Beryllium Ligands

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Complexes with Dative Bonds between d- and s-Block Metals: Synthesis and Structure of [$(Cy_3P)_2Pt{-}Be(Cl)X$] (X = Cl, Me)**

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Dedicated to Professor Helmut Werner on the occasion of his 75th birthday

The chemistry of beryllium has developed in parallel with the awareness of the toxicity of beryllium compounds.[1] Therefore, investigations on beryllium are severely limited, in contrast to its neighboring elements. Recent research has focused on applications in material sciences, owing to the unique properties of beryllium-containing materials,[2] and on the coordination chemistry of Be^{II} in aqueous solutions with regard to its toxicity.[3] The coordination of ligands with neutral main-group donor substituents to Be, which mostly results in the formation of tetrahedral, four-coordinate species, is well-established.[4] Tricoordinate beryllium complexes were discovered as early as their tetracoordinate counterparts, but they are far less numerous.[5] In addition to these species with dative Be−E bonds (E = main-group element), beryllium-containing clusters have attracted further interest.[6] While some of these clusters contain transition metals, in particular Zr, electron-precise bonds between beryllium and transition metals are unknown to date.

Recently, we initiated studies on the behavior of Lewis basic, low-valent Pd and Pt complexes towards Group 13 element halides and their derivatives and consequently elucidated two different reactivity patterns. Boron–bromide and boron–iodide bonds display a propensity to add oxidatively to Pt^0 and Pd^0 centers, respectively, thus furnishing a wide range of boryl and heterodinuclear borylene complexes.[7] Conversely, metal-coordinated boryl and borylene ligands show a unique tendency to form adducts in which the transition metal acts as the Lewis base, with formation of a dative M−B bond (M = Pd, Pt).[8] Likewise, the heavier Group 13 analogues $AlCl_3$ and $GaCl_3$ were found to form similar platinum–base adducts,[9] thus inspiring us to extend this field to strongly Lewis acidic beryllium compounds such as $BeCl_2$. Herein, we report the synthesis and characterization of the first complex with an electron-precise beryllium–transition-metal bond.

Monitoring the reaction of [$Pt(PCy_3)_2$] (Cy = cyclohexyl) with a slight excess of $BeCl_2$ in benzene by $^{31}P\{^1H\}$ NMR spectroscopy revealed the formation of a new species, and conversion was complete after 18 h at 80 °C. The new resonance at $\delta = 53.6$ ppm ($^1J_{Pt,P} = 3240$ Hz) is shifted slightly upfield with respect to the starting material ($\delta = 62.3$ ppm, $^1J_{Pt,P} = 4160$ Hz). The upfield shift is not large enough to suggest formation of a square-planar Pt^{II} complex but fits more comfortably in the range of known Pt^0 adducts of Group 13 compounds.[9] Single crystals suitable for X-ray analysis confirmed the formation of the Pt^0–Be^{II} adduct [$(Cy_3P)_2Pt{-}BeCl_2$] (**1**, Figure 1).

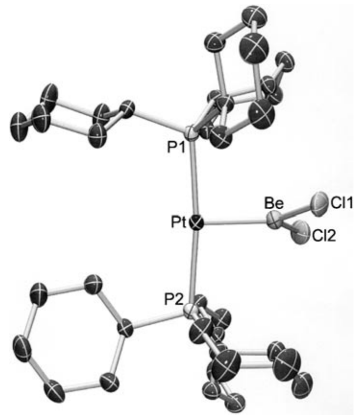

Figure 1. Molecular structure of **1** (thermal ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pt–Be 2.168(4), Be–Cl1 1.923(4), Be–Cl2 1.921(4); P1-Pt1-P2 172.63(2), Cl1-Be-Cl2 118.61(18).

Despite the close relation of **1** to platinum alane and gallane adducts, the P1-Pt-P2 unit in **1** is nearly linear. The P1-Pt-P2 angle (172.63(2)°) is significantly larger than in the former complexes (162.07(2) and 162.21(2)°, respectively). The Cl1-Be1-Cl2 angle (118.61(18)°) indicates almost trigonal-planar coordination of the Be atom, and the $BeCl_2$ fragment is rotated by 71.82° with respect to the P1-Pt-P2 moiety. The average Be−Cl bond length of 1.922 Å is similar to that observed in the Be−N adduct [$Cl_2Be(N(SiMe_3)PEt_3)$] (1.927 Å), a rare example of a three-coordinate beryllium–base adduct reported by Neumueller and Dehnicke in 2004.[10] The Pt−Be bond (2.168(4) Å) is the first example of a classical transition-metal–beryllium bond. Dative interactions from d-block metals to alkaline earth metals have a modicum of precedent: Bergman and co-workers published a complex in which two [$(\eta^5\text{-}C_5Me_5)Ir(PMe_3)H$] fragments are bridged by two MgPh groups. The transition-metal–magnesium bonds are of different lengths, thus suggesting dative-bond character, but no further details were given.[11]

