 2). Also, three different signals appear, again of similar intensities, for three different types of olefinic CH groups, at δ = 78.5, 78.7, and 82.8. Moreover, the signals of the aromatic pro-

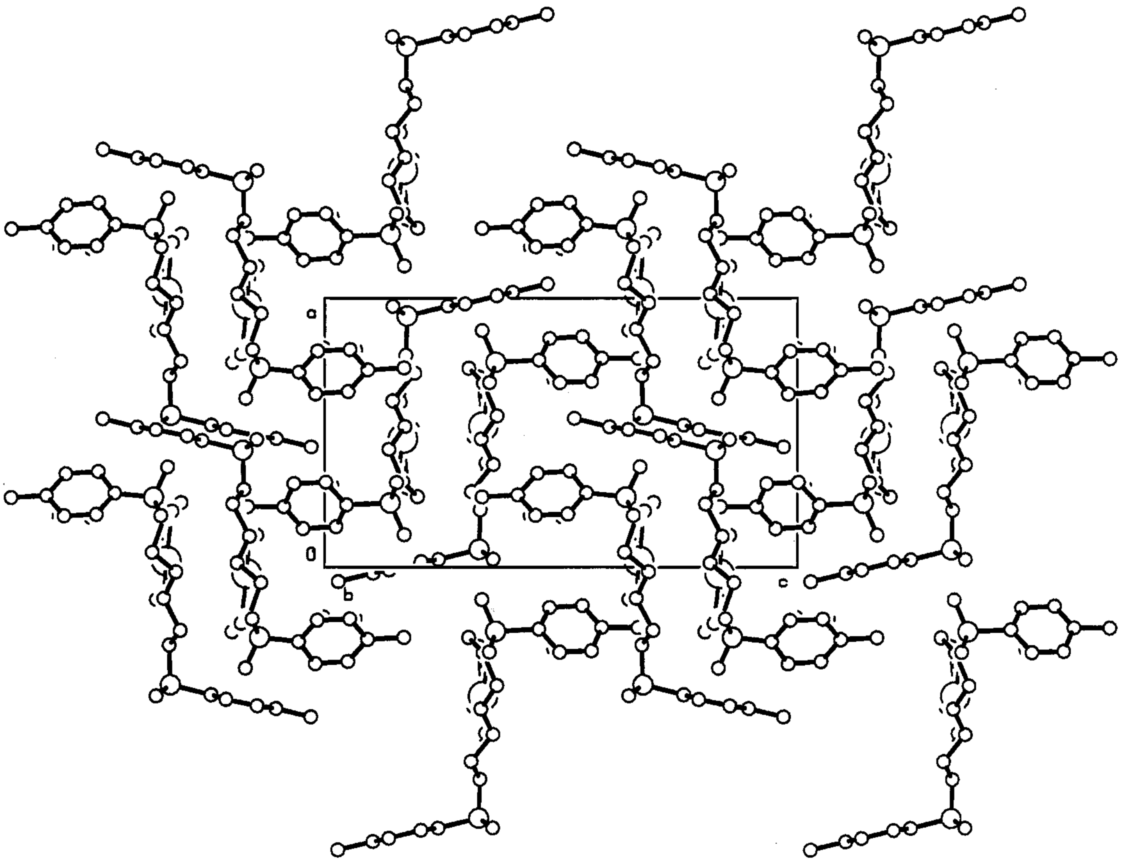


Figure 2. Perspective view of the unit cell of **2a-Pd^0**

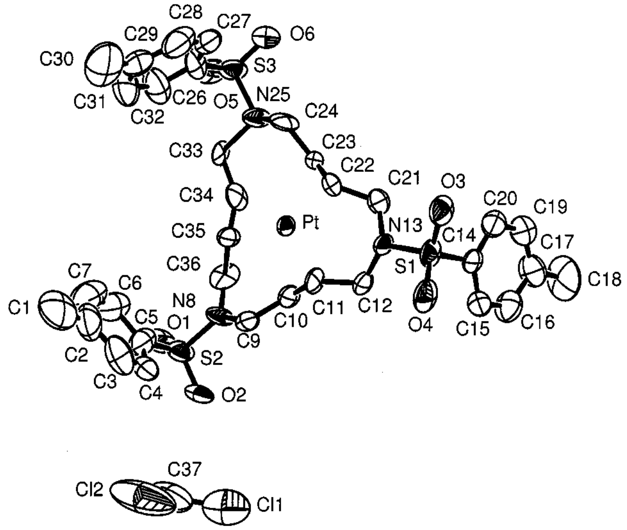


Figure 3. Perspective view of the **2a-Pt^0** molecule with the crystallographic atom numbering; atoms are represented as their thermal vibration ellipsoids (50% probability)

