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Synthesis and Characterization of Heteroleptic 1-Tris(pyrazolyl)borate Beryllium Complexes

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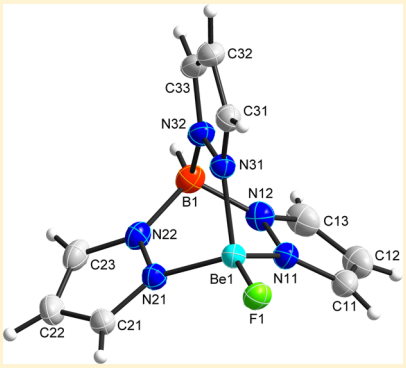
Supporting Information

ABSTRACT: The synthesis and crystal structures of 1-tris(pyrazolyl)borate beryllium halides TpBeX (X = Cl **1**, Br **2**, I **3**, F **4**), the pyrazole adduct of TpBeF (**5**) and of 1-tris(pyrazolyl)borate beryllium hydride, deuteride and azide TpBeX (X = H **6**, ^{2}H (D) **7**, N_3 **8**; Tp = 1-trispyrazolylborate) is described. In addition, ^{9}Be-NMR spectroscopy is introduced as suitable analytical tool for the in situ characterization of heteroleptic organoberyllium halides, pseudohalides and hydrides. Studies in different solvents and solvent mixtures allowed the formulation of a reference guide for the chemical shift of heteroleptic coordination complexes of beryllium only based on variation of the second substituent.



INTRODUCTION

The studies on the coordination chemistry of beryllium are very limited in comparison to almost all other elements in the periodic table. This lack of interest most likely stems from the toxicity of beryllium and its compounds.[1] Almost all publications of the last 20 years concerning organometallic beryllium compounds focused on ligands bonded to alkaline-earth metals, which include the beryllium compound to complete the set.[2−4] However, the interest in beryllium chemistry increased in recent years and an increasing number of reports has been published over the last years, including the synthesis of NHC-stabilized beryllium dihalides and diorganyls[5,6] as well as the Lewis acid−base adducts $[(Cy_3P)_2Pt–Be(Cl)X]$ (X = Cl, Me).[7] The fascinating insertion reaction of NHC-stabilized beryllium hydride (*i*-PrNHC-Be(Me)H) into the NHC after activation this adduct with $PhSiH_3$,[8] which has also been investigated using theoretical calculations,[9,10] can be probably regarded as the overdue awakening kiss of the sleeping beauty of beryllium chemistry. In addition, the synthesis and reactivity of beryllium diorganyls[11] and other complexes[12] as well as the synthesis and reactivity of *β*-diketiminate-substituted beryllium complexes[13,14] including reactions of alcohols, amines and ethers with MesNacnac-BeMe[13,14] have been reported. Moreover, the search for Be(I) complexes[15] and the successful use of BeF_2 as a fluoride acceptor in liquid ammonia is expected to further push the beryllium chemistry in the near future.[16,17]

Since beryllium complexes are very toxic, there is a great interest in the development of suitable analytical tools which allow an in situ characterization of such complexes as well as a monitoring of the reaction process in order to identify possible reaction mechanism. Even though NMR spectroscopy is a well-known method for the in situ characterization of organometallic complexes, systematic ^{9}Be NMR studies with beryllium complexes are limited, even though the quadrupolar ^{9}Be-nucleus with a natural occurrence of 100% and a spin of 3/2 is very sensitive and samples can be quickly and easily measured. In case of small or symmetric complexes the signals are very sharp with line widths of only several Hertz, but in case of larger complexes with low symmetry the signals can broaden to several hundred Hertz. Nevertheless, the ^{9}Be chemical shift is highly dependent on the coordination mode of beryllium and can be used to identify the structure of complexes.[18−22]

We decided to start our ^{9}Be-NMR studies on coordination complexes of beryllium with the well-known 1-tris(pyrazolyl)-borate (Tp) ligand, as synthesis protocols of some of these compounds were published by Parkin et al. in 1992.[23] This publication demonstrated that the beryllium atom typically adopts a tetrahedral coordination sphere in heteroleptic Tp-beryllium complexes, which is the most favored coordination mode of beryllium. As a result, the beryllium metal center adopts a steady chemical environment and the ^{9}Be chemical shift of the complexes is rather influenced by the substituent then by possible flexible coordination modes of the ligand.[3,12,23,24] We also decided to use a nonsubstituted version of the ligand to reduce steric interactions between the ligand and the substituent.

Herein we report on the synthesis of TpBeCl (**1**), TpBeBr (**2**), and TpBeI (**3**) as well as TpBeF (**4**), TpBe(F)pyr (**5**), TpBeH (**6**), TpBeD (**7**), and $TpBeN_3$ (**8**) and the solid state structures of **1**−**5** as determined by single-crystal X-ray diffraction.

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EXPERIMENTAL SECTION

General Procedures. Beryllium compounds are potentially toxic and should be handled with appropriate safety precautions. All manipulations were performed in a Glovebox (MBraun) under an Ar atmosphere or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. BeX_2 (X = F, Cl, Br, I) were prepared according to literature method.[25] K-Pyrazolylborate (TpK) was obtained from Acros and used as received. NMR spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C at 300.1 MHz (^{1}H), 42.2 MHz (^{9}Be), 96.3 MHz (^{11}B), and 75.5 MHz (^{13}C), respectively, and referenced to internal C_6D_5H (^{1}H: δ = 7.154; ^{13}C: δ = 128.0) and internal THF-d_8 (^{1}H: δ = 3.580, 1.730; ^{13}C: δ = 25.2, 67.4), external $BF_3{\cdot}Et_2O$ in $CDCl_3$ ($\delta(^{11}B\{^1H\})$ = 0) and external $BeSO_4$ in D_2O ($\delta(^9Be)$ = 0). IR spectra were recorded on a Bruker ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were not determined due to the potential toxicity of the complexes.

General synthesis of TpBeX (X = Cl 1, Br 2, I 3). Suspensions of 500 mg (2 mmol) of TpK with either 160 mg of $BeCl_2$ or 338 mg of $BeBr_2$ or 526 mg of BeI_2 (2 mmol) were suspended in 50 mL of toluene. The suspensions were stirred at 110 °C for 16 h and filtered after cooling to ambient temperature. The resulting clear, colorless solutions were concentrated to 5 mL and the products crystallized upon storing the solutions at −28 °C for 12 h.

