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Synthesis, catalytic activity and redox properties of palladium(0) complexes with 15-membered triolefinic macrocyclic ligands containing one, two or three ferrocenyl groups

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Abstract—A series of 15-membered triolefinic macrocycles containing ferrocenyl groups and their palladium(0) complexes have been synthesized and characterized. Their catalytic activity has been demonstrated in Suzuki-type cross-coupling and in the Heck reaction. Their redox properties have been investigated by means of cyclic voltammetry. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There is currently great interest in ferrocene-containing complexes owing to their importance in areas of catalysis, asymmetric synthesis, and material science.[1]

Recently, one of us has published synthetic procedures for a novel type of triazatriolefinic macrocycles with the structure of (*E*,*E*,*E*)-1,6,11-tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene,[2a,3] **1** (Fig. 1), as well as the preparation and structures of their complexes with palladium(0), platinum(0) and silver(I).[4] These macrocycles are exceptional, as nitrogen-containing 15-membered macrocycles featuring internal olefinic double bonds have been seldom described in the literature. The few known examples contain only one double bond, and metathesis is the key step for their preparation.[5] On the other hand, the air-stable palladium(0) complex **2** (when $Ar^1 = Ar^2 = 2,4,6$-triisopropylphenyl) (Fig. 1) shows high catalytic activity and recovery in certain Suzuki-type cross-coupling reactions.[2]

All this led us to undertake the preparation of three different macrocycles **1aab**, **1abb** and **1bbb** (Fig. 1) (aryl units in macrocycle **1** have been substituted by one, two or three ferrocenyl groups), as well as their palladium(0) complexes **2**, in order to understand the interaction between palladium metal center and ferrocenyl groups.

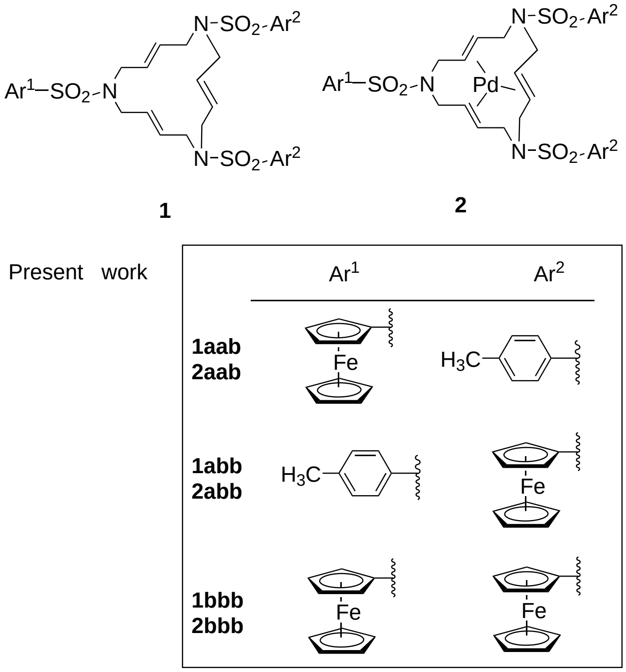

Figure 1. Structure of macrocycles **1aab**, **1abb**, and **1bbb** and their palladium(0) complexes **2** prepared in this work.

Keywords: macrocycles; ferrocene; triene palladium(0) complexes; catalysis.

