Unsaturated Hetero Chains, VIII[+]

First Metal Complexes of Oligonitrile Ligands: Palladium(II) Complexes of *N*-Methoxycarbonyl- and *N*-Thiobenzoyl-1,3,5,7-tetraazaoctatetraenes

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Dedicated to Professor Bernt Krebs at the occasion of his 60th birthday

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Two mononuclear six-membered chelate $PdCl_2$ complexes **2a**, **b** of the two different types of tetrameric oligonitriles **1a**, **b** have been synthesized. Both contain square-planar palladium(II) with a *cis* arrangement of the chloride atoms. In complex **2a** of the ω-amino-substituted *N*-methoxycarbonyl oligonitrile **1a** the metal center is coordinated by the nitrogen atoms N1 and N3. Within the chelate ring alternating bond lengths for the C–N bonds are observed, whereas the non-complexed, more flattened part of the oligonitrile chain shows almost equal C–N bond lengths, indicating strong donor-acceptor interactions involving the terminal amino group and the N3–Pd moiety of the molecule. The complex **2b** is derived from the thiobenzoyl ligand **1b** bearing a terminal (*R*)-fenchylidene group. In **2b** the sulfur atom S1 and the nitrogen atom N2 are involved in complexation. In contrast to **2a**, strong bond-length alternation is observed in **2b** for the complexed and the non-complexed part of the ligand. From the NMR spectra of both complexes no indication for a migration of the $PdCl_2$ unit along the chain could be derived.

Introduction

Recently, variably substituted oligonitriles became available for the first time in monodisperse, well-defined form.[1−4] Although these substances are isoelectronic with polyacetylenes (polyenes), their structural and electronic properties are entirely different. For instance they adopt nonplanar three-dimensional structures (often helices in the crystalline state) without far-reaching conjugation. Of special interest is their behavior in complexation and redox reactions as well as their electrical conductivity[5] and the NLO properties.

In this paper we report on our investigations of the complexation ability of oligonitriles using palladium(II) as metal counterpart. Oligonitriles are expected to serve as potent polydentate ligands since each imine nitrogen atom is a potential σ donor. Furthermore, the numerous C=N bonds may give rise to π complexation. High molecular flexibility due to low barriers of rotation around the C−N single bonds is expected to facilitate complexation additionally.

Results and Discussion

Two different types of substituted oligonitrile molecules have been used, both carrying four adjacent imino bonds ("tetramers") and one additional terminal C=X functionality. Substance **1a** bears a methoxycarbonyl moiety at nitrogen atom N1 whereas **1b** is a thiobenzoyl derivative. For the formation of the complexes the ligands were dissolved in acetonitrile, and bis(benzonitrile)palladium dichloride was added. Crystallization was achieved by adding a surplus of diethyl ether, yielding metal complex **2a**, and **2b**.[6]

Both new compounds **2a** and **2b** were subjected to X-ray analysis. Both are mononuclear 1:1 complexes with a *cis*-$PdCl_2$ unit.

The methoxycarbonyl compound **1a** leads to metal complex **2a** by complexation of nitrogen atom N1 and N3 (crystallographic numbering) to Pd forming a six-membered chelate ring (Figure 1). The palladium center is tetracoordinate forming the expected square-planar geometry[7] as indicated by the sum of angles around palladium (359.88°). Coordinative bond lengths are in the typical range of $Pd^{II}-N(sp^2)$ and $Pd^{II}-Cl$ bonds. As expected for a palladium compound, coordination to nitrogen atoms is clearly preferred over complexation to oxygen atoms of the methoxycarbonyl group. The chelate ring deviates strongly from planarity leading to a twisted-boat-shaped structure. The two other nitrogen atoms N4 and N5 are not involved in complexation. This observation may be explained by

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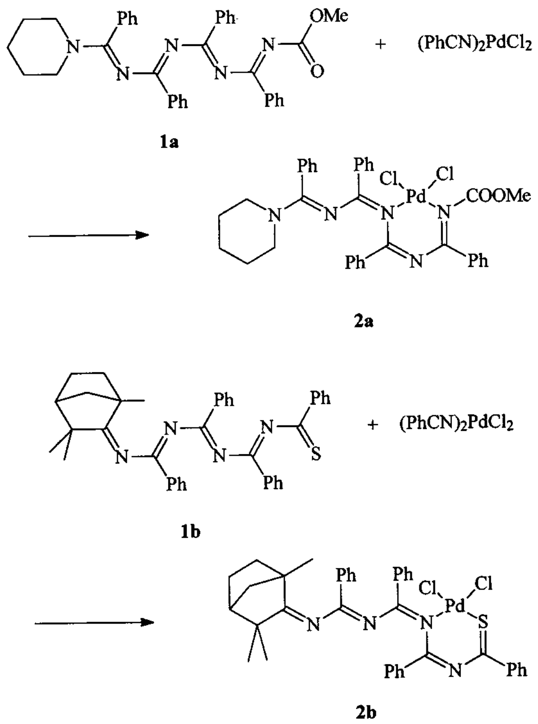

