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Metal complexes of 15-membered triolefinic macrocycles. (*E*,*E*,*Z*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene and its palladium(0), platinum(0), and silver(I) complexes

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Abstract—The preparation of the 15-membered macrocycle (*E*,*E*,*Z*)-1,6,11-tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene is reported. This cyclic triolefin forms stable complexes with palladium(0) and platinum(0), and a moderately stable complex with silver(I) tetrafluoroborate. © 2001 Elsevier Science Ltd. All rights reserved.

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] We have reported the formation of some novel triazatriolefinic macrocycles with the structure of (*E*,*E*,*E*)-1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene by non-selective palladium(0)-catalyzed Tsuji–Trost allylation of arenesulfonamides with (*Z*)-2-butene-1,4-diol biscarbonate.[4] More recently, we have published synthetic procedures for these macrocycles[5,6] as well as on the preparation and structures of their complexes with palladium(0), platinum(0), and silver(I).[7] The air-stable phosphine-free complex **1** (Fig. 1) shows great catalytic activity and recovery in Suzuki cross-couplings.[5] Anchoring to a polystyrene framework affords an insoluble version of the catalyst which can be recovered after filtration and reused several times without loss of catalytic activity.[5]

The complexing behavior of **1** and congeners featuring other aryl groups is reminiscent of the behavior of the geometric isomers of 12-membered cyclododeca-1,5,9-triene in nickel(0) chemistry.[8]

All this led us to undertake the synthesis of the *trans*,*trans*,*cis* isomer: (*E*,*E*,*Z*)-1,6,11-tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (**6**) and to study its complexating ability towards some transition metals.

Macrocycle **6** was prepared by the sequence outlined in Scheme 1. Reaction of **2**[6] with 0.5 equiv. of (*Z*)-1,4-dibromo-2-butene[9] afforded **3**[10] in quantitative yield. Deprotection gave bis-sulfonamide **4**.[10] On the other hand, dibromide **5**[10] was obtained by reaction of 2,4,6-triisopropylbenzenesulfonamide with excess (*E*)-1,4-dibromo-2-butene (9 equiv.). Then, macrocycle **6**[10] was

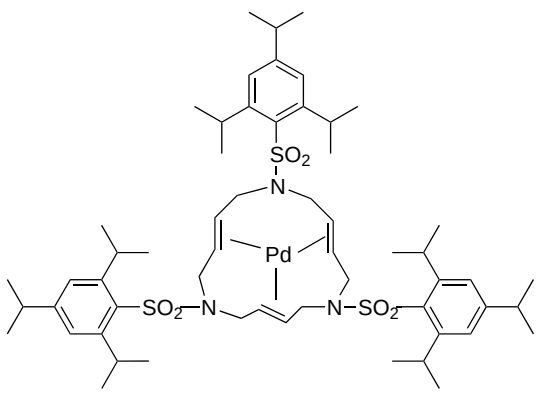

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Figure 1.

Keywords: macrocycles; triene complexes; palladium; platinum; silver.

