Synthesis, Structures, and Donor−Acceptor Adducts of Tris(3,3-dimethyl-1-butynyl)borane

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Dedicated to Prof. Günter Schmid on the occasion of his 65th birthday

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The synthesis and properties of tris(3,3-dimethyl-1-butynyl)borane (**1**), the first donor-free tris(alkynyl)borane, and of its adducts **2** [donor = pyridine (**2a**), triphenylphosphane (**2b**), tetrahydrofuran (**2c**)] are reported. X-ray structure analyses reveal that the B–C bond lengths in **1** are shorter than in **2**; however, the C≡C triple bond lengths are similar to those of the donor-stabilized compounds **2a**, **2b**, and **2c**.

Introduction

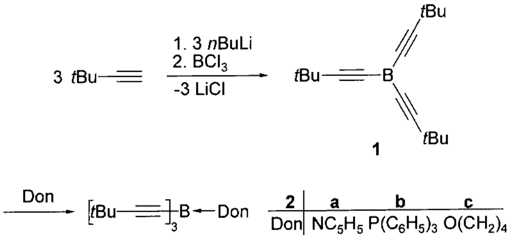
Tris(alkynyl)boranes were first obtained by Krüerke[1] as donor-stabilized compounds by the reaction of tetraphenylalkynylborates with HCl in the presence of tetrahydrofuran and trialkylamines, respectively. Another approach was described by Ashby et al.[2] who treated sodium acetylide or sodium organylacetylides with boron trifluoride−amine to yield the corresponding amine−B-$(C{\equiv}CH_3)_3$ adducts [amine = C_5H_5N, $(CH_3)_3N$, $(CH_3)_2NH$], and $H_5C_5N-B(C{\equiv}CC_6H_5)_3$. Köster et al.[3] prepared tris(alkynyl)borane−trimethylamine adducts by oxidizing alkynylborane adducts of trimethylamine with trimethylamine oxide, the resulting alkynylbis(alkoxy)boranes rearrange to form tris(alkynyl)borane−trimethylamine and tris(alkoxy)borane. Wheatley et al.[4] treated phenylacetylene with *n*-butyllithium and boron trifluoride−diethyl ether in tetrahydrofuran/toluene and obtained the tris(phenylethynyl)borane−tetrahydrofuran adduct as a hydrogen-bonded dimer. Siebert, Cederbaum et al.[5] published the X-ray structure analysis of the adduct $H_5C_5N-B(C{\equiv}CH)_3$ and ab initio calculations on the electronic structure of the donor-free tris(ethynyl)borane. Attempts to synthesize donor-free tris(alkynyl)boranes led to polymeric products.[2]

We report here on the synthesis of tris(3,3-dimethyl-1-butynyl)borane (**1**), the first donor-free tris(alkynyl)borane. Furthermore, the NMR spectroscopic and structural data of **1** and of its pyridine, triphenylphosphane, and tetrahydrofuran adducts **2a−c** are described.

Results and Discussion

Synthesis

Tris(3,3-dimethyl-1-butynyl)borane (**1**) is obtained quantitatively by the reaction of deprotonated 3,3-dimethyl-1-butyne with boron trichloride at −78 °C in pentane. Treatment of **1** with pyridine, triphenylphosphane, and tetrahydrofuran leads to the donor-stabilized tris(alkynyl)boranes **2a−c** (Scheme 1).



Scheme 1

The composition of the new compounds is derived from NMR and mass spectra and confirmed by X-ray structure analyses. The ^{11}B NMR signal of **1** shows a remarkable shift at δ = 38 ppm upfield from shifts for alkyl- and alkenylboranes.[6] The ^1H NMR spectrum of **1** exhibits a resonance at δ = 1.26 ppm for the methyl protons and in the ^{13}C NMR spectrum the broadened signal for the boron-bound α-carbon atoms is detected at δ = 91 ppm. In comparison

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to 3,3-dimethyl-1-butyne[7] [$\delta(^{13}C) = 67.3$] the signal for the α-carbon atom of **1** is shifted by 24 ppm to lower field, while the resonance of the β-carbon atoms ($\delta = 126.3$ ppm) is shifted by 32 ppm to higher field. The signals for the *tert*-butyl substituent are observed at $\delta = 30.5$ ppm for methyl groups and $\delta = 28.7$ ppm for the quaternary carbon atom. An EI mass spectrum of **1** shows the molecular ion peak [M^+] at $m/z = 254$ with an intensity of 72%, and the IR spectrum features for the C≡C triple bond a strong stretching vibration at $\tilde{\nu} = 2171.5$ cm^{-1} indicating that this bond is not elongated (confirmed by X-ray structure data, see below).

