Synthesis and Structural Characterization of the Dinuclear Beryllium Species $[Be_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$

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The synthesis and full characterization of $[Be_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$, which results from the reaction of $[Pd(PCy_3)_2]$ and $BeCl_2$ with concomitant precipitation of elemental palladium, is reported.

Key words: Beryllium, Dinuclear Compound, Lewis Base, Palladium, X-Ray Diffraction

Introduction

Due to the toxicity of beryllium compounds, the chemistry of beryllium is far less developed than that of its neighboring elements [1, 2]. As beryllium-containing materials feature unique properties, most of the corresponding research is done in material sciences [3]. With regard to its toxicity, additional work is focused on the coordination chemistry of Be(II) in aqueous solutions [4, 5]. Thus, tetrahedral four-coordinate Be species, which result from the coordination of ligands containing main group substituents, are well established [6 – 10]. However, the chemistry of transition metal-beryllium interactions was limited to cluster compounds, particularily to examples consisting of Zr [11, 12].

Based on previous success with the facile formation of "metal-only" Lewis pairs between electron-rich Pt^0 complexes and *p*-block metals, *e. g.* in the case of $[(Cy_3P)_2Pt–AlCl_3]$ [13] and $[(Cy_3P)_2Pt–GaCl_3]$ [14], we sought to extend this rather unusual bonding pattern to Lewis-base adducts between *d*- and *s*-block metals. $BeCl_2$ as a strong Lewis acid proved to be a promising starting material, and reaction of $[Pt(PCy_3)_2]$ with $BeCl_2$ in benzene resulted in the platinum beryllium adduct $[(Cy_3P)_2Pt–BeCl_2]$ (**1**) comprising an unprecedented, electron precise bond between beryllium and a *d*-block metal [15]. Recent studies showed that related low-valent palladium complexes also show a propensity to act as metal bases towards metal-coordinate boryl and borylene ligands, and therefore behave similar to their platinum congeners [16 – 19]. In the present paper we report on the reaction of $[Pd(PCy_3)_2]$ with $BeCl_2$, resulting in the formation of a dinuclear beryllium species on a different reaction pathway.

Results and Discussion

The reaction of $[Pd(PCy_3)_2]$ and $BeCl_2$ was conducted under similar conditions as applied to the synthesis of **1**. Thus, a toluene solution of the palladium complex was treated with a slight excess of $BeCl_2$ and heated to 80 °C. The reaction was monitored by ^{31}P NMR spectroscopy, revealing a new signal at 33.3 ppm, which is slightly highfield shifted with regard to that of the starting material (39.2 ppm). Completion of the conversion, though, required additional $BeCl_2$ – two equivalents in total – and extended heating to 80 °C, after which a grey solid precipitated from the yellow-green solution, which we assumed to be elemental palladium. ^9Be NMR spectroscopy of the new compound gave a broad signal at 12.7 ppm, which is comparable to three-coordinate beryllium compounds such as $ArBeCl(OEt_2)$ ($Ar = C_6H_3\text{-}2,6\text{-}Mes_2$) (12.8 ppm), and thus more deshielded than corresponding adducts comprising beryllium in coordination number four, *e. g.* $BeCl_2(OEt_2)_2$ and $Be\{[N(SiMe_3)]_2CPh\}_2$, which exhibit resonances at 2.6 and 5.5 ppm, respectively [20]. It should be noted though, that in case of the corresponding Pt-Be adduct **1** no ^9Be NMR signal could be detected due to unresolved coupling to platinum and phosphorus nuclei. The aforementioned spectroscopic data as well as the required twofold excess of $BeCl_2$ already indicate that $[Pd(PCy_3)_2]$ does not form a Lewis base adduct with $BeCl_2$ in analogy to its plat-

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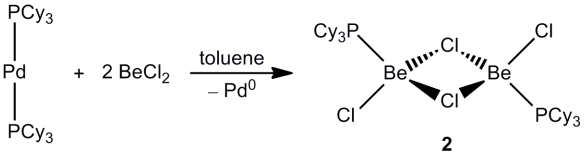

inum congener. Indeed, after work up, 62 % of a colorless, crystalline material was isolated. X-Ray analysis revealed the formation of the dinuclear phosphine adduct [$Be_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2$] (**2**).

