A Novel Organometallic Macrocycle Composed of a Tetranuclear Palladium Acetylide**

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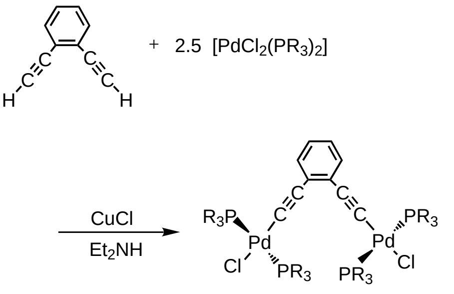
Macrocyclic compounds, which are a fundamental two-dimensional system of molecular networks, have attracted much attention due to their novel properties.[1] Recently, there has been growing interest in macrocycles composed of transition metal complexes and bipyridine ligands.[2] Their structures are strongly influenced by the structure of the bridging ligands and of the metal species. We have been investigating organometallic networks composed of transition metal acetylides,[3] since multinuclear acetylides have potential applications in materials science owing to their characteristic properties such as electronic interaction between metal atoms through bridging acetylide ligands.[4] Here we present a novel macrocyclic multinuclear acetylide complex, the structure of which is determined by the geometry of the bridging ligands and by the steric demand of the phosphane ligands. Although there are a few reports on macrocycles with a metal–acetylide bond,[5] multinuclear complexes are quite rare.[6]

Treatment of *o*-diethynylbenzene[7] with 2.5 equivalents of $[PdCl_2(PEt_3)_2]$ in the presence of a CuCl catalyst in diethylamine at room temperature gave the dipalladium complex **1a** in 62 % yield [Eq. (1)]. The tri-*n*-butylphosphane analogue **1b** was prepared by a similar reaction in 81 % yield. These complexes were fully characterized by spectroscopy. To obtain information on the geometry of the two palladium moieties and *o*-diethynylbenzene ring, an X-ray crystallographic analysis was performed on **1a** (Figure 1).[8] The two acetylene groups are slightly bent away from each other due to steric repulsion between the two bulky Pd moieties. The Pd–C and C≡C bond lengths and the bond angles are similar to those of other palladium acetylide complexes.[9] The noteworthy structural feature of **1a** is that the two palladium coordination planes are twisted out of the C_6H_4 plane of *o*-diethynylbenzene in the same direction to minimize steric repulsion between the triethylphosphane ligands. The dihedral angles are 55.1 and 46.8°.[3b, 5a, 9a, 10]



(1)