The ^{11}B NMR shift of **2a** at $\delta = -15$ ppm indicates a fourfold coordination of the boron atom. In the ^1H NMR spectrum the signal for *tert*-butyl group is observed at $\delta = 1.22$ ppm, and the ^{13}C NMR spectrum exhibits the resonances of the *tert*-butyl substituent at $\delta = 31.4$ ppm for the methyl groups and at $\delta = 29.7$ ppm for the quaternary carbon atom. The boron-bound α-carbon signals appear at $\delta = 106$ ppm, which is shifted to lower field than that of **1**. At $\delta = 128.2$ ppm the resonance for the β-carbon atoms is found.

The ^{11}B NMR signal of **2b** at $\delta = -26$ ppm is upfield relative to that of **2a**. In the ^1H NMR spectrum a singlet is observed for the *tert*-butyl groups at $\delta = 0.88$ ppm. The ^{13}C NMR spectrum exhibits four resonances at $\delta = 29.7$ (CMe_3), 30.9 (CH_3), 107 (broad, CB) and 125.2 ppm (β-carbon atoms). Four signals in the aromatic region are assigned to the triphenylphosphane donor. The ^{31}P NMR signal of **2b** is found at $\delta = 4.0$ ppm. The ^{11}B NMR shift of **2c** at $\delta = -9$ ppm is downfield compared with the values of **2a** and **2b**. The ^1H and ^{13}C NMR signals of complexed **1** in **2c** do not deviate significantly from the data of **2a** and **2b**. In the EI mass spectrum no peak for the molecular ion [M^+] of **2a−c** but that of **1** and peaks for pyridine, triphenylphosphane, and tetrahydrofuran, respectively, are detected.

Attempts to synthesize tris(alkynyl)boranes with a number of terminal alkynes (propyne, 1-butyne, trimethylsilylacetylene, phenylacetylene, mesitylacetylene) were not successful. Instead mixtures of polymeric products of unknown compositions were formed.

Crystal Structures

The molecular structure of **1** was obtained by performing a single-crystal X-ray diffraction analysis. Colorless crystals of **1** were grown from pentane at 4 °C, its molecular structure is shown in Figure 1. In **1** the C≡C triple bond lengths [1.203(2) Å] are similar, but the B−C distances [1.519(2) Å] are shorter than those of the adducts $H_8C_4O{-}B(C{\equiv}C{-}C_6H_5)_3$ [1.209(3), 1.580(4) Å][4] and $H_5C_5N{-}B(C{\equiv}CH)_3$ [1.188(2), 1.586(2) Å].[5] The catecholborylacetylene $H_4C_6O_2B{-}C{\equiv}CH$ [1.195(3), 1.520(4) Å][8] has C≡C and B−C bond lengths similar to those of **1**.

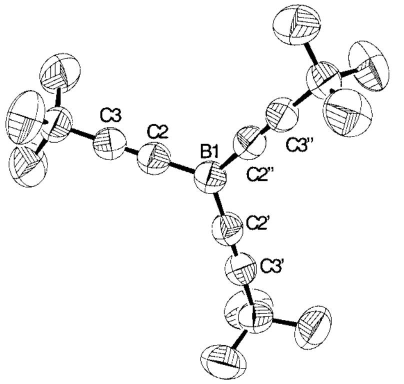

Figure 1. Molecular structure of **1** in the crystal; selected bond lengths [Å] and angles [°]: B1−C2 1.519(2), C2−C3 1.203(2), C3−C4 1.467(2), C2−B1−C2′ 120.00(1), C2−B1−C2′′ 120.00(1), C2′−B1−C2′′ 120.00(1)

Single crystals of **2a** and **2b** were grown from a solution of toluene at −30 °C, while **2c** crystallizes in tetrahydrofuran at −30 °C. Their molecular structures with distorted tetrahedral coordination at the boron atoms are shown in Figures 2−4. The lengths of the C≡C triple bonds [1.196(6)−1.212(1) Å] lie in the range of the donor-free tris(alkynyl)borane **1** [1.203(2) Å], while the B−C bond lengths [1.575(6)−1.593(2) Å] are similar to those in similar adducts of tris(alkynyl)boranes.[4,5] The B−C bonds are elongated compared with those of **1**.

