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Diborane(4)yl and bridged borylene complexes from 1,2-dipyrrolidino- and 1,2-dipiperidinodiborane(4) derivatives

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Abstract

The 1,2-diaminodichlorodiboranes(4) $B_2(NC_4H_8)_2Cl_2$ (**1**) and $B_2(NC_5H_{10})_2Cl_2$ (**2**) served as starting materials for the syntheses of the iron diborane(4)yl complexes $[Cl(R_2N)B{-}B(NR_2)Fe(C_5H_5)(CO)_2]$ (**3a**, $NR_2{=}NC_4H_8$; **3b**, $NR_2{=}NC_5H_{10}$). Upon reaction with the anionic manganese hydride complex $K[(C_5H_4Me)MnH(CO)_2]$, the bridged borylene complexes $[\{(C_5H_4Me)Mn(CO)_2\}_2BNR_2]$ (**4a**, $NR_2{=}NC_4H_8$; **4b**, $NR_2{=}NC_5H_{10}$) were obtained with cleavage of the boron–boron bond, hydrogen migration from manganese to boron, and formation of the corresponding diboranes(6) $(H_2BNR_2)_2$. All complexes were obtained as crystalline materials and fully characterized in solution by IR and multinuclear NMR spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Diborane(4)yl; Bridged borylene complexes; NMR spectroscopy

1. Introduction

Transition metal complexes of boron, which represent a novel class of organometallic compounds, have been established over the past decade [1,2]. Most of these compounds derive from simple boranes, but diboranes(4) also play an important role in the synthesis of these complexes. In the case of the strongly electronegative groups RO^- [3] and F^- [4] as substituents to both boron atoms the corresponding diboranes(4) generally react with cleavage of the boron–boron bond and oxidative addition to suitable metal centers, thus forming products with one to three borylligands. The use of 1,2-diaminodihalodiboranes(4), however, has led to the first diborane(4)yl complexes, which are characterized by a $R_2N{-}B(Hal){-}B(NR_2){-}$ (Hal = Cl, Br) ligand being coordinated via one boron atom to a metal center [5,6]; a cleavage of the boron–boron bond was not observed in these cases. The first bridged borylene complexes $[\{(C_5H_4Me)Mn(CO)_2\}_2BNR_2]$ were also obtained from 1,2-diaminodihalodiboranes(4) by reaction with $K[(C_5H_4Me)MnH(CO)_2]$, in this case, however, again with cleavage of the diborane(4) and hydrogen migration from manganese to boron [7–9]. Interestingly, all products being described so far derive from 1,2-bis-(dimethylamino)dihalodiboranes(4). In the present paper we describe some diborane(4)yl and bridged borylene complexes, which were obtained from $B_2(NC_4H_8)_2Cl_2$ (**1**) and $B_2(NC_5H_{10})_2Cl_2$ (**2**), respectively, thus showing that the syntheses of these complexes are not restricted to the use of $B_2(NMe_2)_2Hal_2$.

2. Results and discussion

Syntheses of the 1,2-diaminodichlorodiboranes(4) $B_2(NC_4H_8)_2Cl_2$ (**1**) and $B_2(NC_5H_{10})_2Cl_2$ (**2**): although compound **1** is known from the literature [10], neither experimental nor spectroscopic details could be found for both diboranes(4), and hence, a brief description is given in this paper. The diaminodichlorodiboranes(4) **1** and **2** were obtained by the well-known reaction [11] of the corresponding tetraaminodiboranes(4) with one equivalent of BCl_3, and with formation of $(R_2N)_2BCl$ according to Eq. (1).