tons appear in two sets, one set of signals being about twice the intensity of the other, confirming that two olefins behave the same both in the ^{1}H NMR and ^{13}C NMR spectra and the third behaves differently. This is a general behavior for complexes **2-Pd^0** and **2-Pt^0**, and can only be compatible with an averaged plane of symmetry rather than with a C_3 symmetry axis. The ^{1}H NMR spectra were further complicated by the fact that the protons pertaining to the same methylene group are not averaged, due to conformational rigidity. These methylenic protons are in different environments and therefore they give signals at very different chemical shifts. Selective 1D TOCSY experiments performed on complexes **2a-Pd^0**, **2a-Pt^0**, and **2b-Pd^0** permitted the determination of the chemical shifts and coupling constants indicated in Table 2. Thus, the pairs of positions C2−C15, C3−C14, C4−C13, and C5−C12 are connected by an averaged plane of symmetry, as are the pairs C7−C10 and C8−C9 (see Scheme 2 for numbering). A simplified representation of the equilibrium causing this averaged response is shown in Scheme 2. As a consequence, the olefinic carbon atoms (and their corresponding hydrogen atoms) in positions C3 and C14 give the same signals, which are different from the signals due to the other bound carbons (positions C4 and C13). Moreover, the third double bond at positions C8 and C9 is different from the others, and positions C8 and C9 give the same signal. In other words the NMR spectroscopic data show that, in solution, two olefins complex the metal with the same strength, and the third one complexes differently, as already shown in the solid phase by X-ray diffraction studies.