TpBeCl **1**. Yield 86% (443 mg). Mp: 188 °C. IR (ATR, 25 °C, 32 scans): ν = 2963 (w), 1507 (m), 1409 (m), 1318 (m), 1260 (m), 1194 (m), 1041 (s), 772 (s), 715 (s), 672 (s), 612 (s), 550 (s) cm^{-1}. ^{1}H NMR (300.1 MHz, 25 °C, C_6D_6): δ = 4.41 (q, 1H, $^1J_{BH}$ = 365.67 Hz, *H*B(N(CHCHCH)N)$_3$BeCl) 5.56 (t, 3H, $^3J_{HH}$ = 6.45 Hz, HB(N-(CHCHC*H*)N)$_3$BeCl), 7.10 (d, 3H, $^3J_{HH}$ = 6.30 Hz, HB(N-(CHC*H*CH)N)$_3$BeCl), 7.71 (d, 3H, $^3J_{HH}$ = 6.93 Hz, HB(N-(C*H*CHCH)N)$_3$BeCl). ^{13}C{^{1}H}-NMR (75.5 MHz, 25 °C, C_6D_6): δ = 105.34 (HB(N(CHCHCH)N)$_3$BeCl), 134.26 (HB(N(CHCHCH)-N)$_3$BeCl), 138.65 (HB(N(CHCHCH)N)$_3$BeCl). ^{11}B{^{1}H}-NMR (21.7 MHz, 25 °C, THF-d$_8$): δ = −4.62. ^{9}Be-NMR (42.2 MHz, 25 °C, THF-d_8): δ = 4.95.

TpBeBr **2**. Yield 82% (495 mg). Mp: 214 °C. IR (ATR, 25 °C, 32 scans): ν = 3110 (w), 2532 (w), 1507 (m), 1409 (s), 1318 (s), 1194 (s), 1109 (w), 1095 (w), 1068 (m), 1043 (s), 985 (s), 909 (w), 825 (w), 802 (m), 780 (s), 745 (s), 716 (s), 671 (s), 615 (m), 556 (m) cm^{-1}. ^{1}H NMR (300.1 MHz, 25 °C, THF-d_8/C_6D_6 2/6): δ = 4.41 (q, 1H, $^1J_{BH}$ = 354.45 Hz, *H*B(N(CHCHCH)N)$_3$BeBr), 5.71 (t, 3H, $^3J_{HH}$ = 6.63 Hz, HB(N(CHCHC*H*)N)$_3$BeBr), 7.26 (d, 3H, $^3J_{HH}$ = 6.60 Hz, HB(N(CHC*H*CH)N)$_3$BeBr), 7.73 (d, 3H, $^3J_{HH}$ = 6.63 Hz, HB(N-(C*H*CHCH)N)$_3$BeBr). ^{13}C{^{1}H}-NMR (75.5 MHz, 25 °C, THF-d_8/C_6D_6 2/6): δ = 106.07 (HB(N(CHCHCH)N)$_3$BeBr), 135.89 (HB(N(CHCHCH)N)$_3$BeBr), 139.48 (HB(N(CHCHCH)N)$_3$BeBr). ^{9}B{^{1}H}-NMR (21.7 MHz, 25 °C, THF-d$_8$): δ = −4.59. ^{9}Be-NMR (42.2 MHz, 25 °C, THF-d_8/C_6D_6 2/6): δ = 5.15.

TpBeI **3**. Yield 70% (489 mg). Mp: 244 °C. IR (ATR, 25 °C, 32 scans): ν = 2525 (m), 1506 (m), 1408 (s), 1317 (s), 1191 (s), 1110 (w), 1097 (w), 1065 (m), 1043 (s), 988 (s), 800 (m), 783 (m), 763 (s), 709 (s), 660 (s), 617 (s), 554 (s) cm^{-1}. ^{1}H NMR (300.1 MHz, 25 °C, THF-d_8): δ = 6.16 (t, 3H, $^3J_{HH}$ = 6.21 Hz, HB(N(CHCHC*H*)-N)$_3$BeI), 7.88 (d, 3H, $^3J_{HH}$ = 6.03 Hz, HB(N(CHC*H*CH)N)$_3$BeI), 8.03 (s (broad), 3H, HB(N(C*H*CHCH)N)$_3$BeI). ^{13}C{^{1}H}-NMR (75.5 MHz, 25 °C, THF-d_8): δ = 106.04 (HB(N(CHCHCH)N)$_3$BeI), 136.04 (HB(N(CHCHCH)N)$_3$BeI), 141.36 (HB(N(CHCHCH)-N)$_3$BeI). ^{9}B{^{1}H}-NMR (21.7 MHz, 25 °C, THF-d$_8$): δ = −3.50. ^{9}Be-NMR (42.2 MHz, 25 °C, THF-d_8): δ = 4.66.

Synthesis of TpBeF 4. A solution of 215 mg (0.88 mmol) difluoro-4-fluoro-iodosobenzene[26−28] and 500 mg (1.66 mmol) **2** in 20 mL of toluene were stirred at ambient temperature for 2 h. Thereafter, all volatiles were removed in vacuum, yielding **4** as colorless solid in almost quantitative yield. Recrystallization from a mixture of thf and toluene yielded colorless crystals of **4**.

Yield 95% (380 mg). Mp: >244 °C decomposition. IR (ATR, 25 °C, 32 scans): ν = 3100 (w), 2748 (w), 1517 (w), 1485 (w), 1409 (m), 1317 (w), 1238 (w), 1204 (w), 1119 (m), 1080 (s), 967 (w), 767 (s), 609 (s), 503 (w), 403 (w) cm^{-1}. ^{1}H NMR (300.1 MHz, 25 °C, THF-d_8/C_7D_8 3/5): δ = 6.07 (m, 3H, HB(N(CHCHC*H*)N)$_3$BeF), 7.42 (m (broad), 6H, HB(N(C*H*CH*C*H)N)$_3$BeF. ^{13}C{^{1}H}: Due to the poor solubility of **4** in common solvents, no ^{13}C NMR spectra with satisfying quality could be obtained. ^{9}Be-NMR (42.2 MHz, 25 °C, THF-d_8/C_7D_8 3/5): δ = 4.54. ^{19}F-NMR (282.4 MHz, 25 °C, THF-d_8/C_7D_8): δ = −149.1.

Synthesis of TpBe(F)pyr 5. A solution of **4** was heated in toluene at 100 °C for 1 h, resulting in decomposition and formation of a brownish solution. Crystals of **5** suitable for a single-crystal X-ray diffraction study were formed upon storage of the solution at 4 °C for 12h.

Yield <5%. ^{1}H NMR (300.1 MHz, 25 °C, THF-d_8/C_7D_8 3/5): δ = 6.06 (m, 4H, HB(N(CHCHC*H*)N)$_3$(NHCHCHC*H*N)BeF), 7.43 (m (broad), 8H, HB(N(C*H*CH*C*H)N)$_3$(NHC*H*CH*C*HN)BeF), 13.99 (1 H, s, HB(N(CHCHCH)N)$_3$(N*H*CHCHCHN)BeF).

Synthesis of TpBeH and TpBeD. Solutions of 500 mg (1.94 mmol) of TpBeCl **1** with either 74 mg (1.94 mmol) of $LiAlH_4$ or 81 mg (1.29 mmol) of $LiAlD_4$ in 50 mL of diethylether were stirred for three days at ambient temperature, followed by filtration and evaporation of all volatiles at ambient temperature. **6** and **7** were obtained as white powders in high yields.

