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A new homobimetallic arenediyl diplatinum(II) unit as building block for macromolecular synthesis. X-ray crystal structure of $[C_6H_2\{CH_2NMe_2\}_2\text{-}1,5\text{-}\{PtCl(PPh_3)\}_2\text{-}2,4]$

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Abstract

Treatment of the diaminobenzene $[C_6H_4\{CH_2NMe_2\}_2\text{-}1,3]$ (NCN-H, **1**) with one or two equivalents of *cis*-$PtCl_2(DMSO)_2$ leads to exclusive formation of the doubly cycloplatinated species $[C_6H_4\{CH_2NMe_2\}_2\text{-}1,5\text{-}\{PtCl(DMSO)\}_2\text{-}2,4]$ (**3**), which upon addition of triphenylphosphine yields the bisphosphine adduct $[C_6H_4\{CH_2NMe_2\}_2\text{-}1,5\text{-}\{PtCl(PPh_3)\}_2\text{-}2,4]$ (**4**). The X-ray molecular structure of **4** revealed the presence of highly distorted square planar Pt(II) centers which is caused by close proximity of the two phosphine donor ligands. Complexes of type **3** can be regarded as suitable starting materials for the directional build-up of larger macromolecular structures. © 2001 Published by Elsevier Science B.V.

Keywords: Arylamine ligands; Building blocks; C–H activation; Platinum

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1. Introduction

Macromolecular synthesis with organometallic complexes is a field of research that is increasingly investigated with the ultimate goal of creating novel materials with unprecedented properties [1]. Prerequisites for the build up of large metal-containing structures seem to be the synthetic availability and stability of such metalated synthons [2]. Additionally, these organometallic complexes should include weak donor ligands which upon exchange with polydentate Lewis bases can give rise to self-assembled structures. Recently, the preparation of metalated (*N*,)*C*,*N*- [3,4] or *S*,*C*,*S*-chelating [5] aryl ligands suitable as fragments of larger synthetic supramolecules has been reported. Simultaneously, the use of platinum(II) dimethylsulfoxides as mild and versatile metalating reagents for introduction of Pt(II) centers onto aromatic ligands has been developed [4,6]. Herein, we report our first results on the synthesis of a doubly cycloplatinated diaminoarene ligand by treatment of $C_6H_4\{CH_2NMe_2\}_2\text{-}1,3$ (**1**, NCN-H) with *cis*-$PtCl_2(DMSO)_2$, and the subsequent exchange of the pendant dimethylsulfoxide ligands for triphenylphosphine donor ligands.

2. Results and discussion

2.1. Synthesis and characterization of diplatinated species

Direct cycloplatination of the NCN-H ligand (**1**) with *cis*-$PtCl_2(DMSO)_2$ in a 1:1 molar ratio was initially aimed at the activation of the 1-position (H_a, Scheme 1), which would afford known **2**. To this end, equimolar amounts of *cis*-$PtCl_2(DMSO)_2$ and **1** (Fig. 1) were mixed in refluxing MeOH in the presence of NaOAc as an external base. After initial dissolution of the platinum salt, a white precipitate was formed, which was isolated (48% yield) and characterized by NMR spec-

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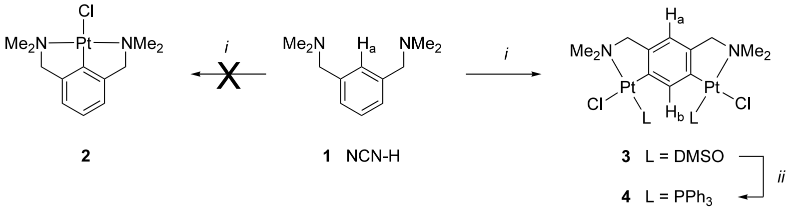
troscopy. The ^{1}H-NMR spectrum displayed the presence of a single organometallic product, which to our surprise was identified as the *doubly* platinated NCN derivative [$C_6H_2\{CH_2NMe_2\}_2$-1,5-$\{PtCl(DMSO)\}_2$-2,4] (**3**). Illustrative in the ^{1}H-NMR spectrum of **3** is the presence of a low-field, singlet resonance at 8.10 ppm with platinum couplings (^3J(Pt–H) = 51.8 Hz), which was attributed to H_b (Scheme 1). Additionally, H_a was observed as a single resonance at 6.78 ppm.