Scheme 1

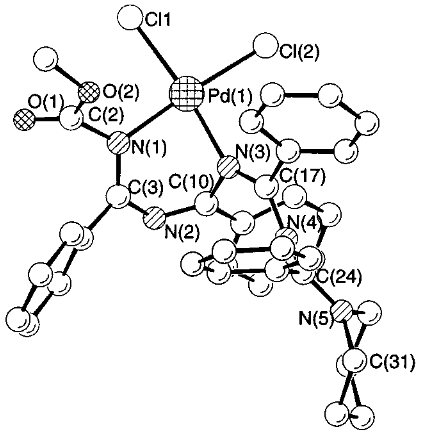

Figure 1. Molecular structure of **2a** (hydrogen atoms omitted for clarity); selected bond lengths [Å], bond angles [°], and torsional angles [°]: bond lengths [Å]: Pd−Cl(1) 2.282(1), Pd−Cl(2) 2.276(1), Pd−N(1) 2.041(2), Pd−N(3) 2.017(2), O(1)−C(2) 1.187(4), C(2)−N(1) 1.434(4), N(1)−C(3) 1.295(4), N(2)−C(3) 1.381(4), N(2)−C(10) 1.285(4), N(3)−C(10) 1.407(4), N(3)−C(17) 1.322(4), N(4)−C(17) 1.330(4), N(4)−C(24) 1.328(4), N(5)−C(24) 1.322(4); bond angles [°]: Cl(1)−Pd−Cl(2) 92.93(3), N(1)−Pd−N(3) 83.45(10), Cl(1)−Pd−N(1) 91.04(7), Cl(2)−Pd−N(3) 92.46(7), O(1)−C(2)−N(1) 123.4(3), C(2)−N(1)−C(3) 120.2(3), N(1)−C(3)−N(2) 120.7(3), C(3)−N(2)−C(10) 121.0(3), N(2)−C(10)−N(3) 120.6(3), C(10)−N(3)−C(17) 118.8(2), N(3)−C(17)−N(4) 118.3(3), C(17)−N(4)−C(24) 124.2(3), N(4)−C(24)−N(5) 118.1(3); torsional angles [°]: O(1)−C(2)−N(1)−C(3) −58.8, C(2)−N(1)−C(3)−N(2) 162.0, N(1)−C(3)−N(2)−C(10) 45.0, C(3)−N(2)−C(10)−N(3) 3.5, N(2)−C(10)−N(3)−C(17) 113.2, C(10)−N(3)−C(17)−N(4) 7.1, N(3)−C(17)−N(4)−C(24) −149.2, C(17)−N(4)−C(24)−N(5) −153.5, N(4)−C(24)−N(5)−C(31) −164.4

strong interactions of the two chlorine atoms to the palladium center which could not be replaced by the nitrogen functionalities.[7] In the six-membered chelate ring of **2a** alternating C=N double bonds (1.29−1.30 Å) and C−N single bonds (1.38−1.41 Å) are found. This structural feature is typical for the free oligonitriles which form nonplanar solid-state structures with alternating bond lengths.[1][2] Similarly, UV/Vis spectra of oligonitriles including **1a** do not indicate long-range conjugation in solution. Much in contrast to this, the exocyclic oligonitrile chain (N3 to N5) of **2a** bears C−N bonds with almost equal bond lengths (1.32−1.33Å). This (*Z*,*E*,*E*)-configured part of **2a** does not deviate much from planarity as the torsional angles indicate (see Figure 1). Both observations indicate a strong conjugative donor−acceptor interaction of N5 (lone pair) and $\mathrm{Pd^{II}}$ coordinated to N3, similar to 2-azavinamidinium-type structures.[8] Unfortunately, interpretation of the UV/Vis spectra of this chromophore is difficult due to strong UV absorptions of $\mathrm{Pd^{II}}$. These favorable electronic interactions as well as steric factors based on the bulky substituents at N4 may lead to the unexpected regioselectivity of the complexation reaction which does not involve the nitrogen atoms N2, N4 or N5 which present better donor groups than the acceptor-substituted N1.