TpBeH **6**. Yield 95% (411 mg). Mp: 195 °C. IR (ATR, 25 °C, 32 scans): ν = 3110 (w), 2532 (w), 1507 (m), 1409 (s), 1318 (s), 1194 (s), 1109 (m), 1095 (w), 1086 (m), 1043 (s), 985 (s), 909 (w), 825 (w), 802 (m), 780 (s), 745 (s), 716 (s), 671 (s), 615 (m), 566 (s) cm^{-1}. ^{1}H NMR (300.1 MHz, 25 °C, THF-d_8/C_6D_6 2/6): δ = 0.19 (s, 1H, HB(N(CHCHCH)N)$_3$Be*H*), 4.40 (q, 1H, $^1J_{BH}$ = 350.91 Hz, *H*B(N(CHCHCH)N)$_3$BeH) 5.75 (t, 3H, $^3J_{HH}$ = 6.51 Hz, HB(N-(CHCHC*H*)N)$_3$BeH), 7.31 (d, 3H, $^3J_{HH}$ = 6.66 Hz, HB(N-(CHC*H*CH)N)$_3$BeH), 7.70 (d, 3H, $^3J_{HH}$ = 5.85 Hz, HB(N-(C*H*CHCH)N)$_3$BeH). ^{13}C{^{1}H}-NMR (75.5 MHz, 25 °C, THF-d_8/C_6D_6 2/6): δ = 105.69 (HB(N(CHCHCH)N)$_3$BeH), 134.87 (HB(N(CHCHCH)N)$_3$BeH), 138.90 (HB(N(CHCHCH)N)$_3$BeH). ^{9}B{^{1}H}-NMR (21.7 MHz, 25 °C, THF-d$_8$): δ = −4.68. ^{9}Be-NMR (42.2 MHz, 25 °C, THF-d_8/C_6D_6 2/6): δ = 5.11.

TpBeD **7**. Yield 98% (426 mg). Mp: 192 °C. IR (ATR, 25 °C, 32 scans): ν = 3112 (w), 2516 (w), 1509 (m), 1431 (w), 1411 (s), 1397 (m), 1316 (s), 1194 (s), 1136 (w), 1113 (w), 1072 (s), 1047 (s), 989 (m), 899 (w), 764 (s), 717 (s), 681 (s), 618 (m), 556 (s), 502 (s) cm^{-1}. ^{1}H NMR (300.1 MHz, 25 °C, THF-d_8): δ = 0.19 (s, 1H, HB(N(CHCHCH)N)$_3$Be*H*), 4.62 (q, 1H, $^1J_{BH}$ = 339.06 Hz, *H*B(N(CHCHCH)N)$_3$BeH), 6.23 (t, 3H, $^3J_{HH}$ = 6.90 Hz, HB(N-(CHCHC*H*)N)$_3$BeH), 7.81 (d, 3H, $^3J_{HH}$ = 6.03 Hz, HB(N-(CHC*H*CH)N)$_3$BeH), 7.84 (d, 3H, $^3J_{HH}$ = 6.90 Hz, HB(N-(C*H*CHCH)N)$_3$BeH). ^{2}H NMR (46.1 MHz, 25 °C, THF): δ = 2.65 (s, 1D, HB(N(CHCHCH)N)$_3$Be*D*). ^{13}C{^{1}H}-NMR (75.5 MHz, 25 °C, THF-d_8/C_6D_6 2/6): δ = 105.02 (HB(N(CHCHCH)N)$_3$BeD), 133.68 (HB(N(CHCHCH)N)$_3$BeD). ^{11}B{^{1}H}-NMR (21.7 MHz, 25 °C, THF-d$_8$): δ = −5.36. ^{9}Be-NMR (42.2 MHz, 25 °C, THF-d$_8$): δ = 4.36.

Synthesis of TpBeN$_3$ 8. A solution of 500 mg (1.94 mmol) TpBeCl **2** in 10 mL of neat trimethylsilylazide was stirred at elevated temperatures (75 °C) for 16 h. All volatiles of the resulting colorless solution were evacuated in vacuum, yielding TpBeN$_3$ **8** as colorless solid, which was recrystallized from a 1:1 mixture of thf and toluene.

Yield 65% (333 mg). Mp: >210 °C decomposition. IR (ATR, 25 °C, 32 scans): ν = 3047 (w) 2525 (w), 2111 (w), 2006 (w), 1589 (w), 1506 (w), 1481 (w), 1434 (w), 1408 (m), 1316 (w), 1260 (m), 1190 (m), 1065 (m), 1041 (m), 799 (m), 781 (m), 762 (m), 712 (s), 667 (m), 615 (m), 550 (m), 491 (m) cm^{-1}. ^{1}H NMR (300.1 MHz, 25 °C, C_6D_6): δ = 4.33 (quar, 1H, $^1J_{BH}$ = 337.08 Hz, *H*B(N(CHCHCH)-N)$_3$BeN$_3$), 5.52 (t, 3H, $^3J_{HH}$ = 6.75 Hz, HB(N(CHCHC*H*)N)$_3$BeN$_3$), 6.72 (d, 3H, $^3J_{HH}$ = 7.02 Hz, HB(N(CHC*H*CH)N)$_3$BeN$_3$), 7.75 (d, 3H, $^3J_{HH}$ = 6.33 Hz, HB(N(C*H*CHCH)N)$_3$BeN$_3$). ^{13}C{^{1}H}-NMR (75.5 MHz, 25 °C, C_6D_6): δ = 105.77 (HB(N(CHCHCH)N)$_3$BeN$_3$), 134.86 (HB(N(CHCHCH)N)$_3$BeN$_3$), 140.31 (HB(N(CHCHCH)-

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$N)_3BeN_3$). $^9B\{^1H\}$-NMR (21.7 MHz, 25 °C, C_6D_6): δ = −4.70. ^9Be-NMR (42.2 MHz, 25 °C, C_6D_6): δ = 4.53.

Crystal Structure Determination of 1 - 5. Figures 1−3, 6, and 7 show the diagrams of the solid-state structures of **1**−**5** and Figures 4, 5,

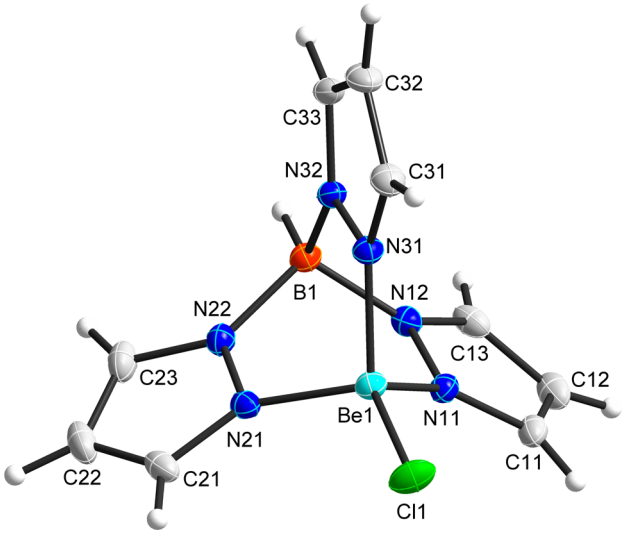

Figure 1. Representation of TpBeCl **1**. Thermal ellipsoids are shown at 50% probability levels except for H atoms.