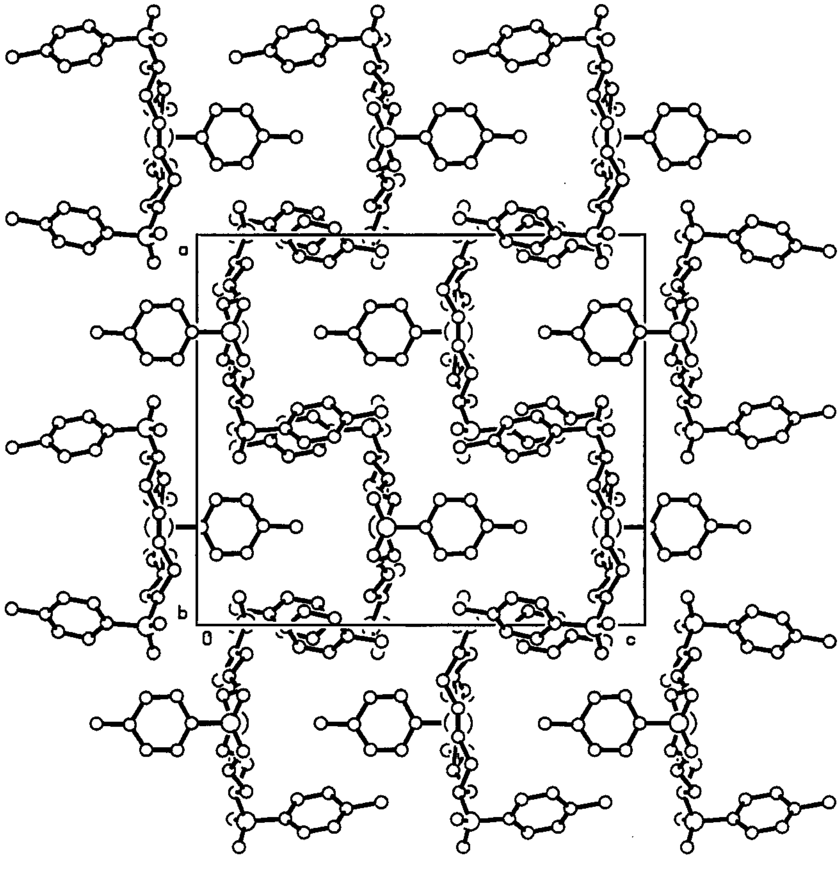


Figure 4. Perspective view of the unit cell of **2a-Pt^0**

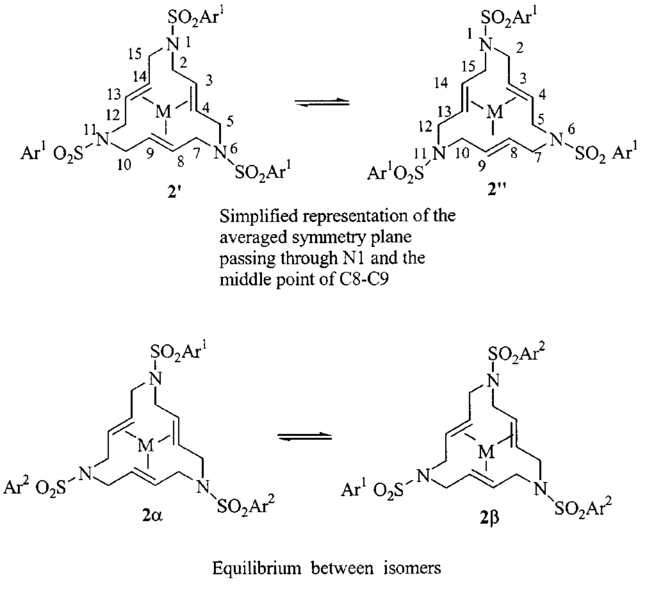
Table 1. Selected bond lengths and angles found in **2a-Pd⁰** and **2a-Pt⁰**

	Pd−olefin distances (Å)		Bond lengths (Å)		Torsion angles (°)	
2a-Pd⁰	Pd−C10 Pd−C11	2.142(6) 2.244(6)	C10−C11	1.301(7)	H10−C10−C11−H11	148.1(9)
2a-Pd⁰	Pd−C22 Pd−C23	2.186(6) 2.261(6)	C22−C23	1.368(7)	H22−C22−C23−H23	146.7(9)
2a-Pd⁰	Pd−C34 Pd−C35	2.167(5) 2.234(6)	C34−C35	1.368(7)	H34−C34−C35−H35	147.9(9)
2a-Pt⁰	Pt−C10 Pt−C11	2.128(15) 2.146(12)	C10−C11	1.365(14)	H10−C10−C11−H11	146.4(12)
2a-Pt⁰	Pt−C22 Pt−C23	2.145(11) 2.154(15)	C22−C23	1.389(14)	H22−C22−C23−H23	145.6(12)
2a-Pt⁰	Pt−C34 Pt−C35	2.135(11) 2.152(11)	C34−C35	1.274(15)	H34−C34−C35−H35	162.6(12)
1a[6]			C10−C11 C22−C23 C34−C35	1.292(7) 1.291(7) 1.277(7)		

Table 2. NMR spectroscopic data for Complexes **2a-Pd⁰**, **2b-Pd⁰**, and **2a-Pt⁰**

Positions	**2a-Pd⁰** [a] ^{1}H NMR	**2a-Pd⁰** ^{13}C NMR	**2b-Pd⁰**[b] ^{1}H NMR	**2b-Pd⁰** ^{13}C NMR	**2a-Pt⁰**[a] ^{1}H NMR	**2a-Pt⁰** ^{13}C NMR
2 and 15 ($-CH_2-$)	3.07 (dd, *J* = 14.2, 11.3) 4.78 (d, *J* = 14.3)	45.1	3.05 (dd, *J* = 12.6, 12.4) 4.55 (d, *J* = 12.6)	43.8	2.98 (dd, *J* = 13.6, 11.5) 5.02 (d, *J* = 12.7)	44.3
3 and 14 (=CH−)	2.79 (t, *J* = 11.7)	82.8	2.80 (t, *J* = 12.4)	83.7	2.07 (td, *J* = 13.3, 2.3)	69.0
4 and 13 (=CH−)	3.93−4.03 (m)	78.7	4.10 (dd, *J* = 12.4, 11.1)	79.3	3.41 (td, *J* = 11.6, 3.8)	63.2
5 and 12 ($-CH_2-$)	1.63 (dd, *J* = 14.3, 10.7) 4.62 (d, *J* = 14.3)	49.5	1.52 (dd, *J* = 15.6, 11.1) 4.22 (dd, *J* = 15.6, 3.2)	47.9	1.34 (dd, *J* = 14.0, 10.9) 4.58 (dd, *J* = 14.0, 3.8)	48.5
7 and 10 ($-CH_2-$)	1.50−1.80 (m) 4.64 (d, *J* = 14.3)	48.2	1.58 (dd, *J* = 15.3, 9.5) 4.30 (d, *J* = 15.3)	46.5	1.35−1.46 (m), 4.62 (d, *J* = 12)	47.2
8 and 9 (=CH−)	3.75 (m)	78.5	3.85 (d, *J* = 9.5)	79.2	3.22−3.25 (m)	62.7

[a] ^{1}H and ^{13}C NMR spectra for **2a-Pd⁰** and **2a-Pt⁰** were recorded in $CDCl_3$. − [b] ^{1}H and ^{13}C NMR spectra for **2b-Pd⁰** were recorded in [D$_8$]toluene.