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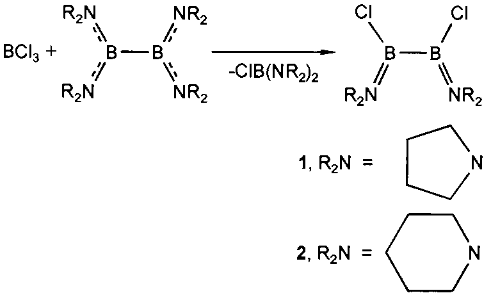
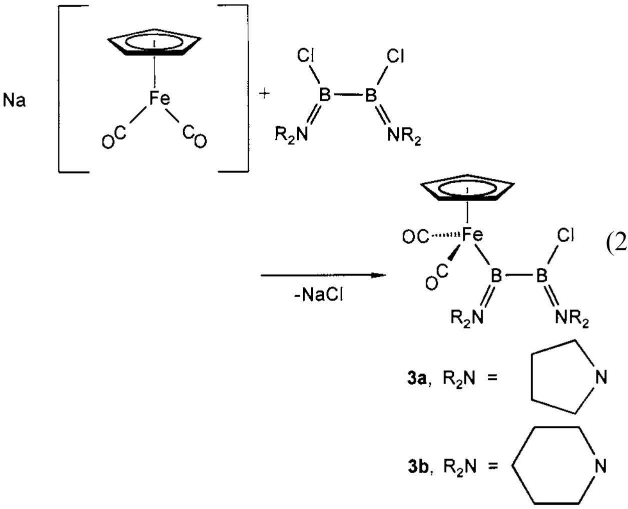


(1)

Both products were obtained in pure form by distillation under reduced pressure as colorless liquids, which solidified on cooling to ambient temperature in yields of 80–96% and characterized by NMR methods.

Syntheses of the diborane(4)yl and bridged borylene complexes: the compounds [Cl(R$_2$N)B–B(NR$_2$)Fe(C$_5$H$_5$)(CO)$_2$] (**3a**, NR$_2$=NC$_4$H$_8$; **3b**, NR$_2$=NC$_5$H$_{10}$) were obtained from reactions of the corresponding diboranes(4) with Na[C$_5$H$_5$Fe(CO)$_2$] at ambient temperature (Eq. (2)) and isolated in pure form as brown (**3a**) or dark red (**3b**) crystalline solids in yields of 22% (**3a**) and 10% (**3b**), respectively.

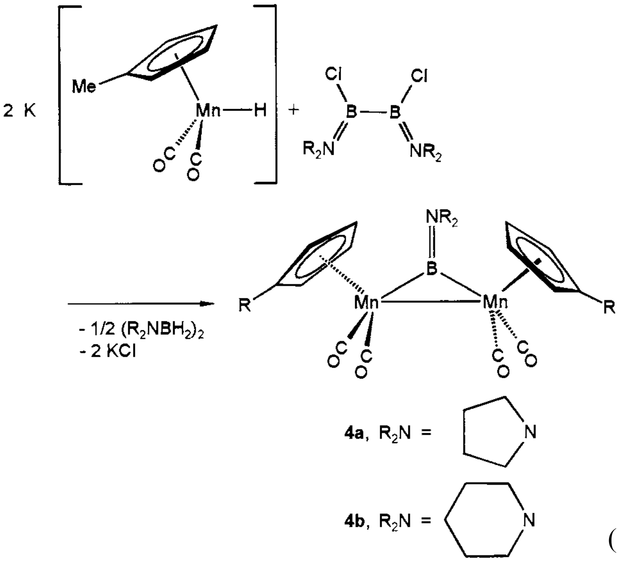


(2)

The low yield of 10% and the required long reaction time of 10 days demonstrate the decreased reactivity of **2** towards Na[C$_5$H$_5$Fe(CO)$_2$].