The thiobenzoyl-substituted oligonitrile **1b** also forms a six-membered chelate **2a** on reaction with $\mathrm{PdCl_2(PhCN)_2}$, but now the sulfur atom is involved in coordination to the palladium center (Figure 2). This is not unexpected in view of the high affinity of the soft $\mathrm{Pd^{II}}$ ion for S ligands. Again a square planar coordination geometry of the palladium center (sum of angles 360.0°) is observed. Due to the chiral (*R*)-fenchyl group, which was introduced enantiomerically pure into the molecule, a chiral space group is required for the crystallization of the substance. However, good adaption was achieved by calculating for the monoclinic space group $P2_1/c$ whereas refinement assuming chiral space groups was unsuccessful. Large U_{iso} values of fenchyl C atoms, which were refined isotropically, and high residual electron density around the fenchyl group may in part be a consequence of the structure solution in the achiral space group. Attempts to apply a split-atom model to the fenchyl group were unsuccessful; however, it is quite likely that (*E*/*Z*) isomers with regard to the N5−C29 bond of **2b** give rise to these difficulties. The C−N bond lengths alternate strongly in the chelate ring and − in contrast to **2a** − also in the uncomplexed part of the chain. This observation supports the postulated donor−acceptor interaction in **2a**, since the imine nitrogen atom N4 and the fenchyl group in **2b** do not have the donor properties of N5 in **2a**. All C=N double bonds show (*Z*) configuration as it is often found in the structures of oligonitriles.[2]

NMR Spectra

The ^{1}H-NMR spectra of complexes **2a** and **2b** at 25 °C in $\mathrm{CDCl_3}$ display broad and poorly resolved signals for the phenyl protons and the piperidyl and fenchyl protons, respectively, due to dynamic properties of the complexes. However, the presence of a single, sharp CO_2CH_3 signal of **2a** at $\delta = 3.8$ (0.3 ppm downfield relative to **1a** in $CDCl_3$[2]) indicates that the N1−N3 coordination in the solid state is retained in solution since metal coordination at N1 reduces the electron density of the ester group. Alternatively, magnetic anisotropy caused by sterically hindered phenyl groups may be responsible for this chemical shift. At −50 °C the phenyl and the alkyl signals of **2a** are much sharper but the CO_2CH_3 signal is very broad. We interpret this effect by a sterically hindered, slow rotation of the ester group around the C2−N1 bond. The ^{13}C-NMR spectrum of **2a** at both 20 °C and −50 °C supports the presence of a single isomer in $CDCl_3$ solution. No indications for a migration of the $PdCl_2$ unit along the chain could be detected in the temperature range used.