Remarkably, no *mono*-metalated species were detected. Earlier results in analogous palladation reactions of the NCN-H ligand with $Pd(OAc)_2$ and $Li_2[PdCl_4]$ also yielded biscyclometalated complexes [3d], [7]. These results suggest strongly that the intermediate monometalated species is more susceptible to electrophilic metalation then NCN-H itself, affording exclusively the bismetalated product. Moreover, the observed regioselectivity suggests that the 1-position of the NCN ligand is more sterically hindered with respect to the 3- and 5-position [8]. We also carried out the analogous cycloplatination reaction of NCN-H (**1**) in the presence of two equivalents of the platinum(II) salt. As expected, **3** was formed selectively (78% isolated yield) and no other platinum species could be detected.

Complex **3** proved to be rather insoluble in common organic solvents. Therefore, a PPh_3-for-DMSO ligand exchange in CH_2Cl_2 was carried out. This procedure afforded the bisphosphine complex **4** in almost quantitative yield as white needles. Complex **4** was analyzed using multinuclear NMR spectroscopy, elemental analyses and also by a single crystal structure determination (see Section 2.2). Of particular note is the high field shift of Ar–H_b positioned at 5.77 ppm (cf., 8.10 ppm in **3**). It seems likely that this high field shift arises from specific shielding caused by the π-electron density of the phenyl rings of each of the PPh_3 ligands in a close proximity to H_b. The proposed *trans*-position of both phosphine ligands (with respect to the NMe_2 donor fragment) in **4** is supported by ^{31}P-NMR spectroscopy, which shows a single singlet flanked by platinum satellites at 15.8 ppm, ^1J(Pt–P) = 4377 Hz. This coupling constant closely relates to previously reported data on similar complexes [4].

2.2. *X-ray crystal structure of 4*

Compound **4** was subjected to an X-ray crystal structure determination. The molecular structure is shown in



Scheme 1. Cycloplatination of the NCN-H ligand (**1**). *Reagents and conditions:* (i) $PtCl_2(DMSO)_2$, NaOAc, MeOH, 65 °C; (ii) PPh_3, CH_2Cl_2.

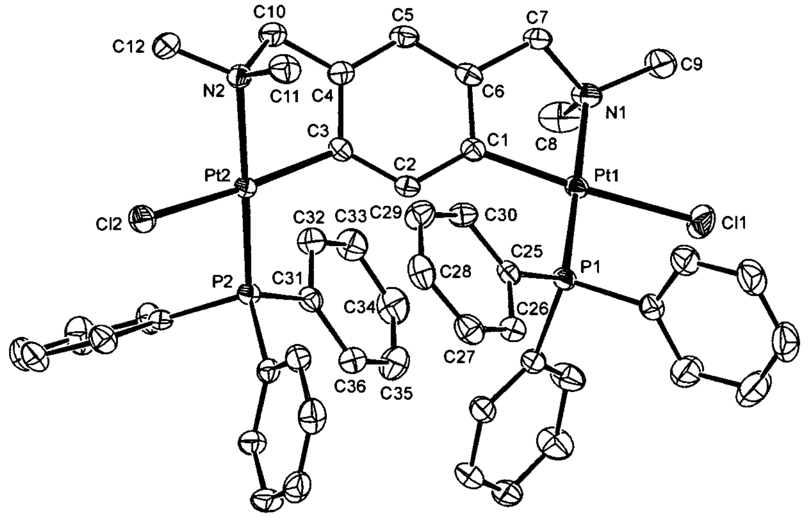


Fig. 1. Displacement ellipsoid plot (50% probability level) of the molecular structure of **4**, with the adopted numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–Cl(1) 2.4007(8), Pt(1)–P(1) 2.2242(7), Pt(1)–N(1) 2.141(3), Pt(1)–C(1) 2.016(3), Pt(2)–Cl(2) 2.4007(6), Pt(2)–P(2) 2.2268(7), Pt(2)–N(2) 2.159(2), Pt(2)–C(3) 2.009(2), C(1)–Pt(1)–N(1) 80.02(10), N(1)–Pt(1)–Cl(1) 90.70, Cl(1)–Pt(1)–P(1) 90.68(3), P(1)–Pt(1)–C(1) 98.75(8), C(1)–Pt(1)–Cl(1) 169.58(8), N(1)–Pt(1)–P(1) 177.68(6), C(3)–Pt(2)–P(2) 96.83(7), P(2)–Pt(2)–Cl(2) 94.38(2), Cl(2)–Pt(2)–N(2) 90.40(6), N(2)–Pt(2)–C(3) 79.99(9), C(3)–Pt(2)–Cl(2) 165.12(7), N(2)–Pt(2)–P(2) 170.54(6).