Both products dissolve readily in benzene or hexane, and such solutions show no signs of decomposition after several days at ambient temperature under an inert gas atmosphere. In the solid state **3a**,**b** can be handled under air for about 1 h. The structure in solution derives from the NMR and IR spectroscopic data. Two ^{11}B-NMR resonances are found for each compound at $\delta = 38.4$ (**3a**) and 37.4 (**3b**) on the one hand, and at $\delta = 66.5$ (**3a**) and 68.0 (**3b**) on the other hand. The distinct low-field shift of the latter signals is characteristic for the metal coordinated boron atoms, while the resonances at about 38 ppm indicate the chlorine-substituted boron atoms [5,6]. The CO stretching frequencies at $\nu = 1980$, 1922 (**3a**) and $\nu = 1981$, 1927 (**3b**) correspond to those of similar iron complexes with aminoborylligands, thus giving evidence for iron–boron σ-bonds without any significant π-interaction [1].

According to Eq. (3) the bridged borylene complexes [{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$BNR$_2$] (**4a**, NR$_2$=NC$_4$H$_8$; **4b**, NR$_2$=NC$_5$H$_{10}$) were obtained as dark red crystalline solids in yields of 48% (**4a**) and 40% (**4b**), respectively.



(3)

This reaction occurs with cleavage of the boron–boron bond of the diboranes(4) and hydrogen migration from manganese to boron, thus giving the corresponding diboranes(6) (H$_2$BNR$_2$)$_2$ in stoichiometric amounts as the second boron containing product. As described before, these diboranes(6) can be separated from the borylene complexes and characterized by NMR methods [7–9]. Both products **4a**,**b** are soluble in hexane or benzene and display a remarkable stability towards oxidation and hydrolysis, since even solutions of these products being exposed to air for several days show no signs of decomposition. Characteristic for such bridged borylene complexes showing two metal–boron bonds are the distinctly low-field-shifted ^{11}B-NMR resonances, which are found at $\delta = 100.3$ (**4a**) and 101.1 (**4b**), respectively. The CO stretching frequencies at $\nu = 1954$, 1916, 1885 (**4a**) and $\nu = 1955$, 1917, 1887 (**4b**) resemble those of both the corresponding dimethylaminoborylene complex [{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$-BNMe$_2$] [7–9], and [{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$CCH$_2$] [12], thus demonstrating the close relationship between bridged aminoborylene complexes and the isoelectronic vinylidene compounds.

3. Experimental

All manipulations were carried out by standard Schlenk techniques under N$_2$. All reagents were purchased from commercial suppliers and used without further purification. Solvents and deuterated solvents for NMR experiments were dried and purified by standard methods. $\mathrm{B_2(NR_2)_4}$ ($\mathrm{NR_2 = NC_4H_8, NC_5H_{10}}$) [13], $\mathrm{Na[C_5H_5Fe(CO)_2]}$ [14], and $\mathrm{K[(C_5H_4Me)MnH(CO)_2]}$ [9] were obtained according to literature methods.

^{1}H-, ^{11}B-, and ^{13}C-NMR data were obtained on a Varian Unity 500 with TMS as internal, and $\mathrm{BF_3{\cdot}OEt_2}$ as external standards. IR spectra were recorded on a Perkin–Elmer FT-IR 1720 X spectrometer. Elemental analyses (C, H, N) were obtained from a Carlo–Erba elemental analyzer, model 1106.

3.1. Synthesis of $\mathit{B_2(NC_4H_8)_2Cl_2}$ *(**1**)*

A total of 2.76 g (23.54 mmol) of $\mathrm{BCl_3}$ was condensed to a solution of 7.11 g (23.54 mmol) $\mathrm{B_2(NC_4H_8)_4}$ in 150 ml of $\mathrm{Et_2O}$ at − 10°C. The reaction mixture was stirred for 1 h at − 10°C, slowly warmed to ambient temperature, and stirred for 4 h. All volatiles were pumped off, and the remaining viscous liquid was distilled at 5×10^{-4} Torr. Pure **1** was obtained at a boiling point of 95–96°C as a colorless liquid, which solidified on cooling to ambient temperature. Yield: 4.40 g (80.50 %). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.78$ (m, 8H, $\mathrm{NCH_2}\mathit{CH_2}$), 3.35 (m, 8H, $\mathrm{NCH_2}$). ^{11}B-NMR ($\mathrm{CDCl_3}$): $\delta = 36.8$. ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 25.12$, 26.57 ($\mathrm{NCH_2}\mathit{CH_2}$), 48.09, 50.38 ($\mathrm{NCH_2}$). Anal. Calc. for $\mathrm{C_8H_{16}B_2Cl_2N_2}$ (232.76): C, 41.28; H, 6.93; N, 12.04. Found: C, 41.15; H, 6.81; N, 12.22.