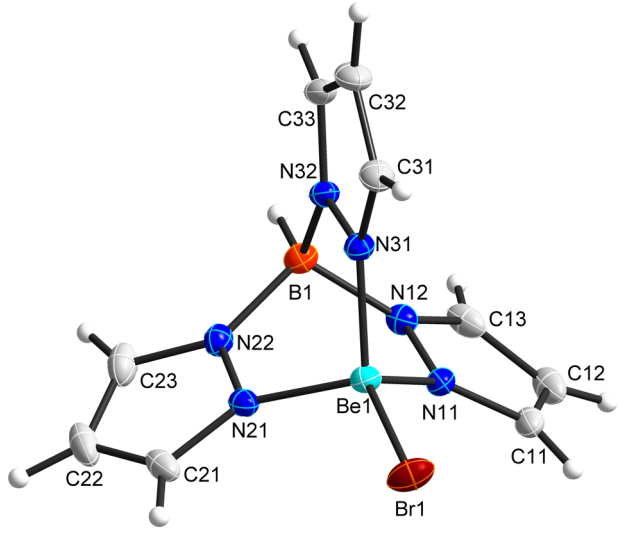

Figure 2. Representation of TpBeBr **2**. Thermal ellipsoids are shown at 50% probability levels except for H atoms.

and 8 show intermolecular interactions as observed in the solid-state structures. Table 1 summarizes the crystallographic data and Table 2 shows selected bond lengths and angles. Tables 3−5 summarize secondary interactions in compounds **1**−**5**. The crystals were mounted on nylon loops in inert oil. Data were collected on a AXS D8 Kappa diffractometer with APEX2 detector (MoK_α radiation, λ = 0.71073 Å; T = 100(1) K **1**, **2**, 180(1) K **3**, **4**). The structures were solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares on F^2.[29] Absorption correction were performed semiempirically from equivalent reflections on basis of multiscans (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms as rigid groups and others by a riding model (SHELXL-97/SHELXL-2013).[30] The crystallographic data (without structure factors) were deposited as supplementary publication no. CCDC-962078 (**1**), CCDC-962079 (**2**), CCDC-962081 (**3**), and CCDC-962080 (**4**) at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge

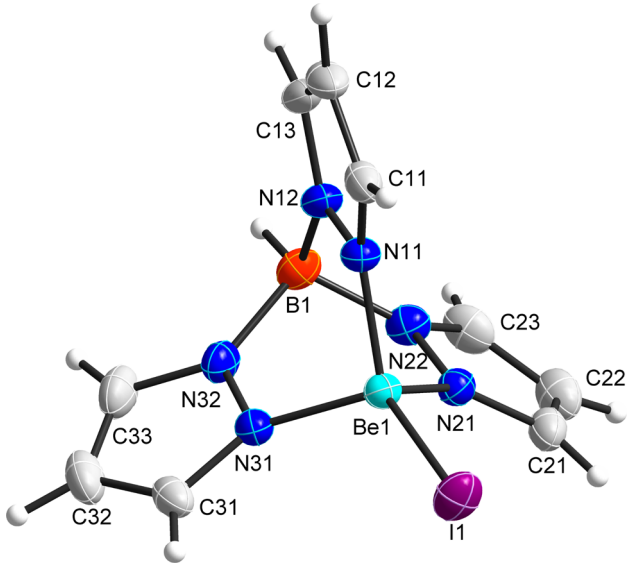

Figure 3. Representation of TpBeI **3**. Thermal ellipsoids are shown at 50% probability levels except for H atoms.

Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam-ak.uk).

RESULTS AND DISCUSSION

TpBeCl **1**, TpBeBr **2**, and TpBeI **3** were obtained in very high yields from the salt-elimination reaction of TpK with the corresponding beryllium halide ($BeCl_2$, $BeBr_2$, and BeI_2) (see Scheme 1). TpBeF **4** was prepared by reaction of TpBeBr **2** with various fluoride transfer reagents such as AgF, XeF_2 and 4−F-$C_6H_4IF_2$, whereas TpBeH **6**, TpBeD **7** and $TpBeN_3$ **8** were synthesized by reaction of TpBeX (X = Cl, Br, I) with suitable hydride, deuteride and azide transfer reagents, e.g., $LiAlH_4$, $LiAlD_4$, and Me_3SiN_3 (see Scheme 1).

The reaction of TpK with $BeCl_2$, $BeBr_2$, and BeI_2 was performed in toluene at 110 °C under vigorous stirring for 16 h. Even though the starting materials are only sparingly soluble in toluene, high yields were obtained. Moreover, all starting materials could be easily separated from the products by filtration. In contrast, THF cannot be used due to the formation of very stable BeX_2-thf complexes, which could not be completely separated from the products TpBeX (X = Cl, Br, I) because of their comparable solubility. The product yields ranged from 68−72% for TpBeI and up to 82 − 86% for TpBeCl and TpBeBr. NMR spectroscopy studies clearly showed that the ^1H and ^{13}C NMR chemical shift of the pyrazolyl rings is not much affected by the (electronically different) nature of the halide substituents. The influence of the second ligand generally seems to be less significant on these nuclei.

Colorless cubical-shaped crystals of **1**−**3** were obtained upon storage of concentrated solutions of **1**−**3** in toluene at −28 °C for 12 h. TpBeCl **1** and TpBeBr **2** crystallize isomorphically in the space group $P2_1/n$, whereas TpBeI **3** crystallizes in the orthorhombic space group *Pbca*. The Be-cation adopts a distorted tetrahedral coordination sphere. The bonding parameters of the 1-tris(pyrazolyl)borate anion do not show any unexpected values and are comparable to those previously observed for this specific ligand.[31] The average N−Be−N bond angles (100.18(20)° **1**, 100.73(29)° **2**, 101.16(65)° **3**) are smaller compared to the average N−Be-X bond angles

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Table 1. Crystallographic Details of 1−5