Because the C≡C triple bonds in **1** are not elongated and the B−C distances are shorter in comparison to those of the donor-stabilized compounds **2a−c** it may be concluded that a small pπ−pπ interaction between the sp-hybridized carbon atoms and the sp^2-boron atom is present. This is supported by ab initio calculations on the unknown tris(ethynyl)borane,[5] which indicate weak π interactions between the boron atom and the C≡C triple bond. Furthermore, ab initio calculations on the model compound ethynylborane ($H_2B{-}C{\equiv}CH$) showed that a (polar) heteroallene structure with a B=C double bond is only of minor import-

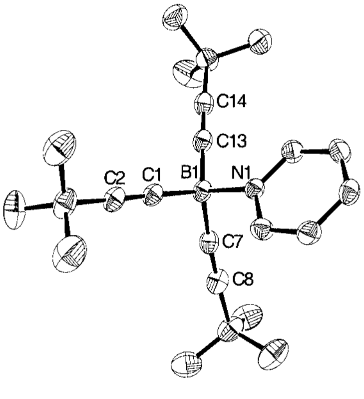

Figure 2. Molecular structure of **2a** in the crystal; selected bond lengths [Å] and angles [°]: B1−C1 1.593(2), B1−C7 1.582(2), B1−C13 1.583(2), C1−C2 1.202(2), C7−C8 1.201(2), C13−C14 1.207(2), B1−N1 1.646(2), C1−B1−N1 106.1(1), C7−B1−N1 103.6(1), C13−B1−N1 107.4(1), C1−B1−C7 111.0(1), C1−B1−C13 113.0(1), C7−B1−C13 114.9(1)

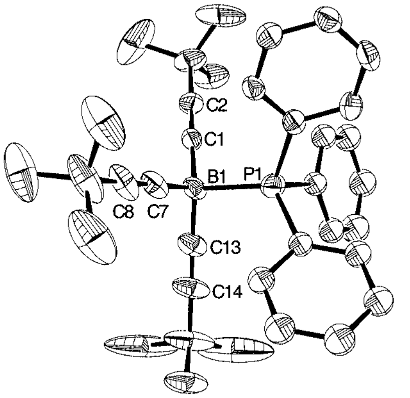

Figure 3. Molecular structure of **2b** in the crystal; selected bond lengths [Å] and angles [°]: B1−C1 1.580(5), B1−C7 1.575(7), B1−C13 1.586(6), C1−C2 1.204(5), C7−C8 1.196(6), C13−C14 1.203(6), B1−P1 2.029(4), C1−B1−P1 103.0(2), C7−B1−P1 108.7(3), C13−B1−P1 102.0(3), C1−B1−C7 114.6(4), C1−B1−C13 114.5(3), C7−B1−C13 112.6(3)

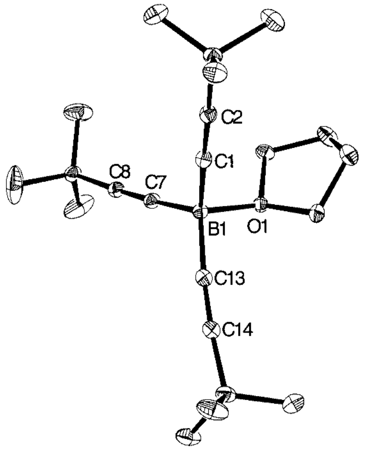

Figure 4. Molecular structure of **2c** in the crystal; selected bond lengths [Å] and angles [°]: B1−C1 1.580(1), B1−C7 1.578(1), B1−C13 1.575(1), C1−C2 1.210(1), C7−C8 1.212(1), C13−C14 1.209(1), B1−O1 1.605(1), C1−B1−O1 104.5(1), C7−B1−O1 104.2(1), C13−B1−O1 103.0(1), C1−B1−C7 112.6(1), C1−B1−C13 115.6(1), C7−B1−C13 115.2(1)

ance.[9] The observed shortening of the B−C bond length may be explained by the different boron hybridizations present in **1** (sp^2) and in the adducts **2** (sp^3).