3.2. Synthesis of $\mathit{B_2(NC_5H_{10})_2Cl_2}$ *(**2**)*

As described for **1**, 2.78 g (23.70 mmol) $\mathrm{BCl_3}$ was reacted with a solution of 8.49 g (23.70 mmol) $\mathrm{B_2(NC_5H_{10})_4}$ in 150 ml of $\mathrm{Et_2O}$ at − 10°C. Pure **2** was obtained at a boiling point of 99–101°C at 5×10^{-4} Torr as a colorless liquid, which solidified on cooling to ambient temperature. Yield: 5.96 g (96.31 %). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.55$ (m, 12H, $\mathrm{NCH_2}\mathit{CH_2CH_2}$), 3.21 (m, 8H, $\mathrm{NCH_2}$). ^{11}B-NMR ($\mathrm{CDCl_3}$): $\delta = 36.4$. ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 24.86$, 27.19, 27.94 ($\mathrm{NCH_2}\mathit{CH_2CH_2}$), 46.58, 52.44 ($\mathrm{NCH_2}$). Anal. Calc. for $\mathrm{C_{10}H_{20}B_2Cl_2N_2}$ (260.81): C, 46.05; H, 7.73; N, 10.74. Found: C, 45.45; H, 7.31; N, 10.22.

3.3. Synthesis of $\mathit{[Cl\{(C_4H_8)_2N\}B\text{-}B\{N(C_4H_8)_2\}Fe(C_5H_5)(CO)_2]}$ *(**3a**)*

A total of 1.88 g (8.08 mmol) of $\mathrm{B_2(NC_4H_8)_2Cl_2}$ (**1**) was added to a suspension of 1.62 g (8.08 mmol) of $\mathrm{Na[(C_5H_5)Fe(CO)_2]}$ in 40 ml of benzene at ambient temperature. The reaction mixture was stirred for 1 day, all volatiles were pumped off in high vacuum, and the remaining solid was extracted with 40 ml of hexane. After filtration and cooling to − 30°C pure **3a** was obtained as a brown crystalline solid. Yield: 0.65 g (21.50 %); m.p. 65°C. ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.53$ (m, 8H, $\mathrm{NCH_2}\mathit{CH_2}$), 2.90–3.60 (m, 8H, $\mathrm{NCH_2}$), 4.43 (s, 5H, $\mathrm{C_5H_5}$). ^{11}B-NMR ($\mathrm{CDCl_3}$): $\delta = 38.4$ (BCl), 66.5 (BFe). ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 25.51$, 26.73, 26.83 ($\mathrm{NCH_2}\mathit{CH_2}$), 47.40, 49.83, 52.62, 55.45 ($\mathrm{NCH_2}$), 83.73 ($\mathrm{C_5H_5}$), 217.37, 217.54 (CO). IR (hexane) $\nu_{\mathrm{CO}} = 1980$ (m), 1922 (m). Anal. Calc. for $\mathrm{C_{15}H_{21}B_2ClFeN_2O_2}$ (374.26): C, 48.14; H, 5.66; N, 7.48. Found: C, 47.58; H, 5.73; N, 7.27.