Scheme 2. Averaged plane of symmetry and equilibrium between isomers in complexes **2**

In the case of different N-substituents, as for **2c-Pd⁰**, two different isomers are expected depending on which substituent occupies the position opposite to the singular olefin. Although no attempts have been performed to separate these possible isomers, the ^{13}C NMR spectrum for **2c-Pd⁰** confirms this situation in solution. Thus, the **2α** isomer (Scheme 2) has the unique (2,4,6-triisopropyl)phenylsulfonyl group opposite the singular olefin, and therefore it has an averaged plane of symmetry and three different signals are predicted for the olefinic protons and for the ring methylene protons, whereas the **2β** isomer has no symmetry whatsoever, and therefore six different signals are predicted for the olefinic protons and for the methylenic protons. The experimental result is that **2c-Pd⁰** has nine signals in the olefinic region between δ = 77.6 and 88.4 and eight signals in the CH_2 region between δ = 43.7 and 49.5. Efforts are presently being made to prepare crystals of different N-substituted macrocycles.

The silver complexes were not stable and could not be studied in depth.

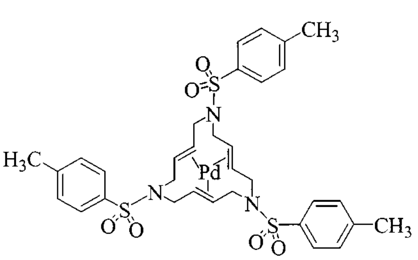
Conclusion

Preparations of the first Pd^0, Pt^0, and Ag^I complexes of 15-membered macrocyclic triolefins are described. X-ray analysis and NMR spectroscopic data indicate that the complexes have an averaged plane of symmetry rather than a C_3 axis.

Experimental Section

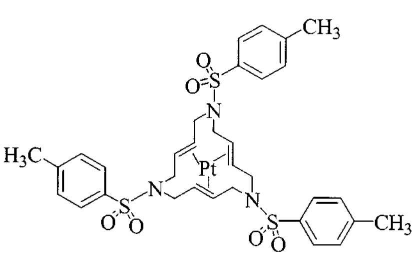
General: Macrocycles **1** were prepared as described previously.[5,6] Melting points were determined with a Kofler apparatus and are uncorrected. − IR spectra were recorded with a Nicolet FT-IR 510 ZDX. − NMR spectra were recorded with a Bruker-Analytik AC250. ^1H NMR (250 MHz) chemical shifts are reported relative to $CHCl_3$ at $\delta = 7.26$ or tetramethylsilane at $\delta = 0.00$. Coupling constants are reported in Hz. ^{13}C NMR (62.5 MHz) chemical shifts are expressed relative to $CDCl_3$ at $\delta = 77.00$ or tetramethylsilane at $\delta = 0.00$. Mass spectra (EIMS) were obtained with a Hewlett−Packard 5989A spectrometer and determined at an ionizing voltage of 70 eV. MALDI-TOF spectra were recorded on a BIFLEX spectrometer (Bruker−Franzen Analytik) equipped with a pulsed nitrogen laser (337 nm), operating in positive-ion reflector mode, and using 19 kV acceleration voltage. Matrices (α-cyanocinnamic acid) were prepared at 5 mg/mL in THF. Analytes were dissolved at concentrations between 0.1 and 5 mg/mL in THF or chloroform. − Elemental analyses were determined at the Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