	TpBeCl **1**	TpBeBr **2**	TpBeI **3**	TpBeF **4**	TpBe(F)pyr **5**
empirical formula	$C_9H_{10}BBeClN_6$	$C_9H_{10}BBeBrN_6$	$C_9H_{10}BBeIN_6$	$2(C_9H_{10}BBeFN_6)*C_7H_8$	$C_{12}H_{14}BBeFN_8$
M	257.50	301.96	348.95	574.23	309.13
cryst size (mm^3)	0.270 × 0.230 × 0.080	0.35 × 0.3 × 0.3	0.380 × 0.350 × 0.280	0.250 × 0.220 × 0.170	0.250 × 0.220 × 0.150
T (K)	100(1)	100(1)	180(1)	180(1)	180(1)
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$Pbca$	$P2_1/c$	$P2_1/n$
a (Å)	7.6712(5)	7.7158(2)	12.7981(11)	7.9099(3)	7.7207(8)
b (Å)	12.6310(9)	12.6696(3)	14.2608(13)	12.7438(6)	15.7986(17)
c (Å)	12.9757(8)	13.1953(3)	14.5214(13)	14.6259(7)	12.7865(13)
α (deg)	90	90	90	90	90
β (deg)	99.740(4)	100.1890(10)	90	104.383(2)	101.130(6)
γ (deg)	90	90	90	90	90
V [Å^3]	1239.16(14)	1269.58(5)	2650.3(4)	1428.11(11)	1530.3(3)
Z	4	4	8	2	4
D_{calcd} (g cm^{-1})	1.380	1.580	1.749	1.335	1.342
μ(MoK_α (mm^{-1}))	0.296	3.226	2.405	0.093	0.096
transmissions	0.75/0.67	0.75/0.62	0.75/0.51	0.75/0.66	0.75/0.65
F(000)	528	600	1344	596	640
index ranges	$-10 \le h \le 10$	$-11 \le h \le 11$	$-19 \le h \le 17$	$-10 \le h \le 9$	$-10 \le h \le 10$
	$-17 \le k \le 16$	$-19 \le k \le 19$	$-21 \le k \le 21$	$-16 \le k \le 16$	$-20 \le k \le 20$
	$-18 \le l \le 18$	$-20 \le l \le 20$	$-21 \le l \le 20$	$-18 \le l \le 19$	$-16 \le l \le 16$
θ_{max} (deg)	30.533	33.14	32.721	27.972	27.651
no. of reflns collected	18765	22811	48086	22326	23592
no. of independent reflns	3743	4720	4822	3425	3508
R_{int}	0.0220	0.0199	0.0320	0.0261	0.0458
refined param	163	163	163	214	212
R_1 [$I > 2\sigma(I)$]^a	0.0313	0.0244	0.0239	0.0368	0.0454
wR_2 [all data]^b	0.0854	0.0656	0.0630	0.1035	0.1282
GOF^c	1.067	1.045	1.060	1.059	1.021
$\Delta\rho_{final}$ (max/min) (e Å^{-3})	0.399/−0.202	0.635/−0.605	0.711/−1.311	0.237/−0.177	0.294/−0.209

$^a R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ (for iI > $2\sigma(I)$). $^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. ^{c}Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{obsv} - N_{params})\}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ with $P = [F_o^2 + 2F_c^2]/3$, a and b are constants chosen by the program.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 1-Tris(pyrazolyl)borate Halides 1−5

	TpBeCl **1**	TpBeBr **2**	TpBeI **3**	TpBeF **4**	TpBe(F)pyr **5**
Be1-X1 (X = halide)	1.9310(12)	2.0922(14)	2.3303(18)	1.4533(15)	1.479(2)
Be1−N11	1.7336(15)	1.7248(17)	1.715(2)	1.7584(17)	
Be1−N21	1.7312(14)	1.7195(17)	1.716(2)	1.7495(17)	1.735(3)
Be1−N31	1.7279(15)	1.7245(16)	1.724(2)	1.7574(17)	1.726(3)
Be1−N41					1.736(2)
B1−N12	1.5511(13)	1.5479(15)	1.545(2)	1.5519(17)	1.545(2)
B1−N22	1.5491(13)	1.5488(16)	1.545(2)	1.5467(17)	1.537(2)
B1−N32	1.5495(14)	1.5519(15)	1.550(2)	1.5479(17)	1.552(2)
N11−N12	1.3651(11)	1.3612(13)	1.3648(18)	1.3639(14)	1.3645(19)
N21−N22	1.3633(11)	1.3615(14)	1.3655(17)	1.3665(13)	1.3683(18)
N31−N32	1.3622(12)	1.3650(13)	1.3625(17)	1.3648(13)	1.363(2)
N41−N42					1.3371(19)
X1−Be1−N11	118.33(7)	117.64(8)	117.46(10)	117.62(10)	
X1−Be1−N21	118.57(7)	115.40(8)	115.79(10)	118.67(10)	116.06(15)
X1−Be1−N31	116.06(7)	118.61(8)	117.35(10)	118.64(10)	112.26(14)
X1−Be1−N41					107.09(14)
N11−Be1−N21	99.72(7)	101.27(8)	102.24(11)	99.03(8)	
N11−Be1−N31	100.30(7)	100.09(8)	99.62(11)	99.37(8)	
N21−Be1−N31	100.53(7)	100.85(8)	101.64(11)	99.68(8)	102.21(13)
N21−Be1−N41					109.64(13)
N31−Be1−N41					109.44(14)
N12−B1−N22	105.61(8)	106.17(9)	106.36(13)	106.28(10)	110.34(14)
N12−B1−N32	105.90(7)	105.64(9)	105.20(13)	106.13(10)	111.58(14)
N22−B1−N32	106.23(8)	105.81(9)	106.20(12)	106.33(9)	109.41(14)

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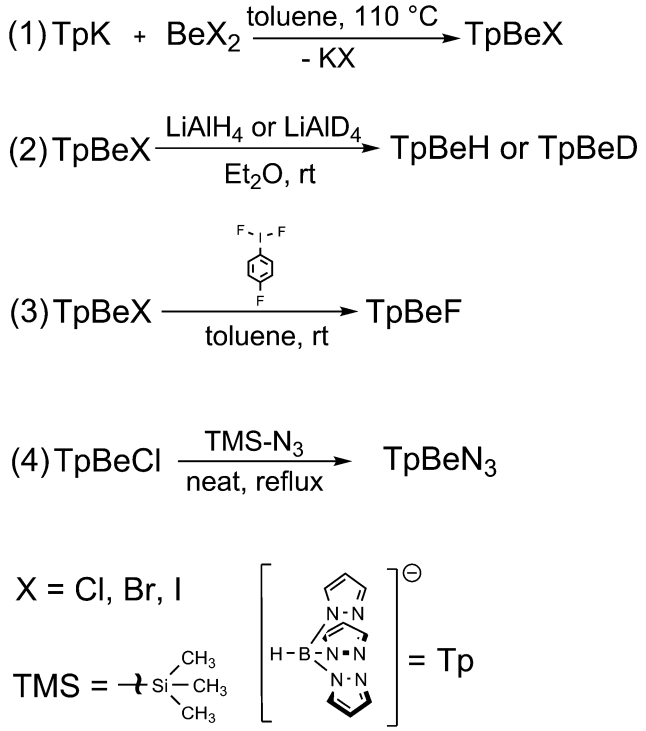
Scheme 1. Synthesis of 1-Tris(pyrazolyl)borate Beryllium Complexes 1−8



(117.65(65)° **1**, 117.22(78)° **2**, 116.87(44)° **3**). The average Be−N bond lengths are also almost identical (1.7309(16) Å **1**, 1.7229(17) Å **2**, 1.718(3) Å **3**), whereas the Be-X bond lengths increase with increasing atomic number as was expected. Comparable Be−N and Be−X bond lengths were reported for *β*-diketiminate complexes LBeX (L = HC[C(Me)NDipp]$_2$, HC[C(Ph)NDipp]$_2$; X = Cl, I)[13,14] as well as in a Cambridge structural database search.[31]

The packing of the isomorphous compounds **1** and **2** is dominated by layers parallel to (001). These layers are constituted by the CH···*π* interactions (edge to face, iv,v and vi,vii; see Table 3 and Figure 4) as well as the three-centered interaction (i,ii). The CH···*π* interactions (iv,v and vi,vii) generate endless chains by 2_1 symmetry, which are then connected by the three-centered interaction (i,ii) to complete the layer. CH···X hydrogen bonds can also be found in between these layers, completing the set of structure-determining interactions.