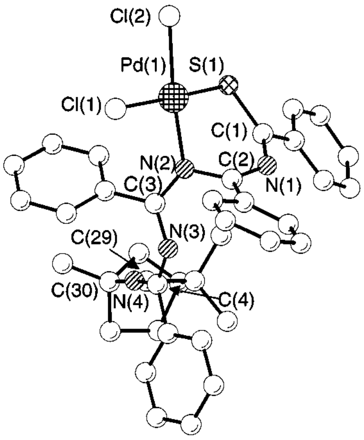

Figure 2. Molecular structure of **2b** (hydrogen atoms omitted for clarity); selected bond lengths [Å], bond angles [°], and torsional angles [°]: bond lengths [Å]: Pd−Cl(1) 2.341(1), Pd−Cl(2) 2.291(1), Pd−S 2.237(1), Pd−N(2) 2.039(4), S−C(1) 1.677(5), N(1)−C(1) 1.372(6), N(1)−C(2) 1.303(7), N(2)−C(2) 1.396(6), N(2)−C(3) 1.310(6), N(3)−C(3) 1.350(6), N(3)−C(4) 1.302(7), N(4)−C(4) 1.347(6), N(4)−C(29) 1.273(7); bond angles [°]: Cl(1)−Pd−Cl(2) 95.34(5), S−Pd−N(2) 89.57(12), S−Pd−Cl(2) 83.46(5), Cl(1)−Pd−N(2) 91.63(12), S−C(1)−N(1) 122.9(4), C(1)−N(1)−C(2) 125.2(4), N(1)−C(2)−N(2) 122.0(5), C(2)−N(2)−C(3) 120.1(4), N(2)−C(3)−N(3) 119.7(5), C(3)−N(3)−C(4) 125.2(4), N(3)−C(4)−N(4) 125.0(5), C(4)−N(4)−C(29) 136.2(5), N(4)−C(29)−C(39) 121.7(5); torsional angles [°]: S−(1)−N(1)−C(2) −38.6(7), C(1)−N(1)−C(2)−N(2) −11.8(8), N(1)−C(2)−N(2)−C(3) −113.8(6), C(2)−N(2)−C(3)−N(3) −10.6(7), N(2)−C(3)−N(3)−C(4) 142.6(5), C(3)−N(3)−C(4)−N(4) −5.9(9), N(3)−C(4)−N(4)−C(29) −100.5(8), C(4)−N(4)−C(29)−C(30) −172.4(6)

Experimental Section

Materials and Methods: Compounds **1a** and **1b** were prepared as previously described.[2][3] Commercially available solvents (p.a. quality) were used without further purification. − CHN analyses were performed with a DiaCHN 240 (Perkin−Elmer). − IR spectra were recorded with a Bruker FT-IR IFS 48 spectrophotometer as KBr pellets. − UV/Vis spectra were recorded using an HP 8453 diode array spectrophotometer (Hewlett-Packard). − ^1H- and ^{13}C-NMR spectra were obtained using a Bruker AC 200 and Varian Unity 600 spectrometer.

$PdCl_2$ Complex of *N*-Methoxycarbonyl-2,4,6,8-tetraphenyl-8-piperidino-1,3,5,7-tetraazaoctatetraene (2a): 27 mg (0.049 mmol) of **1a**[2] was treated at room temperature with 19 mg (0.049 mmol) of $(PhCN)_2PdCl_2$ in 1 mL of acetonitrile. After stirring for 10 min, a clear, orange solution was formed, which was treated with 1 mL of diethyl ether. Later, 10 mL of diethyl ether and 10 mL of pentane were added carefully in such a way that an upper layer was formed. After 5 d, red crystals of **2a** were collected [31 mg (0.042 mmol), 21% yield]. − UV/Vis($CDCl_3$): λ_{max} [nm] (ε) = 445 (100), 375 (shd), 300 (2900). − ^1H NMR(600 MHz, 298 K, $CDCl_3$): δ = 1.31 (br., 4 H, CH_2), 1.52 (br., 2 H, CH_2), 3.07 (br., 4 H, NCH_2), 3.80 (s, 3 H, OCH_3), 6.35, 6.85, 7.10, 7.35, 7.54 (br., phenyl-CH), 7.55, 7.63 (t, phenyl-CH), 7.80, 7.99 (s, br., phenyl-CH), 8.25 (br., phenyl-CH). − ^{13}C NMR(150.85 MHz, 298 K, $CDCl_3$): δ = 23.72, 24.78, 26.40 (CH_2), 49.76 (NCH_2), 54.71 (OCH_3), 128.19, 128.64, 128.89, 128.98, 130.42, 130.60 (CH), 131.69, 132.51 (C_i), 132.91, 133.24 (CH), 137.68 (C_i), 157.94, 162.54, 164.85, 166.76 (CN, CO). −$C_{35}H_{33}Cl_2N_5O_2Pd \cdot Et_2O$ (807.08): calcd. C 57.71 H 4.97 N 9.09; found C 57.26 H 5.13 N 9.02.

X-ray Diffraction Analysis of 2a · Et_2O ($C_{35}H_{33}Cl_2N_5O_2Pd \cdot Et_2O$):[9] The red single crystals were analyzed with a Siemens P3 diffractometer using Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator at 170(2) K. Crystal system: monoclinic, space group $P2_1/n$ with cell parameters a = 10.186(2), b = 22.633(5), c = 16.221(3) Å, β = 95.73(3)°, V = 3720.9(13) $Å^3$, $\rho_{calcd.}$ = 1.441 g cm^{-3}, Z = 4. Crystal size: 0.38 × 0.34 × 0.15 mm. 8573 reflections were collected leading to 8118 independent and 6422 observed [$I > 2\,\sigma(I)$] reflections. Absorption coefficient μ = 0.687 mm^{-1}, no absorption correction, 452 refined parameters. Non-hydrogen atoms were refined anisotropically. H atoms were geometrically positioned (riding model). $R(F)$ = 0.0417, $wR(F^2)$ = 0.0904; residual electron density: 0.551/−1.097 e $Å^{-3}$. The structure was solved and refined using SHELXS-86 and SHELXL-93.[10]