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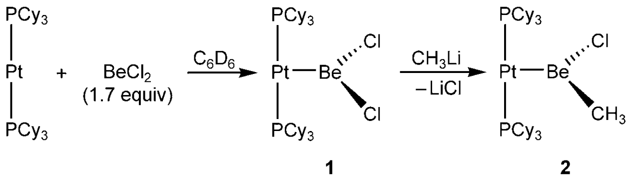
Formation of a $\mathrm{Pt^0 \rightarrow Be^{II}}$ adduct, although unprecedented, is consistent with theoretical work of Frenking and co-workers on beryllium chloro complexes with nitrogen donors in which $BeCl_2$ was determined to be strongly Lewis acidic.[12] To gain an estimation of the bond strength, we treated **1** with 4-methylpyridine, which led to abstraction of the $BeCl_2$ moiety as a 4-methylpyridine adduct and to liberated $[Pt(PCy_3)_2]$. The monopyridine adduct was confirmed by ^{9}Be NMR spectroscopy in which a single resonance was found at $\delta = 7.08$ ppm (in C_6D_6). When the reaction of $[Pt(PCy_3)_2]$ and $BeCl_2$ was performed in diethyl ether, no formation of **1** was observed by NMR spectroscopy, and treatment of preformed **1** with diethyl ether led to liberation of $[Pt(PCy_3)_2]$, as with 4-methylpyridine.

To gain further information about the new species, **1** was treated with a slight excess of methyllithium, which resulted in a new resonance at $\delta = 54.2$ ppm ($^1J_{\mathrm{Pt,P}} = 3460$ Hz) in the ^{31}P{^{1}H} NMR spectrum. In the ^{1}H NMR spectrum, a characteristic resonance was detected at $\delta = 0.14$ ppm, in accordance with a new broad singlet at $\delta = 0.6$ ppm in the ^{13}C{^{1}H} NMR spectrum. Filtration of the reaction mixture and layering of the filtrate with hexane yielded $[(Cy_3P)_2Pt{-}Be(Cl)CH_3]$ (**2**) as cubic crystals (Scheme 1, Figure 2).



Scheme 1. Formation of **1** and **2**.

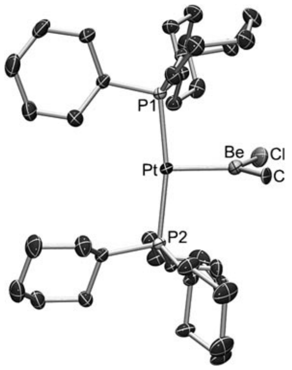


Figure 2. Molecular structure of **2** (thermal ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pt–Be 2.195(3), Be–Cl 1.933(3), Be–C 1.788(4); P1-Pt-P2 167.34(2), Cl-Be-C 123.70(17), Pt-Be-Cl 116.12(15), Pt-Be-C 120.18(18).

The facile substitution of chloride upon treatment with methyllithium has also been observed for the half-sandwich complex $[(\eta^5\text{-}C_5Me_5)BeCl]$.[13] Nevertheless, to our knowledge no complexes of the heteroleptic Cl-Be-CH_3 fragment with a donor ligand exist.

In comparison to **1** (2.168(4) Å), the Pt–Be bond in **2** is slightly elongated (2.195(3) Å), and the Cl-Be-C angle of **2** (123.70(17)°) is wider than the Cl1-Be-Cl2 angle of **1** (118.61(18)°). The assumption that a shorter Pt–Be bond and a smaller Cl-Be-Cl angle are indicative of a stronger platinum–beryllium interaction in **1** was supported by DFT calculations on model compounds $[(H_3P)_2Pt{-}Be(Cl)X]$ ($X = Cl$, Me).[14] The use of smaller phosphane ligands in computations leads to shortening of the Pt–Be bonds by approximately 0.1 Å and to wider (by 15°) Cl-Be-X angles for both molecules. The Pt–Be bond dissociation energies (D_0) are 77.6 and 47.8 kJ mol^{-1} for $X = Cl$ and Me, respectively, and thus corroborate stronger Pt–Be interactions for the more Lewis acidic $BeCl_2$.

In conclusion, the platinum–beryllium adducts $[(Cy_3P)_2Pt{-}Be(Cl)X]$ ($X = Cl$, Me) reported herein display unprecedented two-center two-electron transition-metal–beryllium bonds. The reactivity of the beryllium dichloride adduct was investigated, and X-ray structure analyses and theoretical calculations of both complexes allow a deeper insight into the Pt–Be bond strength.

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.

All manipulations were performed in an inert atmosphere of dry argon using standard Schlenk and glovebox techniques. 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, and $[Pt(PCy_3)_2]$ was prepared according to known methods.[15] 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. NMR spectra of reaction controls were recorded on a Bruker Avance 200 (^{1}H: 200.13 MHz; ^{31}P: 81.01 MHz) FT-NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS using the residual protio signal of the solvent (^{1}H) or the solvent itself (^{13}C). ^{31}P{^{1}H} NMR spectra were referenced to 85% H_3PO_4; ^{9}Be NMR spectra were referenced to an aqueous solution of $BeCl_2$. The ^{9}Be NMR resonances of **1** and **2** were significantly broadened owing to unresolved coupling to platinum and phosphorus nuclei such that no definitive signal was observed.[7c] Microanalyses were performed on an Elementar vario MICRO cube elemental analyzer.