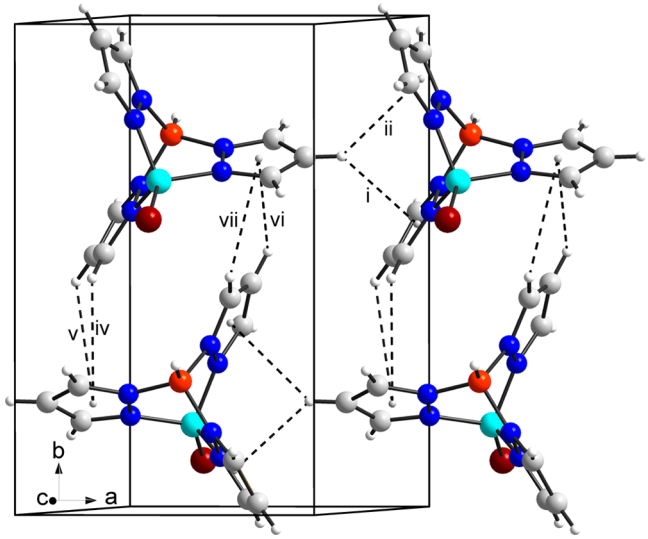


Figure 4. CH···*π* interactions within the layers in **1** and **2**.

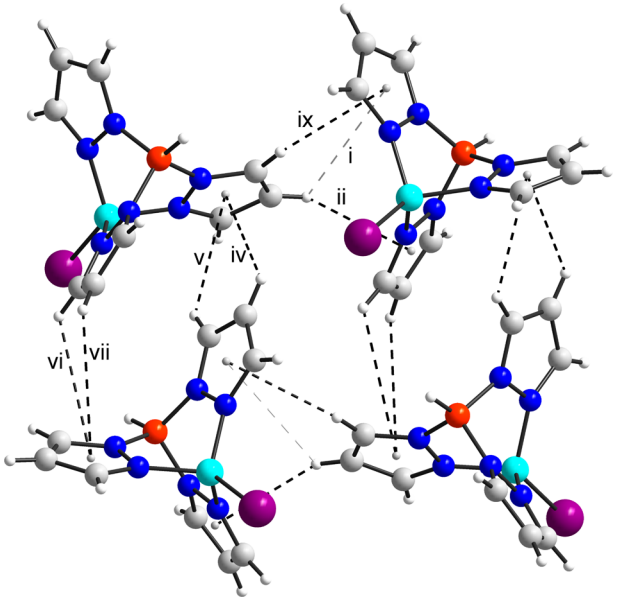


Figure 5. Interaction within the layers in **3**. CH···*π* interaction (i) was added for comparison with **1** and **2**, but it should not be considered as an attractive interaction. View parallel to the *b* axis.

Table 3. Secondary Interactions in the Packing of 1 and 2[a]

			H···A		D−H···A		H···R		H···AR	
Nr	D−H···A	sym. operation	1	2	1	2	1	2	1	2
i	C12−H12···M2	1 + *x*, +*y*, +*z*	2.72	2.81	130.8	131.0	2.6392(11)	2.6826(13)	76.0	72.7
ii	C12−H12···M3	1 + *x*, +*y*, +*z*	2.96	2.97	134.7	136.0	2.7687(12)	2.7920(13)	69.3	70.1
iii	C13−H13···X1	1/2 + *x*, 3/2 − *y*, −1/2 + *z*	2.74	2.81	150.6	152.0				
iv	C21−H21···M1	1/2− *x*, −1/2 + *y*, 1/2 − *z*	3.41	3.42	109.5	114.4	2.4140(18)	2.4847(19)	45.1	46.6
v	C22−H22···M1	1/2 − *x*, −1/2 + *y*, 1/2 − *z*	3.23	3.45	114.9	112.3	3.2231(14)	3.4013(17)	86.3	80.4
vi	C32−H32···M1	1/2 − *x*, 1/2 + *y*, 1/2 − *z*	3.09	3.10	121.3	119.3	2.9750(13)	3.0236(14)	74.3	77.3
vii	C33−H33···M1	1/2 − *x*, 1/2 + *y*, 1/2 − *z*	3.26	3.16	115.4	117.8	2.6380(14)	2.5881(16)	54.0	55.0
viii	C33−H33···X1	−1/2 + *x*, 3/2 − *y*, −1/2 + *z*	2.95	3.07	121.1	119.2				

[a]M*x* is the centroid of the ring (and its best plane, respectively) R formed by N*x*1, N*x*2, C*x*1, C*x*2, and C*x*3.

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Table 4. Secondary Interactions in the Packing of 3

Nr	D−H···A	sym. operation	H···A	D−H···A	H···R	H···AR
i	C32−H32···M1	$+x, 1/2- y, -1/2 + z$	4.09	98.4	3.7724(25)	67.3
ii	C32−H32···M2	$+x, 1/2 - y, -1/2 + z$	2.97	130.2	2.9588(19)	85.0
iii	CH···I		>3.5			
iv	C12−H12···M3	$-1/2 + x, 1/2 - y, 1 - z$	3.11	116.9	2.9485(21)	71.5
v	C13−H13···M3	$-1/2 + x, 1/2 -y, 1 - z$	3.02	121.7	2.5666(21)	58.2
vi	C21−H21···M3	$1/2 + x, 1/2 - y, 1 - z$	3.66	115.1	2.6687(28)	46.8
vii	C22−H22···M3	$1/2 + x, 1/2 - y, 1 - z$	3.76	110.66	3.6991(23)	79.7
viii	CH···I		>3.5			
ix	C33−H33···M1	$+x, 1/2 - y, -1/2 + z$	2.98	147.5	2.6003(22)	60.8

Mx is the centroid of the ring (and its best plane, respectively) R formed by N*x*1, N*x*2, C*x*1, C*x*2 and C*x*3.

The packing of **3** (Figure 5, Table 4) is similar, even though the iodine atoms do not take part in any hydrogen bonding or other intermolecular interactions. The molecules adopt a slightly different orientation, most likely caused by the longer Be−I bond and the resulting demands for the packing density. As a consequence, the comparable interactions found in **1** and **2** are distorted and a change of the space group is observed. Especially the connection of the chains is altered. The CH···π interaction (i) now hardly fulfills criteria of a CH···π interaction and is replaced by CH···π interaction (ix). Because of the change in symmetry, the chains are related by 2_1 instead of translation and thus the orientation of the "iodine end" of the molecules is alternating.