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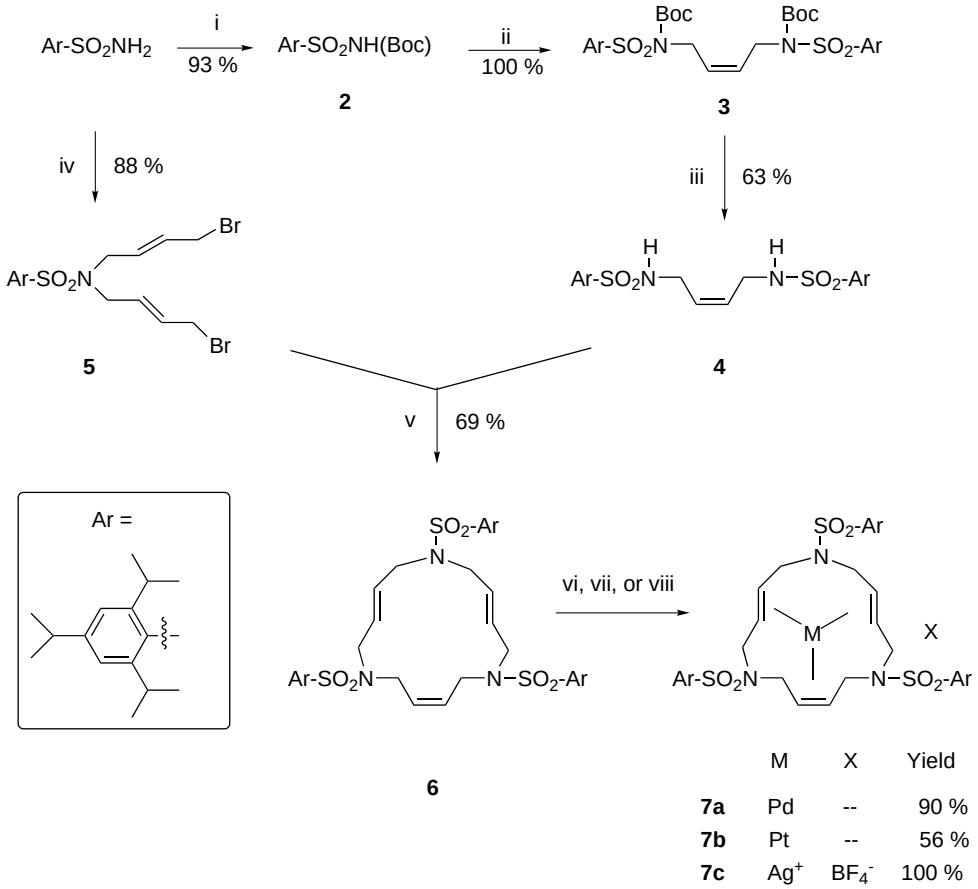

Scheme 1. (i) $(^tBuOCO)_2O$, Et_3N, DMAP, CH_2Cl_2, rt, 24 h; (ii) (*Z*)-1,4-dibromo-2-butene[9] (0.5 equiv.), K_2CO_3, refluxing CH_3CN, 20 h; (iii) TFAA, CH_2Cl_2, rt, 3 h; (iv) (*E*)-1,4-dibromo-2-butene (9 equiv.), DMF, 100°C, 6 h, then column chromatography; (v) K_2CO_3, refluxing CH_3CN, 24 h; (vi) $Pd(PPh_3)_4$, refluxing THF, 5 h; (vii) $Pt(PPh_3)_4$, DMF, 130°C, 96 h; (viii) $AgBF_4$, refluxing acetone, 5 h.

formed in 69% yield by reaction of equimolar amounts of **4** and **5** in refluxing acetonitrile using potassium carbonate as a base. Concentrations below 0.02 M are optimal.

Macrocycle **6** shows a complexing ability towards transition metals which is comparable to those obtained before for its *trans*,*trans*,*trans* isomer **1**.[7] Thus, reaction of **6** with 1 equiv. of tetrakis(triphenylphosphine)palladium(0) led to complex **7a**.[10] The related Pt(0) complex (**7b**)[10] was formed by treating **6** with tetrakis(triphenylphosphine)platinum(0) in DMF at 130°C. Both **7a** and **7b** are air-stable and have been purified by column chromatography in silica gel giving correct elementary analysis. Their ^1H NMR spectra are quite similar to each other showing the classical displacement of the signals of the olefinic protons to higher fields with respect to the free ligand **6**.

Reaction of **6** with 1 equiv. of silver tetrafluoroborate in refluxing acetone under a nitrogen atmosphere gives the ionic complex **7c**[10] in quantitative yield. On the contrary to **7a** and to **7b**, **7c** showed low stability when treated with most solvents. It was characterized by NMR and MALDI-TOF MS. Its ^1H NMR spectrum was quite different to those of **7a** and **7b**, with chemical shift displacement of the olefinic signals to lower field being observed.

In summary, the novel triolefinic macrocycle **6** forms stable complexes with Pd(0) and with Pt(0).