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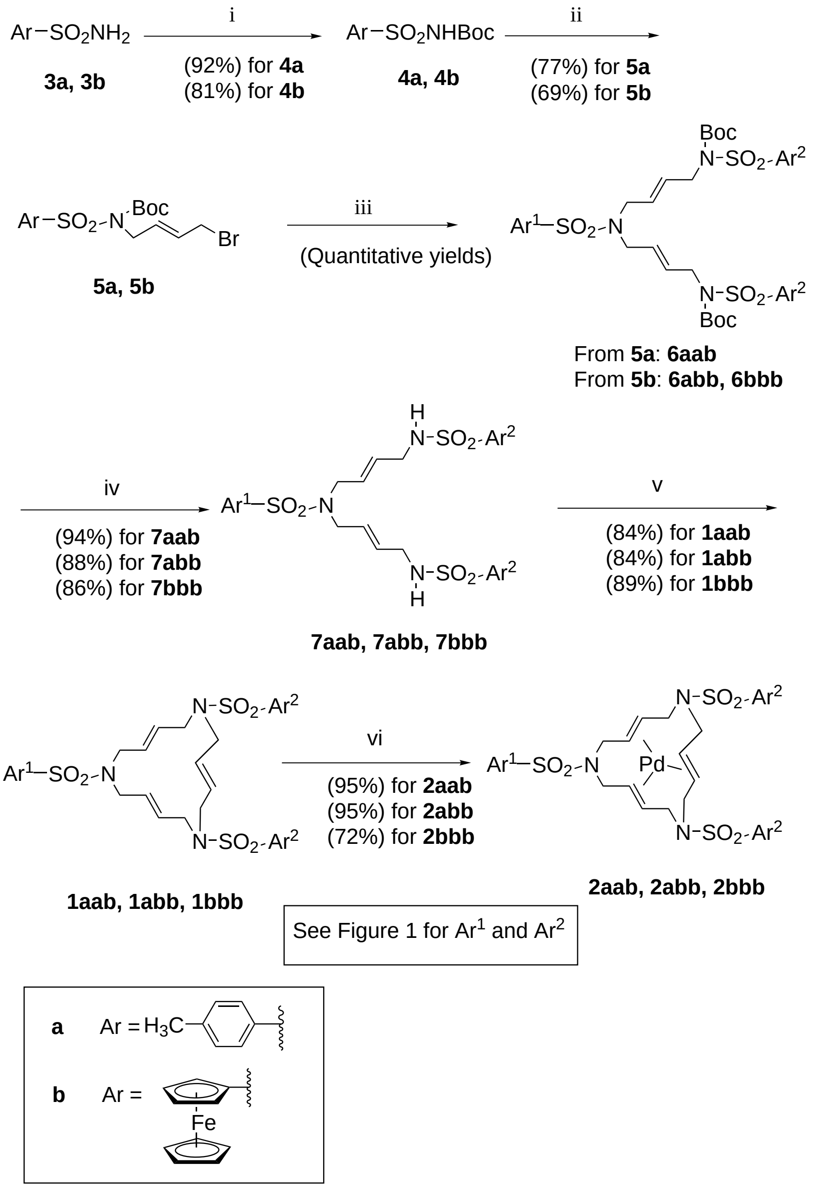
2. Synthesis of macrocyclic ligands, 1, and their palladium(0) complexes, 2. Catalytic activity of complexes 2

Macrocycles **1aab**, **1abb** and **1bbb** were prepared by the sequences outlined in Scheme 1. Compounds **4a** and **4b** were prepared from the corresponding sulfonamides **3a** and **3b**[6] according to the general method described in the literature.[7] Reaction of **4a** and **4b** with 4 equiv. of (*E*)-1,4-dibromo-2-butene afforded **5a**[3] and **5b**[8] in 77 and 69% yield, respectively. Reaction of **5a** with 0.5 equiv. of ferrocenesulfonamide **3b** in refluxing acetonitrile and potassium carbonate as a base, gave **6aab**[8] in quantitative yield. Under the same conditions as for compound **5a**, compound **5b** reacts, respectively, with 0.5 equiv. of *p*-toluenesulfonamide **3a** and ferrocenesulfonamide **3b** to give **6abb**[8] and **6bbb**,[8] both in quantitative yields. Deprotection of the three compounds **6aab**, **6abb** and **6bbb** was carried out with trifluoroacetic acid giving the respective deprotected compounds **7aab**[8] (94% yield), **7abb**[8] (88% yield) and **7bbb**[8] (86% yield). Then, macrocycles **1aab**,[8] **1abb**[8] and **1bbb**[8] were formed in 84, 84 and 89% yield by reaction of equimolar amounts of compounds **7** and (*E*)-1,4-dibromo-2-butene using potassium carbonate as a base in refluxing acetonitrile.

Tetrakis(triphenylphosphine)palladium(0) was used as a source of palladium(0) to prepare complexes **2aab**,[8] **2abb**[8] and **2bbb**[8] (Scheme 1). Thus, macrocycles **1aab**,