(*E,E,E*)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (2a-Pd^0): A solution of macrocycle **1a** (0.150 g, 0.125 mmol) and tetrakis(triphenylphosphane)palladium(0) (0.100 g, 0.150 mmol) in tetrahydrofuran (4 mL) was refluxed for 24 h. More tetrakis(triphenylphosphane)palladium(0) (0.50 g, 0.75 mol) was then added and the reflux continued for a further 24 h. The solvent was then evaporated and the residue was passed through a silica gel column with hexane/ethyl acetate/dichloromethane (2:1:1) as eluent to afford **2a-Pd^0** (0.164 g, 95%) as a solid, m.p. 237−240 °C (dec). − IR (KBr): $\tilde{\nu}$ = 1340, 1162, 1094, 904, 657 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.60 (m, 2 H), 1.63 (dd, J = 14.3 and 10.7 Hz, 2 H), 2.39 (s, 9 H), 2.79 (t, J = 11.7 Hz, 2 H), 3.07 (dd, J = 14.2 and 11.3 Hz, 2 H), 3.75 (d, J = 8.9 Hz, 2 H), 3.93−4.03 (m, 2 H), 4.62 (d, J = 14.0 Hz, 2 H), 4.64 (d, J = 14.3 Hz, 2 H), 4.78 (d, J = 14.3 Hz, 2 H), 7.28 (d, J = 8.2, 6 H), 7.64 (d, J = 8.2 Hz, 4 H), 7.71 (d, J = 8.2 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.5, 45.1, 48.2, 49.5, 78.5, 78.7, 82.8, 127.0, 127.2, 129.8, 135.2, 136.1, 143.4, 143.6. − MALDI-TOF MS: m/z (%) = 774.9 $[M]^+$, 798.1 $[M + Na]^+$, 813.9 $[M + K]^+$. − $C_{33}H_{39}N_3O_6PdS_3 \cdot CH_2Cl_2$ (861.2): calcd. C 47.42, H 4.80, N 4.88, S 11.15; found C 47.47 and 47.46, H 4.82 and 4.80, N 4.71 and 4.67, S 10.76 and 10.89.



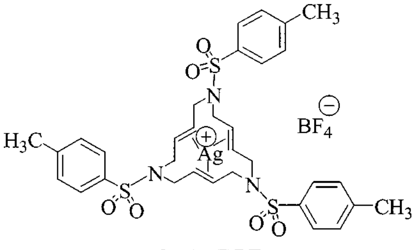
2a-Pd(0)

(*E,E,E*)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trieneplatinum(0) (2a-Pt^0): A solution of macrocycle **1a** (0.186 g, 0.149 mmol) and tetrakis(triphenylphosphane)platinum(0) (0.186 g, 0.149 mmol) in tetrahydrofuran (6 mL) was refluxed for 144 h. The solvent was then evaporated and the residue was passed through a silica gel column with hexane/ethyl acetate/dichloromethane (2:1:1) as eluent to afford **2a-Pt^0** (0.078 g, 60%) as a solid, m.p. 260−263 °C (dec., change of crystalline structure at 168−172 °C). − IR (KBr): $\tilde{\nu}$ = 1340, 1162, 1092, 909, 661 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34−1.46 (m, 4 H), 2.07 (td, J = 13.3 and 2.3 Hz, 2 H), 2.40 (s, 9 H), 2.98 (dd, J = 13.6 and 11.5 Hz, 2 H), 3.22−3.25 (m, 2 H), 3.41 (td, J = 11.6 and 3.8 Hz, 2 H), 4.58 (dd, J = 13.6 and 3.8 Hz, 2 H), 4.62 (d, J = 12.0 Hz, 2 H), 5.02 (d, J = 12.7 Hz, 2 H), 7.26 (d, J = 8.2 Hz, 6 H), 7.62 (d, J = 8.2 Hz, 4 H), 7.65 (d, J = 8.2 Hz, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.5, 44.3, 47.2, 48.5, 62.7, 63.2, 69.0, 127.0, 127.2, 129.8, 135.0, 136.0, 143.4, 143.6. − MALDI-TOF MS: m/z (%) = 864.9 $[M]^+$, 887.9 $[M + Na]^+$, 903.9 $[M + K]^+$. − $C_{33}H_{39}N_3O_6PtS_3 \cdot CH_2Cl_2$ (949.9): calcd. C 43.00, H 4.35, N 4.42, S 10.11; found C 43.57, H 4.07, N 4.15, S 9.73.