In the crystal, **2** displays C_{2h} symmetry, and each beryllium center is surrounded by a phosphine group, two bridging and one terminal chloride substitutent, thus exhibiting a distorted tetrahedral geometry (Fig. 1).

The Be–P bond length in **2** (1.932(2) Å) is significantly shorter than in a related bisphosphine complex of beryllium [$BeCl_2(Ph_2PCH_2PPh_2)_2$] (2.206(3) Å), recently reported by Dehnicke *et al.* [21]. The P–Be–Cl1 plane in **2** is orientated almost perpendicular with respect to the central Be–Cl2–Be_a–Cl2_a plane (88.2°). As to be expected, the exocyclic Be–Cl1 distance of 1.932(2) Å is shorter than the endocyclic Be–Cl separations (Be–Cl2 2.088(2) Å). Comparison to the structurally related $(Ph_4P)_2[Be_2Cl_6]$ reveals many similarities [22]. Thus, the terminal (1.952(3) Å) and the bridging Be–Cl bonds (2.102(3) Å) in the latter species are only slighthly longer than those in **2**. Likewise, the central four-membered ring in **2** displays an angle of 97.13(9)° (Cl2–Be–Cl2_a), which resembles that in $[Be_2Cl_6]^{2-}$ (95.6(1)°). Somewhat surprising, a CCDC search provided no information as to other structurally characterized beryllium chloride species of the type *trans*-(L)ClBe-(μ-Cl)$_2$-BeCl(L) (L = neutral donor), wherein one donating ligand stabilizes a tetrahedral beryllium center. However, similar structural motifs are known from *d*-block metal species such as the corresponding dinuclear mercury compound [$Hg_2(Cl)_2(\mu\text{-}Cl)_2(PCy_3)_2$] [23] and the palladium complex [$Pd_2(Cl)_2(\mu\text{-}Cl)_2(PCy_3)_2$] [24]. However, the latter compound displays the expected square-planar geometry at the palladium centers.

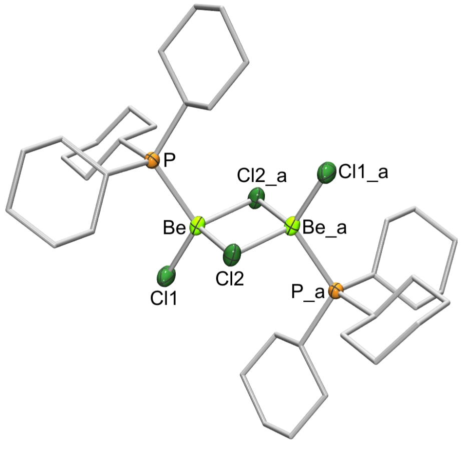

Fig. 1. Molecular structure of [$Be_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2$] (**2**). Displacement ellipsoids are at the 50 % probability level. Symmetry related positions ($-x+1$, $-y$, $-z+1$) are marked with _a. Selected bond lenghts (Å) and angles (deg): Be–Cl1 1.932(2), Be–P 2.216(2), Be–Cl2 2.088(2); P–Be–Cl1 114.47(10), P–Be–Cl2 110.54(10), Cl2–Be–Cl2_a 97.13(9).

In conclusion, we have shown that the reaction of [$Pd(PCy_3)_2$] with $BeCl_2$ takes a completely different course than that of the corresponding platinum phosphine species. In case of the former, $BeCl_2$ abstracts the phosphine ligands with formation of a dinuclear, structurally rare Be-P adduct, without any indication for the formation of a palladium-beryllium complex. Presumably, this finding can be ascribed to a decreased Lewis basicity of Pd in comparison to Pt.