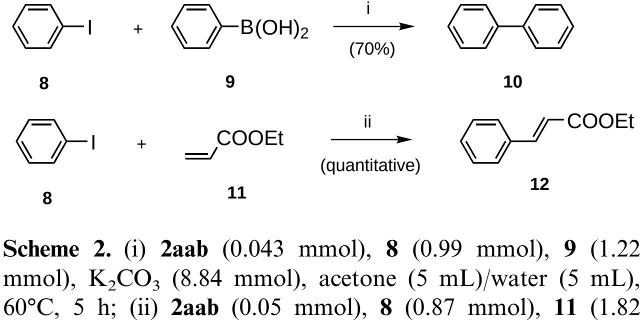
Scheme 1. (i) $(^t\mathrm{BuOCO})_2\mathrm{O}$, $\mathrm{Et_3N}$, DMAP, $\mathrm{CH_2Cl_2}$, 2.5 h.; (ii) 4 equiv. (*E*)-1,4-dibromo-2-butene, $\mathrm{K_2CO_3}$, $\mathrm{CH_3CN}$, reflux, 6 h (for **5a**), 21 h (for **5b**); (iii) to give **6aab** and **6bbb**: 0.5 equiv. ferrocenesulfonamide **3b**, $\mathrm{K_2CO_3}$, $\mathrm{CH_3CN}$, reflux, 7 h (for **6aab**), 18 h (for **6bbb**); to give **6abb**: 0.5 equiv. *p*-toluenesulfonamide **3a**, $\mathrm{K_2CO_3}$, $\mathrm{CH_3CN}$, reflux, 24 h; (iv) TFAA, $\mathrm{CH_2Cl_2}$, rt, 2 h; (v) 1 equiv. (*E*)-1,4-dibromo-2-butene, $\mathrm{K_2CO_3}$, $\mathrm{CH_3CN}$, reflux, 23 h (for **1aab**), 20 h (for **1abb**), and 23 h (for **1bbb**); (vi) 1.5 equiv. $\mathrm{Pd(PPh_3)_4}$, THF, reflux, 2 days (for **2aab**), 26 h (for **2abb**) and 7 h (for **2bbb**).

1abb and **1bbb** were treated with 1.5 equiv. of Pd(PPh$_3$)$_4$ in refluxing THF to give the three complexes in 95, 95 and 72% yield, respectively. The three complexes **2aab**, **2abb** and **2bbb** are air-stable and have been purified by recrystallization from ethyl acetate/hexane giving correct elemental analysis. Their ^{1}H NMR spectra are similar to others already published showing a strong displacement of the signals of the olefinic protons to higher fields with respect to the free ligands **1**.[4]

Palladium(0) complex **2aab** catalyses the Suzuki-type cross-coupling reaction of iodobenzene (**8**) with benzeneboronic acid (**9**) to afford biphenyl (**10**) (70% yield) and the Heck reaction of ethyl acrylate (**11**) with iodobenzene (**8**) leading to ethyl cinnamate (**12**) in quantitative yield (Scheme 2). In both cases complex **2aab** was recovered by column chromatography on silica gel in 95 and 55% yield, respectively. For the Heck reaction the rest of the macrocycle is recovered as uncomplexed **2aab**.

3. Redox properties[9]

Macrocyclic ferrocenyl ligands **1aab**, **1abb** and **1bbb**, display a reversible wave at approximately 700 mV in acetonitrile, which can be associated to the Fe^{III}/Fe^{II} ferrocenyl moiety couple.[10] Their corresponding Pd(0) complexes **2aab**, **2abb** and **2bbb**, besides the Fe^{III}/Fe^{II} couple, display a new chemically irreversible wave ($E_{p,a} = 1.3$ V) due to the irreversible oxidation of Pd(0). In the specific case of **2abb**, both waves exhibit similar intensities. For the corresponding Pd(0) complexes, not containing the ferrocenyl group[2,3] (palladium(0) complex **2** with Ar^1 = Ar^2 = 2,4,6-triisopropylphenyl, see Fig. 1), this wave is also observed but with very low intensity. Thus, the ferrocenyl group in **2aab**, **2abb** and **2bbb** is responsible for inducing an enhancement of the heterogeneous electron transfer rate constant in the Pd based wave. These experiments clearly reveal that the ferrocenyl group is not simply acting as a spectator ligand, but on the contrary is strongly influencing the Pd(0) redox properties. We are at the moment investigating the potential origins of this phenomena which will be reported as a full paper in the near future.



Scheme 2. (i) **2aab** (0.043 mmol), **8** (0.99 mmol), **9** (1.22 mmol), K$_2$CO$_3$ (8.84 mmol), acetone (5 mL)/water (5 mL), 60°C, 5 h; (ii) **2aab** (0.05 mmol), **8** (0.87 mmol), **11** (1.82 mmol), KOAc (1.76 mmol), Bu$_4$NBr (0.96 mmol), DMF (10 mL), 60°C, 2.5 h.