Conclusion

In this paper we report on the synthesis of the first donor-free tris(alkynyl)borane. By treating of 3,3-dimethyl-1-butynyllithium with boron trichloride in a ratio of 3:1 tris(3,3-dimethyl-1-butynyl)borane (**1**) is formed. Reactions with several other terminal alkynes did not yield the corresponding tris(alkynyl)boranes, but mixtures of polymeric products with unknown compositions were obtained. Addition of pyridine, triphenylphosphane or tetrahydrofuran to **1** yields the donor-stabilized derivatives **2a**, **2b**, and **2c**, respectively. X-ray structure analyses of **1**, **2a**, **2b**, and **2c** show that the lengths of the C≡C triple bonds of **1** are similar to the C≡C triple bonds of **2a−c**, while the B−C bonds in **1** are shorter compared with the B−C bonds in **2a−c**. This result seems to be in agreement with the presence of a (C−B)π interaction as indicated by ab initio calculations on the nonexistent tris(ethynyl)borane[5] and by NMR studies of several alkenyl- and alkynylboranes.[6] However, the elongation of the B−C bonds more likely is a consequence of the decrease of the 2s character in the boron−carbon bonds of **2a−c**, rather than a (C−B)π bond in **1**.

Experimental Section

General: Reactions were carried out under dry argon or nitrogen, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun under high vacuum. ^{1}H, ^{13}C, ^{31}P and ^{11}B NMR: Bruker DRX 200 spectrometer, $Et_2O·BF_3$ was used as external standard for ^{11}B NMR, 30% H_3PO_4 for ^{31}P NMR. As internal references for ^{1}H and ^{13}C NMR spectra the signals of the deuterated solvents were used and calculated for TMS. The mass spectra were measured with a ZAB-2F VH Micromass CTD spectrometer and with a Jeol MS station JMS 700 using EI and HR-EI techniques. IR spectra were recorded with a Perkin−Elmer 983G spectrometer. Melting points (uncorrected) were measured with a Büchi apparatus using capillaries, which were filled under argon or nitrogen, and sealed.

Tris(3,3-dimethyl-1-butynyl)borane (1): To a solution of 5 g (61 mmol) of 3,3-dimethyl-1-butyne in 140 mL of pentane 61 mmol of *n*BuLi was added at −20 °C. The mixture was allowed to warm to room temp. and stirred for 1 h. Then the suspension was cooled to −78 °C and transferred to a solution of 3.3 g (28 mmol) of BCl_3 in 40 mL of pentane at −78 °C. The reaction mixture was allowed to warm slowly to room temp. and was stirred for 12 h. After filtration, the solvent was evaporated to give **1** as colorless solid (5.04 g, 97.5%, m.p. 48 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26 [s, 27 H, $C(CH_3)_3$] ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 38 ppm ($\Delta_{1/2}$ = 580 Hz). $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 28.7 [$\mathit{C}(CH_3)_3$], 30.5 [$C(\mathit{C}H_3)_3$], 91 (br., B*C*≡C), 126.3 ppm (BC≡*C*). EI-MS: *m/z* (%) = 254 (72) [M^+], 239 (38) [$M^+ - CH_3$], 197 (78) [$M^+ - C_4H_9$], 173 (20) [$M^+ - C_6H_9$], 67 (100) [$C_5H_7^+$], 57 (43) [$C_4H_9^+$], 41 (74) [$C_3H_5^+$]. HR-MS (EI): *m/z* = 254.2208 [M^+]; calcd. for $^{12}C_{18}{}^{1}H_{27}{}^{11}B_1$: 254.2206 (Δ = 0.2 mmu). IR: $\tilde{\nu}$ = 2171.5 cm^{-1} (C≡C).