The synthesis of the TpBeF **4** was quite challenging compared to the synthesis of **1**−**3**, since the salt elimination reaction between TpBeK and BeF_2 completely failed and halide exchange reactions between TpBeX (X = Cl **1**, Br **2**, I **3**) and typical fluorination reagents only gave unsatisfying yields. The salt elimination reaction of TpK with metal fluorides is generally thermodynamically hindered due to the strong metal fluoride bond, resulting from the high electron-withdrawing properties of fluorine in compounds. This often leads to poor solubility of the metal-fluoride in common organic solvents, which is particularly true for electron-deficient BeF_2, which additionally forms polymeric chains in the solid state. Therefore, the halide exchange reaction between TpBeX (X = Cl, Br, I) and a fluoride-source is the more promising way to synthesize TpBeF **4**. Several inorganic fluorination reagents such as HgF_2, Hg_2F_2, AgF_2, CuF_2, NaF, KF, and CsF failed, whereas the reaction of TpBeBr **2** with AgF in toluene at 95 °C for 3 days gave **4** in approximately 35% yield. The synthesis has to be performed under exclusion of light to prevent formation of elemental silver and bromine radicals, which disturb the reaction in general. Because the yield of this reaction was still rather unsatisfying, we investigated reactions in which the TpBeF **4** might be formed under oxidative conditions. The best reagents for these reactions seemed to be elemental fluorine F_2, XeF_2, or 4-R-$C_6H_4IF_2$ (R = H, F, *t*-Bu) derivatives, whose oxidative fluorination properties were reported by Yoneda, Hara, and Frohn.[26−28] Because the handling of elemental fluorine needs specific safety procedures and XeF_2 is expensive, we concentrated on the use of 4-F-$C_6H_4IF_2$. Its reaction with **2** in toluene at ambient temperature yielded **4** in almost quantitative yield after only 2 h. For proof of principle, the reaction between TpBeBr and XeF_2 was also performed in toluene and **4** was obtained under almost identical reaction conditions in yields higher than 80%. In contrast to **1**−**3**, TpBeF **4** is only sparingly soluble in noncoordinating solvents. Moreover, **4** is thermally less stable compared to **1**−**3** and decomposes upon heating above 60 °C under ligand cleavage and subsequent formation of the Lewis acid−base adduct TpBe(F)pyr (pyr = $N_2C_3H_4$) **5**.

Colorless crystals of **4** were obtained upon recrystallization from a solution in thf and toluene. The crystal structure of **4** as determined by single-crystal X-ray diffraction is shown in Figure 6. **4** crystallizes along with a disordered toluene molecule. The Be atom is tetrahedrally coordinated and the bond angles, which vary from 99.03(8)° to 118.67(10)°, are only slightly distorted. The average N−Be bond length of 1.7551(25) Å is within the typical range observed for Be−N bonds containing 4-fold coordinated Be atoms and 3-fold coordinated N atoms, whereas the Be−F bond length of 1.4533(15) Å is among the shortest Be−F bond lengths ever reported.[31] However, all CSD entries contain BeF_4 units, whereas **4** represents the first Be complex with only one fluorido ligand.

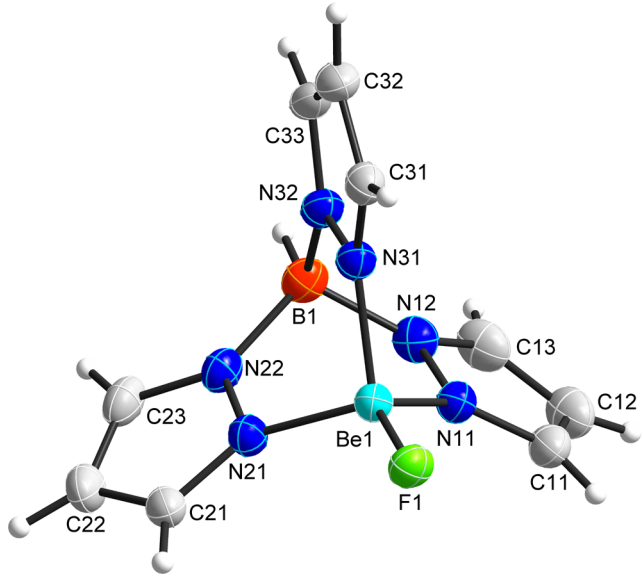

Figure 6. Representation of TpBeF **4**. Thermal ellipsoids are shown at 50% probability levels except for H atoms.

5 represents the Lewis acid−base adduct between **4** and neutral pyrazole, that is formed by thermal decomposition of the trispyrazolyl ligand (see Figure 7). The neutral pyrozole molecule coordinates to the electrophilic Be atom and replaces one pyrazolyl arm of the Tp ligand, which is stabilized by a classical N11···H−N42 hydrogen bond (H···A 1.818 Å, D−H···A 173.64°). The bond lengths and angles are comparable to those of **4** (Be−N21 1.735(3), Be−N31 1.726(3), Be−F1

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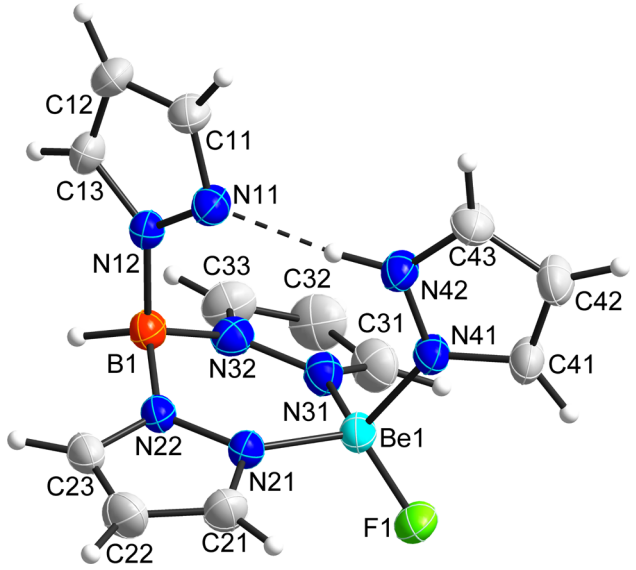

Figure 7. Representation of TpBe(F)pyr **5**. Thermal ellipsoids are shown at 50% probability levels except for H atoms.

1.479(2), Å). The Be−N41 bond length (1.736(2) Å) is comparable to the Be−N bonds of the Tp ligand. Be, B and the N atoms of the coordinating rings of the Tp ligand form a nearly flat six-membered ring (rms deviation from the best plane 0.1337 Å; Be and B deviate most from the plane (0.1326(12) and 0.2220(12) Å, 0.1250(29) and 0.3925(26) Å from the best plane of the N atoms) resulting in a shallow boat-type conformation.