Acknowledgements

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8. Selected data for all new compounds:
   4b, mp 149–151°C; **5b**, mp 122–124°C; **6aab**, mp 57–59°C; **6abb**, 65–67°C; **6bbb**, mp 82–84°C; **7aab**, mp 46–49°C; **7abb**, mp 54–56°C; **7bbb**, mp 71–74°C.
   1aab, (*E*,*E*,*E*)-1-Ferrocenylsulfonyl-6,11-bis[(4-methylphenyl)sulfonyl] - 1,6,11 - triaza cyclopentadeca - 3,8,13-triene: mp 195–197°C; IR (KBr) 2922, 2859, 1338, 1151 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz): δ 2.44 (s, 6H), 3.55–3.66 (m, 12H), 4.39 (apparent t, J = 1.8 Hz, 2H), 4.41 (s, 5H), 4.57 (apparent t, J = 1.8 Hz, 2H), 5.53–5.55 (m, 6H), 7.31 (m, 4H), 7.65 (m, 4H); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 21.5, 50.5, 50.6, 50.7, 68.6, 70.6, 70.8, 86.2, 127.2, 129.0, 129.4, 129.6, 129.8, 136.1, 143.5; ESI-MS (*m*/*z*) 786 [M+Na]$^+$, 781 [M+NH$_4$]$^+$, 764 [M+H]$^+$, 763 [M]$^+$. C$_{36}$H$_{41}$FeN$_3$O$_6$S$_3$ (763.8) calcd: C, 56.61; H, 5.41; N, 5.50. Found: C, 56.57 and 56.47; H, 5.29 and 5.39; N, 5.50 and 5.42.
   1abb, (*E*,*E*,*E*)-1,6-Bis(ferrocenylsulfonyl)-11-[(4-methylphenyl)sulfonyl] - 1,6,11 - triazacyclopentadeca - 3,8,13-triene: mp 103–105°C; IR (KBr) 2921, 2853, 1338, 1157 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz): δ 2.44 (s, 3H), 3.55–3.64 (m, 12H), 4.39 (s, 10H), 4.10–4.42 (m, 4H), 4.56 (apparent t, J = 1.9 Hz, 4H), 5.50–5.52 (m, 6H), 7.31 (m, 2H), 7.64 (m, 2H); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 21.9, 50.5, 50.6, 50.7, 68.6, 70.6, 70.8, 86.2, 127.1, 128.9, 129.2, 129.6, 129.8, 136.0, 143.5; ESI-MS (*m*/*z*) 880 [M+Na]$^+$, 857 [M]$^+$. C$_{39}$H$_{43}$Fe$_2$N$_3$O$_6$S$_3$ (857.7) calcd: C, 54.62; H, 5.05; N, 4.90. Found: C, 54.74 and 54.78; H, 5.43 and 5.44; N, 4.54 and 4.57.
   1bbb, (*E*,*E*,*E*)-1,6,11-Tris(ferrocenylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene: mp 225–226°C; IR (KBr) 2919, 2850, 1332, 1187, 1131 cm^{-1}; ^{1}H NMR

($CDCl_3$, 200 MHz): δ 3.57 (br absorption, 12H), 4.42 (apparent t, $J=1.9$ Hz, 6H), 4.44 (s, 15H), 4.60 (apparent t, $J=1.9$ Hz, 6H), 5.46 (br. absorption, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 50.6, 68.6, 70.6, 70.8, 86.4, 129.2; ESI-MS (*m*/*z*) 968 [M+Na]$^+$, 952 [M+H]$^+$, 951 [M]$^+$. $C_{42}H_{45}Fe_3N_3O_6S_3$ (951.5) calcd: C, 53.01; H, 4.77; N, 4.42. Found: C, 53.27 and 53.48; H, 4.82 and 4.88; N, 4.41 and 4.42.