Tris(3,3-dimethyl-1-butynyl)borane−Pyridine Adduct (2a): 133 mg (0.52 mmol) of **1** was dissolved in 15 mL of pentane and treated with 45 mg (0.57 mmol) of pyridine at −10 °C. The mixture was allowed to warm to room temp. and was stirred for 4 h. Then the solvent was removed under vacuum to yield **2a** as colorless solid (168 mg, 96.3%, m.p. 74 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22 [s, 27 H, $C(CH_3)_3$], 7.62 (m, 2 H, H_{py}), 8.03 (m, 1 H, H_{py}), 9.28 ppm (m, 2 H, H_{py}). ^{11}B NMR (64 MHz, $CDCl_3$): δ = −15 ppm ($\Delta_{1/2}$ = 139 Hz). $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 29.7 [$\mathit{C}(CH_3)_3$], 31.4 [$C(\mathit{C}H_3)_3$], 106 (br., B*C*≡C), 128.2 (BC≡*C*), 125.1, 140.6, 146.1 ppm (C_{py}). EI-MS: *m/z* (%) = 254 (81) [M^+ −py], 239 (49) [M^+ − py − CH_3], 197 (100) [M^+ − py − C_4H_9], 173 (22) [M^+ − py − C_6H_9], 79 (96) [py^+], 67 (60) [$C_5H_7^+$], 57 (36) [$C_4H_9^+$], 52 (87) [$C_4H_4^+$], 41 (86) [$C_3H_5^+$].

Tris(3,3-dimethyl-1-butynyl)borane−Triphenylphosphane Adduct (2b): 90 mg (0.35 mmol) of **1** was dissolved in 20 mL of toluene, and a solution of 93 mg (0.35 mmol) of PPh_3 in 10 mL of toluene was added at room temp. After 4 h of stirring, the solvent was

Table 1. Crystal data and details of the structure determinations

	1	**2a**	**2b**	**2c**
Empirical formula	$C_{18}H_{27}B$	$C_{23}H_{32}BN{\cdot}0.5\ C_7H_8$	$C_{36}H_{42}BP$	$C_{22}H_{35}BO$
Formula mass	254.22	379.37	516.51	326.31
Temperature [K]	293(2)	173(2)	173(2)	100(2)
Crystal system	hexagonal	trigonal	monoclinic	triclinic
Space group	$P6_3/m$	$P3_121$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions				
a [Å]	11.530(2)	14.2708(1)	14.188(2)	10.5829(5)
b [Å]	11.530(2)	14.2708(1)	16.857(2)	10.9449(5)
c [Å]	8.552(2)	21.7049(3)	15.003(2)	11.5218(5)
α [°]	90	90	90	96.675(1)
β [°]	90	90	114.358(3)	107.182(1)
γ [°]	120	120	90	117.710(1)
Volume [Å^3]	984.6(3)	3828.11(7)	3268.9(8)	1076.84(8)
Z	2	6	4	2
Calcd. density [g/cm^3]	0.857	0.987	1.049	1.006
Absorp. coeff. [mm^{-1}]	0.047	0.055	0.105	0.058
F(000)	280	1242	1112	360
Crystal size [mm]	0.72 × 0.46 × 0.44	0.42 × 0.33 × 0.28	0.75 × 0.33 × 0.26	0.42 × 0.25 × 0.22
Θ_{max} [°]	26.33	26.37	24.41	32.00
Index ranges	−11/7, 0/14, −10/10	−17/8, 0/17, −0/27	−16/15, 0/19, 0/17	−15/14, −16/16, 0/17
No. of reflections				
Unique	717	5232	5393	7287
Observed [$I > 2\sigma(I)$]	561	4326	3810	5906
Parameters	49	399	331	357
Final R indices				
$R1$ [$I > 2\sigma(I)$]	0.0535	0.0401	0.0927	0.0472
$wR2$	0.1583	0.1101	0.2360	0.1230
Largest diff. peak/hole [e/Å^3]	+0.104/−0.127	+0.171/−0.124	+0.509/−0.475	+0.477/−0.276