Acknowledgements

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10. Selected data for all new compounds:
Compound **3**: mp 106–107°C.
Compound **4**: mp 129–131°C.
Compound **5**: mp 83–86°C.[5]
Compound **6**: mp 198–199°C; IR (KBr): 2961, 1317, 1153 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.17–1.25 (m, 54H), 2.87 (sept., $J=7.3$ Hz, 3H), 3.73 (d, $J=3.2$ Hz, 4H), 3.76 (d, $J=6.4$ Hz, 4H), 3.78 (d, $J=6.2$ Hz, 4H), 4.04 (sept., $J=6.6$ Hz, 4+2H), 5.50 (t, $J=3.2$ Hz, 2H), 5.55 (dt $J=15.6$ and 6.4 Hz, 2H), 5.75 (dt, $J=15.6$ and 6.2 Hz, 2H), 7.12 (s, 2+4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 23.5, 24.8, 29.3, 34.2, 41.4, 46.4, 49.9, 124.0, 127.5, 128.9, 130.6, 132.8, 151.5, 153.3, 153.4; LSI MS (3-nitrobenzyl alcohol matrix): m/z 472 (100, M–$2SO_2Ar$), 741 (48, M–SO_2Ar), 1007 (54, M).
Compound **7a**: mp 263–267°C (dec.); IR (KBr): 2956, 1319, 1151 cm^{-1}; from TOCSY 1D, COSY, NOESY 2D, and ^1H–^{13}C HSQC experiments the following information was acquired:[11] ^1H NMR ($CDCl_3$, 400 MHz): δ 1.17–1.25 (m, 54H), 2.07 (dd, $J=10.0$ and 4.0, 2H), 2.08 (dd, $J=10.0$ and 4.0, 2H), 2.26 (dd, $J=14.6$ and 9.2 Hz, 2H), 2.88 (sept., $J=7.0$, 1H), 2.90 (sept., $J=7.0$, 2H), 3.98 (t, $J=10.0$ Hz, 2H), 4.09 (t, $J=10.0$, 2H), 4.17 (d, $J=14.6$, 2H), 4.18 (sept., $J=7.0$ Hz, 6H), 4.20 (d, $J=9.2$ Hz, 2H), 4.44 (m, 2H), 4.49 (m, 2H), 7.15 (s, 2H), 7.16 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.6, 24.9, 29.3, 34.2, 42.5, 46.5, 47.4, 75.9, 76.7, 77.2, 124.0, 131.0, 151.3, 151.4, 153.3; MALDI-TOF MS: m/z from 1108.48 to 1116.47, all peaks appear differing by 1 a.m.u. and corresponding to the molecular isotopic distribution for $C_{57}H_{87}N_3O_6PdS_3$. An additional system of peaks corresponding to [M+K] also appeared.
Compound **7b**: mp 271–274°C (dec.); IR (KBr): 2958, 1319, 1151 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.20–1.26 (m, 54H), 1.85 (dd, $J=10.4$ and 4.8 Hz, 2H), 1.88 (dd, $J=10.2$ and 5.3 Hz, 2H), 2.04 (dd, $J=14.1$ and 9.0 Hz, 2H), 2.89 (sept., $J=6.9$ Hz, 3H), 3.42 (t, $J=10.4$ Hz, 2H), 3.55 (t, $J=10.2$ Hz, 2H), 3.82 (d, $J=9.0$ Hz, 2H), 4.10–4.30 (m, 8H), 4.40 (m, 2H), 4.46 (m, 2H), 7.15 (s, 2H), 7.16 (s, 4H); MALDI-TOF MS: m/z from 1198.72 to 1202.69, all peaks appear differing by 1 a.m.u. and corresponding to the molecular isotopic distribution for $C_{57}H_{87}N_3O_6PtS_3$. An additional system of peaks corresponding to [M+Na] also appeared.
Compound **7c**: mp 177–180°C (dec.); IR (KBr): 2962, 1322, 1154, 1104, 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.19–1.25 (m, 54H), 2.86 (sept., $J=6.9$ Hz, 3H), 3.25 (m, 2H), 3.45 (m, 2H), 3.60 (m, 2H), 3.94 (sept., $J=7.1$ Hz, 6H), 4.10–4.50 (m, 6H), 6.07 (br s, 2H), 6.15 (br s, 4H), 7.14 (s, 4H), 7.16 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 23.5, 24.6, 24.7, 29.4, 34.2, 42.8, 46.4, 47.2, 118.5 (br m), 120.5 (br), 124.2, 124.3, 129.9, 130.3, 151.4, 151.6, 153.7, 153.9; MALDI-TOF MS: m/z from 1113.40 to 1117.27, all peaks appear differing by 1 a.m.u. and corresponding to the molecular isotopic distribution for the $C_{57}H_{87}AgN_3O_6S_3$ cation.
Good elemental analyses were secured for products **4**, **6**, and **7a**.
11. To be published elsewhere.