

Synthesis and Structural Characterization of the Dinuclear Beryllium Species $[\text{Be}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$

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The synthesis and full characterization of $[\text{Be}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$, which results from the reaction of $[\text{Pd}(\text{PCy}_3)_2]$ and BeCl_2 with concomitant precipitation of elemental palladium, is reported.

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

Introduction

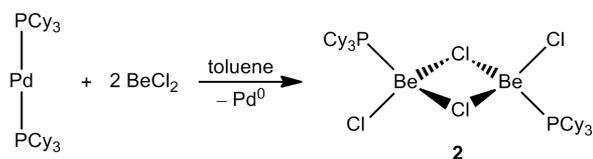
Due to the toxicity of beryllium compounds, the chemistry of beryllium is far less developed than that of its neighboring elements [1, 2]. As beryllium-containing materials feature unique properties, most of the corresponding research is done in material sciences [3]. With regard to its toxicity, additional 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, particularly 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 $[(\text{Cy}_3\text{P})_2\text{Pt}-\text{AlCl}_3]$ [13] and $[(\text{Cy}_3\text{P})_2\text{Pt}-\text{GaCl}_3]$ [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 $[\text{Pt}(\text{PCy}_3)_2]$ with BeCl_2 in benzene resulted in the platinum beryllium adduct $[(\text{Cy}_3\text{P})_2\text{Pt}-\text{BeCl}_2]$ (**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 $[\text{Pd}(\text{PCy}_3)_2]$ with

BeCl_2 , resulting in the formation of a dinuclear beryllium species on a different reaction pathway.

Results and Discussion

The reaction of $[\text{Pd}(\text{PCy}_3)_2]$ 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 $\text{ArBeCl}(\text{OEt}_2)$ ($\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-Me}_2$) (12.8 ppm), and thus more deshielded than corresponding adducts comprising beryllium in coordination number four, *e. g.* $\text{BeCl}_2(\text{OEt}_2)_2$ and $\text{Be}\{[\text{N}(\text{SiMe}_3)]_2\text{CPh}\}_2$, 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 $[\text{Pd}(\text{PCy}_3)_2]$ does not form a Lewis base adduct with BeCl_2 in analogy to its plat-



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 $[\text{Be}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ (**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 substituent, 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 $[\text{BeCl}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ (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 $(\text{Ph}_4\text{P})_2[\text{Be}_2\text{Cl}_6]$ 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 slightly 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

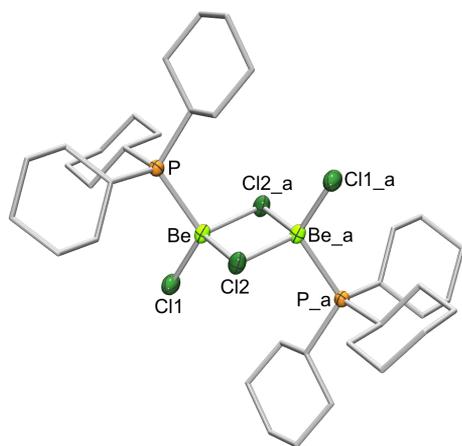


Fig. 1. Molecular structure of $[\text{Be}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ (**2**). Displacement ellipsoids are at the 50 % probability level. Symmetry related positions ($-x+1, -y, -z+1$) are marked with _a. Selected bond lengths (Å) and angles (deg): Be–Cl1 1.932(2), Be–P 2.216(2), Be–Cl2 2.088(2); P–Be–Cl1 114.47(10), P–Be–Cl2 110.54(10), Cl2–Be–Cl2_a 97.13(9).

that in $[\text{Be}_2\text{Cl}_6]^{2-}$ (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-($\mu\text{-Cl}$)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 $[\text{Hg}_2(\text{Cl})_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ [23] and the palladium complex $[\text{Pd}_2(\text{Cl})_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ [24]. However, the latter compound displays the expected square-planar geometry at the palladium centers.

In conclusion, we have shown that the reaction of $[\text{Pd}(\text{PCy}_3)_2]$ 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, $[\text{Pd}(\text{PCy}_3)_2]$ was prepared according to known methods [25]. The NMR spectra were recorded on a Bruker Avance 500 (^1H : 500.13 MHz; ^{13}C : 125.76 MHz; ^{31}P : 202.45 MHz; ^9Be : 70.28 MHz) FT-NMR spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to external TMS *via* the signal of the residual protons of the solvent (^1H) or *via* the solvent itself (^{13}C). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to 85 % H_3PO_4 , ^9Be 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 $[\text{Pd}(\text{PCy}_3)_2]$ (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 C₆D₆ for spectroscopic characterization. – ¹H NMR (500.13 MHz, C₆D₆): δ = 1.26 (br s, 18H, Cy), 1.75–1.61 (m, 30H, Cy), 2.11–2.05 (m, 18H, Cy). – ¹³C NMR (125.76 MHz, C₆D₆): δ = 26.55 (s, C⁴, Cy), 27.81 (virtual triplet, *N* [26] = 11 Hz, C², C⁶, Cy), 31.45 (s, C³, C⁵, Cy), 34.14 (virtual triplet, *N* [27] = 18 Hz, C¹, Cy). – ³¹P{¹H} NMR (202.46 MHz, C₆D₆): δ = 33.25. – ⁹Be NMR (70.28 MHz, C₆D₆): δ = 12.72 (br s). – C₃₆H₆₆Be₂Cl₄P₂ (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**: C₄₂H₇₂Be₂Cl₄P₂, *M_r* = 798.76, colorless block, 0.28 × 0.1 × 0.1 mm³, monoclinic space group *P*2₁/*c*, *a* = 15.583(1), *b* = 8.2539(6), *c* = 18.4827(13) Å, β = 112.999(1)°, *V* = 2188.3(3) Å³, *Z* = 2, ρ_{calcd} = 1.21 g cm⁻³, μ = 0.4 mm⁻¹, *F*(000) = 860 e, *T* = 168(2) K, *R*1 = 0.0441, *wR*2 = 0.0911 for 4281 independent reflections [2θ ≤ 52.02°] and 226 refined parameters, Δρ (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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