Fig. 1. Relevant bond angles and distances have been deposited as Section 5.

The two platinum centers are positioned opposite to the central arene plane, 0.221(1) Å above the plane for Pt1 and 0.253 Å below the plane for Pt2, respectively. They are in distorted planar environments with dihedral angles of 5.15(9) and 14.06(11)° between the N–Pt–C and P–Pt–Cl planes for Pt1 and Pt2, respectively. This distortion is caused by the strain of the two five membered chelate rings. Interestingly, these chelate rings have different conformations: the first ring is best described as a twist conformation with N1 0.774(2) Å above the plane of the central arene ring; the second ring is in an envelope conformation with N2 1.212(2) Å below the central arene plane. The N–Pt–C bite angles of 80.03(9) and 79.98(9)° are significantly smaller than the ideal values. The two PPh_3 ligands are located *trans* to the amino groups. The conformations of the PPh_3 groups slightly differ: the first ligand is in a *gauche* conformation with respect to the Pt1–Cl1 bond, while the second ligand is in a *staggered* conformation to Pt2–Cl2. We assume that the PPh_3 ligands behave like 'cogwheels' and that this interaction between them determines the conformation. Moreover, in this conformation, a close proximity between the aromatic hydrogen H2 and the two phenyl groups of the PPh_3 ligands is present, as supported by the NMR spectroscopic studies. The distance between H2 and C31 is 2.79 Å, which is significantly shorter than the sum of the covalent radii (C + H = 2.90 Å). Moreover, the H2–C30 (3.03 Å) and H2–C25 (2.23 Å) distances are indicative for the close proximity of H2 and the phenyl groups.

3. Conclusions

The presented results show that bisplatinum(II) derivatives of the diaminoarene ligand NCN-H are easily accessible via a direct and selective cycloplatination route. Moreover, recent experiments have unambiguously demonstrated the chemical stability of complexes of type **4** in subsequent synthesis [4c,d]. Future research programmes are focused on application of the presented building blocks in macromolecular synthesis by using suitable ligands with a predefined directional character.

4. Experimental

4.1. General

All chemicals were purchased from Acros/Aldrich and used without further purification. Solvents were distilled from appropriate drying agents *prior* to use. The starting materials *cis*-$PtCl_2(DMSO)_2$ [6] and NCN-H (**1**) [9] were prepared according to literature. NMR spectroscopic measurements were carried out on a Varian Inova 300 MHz spectrometer at room temperature (r.t.). Chemicals shifts are in ppm and referenced to residual solvent resonances. Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisch Labor, Mülheim a/d Ruhr, Germany.

4.2. $[C_6H_2\{CH_2NMe_2\}_2$-1,5-$\{PtCl(DMSO)\}_2$-2,4] (**3**)

To a solution of $C_6H_4(CH_2NMe_2)_2$-1,3 (0.32 g, 1.70 mmol) in MeOH (40 ml) was added solid *cis*-$PtCl_2(DMSO)_2$ (1.45 g, 3.43 mmol) and NaOAc (0.29 g, 3.45 mmol). The reaction mixture was stirred at 65 °C and within 15 min a clear yellow solution was obtained. The solution was stirred at 65 °C for 3 h whereupon a white solid precipitated from solution. The product was collected by decantation, washed with MeOH (50 ml), Et_2O (2×50 ml) and dried in vacuo to yield a white solid (1.07 g, 78%). ^{1}H-NMR ($CDCl_3$): δ 8.10 (s, ^3J(Pt–H) = 51.8 Hz, 1H, Ar-H_{ortho}), 6.78 (s, 1H, Ar-H), 3.89 (s, ^3J(Pt–H) = 40.6 Hz, 4H, CH_2N), 3.54 (s, ^3J(Pt–H) = 23.4 Hz, 12H, SCH_3), 2.90 (s, ^3J(Pt–H) = 33.2 Hz, 12H, NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.5, 139.6 (^2J(Pt–C) = 65.9 Hz), 134.9, 115.2 (^3J(Pt–C) = 40.2 Hz), 74.8 (^2J(Pt–C) = 54.8 Hz, CH$_2$N), 52.0 (NCH$_3$), 46.4 (^2J(Pt–C) = 65.5 Hz, SCH$_3$). The compound proved to be insoluble for a decent ^{13}C{^{1}H} NMR spectroscopic analysis. Anal. Calcd. for $C_{16}H_{30}Cl_2N_2O_2Pt_2S_2$: C, 23.79; H, 3.74; N, 3.47. Found: C, 23.81; H, 3.72; N, 3.39%.