$PdCl_2$ Complex of 2,4,6,8-Tetraphenyl-8-(1,3,3-trimethylbicyclo-[2.2.1]hept-2-ylidene)amino-1-thia-1,3,5,7-octatetraene (2b): 24 mg (0.042 mmol) of **1b**[3] was suspended in 1 mL of acetonitrile and treated with a solution of 18.8 mg (0.049 mmol) of $(PhCN)_2PdCl_2$ in 2 mL of acetonitrile. After stirring for 5 min, a clear, deeply red solution has formed, from which after 30 min a red, powder-like solid precipitated. The solid was separated by filtration, washed with little acetonitrile and dried in vacuo. Yield: 17 mg (0.022 mmol; 53%). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3058 (w), 2962−2868 (w), 1734 (m), 1585 (m), 1560 (s), 1495 (s), 1478 (s), 1450 (s), 1345 (m), 1323 (m), 1309 (m), 1285 (m), 1267 (m), 1205 (m), 766 (m), 696 (m). − $C_{38}H_{36}Cl_2N_4PdS$(758.07): calcd. C 60.20 H 4.78 N 7.39; found C 59.04 H 5.06 N 7.68.

X-ray Diffraction Analysis of 2b ($C_{38}H_{36}Cl_2N_4PdS$):[9] The red single crystals were analyzed at 170(2) K with a Siemens P3 diffractometer using Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. Crystal system: monoclinic, space group $P2_1/c$ (see text) with cell parameters a = 11.244(2), b = 30.714(4), c = 11.562(2) Å, β = 118.42(3)°, V = 3511.7(10) $Å^3$, $\rho_{calcd.}$ = 1.434 g cm^{-3}, Z = 4; crystal size 0.12 × 0.20 × 0.38 mm). 8037 reflections were collected leading to 7657 independent and 5399 observed [$I > 2\,\sigma(I)$] reflections. Absorption coefficient μ = 0.773 mm^{-1}, no absorption correction. 379 refined parameters. Non-hydrogen atoms were refined anisotropically with exception of the fenchyl C atoms which were refined isotropically. H atoms were geometrically positioned (riding model). $R(F)$ = 0.0594, $wR(F^2)$ = 0.1625; residual electron density: 2.072/−0.887 e $Å^{-3}$. The structure was solved and refined using SHELXS-97 and SHELXL-97.[10]

Acknowledgments

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[1] M. Buhmann, M. H. Möller, U. Rodewald, E.-U. Würthwein, *Angew. Chem.* **1994, 106,** 2386; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2337.

[2] N. C. Aust, R. Fröhlich, J. Hecht, E.-U. Würthwein, *Liebigs Ann.* **1997**, 1593.

[3] A. Beckmann, R. Fröhlich, E.-U. Würthwein, *Tetrahedron Lett.* **1997**, *38*, 5481; see also: A. Beckmann, Ph.D. thesis, Univ. of Münster, **1996**.

[4] N. Schulte, R. Fröhlich, J. Hecht, E.-U. Würthwein, *Liebigs Ann.* **1996**, 371.

[5] D. Wöhrle, *Makromol. Chem.* **1974**, *175*, 1751−1760.

[6] From **1a** and $[Pd(MeCN)_4]^{2+}(BF_4^-)_2$ a yellow oil was obtained which could not be crystallized. Due to broad ^{1}H-NMR signals, a satisfying structural assignment was not possible.

[7] C. F. Barnard, M. J. H. Russel, in *Comprehensive Coordination Chemistry*, vol 5 (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, Oxford, **1987**, p. 1115.

[8] H. Pritzkow, H. Hartl, *Acta Crystallogr.* **1973**, *B29*, 1777−1784.

[9] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112052 (**2a**) and -112053(**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

[10] G. M. Sheldrick, *SHELXS-86, Program for crystal structure solution*, Universität Göttingen, Germany, **1986**. G. M. Sheldrick, *SHELXL-93, Program for the refinement of crystal structures*, Universität Göttingen, Germany, **1993**; G. M. Sheldrick, *SHELX-97*, Universität Göttingen, **1997**.

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