Experimental Section

Safety note: in view of the toxicity of beryllium and its compounds, all necessary safety measures were undertaken. All reactions were carried out on a small scale, and for NMR spectroscopy we used exclusively J. Young NMR tubes. The glassware was cleaned separately, and all waste was collected in suitable containers.

General considerations: All manipulations were performed under an inert atmosphere of dry argon using either standard Schlenk-line or glovebox techniques. Toluene was distilled over sodium and stored over molecular sieves prior to use. C_6D_6 was dried over molecular sieves and degassed by three freeze-pump-thaw cycles before use. Anhydrous $BeCl_2$ was purchased from Aldrich, [$Pd(PCy_3)_2$] was prepared according to known methods [25]. The NMR spectra were recorded on a Bruker Avance 500 (^{1}H: 500.13 MHz; ^{13}C: 125.76 MHz; ^{31}P: 202.45 MHz; ^{9}Be: 70.28 MHz) FT-NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS *via* the signal of the residual protons of the solvent (^{1}H) or *via* the solvent itself (^{13}C). ^{31}P{^{1}H} NMR spectra were referenced to 85 % H_3PO_4, ^{9}Be NMR spectra to an aqueous solution of $BeCl_2$.

Di-μ-chloro-trans-dichloro-bis[tricyclohexylphosphine]-diberyllium (2)

A small excess of $BeCl_2$ (2.8 mg, 0.035 mmol) was added to a pale-yellow solution of [$Pd(PCy_3)_2$] (20 mg, 0.030 mmol) in toluene (0.4 mL). The reaction was heated for 18 h at 80 °C. A second portion of $BeCl_2$ (2.0 mg, 0.025 mmol) was added, and the reaction mixture was again heated for 18 h at 80 °C to complete the conversion. No ligand exchange was observed in solution. Palladium precipitated as a dark-grey solid from the yellow-green solution, and after filtration the latter was layered with hexane. After slow evaporation in a glovebox at r. t., **2** was obtained as colorless crystals (13 mg, 62 %). The crystals were redissolved in C_6D_6 for spectroscopic characterization. – ^{1}H NMR (500.13 MHz, C_6D_6): δ = 1.26 (br s, 18H, Cy), 1.75 – 1.61 (m, 30H, Cy), 2.11 – 2.05 (m, 18H, Cy). – ^{13}C NMR (125.76 MHz, C_6D_6): δ = 26.55 (s, C^4, Cy), 27.81 (virtual triplet, N [26] = 11 Hz, C^2, C^6, Cy), 31.45 (s, C^3, C^5, Cy), 34.14 (virtual triplet, N [27] = 18 Hz, C^1, Cy). – $^{31}P\{^1H\}$ NMR (202.46 MHz, C_6D_6): δ = 33.25. – ^{9}Be NMR (70.28 MHz, C_6D_6): δ = 12.72 (br s). – $C_{36}H_{66}Be_2Cl_4P_2$ (720.70): calcd. C 60.00, H 9.23; found C 59.19, H 8.58.

X-Ray structure determination

The crystal data of **2** were collected on a Bruker APEX diffractometer with CCD area detector and graphite-monochromatized MoK_α radiation. The structure was solved using Direct Methods, expanded using Fourier techniques and refined with the SHELX software package [28]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystal data for **2**: $C_{42}H_{72}Be_2Cl_4P_2$, M_r = 798.76, colorless block, 0.28 × 0.1 × 0.1 mm^3, monoclinic space group $P2_1/c$, a = 15.583(1), b = 8.2539(6), c = 18.4827(13) Å, β = 112.999(1)°, V = 2188.3(3) Å^3, Z = 2, ρ_{calcd} = 1.21 g cm^{-3}, μ = 0.4 mm^{-1}, $F(000)$ = 860 e, T = 168(2) K, $R1$ = 0.0441, $wR2$ = 0.0911 for 4281 independent reflections [$2\theta \leq$ 52.02°] and 226 refined parameters, $\Delta\rho$ (max / min) = 0.495 / −0.363 e Å^{-3}.

CCDC 795511 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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