4.3. $[C_6H_2\{CH_2NMe_2\}_2$-1,5-$\{PtCl(PPh_3)\}_2$-2,4] (**4**)

To a suspension of **1** (0.18 g, 0.19 mmol) in CH_2Cl_2 (10 ml) was added PPh_3 (0.16 g, 0.61 mmol) dissolved in CH_2Cl_2 (5 ml). The suspension gradually turned into a clear, yellow solution. After 4 h, Et_2O (60 ml) was added to the mixture whereupon white crystals separated from the solution, which were dried in vacuo (0.22 g, 95%). ^{1}H-NMR ($CDCl_3$): δ 7.39–7.24 (m, 20H, PAr–H), 7.14–7.06 (m, 10H, PAr–H), 6.82 (s, 1H, Ar–H), 5.77 (s, ^4J(P–H) = 5.20 Hz, ^3J(Pt–H) = 55.0 Hz, 1H, Ar–H_{ortho}), 3.94 (s, 4H, ^3J(Pt–H) = 30.0 Hz, CH_2N), 2.70 (d, ^3J(Pt–H) = 31.4 Hz, ^3J(P–H) = 1.8 Hz, 12H, NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.7 (^2J(P–C) = 4.8 Hz), 140.2, 137.8 (^1J(P–C) = 7.0 Hz, PAr–C_{ipso}), 134.9 (^2J(P–C) = 11.8 Hz, PAr–C_{ortho}), 131.3, 130.5, 129.8 (^4J(P–C) = 2.5 Hz, PAr–C_{para}), 127.4 (^3J(P–C) = 10.9 Hz, PAr–C_{meta}), 115.1 (^3J(Pt–C) = 34.8 Hz), 73.9 (^2J(Pt–C) = 50.7 Hz, CH_2N), 50.1 (NMe_2). ^{31}P{^{1}H}-NMR ($CDCl_3$, 81 MHz): δ 15.8 (^1J(Pt–P) = 4377 Hz). Anal. Calcd. for $C_{48}H_{48}Cl_2N_2P_2Pt_2$: C, 49.03; H, 4.11; N 2.38. Found: C, 48.88; H, 4.18; N, 2.31%.

*4.4. Crystal structure determinaton of **4***

Complex **4**: $C_{48}H_{48}Cl_2N_2P_2Pt_2\cdot C_4H_{10}O$, $F_w = 1250.02$, colourless needle, $0.48 \times 0.09 \times 0.06$ mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 13.2504(1)$, $b = 23.3587(2)$, $c = 17.2594(2)$ Å, $\beta = 116.5033(6)°$, $V = 4780.59(8)$ Å^3, $Z = 4$, $\rho = 1.737$ g cm^{-3}, 76701 measured reflections, 10999 unique reflections ($R_{int} = 0.051$). Intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (Mo–K_α, $\lambda = 0.71073$ Å) at a temperature of 150 K. Analytical absorption correction with the program PLATON [10] (routine TOMPA, $\mu = 6.06$ mm^{-1}, 0.19–0.82 transmission). The structure was solved with automated Patterson methods with the program DIRDIF97 [11] and refined with the program SHELXL97 [12] against F^2 of all reflections up to a resolution of $(\sin \vartheta/\lambda)_{max} = 0.65$ Å^{-1}. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. The crystal structure contains disordered diethyl ether solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON [10], CALC SQUEEZE, 172 e$^-$/unit cell in voids of 635.7 Å^3 per unit cell). R ($I > 2\sigma(I)$): $R1 = 0.0209$, $wR2 = 0.0433$. R (all data): $R1 = 0.0269$, $wR2 = 0.0446$. $S = 1.036$. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON [10].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 163055 for compound **4.** Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)

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[7] Note that reaction of NCN-H with $Pd(OAc)_2$ yielded mixtures of mono- and bispalladated products, dependent on the experimental conditions, see [3d].

[8] For selective metalation on the 1-position, this position should be activated prior to the transmetallation reaction, for example, by introducing 1-$SiMe_3$ groups or by C–H activation at the 1-position by lithium reagents (see, for example, [2] and [3d]).

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