1a: R = Et
1b: R = Bu

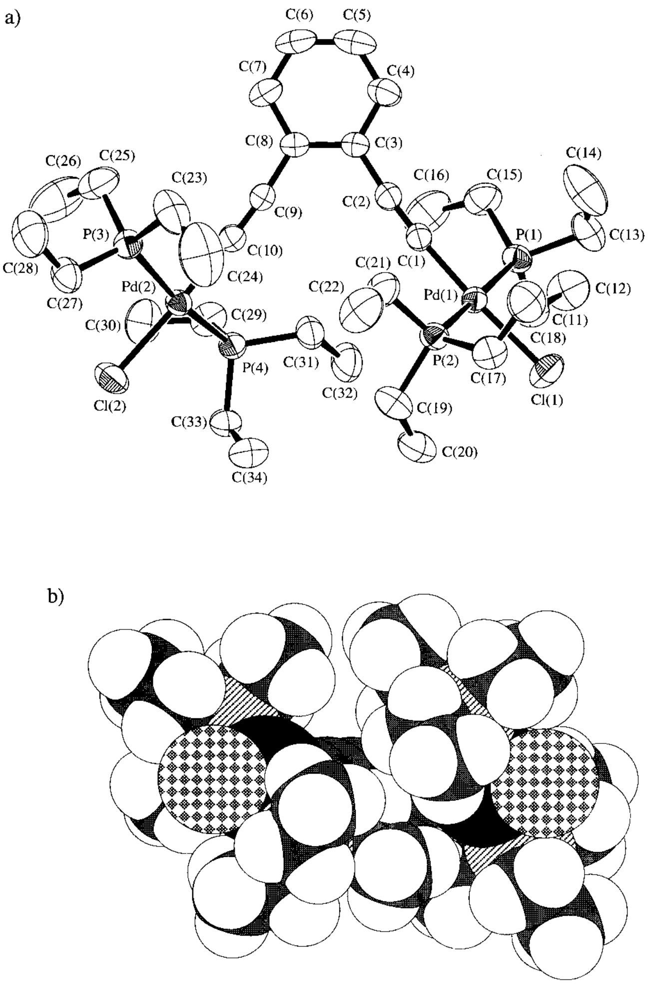


Figure 1. Molecular structure of **1a**. a) ORTEP plot (top view). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(1) 1.951(3), Pd(2)–C(10) 1.956(4), C(1)–C(2) 1.192(5), C(9)–C(10) 1.195(5); Cl(1)-Pd(1)-C(1) 175.8(1), P(1)-Pd(1)-P(2) 176.16(4), Cl(2)-Pd(2)-C(10) 178.0(1), P(3)-Pd(2)-P(4) 169.58(4), Pd(1)-C(1)-C(2) 175.1(3), C(1)-C(2)-C(3) 175.1(4), C(2)-C(3)-C(8) 122.5(3), C(3)-C(8)-C(9) 121.1(3), C(8)-C(9)-C(10) 175.8(4), Pd(2)-C(10)-C(9) 176.1(3). b) Space-filling representation (side view).

When *o*-diethynylbenzene was treated with an equimolar amount of $[PdCl_2(PEt_3)_2]$ under similar conditions [Eq. (2)], the oligomeric complex **2** was formed along with small amounts of polymeric complexes, as confirmed by gel permeation chromatography.[11] Purification by column chromatography on alumina followed by recrystallization from CH_2Cl_2/hexane gave pale yellow crystals of **2** in 33 % yield. Formation of M–C bonds was indicated by a characteristic band for ν(C≡C) of palladium acetylides at 2088 cm^{-1} in the IR spectrum of **2**. Although **2** is an oligomer, its NMR spectra show simple patterns. For example, the ^{31}P NMR spectrum exhibits a singlet at $\delta = 19.3$, and single sets of signals for the acetylenic and aromatic carbon atoms were observed in the

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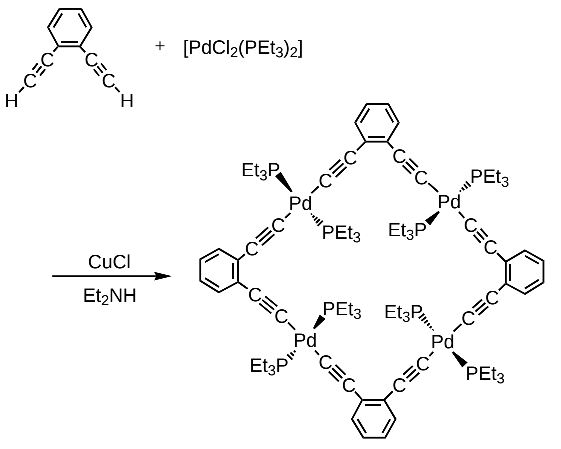

(2)

2

^{13}C NMR spectrum. These spectroscopic data suggest that **2** is a macrocyclic complex. Elemental analysis gave the composition $(C_{22}H_{34}P_2Pd)_n$, which also suggests a macrocyclic structure. Since the angle between two acetylene groups in *o*-diethynylbenzene is 60°, we assumed that **2** would be trinuclear.[2, 12] However, the average molecular weight of **2** determined by vapor pressure osmometry was 1850, which corresponds to a tetranuclear complex. Finally, the tetranuclear, macrocyclic structure of **2** was confirmed an X-ray structural analysis (Figure 2).[13] The molecule of **2** has D_{2d} symmetry in the solid state. The macrocyclic skeleton of palladium atoms, acetylide groups, and aromatic rings lies almost in a plane. The Pd–C bonds are slightly longer than those of **1a** due to the larger *trans* influence of an alkynyl group relative to a chloride ligand. The coordination plane of the Pd center forms dihedral angles of 63.9 and 69.6° with the C_6H_4 plane, which are larger than those of **1a**. The ethyl groups of the phosphane ligands are directed into the center of the macrocycle (Figure 3), so that there is no significant space for the inclusion of organic guest molecules.