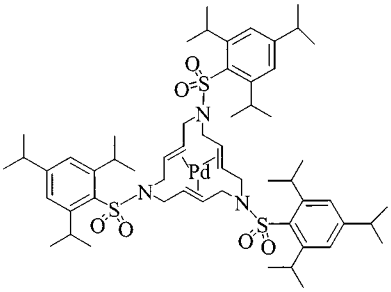
2a-Pt(0)

(*E,E,E*)-1,6,11-Tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienesilver(I) Tetrafluoroborate (2a-Ag^{I}BF$_4$): A solution of macrocycle **1a** (0.300 g, 0.45 mmol) and silver tetrafluoroborate (0.216 g, 0.90 mmol) in acetone (12 mL) was stirred for 5 min. at room temperature and the mixture was then left for 20 h. The formed precipitate was filtered off to afford **2a-Ag^{I}BF$_4$** as a white solid (0.200 g, 54%), m.p. 206−208 °C (dec). − IR (KBr): $\tilde{\nu}$ = 1700, 1392, 1349, 1165, 1092, 1058, 1009, 939, 904, 815, 754, 659 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 9 H), 3.75 (s, 12 H), 5.74 (s, 6 H), 7.33 (d, J = 7.9 Hz, 6 H), 7.66 (d, J = 7.9 Hz, 6 H). − MALDI-TOF MS: m/z (%) = 776.1 [M of cation]$^+$, 692.2 $[M - Ag + Na]^+$. − $C_{33}H_{39}AgBF_4N_3O_6S_3 \cdot CH_3COCH_3$ (922.6): calcd. C 46.87, H 4.92, N 4.55, S 10.42; found C 46.91 and 46.90, H 4.98 and 4.89, N 4.71 and 4.60, S 10.52 and 10.48.



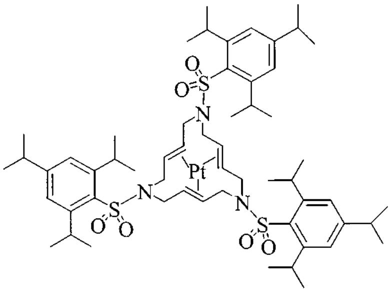
2a-Ag(I)BF$_4$

(*E,E,E*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (2b-Pd^0): This compound was prepared as for **2a-Pd^0** according to ref.[5]



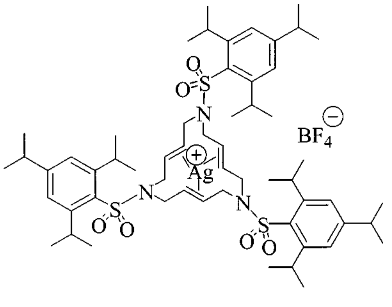
2b-Pd(0)

(E,E,E)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trieneplatinum(0) (2b-Pt^0): A solution of macrocycle **1b** (0.083 g, 0.08 mmol) and tetrakis(triphenylphosphane)platinum(0) (0.200 g, 0.17 mmol) in DMF (2.5 mL) was heated at 130 °C for four days. The solvent was then distilled off at reduced pressure and the residue was passed through a column of silica gel with hexane/ethyl acetate (5:1) as eluent to afford **2b-Pt^0** (0.07 g, 70%) as a white solid, m.p. 286−287 °C (dec). − IR (KBr): $\tilde{\nu}$ = 2960, 1601, 1461, 1427, 1363, 1315, 1262, 1151, 1103, 1047 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20−1.26 (m, 54 H), 1.84 (m, 4 H), 2.49 (t, J = 11.1 Hz, 2 H), 2.89 (septet, J = 6.9 Hz, 3 H), 3.14 (t, J = 11.1 Hz, 2 H), 3.38 (d, J = 8.6 Hz, 2 H), 3.58 (dt, J = 12.5 and 3.8 Hz, 2 H), 4.17 (septet, J = 6.8 Hz, 6 H), 4.36−4.40 (m, 2 H), 4.45 (d, J = 14.7 Hz, 2 H), 4.82 (d, J = 12.4 Hz, 2 H), 7.16 (s, 6 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.8, 29.3, 34.2, 43.1, 45.6, 47.0, 62.9, 63.4, 69.7, 123.9, 131.3, 151.4, 153.2. − MALDI-TOF MS: m/z (%) = 1201.3 [M]$^+$, 935.1 [M − SO_2Ar]$^+$, 667.6 [M − $2SO_2Ar$]$^+$. − $C_{57}H_{87}N_3O_6PtS_3$ (1201.6): calcd. C 56.98, H 7.30, N 3.50, S 8.00; found C 56.97 and 56.91, H 7.18 and 7.27, N 3.52 and 3.48, S 7.85 and 7.83.