removed under vacuum to give **2b** as colorless solid (143 mg, 78.3%, m.p. 96 °C). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.88 [s, 27 H, C(CH$_3$)$_3$], 7.10−7.20 ppm (m, 15 H, Ar-H). ^{11}B NMR (64 MHz, CDCl$_3$): δ = −26 ppm (Δ1/2 = 174 Hz). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ = 29.7 [*C*(CH$_3$)$_3$], 30.9 [C(*C*H$_3$)$_3$], 107 (br., B*C*≡C), 125.3 (BC≡*C*), 128.2, 129.0, 134.0, 137.8 ppm (Ar-C). ^{31}P NMR (81 MHz, CDCl$_3$): δ = 4.0 ppm. EI-MS: *m/z* (%) = 262 100) [PPh$_3$$^+$], 254 (14) [M$^+$ − PPh$_3$], 239 (12) [M$^+$ − PPh$_3$ − CH$_3$], 197 (36) [M$^+$ − PPh$_3$ − C$_4$H$_9$], 108 (33) [PPh$^+$].

Tris(3,3-dimethyl-1-butynyl)borane−Tetrahydrofuran Adduct (2c): 169 mg (0.67 mmol) of **1** was dissolved in 15 mL of pentane and treated with 5 mL of tetrahydrofuran at −10 °C. The mixture was allowed to warm up to room temp. and was stirred for 4 h. Then the solvents were removed under vacuum to yield **2c** as colorless solid (202 mg, 92.4%, m.p. 63 °C). ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.15 [s, 27 H, C(CH$_3$)$_3$], 1.78 (m, 4 H, β-H$_{thf}$), 3.63 ppm (m, 4 H, α-H$_{thf}$). ^{11}B NMR (64 MHz, [D$_8$]THF): δ = −8 ppm ($\Delta_{1/2}$ = 412 Hz). ^{13}C{^{1}H} NMR (50 MHz, [D$_8$]THF): δ = 26.5 (β-C$_{thf}$), 31.5 [*C*(CH$_3$)$_3$], 32.0 [C(*C*H$_3$)$_3$], 68.5 (α-C$_{thf}$), 89 (br., B*C*≡C), 104.6 ppm (BC≡*C*). EI-MS: *m/z* (%) = 254 (64) [M$^+$ − THF], 239 (43) [M$^+$ − THF − CH$_3$], 197 (100) [M$^+$ − THF − C$_4$H$_9$], 72 (84) [THF$^+$], 57 (14) [C$_4$H$_9$$^+$].

X-ray Crystal Structure Analyses of 1, 2a, 2b, and 2c: Crystal data and details of the structure determinations are compiled in Table 1. Intensity data were collected with a Bruker AXS Smart 1000 CCD area detector (Mo-K_α radiation, λ = 0.71073 Å, ω-scan). An empirical absorption correction was applied (SADABS). The structures were solved by direct methods and refined by full-matrix least squares based on F^2 with all measured reflections.[10] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms for **2a** were located in a difference Fourier map and refined isotropically, for **1** and **2b** they were inserted in calculated positions. CCDC-179205−179209 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] U. Krüerke, *Z. Naturforsch., Teil B* **1956**, *11*, 676−677.

[2] E. C. Ashby, W. E. Foster, *J. Org. Chem.* **1964**, *29*, 3225−3229.

[3] R. Köster, H.-J. Horstschäfer, P. Binger, *Justus Liebigs Ann. Chem.* **1968**, *717*, 1−20.

[4] J. E. Davies, P. R. Raithby, R. Snaith, A. E. H. Wheatley, *Chem. Commun.* **1997**, 1797−1798.

[5] A. Maderna, H. Pritzkow, W. Siebert, T. Sommerfeld, L. S. Cederbaum, *Z. Naturforsch., Teil B* **1997**, *52*, 1315−1320.

[6] B. Wrackmeyer, H. Nöth, *Chem. Ber.* **1977**, *110*, 1086−1094.

[7] G. Fraenkel, P. Pramanik, *J. Chem. Soc., Chem. Commun.* **1983**, 1527−1528.

[8] Y. Gu, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2001**, 373−379.

[9] V. Bachler, N. Metzler-Nolte, *Eur. J. Inorg. Chem.* **1998**, 733−744.

[10] G. M. Sheldrick, SHELXTL V5.1, Bruker AXS, Madison, Wisconsin, **1998**.

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