The packing of **4** completely differs from those observed for **1**−**3**, most likely due to the presence of additional solvent molecules. A three-dimensional network constituted of CH···F nonclassical hydrogen bonds is formed in **4** (Figure 8, Table 5),

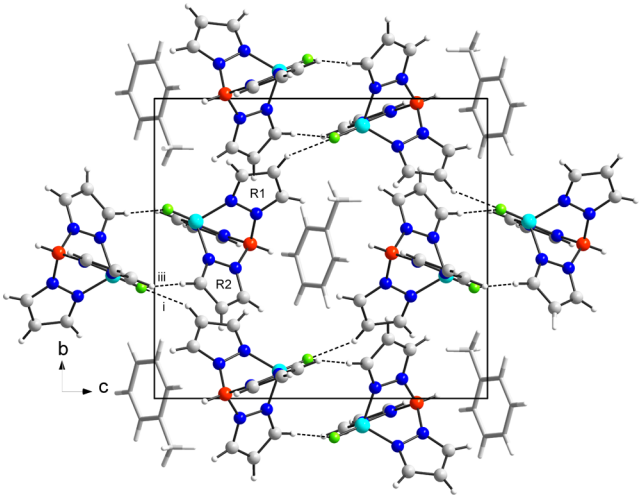

Figure 8. Two-dimensional substructure of **4**. Only one component of the disordered solvent is shown.

whose cavities host the toluene molecules. Hydrogen bonds (i) and (iii) generate a two-dimensional substructure and intersubstructure hydrogen bonds (vi) complete the network. These are accompanied by CH···π interaction (ii) and (iv,v). The solvent is incorporated via CH···π interaction to R1 and R2, which cannot be quantified because of the disorder.

TpBeH **6** and TpBeD **7** were synthesized by reaction of TpBeCl **1** with $LiAlH_4$ and $LiAlD_4$, respectively, and obtained after workup as white powders in 50−60% yields. Both hydride derivatives are only sparingly soluble in noncoordinating solvents as was observed for TpBeF **4**. The ^{1}H and ^{13}C NMR spectra of **6** show the expected resonances of the Tp ligand. In addition, a resonance at 0.19 ppm was observed for the Be−H group. For the Be−D group, a resonance was found at 2.65. Unfortunately, **6** and **7** are not stable in coordinating solvents (thf or diethylether) at elevated temperatures. The decomposition in thf occurs much faster than in Et_2O, probably because of its stronger coordination properties.

The reaction of TpBeCl **2** with neat trimethylsilylazide at elevated temperatures yielded in the formation of $TpBeN_3$ **8** after 16 h. The product is well soluble in noncoordinating solvents like toluene or benzene. The ^{1}H and ^{13}C NMR spectra of **8** are comparable to those observed for **1**−**7**, demonstrating a rather negligible electronic influence of the second ligand on the ^{1}H and ^{13}C NMR resonance shift of the Tp ligand. The formation of **8** was clearly proven by means of IR spectroscopy, since very strong absorption bands due to the asymmetric N_α-N_β-N_γ stretching mode (ν = 2111, 2006 cm^{-1}) were observed.

Since coordination complexes of beryllium are potentially harmful, there is a strong interest in the development of an in situ analytical tool, that allows their characterization as well as the identification of reaction mechanism during their synthesis in solution. Because ^{9}Be NMR fulfils this demand, we became interested in identifying the most prominent electronic parameters which influence the ^{9}Be NMR shift of beryllium complexes. The heteroleptic 1-tris(pyrazolyl)borate beryllium complexes **1**−**8** provide a suitable prototype for these investigations because they contain a constant Tp ligand and a varying second substituent. The influence of the second ligand in heteroleptic complexes on the ^{9}Be-NMR chemical shift was studied in different solvents and solvent mixtures to get a brief overview in this field (Table 6).

In accordance to the HSAB-theory, soft bases such as H^-, Br^-, and I^- lead to a slight highfield-shift of the ^{9}Be-resonance compared to hard bases such as N_3^- and Cl^-. The lowfield shift in the case of the F^- substituent most likely occurs because of its strong electron-withdrawing properties. The addition of coordinating solvent molecules such as thf leads to a highfield-shift of the ^{9}Be-resonance in comparison to less coordinating solvents or mixtures, most likely caused by the different polarity of the organic solvent. In contrast, the second ligand has no strong influence on the ^{11}B-NMR chemical shift of the Tp ligand, which is typically observed at −4.6 ± 0.2 ppm for all complexes.

To summarize, 1-tris(pyrazolyl)borate beryllium halides TpBeX (X = Cl **1**, Br **2**, I **3**, F **4**), hydride, deuteride and azide TpBeX (X = H **6**, ^{2}H (D) **7**, N_3 **8**; Tp = 1-trispyrazolylborate) complexes were synthesized in high yields and structurally characterized (**1**−**5**). In addition, ^{9}Be-NMR spectroscopy is demonstrated to be a suitable analytical tool for the in situ characterization of such heteroleptic coordination complexes. Studies in different solvents and solvent mixtures revealed the electronic influence of the variable second ligand X, whereas the Tp ligand in these complexes as well as the coordination mode of the beryllium center was kept constant.

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Table 5. Secondary Interactions in the Packing of 4

Nr	D−H···A	sym. operation	H···A	D−H···A	H···R	H···AR
i	C12−H12···F1	$+x, 3/2 - y, 1/2 + z$	2.57	152.3		
ii	C12−H12···M3	$2 - x, 1/2 + y, 1/2 - z$	3.38	122.8	3.2816(17)	80.0
iii	C21−H21···F1	$1 - x, 1 - y, -z$	2.31	175.3		
iv	C22−H22···M3	$2 - x, -1/2 + y, 1/2 - z$	3.16	118.5	2.8252(16)	63.4
v	C23−H23···M3	$2 - x, 1/2+ y, 1/2 - z$	3.11	121.4	2.8709(14)	67.4
vi	C32−H32···F1	$1 + x, +y, +z$	2.60	169.0		

M*x* is the centroid of the ring (and its best plane, respectively) R formed by N*x*1, N*x*2, C*x*1, C*x*2 and C*x*3.

Table 6. ^{9}Be NMR Shifts of Complexes 1−4 and 6−8

	solvent	1	2	3	4	6	7	8
^{9}Be [ppm]	C_6D_6	5.42						4.35
	C_6D_6/THF-d_8 (4:2)	5.23	5.15	4.85	4.54	5.11		3.30
	THF-d_8	4.95	4.83	4.66			4.36	

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for complex **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Dr. W. Bensch on the occasion of his 60th birthday

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Tp ligand's structural parameters were found to be N−B 1.540(2) Å, N−N 1.371(15) Å, N−B−N 109,1(16)° from 2612 TpM complexes with many metals. In the following searches Be−X (X = F, Cl, Br, I) fragments were used. The coordination number of Be was restricted to 4 in all cases and to 1 for all halogen atoms. The bond type was set to "any". The mean Be−N bond length was found to be 1.743(43) Å (min. 1.595 Å, max. 1.917 Å) based on 78 hits with 261 bonds. The mean Be−Cl bond length was found to be 2.007(39) Å (min. 1.865 Å, max. 2.155 Å) based on 46 hits with 126 bonds. The mean Be−Br bond length was found to be 2.143(23) Å (min. 2.121 Å, max. 2.192 Å) based on 6 hits with 13 bonds. Only one complex containing a Be−I bond was found (Ref.-code KIFZIJ[32]), showing a Be−I bond length of 2.41 . A search for Be−F with bond type "any" produced bond lengths from 1.487 to 1.587 Å (Mean: 1.539(23) Å) from 17 structures with 45 Be-F bonds in total

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