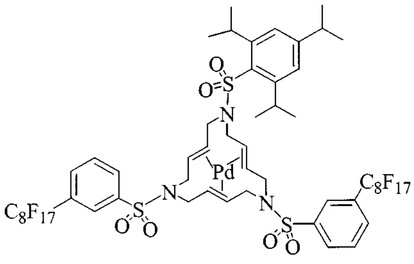
2b-Pt(0)

(E,E,E)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienesilver(I) Tetrafluoroborate (2b-Ag^{I}BF$_4$): A solution of macrocycle **1b** (0.100 g, 0.1 mmol) and silver tetrafluoroborate (0.020 g, 0.1 mmol) in acetone (0.5 mL) was refluxed for 5 h in a round-bottomed flask kept in the dark. The solvent was eliminated by passing a stream of nitrogen though the flask to afford complex **2b-Ag^{I}BF$_4$** quantitatively: This compound was not stable to further purification procedures. M.p. 213−216 °C (dec). − IR (KBr): $\tilde{\nu}$ = 2960, 1602, 1464, 1428, 1364, 1322, 1154, 1108, 1041, 997 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$, at 328 K): δ = 1.22 (m, 54 H), 2.87 (septet, J = 7.0, 3 H), 3.75−4.10 (m, 18 H), 6.06 (br. s, 6 H), 7.15 (s, 6 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 23.5, 24.7, 29.4, 34.2, 47.3, 123.7, 123.9, 124.2, 130.1, 151.6, 153.8. − MALDI-TOF MS: m/z (%) = 1112.5 [M of cation]$^+$.



2b-Ag(I)BF$_4$

(E,E,E)-1,6-Bis[(3-perfluorooctylphenyl)sulfonyl]-11-[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (2c-Pd^0): A solution of macrocycle **1c** (1.920 g, 1.21 mmol) and bis(dibenzylideneacetone)palladium(0) (0.760 g, 1.33 mmol) in tetrahydrofuran (60 mL) was maintained at room temperature for 24 h. The mixture was filtered, the solvent was removed from the filtrate in vacuo and the residue was washed with hexane and passed through a silica gel column with hexane/ethyl acetate (10:1) as eluent to afford **2c-Pd^0** (1.95 g, 95%) as a solid, m.p. 141−142 °C (dec). − IR (KBr): $\tilde{\nu}$ = 1351, 1240, 1212, 1162, 1117, 908, 658 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$, α+β forms): δ = 1.21 (m, 18 H), 1.5−1.9 (m, 2 H), 1.95−2.2 (m, 2 H), 2.72 (bt, J ≈ 12.4 Hz), 2.85−3.00 (m) and 3.0−3.3 (m) (the three groups of signals, 6 H), 3.7−4.0 (m, 2 H), 4.0−4.3 (m, 3 H), 4.47 (bt, J ≈ 15 Hz, 2 H), 4.68 (bt, J ≈ 14 Hz, 2 H), 4.83 (bd, J ≈ 15 Hz, 2 H), 7.07, 7.12, and 7.19 (three s, 2 H), 7.40−7.45 (m, 2 H), 7.6−7.85 (m, 4 H), 7.95−8.1 (m, 2 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$, α+β forms): δ = 23.5, 24.7, 24.8, 29.3, 34.1, 43.7, 45.2, 45.4, 46.3, 47.6, 48.2, 49.3, 49.5, 77.6, 77.9, 78.6, 78.8, 79.7, 79.9, 81.9, 82.8, 84.4, 123.9−153.4 (m). − MALDI-TOF MS: m/z (%) = 1695.1 [M]$^+$, 1718.1 [M + Na]$^+$, 1734.1 [M + K]$^+$. − $C_{55}H_{49}F_{34}N_3O_6PdS_3$ (1696.6): calcd. C 38.94, H 2.91, N 2.48, S 5.67; found C 39.03 and 39.02, H 3.18 and 3.30, N 2.45 and 2.44, S 5.47 and 5.42.



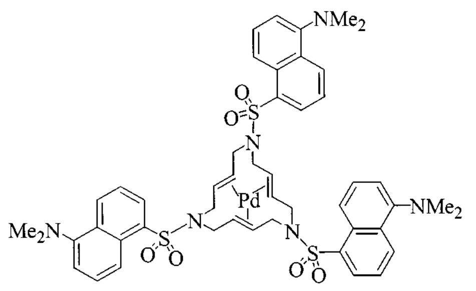
2c-Pd(0)