2aab, (*E*,*E*,*E*)-1-Ferrocenylsulfonyl-6,11-bis[(4-methylphenyl)sulfonyl] - 1,6,11 - triaza cyclopentadeca - 3,8,13-trienepalladium(0): mp 127–129 (dec.); IR (KBr) 2918, 1333, 1157, 901, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.50–1.70 (m, 4H), 2.38 (s, 6H), 2.76 (apparent t, $J=12$ Hz, 2H), 3.03 (apparent q, $J=12$ Hz, 2H), 3.70 (m, 2H), 3.93 (m, 2H), 4.41 (s, 5H), 4.32–4.80 (m, 10H), 7.26 (m, 4H), 7.68 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.4, 45.1, 48.1, 48.2, 49.3, 49.4, 68.3, 68.4, 70.6, 70.7, 78.1, 78.2, 78.3, 78.4, 78.6, 78.7, 82.5, 82.6, 82.9, 85.4, 85.8, 126.9, 127.1, 129.7, 129.8, 135.3, 136.0, 143.3, 143.5; ESI-MS (*m*/*z*) 892 [M+Na]$^+$, 887 [M+NH$_4$]$^+$, 869 [M]$^+$, 781 [M−Pd+NH$_4$]$^+$, 764 [M−Pd+H]$^+$, 763 [M−Pd]$^+$. $C_{36}H_{41}FeN_3O_6PdS_3$ (870.2) calcd: C, 49.69; H, 4.75; N, 4.83. Found: C, 49.50 and 49.66; H, 4.84 and 4.87; N, 4.45 and 4.47.

2abb, (*E*,*E*,*E*)-1,6-Bis(ferrocenylsulfonyl)-11-[(4-methylphenyl)sulfonyl] - 1,6,11 - triazacyclopentadeca - 3,8,13-trienepalladium(0): mp 144–146°C (dec.); IR (KBr) 2920, 1337, 1136, 900, 614 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.48–1.70 (m, 4H), 2.38 (s, 3H), 2.73 (apparent t, $J=12$ Hz, 2H), 3.02 (apparent q, $J=11$ Hz, 2H), 3.68 (m, 2H), 3.89 (m, 2H), 4.41 (s, 10H), 4.30–4.80 (m, 14H), 7.26 (m, 2H), 7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.5, 45.1, 48.1, 48.2, 49.4, 49.5, 68.4, 68.5, 70.5, 70.6, 70.8, 78.0, 78.2, 78.3, 78.4, 78.7, 82.4, 82.7, 82.8, 85.5, 85.9, 127.0, 127.1, 129.7, 129.8, 135.4, 136.1, 143.3, 143.5; ESI-MS (*m*/*z*) 963 [M]$^+$, 857 [M−Pd]$^+$. $C_{39}H_{43}Fe_2N_3O_6PdS_3$ (964.1) calcd: C, 48.59; H, 4.50; N, 4.36. Found: C, 48.91 and 49.06; H, 4.67 and 4.65; N, 4.11 and 4.09.

2bbb,(*E*,*E*,*E*)-1,6,11-Tris(ferrocenylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0): mp 178–180°C (dec.); IR (KBr) 2917, 1332, 1132, 900, 611 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.42–1.59 (m, 4H), 2.64 (t, $J=11$ Hz, 2H), 2.90 (dd, $J=14$ and 11 Hz, 2H), 3.47–3.73 (m, 2H), 3.74–3.88 (m, 2H), 4.24–4.47 (m, 18H), 4.34 (s, 15H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 45.6, 48.6, 49.8, 68.8, 68.9, 70.9, 71.0, 71.2, 78.5, 78.8, 83.0, 85.9, 86.3; ESI-MS (*m*/*z*) 1080 [M+Na]$^+$, 1075 [M+NH$_4$]$^+$, 1057 [M]$^+$, 951 [M−Pd]$^+$. $C_{42}H_{45}Fe_3N_3O_6PdS_3$ (1057.9) calcd: C, 47.68; H, 4.29; N, 3.97. Found: C, 47.27 and 47.61; H, 4.39 and 4.43; N, 3.84 and 3.89.

9. The redox properties have been investigated by means of cyclic voltammetry experiments. Those CV experiments have been carried out using approximately 1 mM sample complexes in a standard three-electrode cell using acetonitrile, dichloromethane or mixtures of them as solvent under Ar or N_2 atmospheres. Glassy carbon disks (3 mm diameter) were used as the working electrode, platinum wire as auxiliary and SSCE as the reference electrode. All $E_{1/2}$ redox potentials are thus reported versus SSCE.
10. $E_{1/2}=706$ mV, $E_{p,a}=756$ mV, $E_{p,c}=656$ mV, $\Delta E=100$ mV for **1aab**; $E_{1/2}=711$ mV, $E_{p,a}=762$ mV, $E_{p,c}=660$ mV, $\Delta E=102$ mV for **1abb**; $E_{1/2}=713$ mV, $E_{p,a}=762$ mV, $E_{p,c}=664$ mV, $\Delta E=102$ mV for **1bbb**.