1: $BeCl_2$ (5.4 mg, 0.068 mmol) was added to a pale yellow solution of $[Pt(PCy_3)_2]$ (0.030 g, 0.040 mmol) in C_6D_6 (0.5 mL). The reaction was heated for 18 h at 80 °C. The light yellow solution was layered with hexane and allowed to evaporate slowly in a glovebox at room temperature to yield **1** as colorless crystals (0.029 g, 87%). ^{1}H NMR (500.1 MHz, C_6D_6): $\delta = 2.31$–2.26 (m, 6H, Cy), 2.12–2.09 (m, 12H, Cy), 1.76–1.60 (m, 30H, Cy), 1.27–1.21 ppm (m, 18H, Cy); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): $\delta = 35.3$ (virtual triplet, $N^{[16]} = 21$ Hz, C^1, Cy), 31.1 (s, C^{3,5}, Cy), 27.7 (virtual triplet, $N^{[17]} = 9$ Hz, C^{2,6}, Cy), 26.5 ppm (s, C^4, Cy); ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6): $\delta = 53.6$ ppm ($^1J_{\mathrm{Pt,P}} = 3240$ Hz); elemental analysis (%) calcd for $C_{36}H_{66}BeCl_2P_2Pt$: C 51.73, H 7.96; found: C 52.44, H 7.92.

2: Compound **1** was used without prior isolation and treated with 2.4 equivalents methyllithium (2.1 mg, 0.096 mmol) in a sealable NMR tube. The reaction mixture became lighter in color, and a fine white solid precipitated immediately. The NMR tube was placed in an ultrasonic bath for 1 min and heated for 18 h at 80 °C to complete the reaction. The dark precipitate was filtered off and discarded, and the resulting orange solution was layered with hexane and allowed to evaporate slowly in a glovebox at room temperature to yield **2** as colorless cubic crystals (0.020 g, 71 %). ^{1}H NMR (500.1 MHz, C_6D_6): $\delta = 2.22$–2.17 (m, 6H, Cy), 2.14–2.12 (m, 12H, Cy), 1.78–1.62 (m, 30H, Cy), 1.26 ppm (m, 18H, Cy), 0.14 ppm (s, 3H, Be-CH_3); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): $\delta = 35.5$ (virtual triplet, $N^{[16]} = 27$ Hz, C^1, Cy), 31.2 (s, $C^{3,5}$, Cy), 27.8 (virtual triplet, $N^{[17]} = 11$ Hz, $C^{2,6}$, Cy), 26.7 ppm (s, C^4, Cy), 0.6 (br s, CH_3); ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6): $\delta = 54.2$ ppm ($^1J_{\mathrm{Pt,P}} = 3460$ Hz); elemental analysis (%) calcd for $C_{37}H_{69}BeClP_2Pt$: C 54.50, H 8.53; found: C 54.93, H 8.45.

The crystal data of **1** and **2** were collected on a Bruker D8 diffractometer with an Apex CCD area detector and graphite-monochromated $Mo_{K\alpha}$ radiation. The structures were solved using direct methods, refined with the Shelx software package (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations.

Crystal data for **1**: $C_{42}H_{72}BeCl_2P_2Pt$, $M_r = 913.94$, colorless block, $0.23 \times 0.14 \times 0.11$ mm^3, monoclinic space group $P2_1/c$, $a = 14.8648(18)$ Å, $b = 16.0483(19)$ Å, $c = 18.741(2)$ Å, $\beta = 104.196(2)°$, $V = 4334.2(9)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.401$ g cm^{-3}, $\mu = 3.462$ mm^{-1}, $F(000) = 1880$, $T = 168(2)$ K, $R_1 = 0.0262$, $wR^2 = 0.0564$, 8619 independent reflections [$2\theta \leq 52.22°$] and 433 parameters.

Crystal data for **2**: $C_{37}H_{69}BeClP_2Pt$, $M_r = 815.41$, colorless block, $0.48 \times 0.28 \times 0.26$ mm^3, monoclinic space group $P2_1/n$, $a = 12.1749(13)$ Å, $b = 17.1299(18)$ Å, $c = 19.111(2)$ Å, $\beta = 107.3470(10)°$, $V = 3804.4(7)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.424$ g cm^{-3}, $\mu = 3.866$ mm^{-1}, $F(000) = 1680$, $T = 169(2)$ K, $R_1 = 0.0218$, $wR^2 = 0.0508$, 9552 independent reflections [$2\theta \leq 56.9°$] and 380 parameters.

CCDC 717995 (**1**) and 717996 (**2**) contain 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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