(E,E,E)-1,6,11-Tris[(5-dimethylaminonaphthyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (2d-Pd^0): A solution of macrocycle **1d** (0.180 g, 0.20 mmol) and bis(dibenzylideneacetone)palladium(0) (0.127 g, 0.22 mmol) in tetrahydrofuran (10 mL) was refluxed for 5 h. The mixture was filtered, the solvent was removed from the filtrate in vacuo and the solid residue (0.270 g) was passed through a silica gel column with hexane/ethyl acetate (8:2) as eluent to afford dibenzylideneacetone (0.054 g) and **2d-Pd^0** (0.180 g, 89%) as a solid, m.p. 167−169 °C (hexane/ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 2940, 2832, 1574, 1457, 1401, 1322, 1144, 1068, 938, 903, 833, 789, 750 cm^{-1}. − UV/Vis (THF): λ (log ε) = 340 (4.11), 254 (4.61). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.86−2.02 (m, 4 H), 2.85−2.86 (two s, 18 H), 2.93−2.98 (m, 2 H), 3.18 (dd, J = 14.0 and 10.7 Hz, 2 H), 3.79−3.82 (m, 2 H), 4.01−4.12 (m, 2 H), 4.63 (t, J ≈ 13.5 Hz, 4 H), 4.89 (d, J ≈ 13.5 Hz, 2 H), 7.15 (dd, J = 7.5

Table 3. The crystal data and structure refinement for **2a-Pd⁰** and **2a-Pt⁰**

	2a-Pd⁰	**2a-Pt⁰**
Formula	$C_{34}H_{41}Cl_2N_3O_6PdS_3$	$C_{34}H_{41}Cl_2N_3O_6PtS_3$
Molecular weight	861.18	949.87
Crystal size [mm]	0.53 × 0.23 × 0.21	0.39 × 0.16 × 0.07
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a [Å]	11.1844 (13)	17.15 (9)
b [Å]	17.1818(12)	11.199 (10)
c [Å]	19.713(3)	19.74 (4)
β [°]	−	90.03 (2)
V [Å^3]	3788 (2)	3793 (2)
Z	4	4
ρ_{calc} [Mg m^{-3}]	1.510	1.663
Temperature [K]	293 (2)	293 (2)
F(000)	1768	1896
Wavelength [Å]	Mo-K_α, 0.710739	Mo-K_α, 0.710739
Absorption coefficient [mm^{-1}]	0.843	4.052
hkl range	−13/13, 0/20, 0/23	−20/20, 0/13, 0/23
Reflections collected	6633	6658
Data/restraints/parameters	6633 / 69/442	6658/5/460
Goodness of fit on F^2	1.087	0.976
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0667$ $wR2 = 0.1831$	$R1 = 0.0622$ $wR2 = 0.1091$
R indices (all data)	$R1 = 0.0956$ $wR2 = 0.2018$	$R1 = 0.1370$ $wR2 = 0.1228$
Largest diff. peak and hole	1.378/−0.861	0.838/−1.220

and 5.7 Hz, 3 H), 7.48−7.56 (m, 6 H), 8.19 (dd, J = 7.5 and 1.4 Hz, 3 H), 8.24−8.31 (m, 3 H), 8.53 (br. d, J = 8.2 Hz, 3 H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 14.5, 22.7, 34.5, 45.1, 45.8, 48.0, 49.2, 79.6, 79.8, 83.9, 115.7, 119.6, 123.6, 128.6, 130.3, 130.4, 130.8, 131.0, 134.9, 152.3. − MALDI-TOF MS: m/z (%) = 1012.5 [M]$^+$, 929.7 [M − Pd + Na]$^+$. − $C_{48}H_{54}N_6O_6PdS_3$ (1013.6): calcd. C 56.88, H 5.37, N 8.29; found C 57.34 and 57.31, H 5.38 and 5.49, N 7.96 and 8.19.



2d-Pd(0)

X-ray Analysis of 2a-Pd⁰ and 2a-Pt⁰. Data Collection and Processing: Crystal data and experimental conditions for the two complexes are listed in Table 3. The collected reflections were corrected for Lorentz, polarization and absorption effects [empirical Difabs, max. and min. transmission were 0.8669−0.3950 for **2a-Pd⁰**, and 0.5907−0.3170 for **2a-Pt⁰**]. The lattice constants were determined by least-squares fitting of the setting angles of 25 reflections. Data were recorded using the ω-2θ scan mode up to a 2θ of 49.98 for **2a-Pd⁰** and 50.02 for **2a-Pt⁰**.

The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods on F^2 over the complete set of data using SHELXL-97. Anisotropic thermal parameters were refined for the non-hydrogen atoms and the hydrogen atoms were introduced in calculated positions.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic data center as supplementary publications nos. CCDC-150655 and -150656 for **2a-Pd⁰** and **2a-Pt⁰**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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