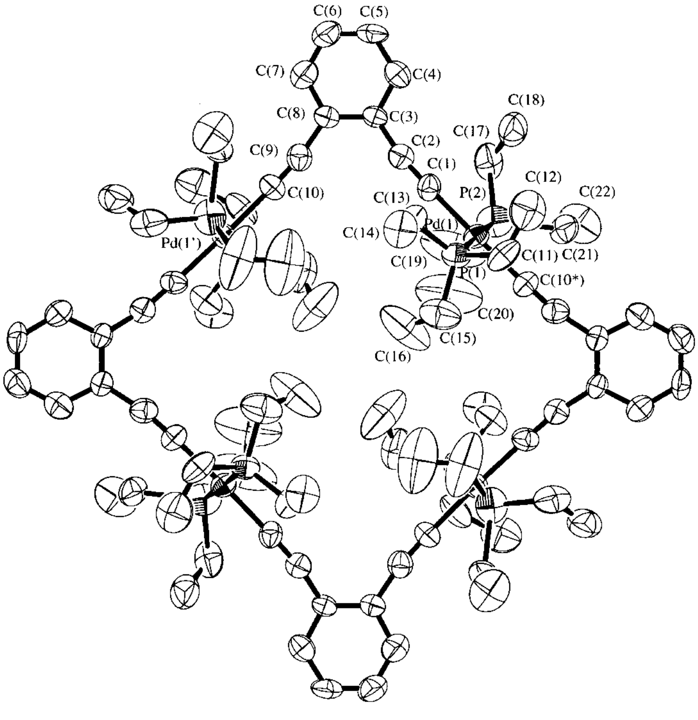

Figure 2. ORTEP plot of the molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(1) 1.996(8), Pd(1)–C(10*) 2.013(8), C(1)–C(2) 1.22(1), C(9)–C(10) 1.18(1); P(1)-Pd(1)-P(2) 176.82(9), C(1)-Pd(1)-C(10*) 177.6(3), Pd(1)-C(1)-C(2) 178.2(7), C(1)-C(2)-C(3) 170.7(8), C(2)-C(3)-C(8) 122.7(7), C(3)-C(8)-C(9) 123.1(7), C(8)-C(9)-C(10) 171.1(9), Pd(1')-C(10)-C(9) 177.1(3).

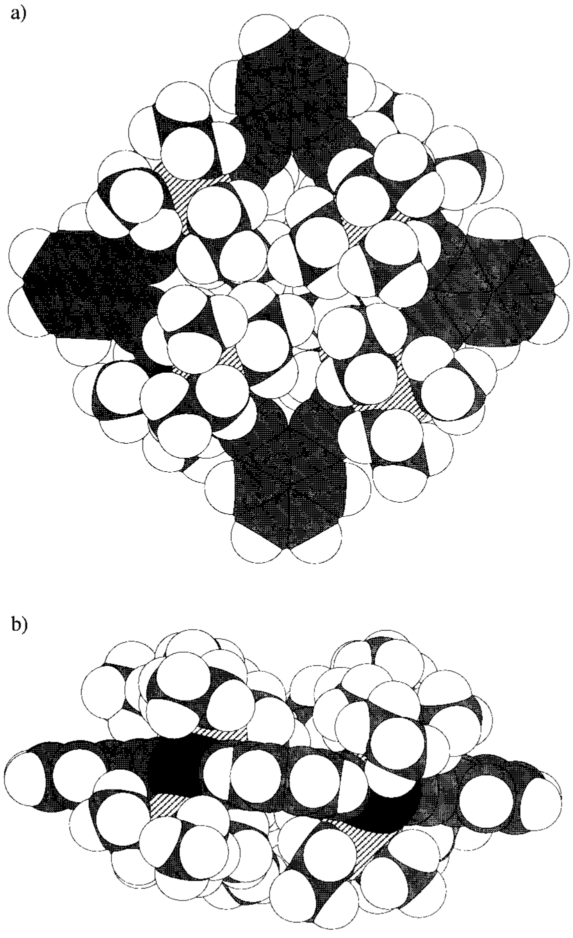

Figure 3. Space-filling representation of **2**. a) Top view. b) Side view.

The molecular structure provides information on the selective formation of **2**. In each $Pd(PEt_3)_2(o\text{-}C{\equiv}CC_6H_4C{\equiv}C)\text{-}Pd(PEt_3)_2$ moiety, the two coordination planes are twisted out of the C_6H_4 plane in the same direction to avoid steric steric interactions, as is observed in **1a**. Consequently, the P-Pd-P axes are inclined alternatingly in opposite directions with respect to the macrocycle, and the triethylphosphane ligands on one side of the macrocycle plane are alternatingly situated on the outside and inside of the macrocycle. Therefore, the number of palladium atoms in the macrocycle must be even. Because dinuclear and hexanuclear macrocycles are highly strained, the tetranuclear complex **2** with minimum strain is selectively formed.

Treatment of *o*-diethynylbenzene with an equimolar amount of $[PdCl_2(PnBu_3)_2]$ did not give a macrocycle, but a mixture of linear oligomeric complexes owing to the slightly larger steric bulk of tri-*n*-butylphosphane relative to triethylphosphane.

We have demonstrated a novel route to a macrocycle with palladium acetylide units in the backbone. We are currently investigating the extension of this method to the formation of macrocycles with other bridging acetylide ligands.

Experimental Section

1a: A mixture of *o*-diethynylbenzene (126 mg, 1 mmol) and [$PdCl_2(PEt_3)_2$] (1.034 g, 2.5 mmol) in diethylamine (50 mL) in the presence of CuCl (ca. 2 mol%) was stirred at room temperature for 18 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina with CH_2Cl_2 as eluent. Recrystallization from CH_2Cl_2/hexane gave pale yellow crystals (544 mg, 62%). IR (KBr): $\tilde{\nu}$ = 2114 cm^{-1} ($C\equiv C$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.22$ (dd, $J = 5.8, 3.5$ Hz, 2H), 6.99 (dd, $J = 5.8, 3.5$ Hz, 2H), 2.00–1.93 (m, 24H), 1.19 (dt, $J = 16.6$, 8.0 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.3$, 127.9, 124.9, 107.0 (t, $J_{P,C} = 5.8$ Hz), 98.2 (t, $J_{P,C} = 16.5$ Hz), 15.4 (vt, $N = 14.1$ Hz), 8.43; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 18.2$; satisfactory elemental analysis.

2: An equimolar mixture of *o*-diethynylbenzene and [$Pd(PEt_3)_2Cl_2$] was treated as for **1a** to give pale yellow crystals in 33% yield. IR (KBr): $\tilde{\nu}$ = 2088 cm^{-1} ($C\equiv C$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.23$ (dd, $J = 5.9, 3.4$ Hz, 8H), 6.99 (dd, $J = 5.9, 3.4$ Hz, 8H), 2.05–2.00 (m, 48H), 1.21 (dt, $J = 16.3$, 8.0 Hz, 72H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 132.4$, 128.6, 124.0, 114.2 (t, $J_{P,C} = 17.4$ Hz), 111.1 (t, $J_{P,C} = 3.7$ Hz), 17.2 (vt, $N = 14.1$ Hz), 8.9; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 19.3$; satisfactory elemental analysis.

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[8] Crystallographic data for **1a**: $C_{34}H_{64}Cl_2P_4Pd_2$ ($M_r = 592.54$), monoclinic, space group $P2_1/c$ (no. 14), $a = 17.681(2)$, $b = 11.080(1)$, $c = 22.446(2)$ Å, $\beta = 103.810(8)^\circ$, $V = 4270.3(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.369$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 11.38$ cm^{-1}, $T = -75\,^\circ C$, $\omega/2\theta$ scans, $6 < 2\theta < 60^\circ$, $R = 0.035$ and $R_w = 0.054$ for 379 parameters against 8528 reflections with $I > 3.0\sigma(I)$ out of 13341 unique reflections by full-matrix least-squares method, GOF = 1.12.[13b]

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[13] a) Crystallographic data for **2**: $C_{88}H_{136}P_8Pd_4$ ($M_r = 1867.43$), tetragonal, space group $P4_2/n$ (no. 86), $a = 18.429(4)$, $c = 14.440(4)$ Å, $V = 4904(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.264$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 8.90$ cm^{-1}, $T = -75\,^\circ C$, $\omega/2\theta$ scans, $6 < 2\theta < 55^\circ$, $R = 0.068$ $R_w = 0.110$ for 244 parameters against 2711 reflections with $I > 3.0\sigma(I)$ out of 4573 unique reflections by full-matrix least-squares method, GOF = 1.24. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101904 (**1a**) and CCDC-101905 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Completely Regioselective Synthesis of Directly Linked *meso,meso* and *meso,β* Porphyrin Dimers by One-Pot Electrochemical Oxidation of Metalloporphyrins**

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Porphyrin dimers have been attracting considerable attention as biomimetic models of photosynthetic systems, and as photonic materials and functional molecular devices.[1–7] Since the type of bond connecting the porphyrin rings influences the electronic communication in the dimer, a variety of porphyrin arrays has been explored.[8–10] Directly linked porphyrin arrays are one interesting class of these compounds, because of the strong interaction between the two porphyrin rings.[1, 7, 11–14]

We previously reported that electrochemical oxidation has an advantage over silver salt oxidation for obtaining directly linked *meso,meso* porphyrins, since the former method can be

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author. The following data are available as supporting information: a preliminary X-ray crystal structure of **10**, the ROESY NMR spectrum of **11**, and cyclic and differential-pulse voltammograms of **2**, **4**, **5**, **8**, **10**, **11**, and **13**–**15**.