3.4. Synthesis of $\mathit{[Cl\{(C_5H_{10})_2N\}B\text{-}B\{N(C_5H_{10})_2\}Fe(C_5H_5)(CO)_2]}$ *(**3b**)*

As described for **3a**, 2.98 g (11.40 mmol) of $\mathrm{B_2(NC_5H_{10})_2Cl_2}$ (**2**) was added to a suspension of 2.28 g (11.40 mmol) of $\mathrm{Na[(C_5H_5)Fe(CO)_2]}$ in 40 ml of benzene at ambient temperature and the reaction mixture was stirred for 10 days. Pure **3b** was obtained as a dark red crystalline solid. Yield: 0.46 g (10.00%); m.p. 118°C. ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.43$ (m, 12H, $\mathrm{NCH_2}\mathit{CH_2CH_2}$), 3.60 (m, 8H, $\mathrm{NCH_2}$), 4.41 (s, 5H, $\mathrm{C_5H_5}$). ^{11}B-NMR ($\mathrm{CDCl_3}$): $\delta = 37.8$ (BCl), 68.0 (BFe). ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 25.19$, 25.22, 27.40, 27.71, 27.91, 28,68 ($\mathrm{NCH_2}\mathit{CH_2CH_2}$), 46.24, 51.42, 58.62, 58.64 ($\mathrm{NCH_2}$), 83.68 ($\mathrm{C_5H_5}$), 217.48, 217.51 (CO). IR (hexane) $\nu_{\mathrm{CO}} =$ 1981 (m), 1927 (m). Anal. Calc. for $\mathrm{C_{17}H_{25}B_2ClFeN_2O_2}$ (402.32): C, 50.75; H, 6.26; N, 6.96. Found: C, 50.54; H, 6.31; N, 6.77.

3.5. Synthesis of $\mathit{[\{(C_5H_4Me)Mn(CO)_2\}_2BNC_4H_8]}$ *(**4a**)*

A total of 0.97 g (4.17 mmol) of $\mathrm{B_2(NC_4H_8)_2Cl_2}$ (**1**) was added to a suspension of 1.92 g (8.34 mmol) of $\mathrm{K[(C_5H_4Me)MnH(CO)_2]}$ in 20 ml of benzene at ambient temperature. The reaction mixture was stirred for 1 day, all volatiles were pumped off in high vacuum, and the remaining solid was extracted with 50 ml of hexane. After filtration and cooling to − 30°C pure **4a** was obtained as a red crystalline solid. Yield: 1.02 g (48.42 %); m.p. 98°C. ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta = 1.48$ (m, 4H, $\mathrm{NCH_2}\mathit{CH_2}$), 1.90 (s, 6H, Me) 3.16–3.86 (m, 4H, $\mathrm{NCH_2}$), 4.05–4.22 (m, 4H, $\mathrm{C_5H_4}$). ^{11}B-NMR ($\mathrm{CDCl_3}$): $\delta = 100.3$. ^{13}C-NMR ($\mathrm{CDCl_3}$): $\delta = 13.50$ (Me), 26.77 ($\mathrm{NCH_2}\mathit{CH_2}$), 52.99 ($\mathrm{NCH_2}$), 81.44, 83.37, 85.54, 87.87, 101.34 ($\mathrm{C_5H_4}$), 230.29, 233.79 (CO). IR (hexane) $\nu_{\mathrm{CO}} =$ 1954 (m), 1916 (m), 1885 (m). Anal. Calc. for $\mathrm{C_{20}H_{22}BMn_2NO_4}$ (461.08): C, 52.10; H, 4.81; N, 3.04. Found: C, 51.73; H, 4.89; N, 3.05.

3.6. Synthesis of $\mathit{[\{(C_5H_4Me)Mn(CO)_2\}_2BNC_5H_{10}]}$ *(**4b**)*

As described for **4a**, 1.31 g (5.02 mmol) of $\mathrm{B_2(NC_5H_{10})_2Cl_2}$ (**2**) was added to a suspension of 2.30 g (10.00 mmol) of $\mathrm{K[(C_5H_4Me)MnH(CO)_2]}$ in 20 ml of benzene at ambient temperature. Pure **4b** was obtained as a red crystalline solid. Yield: 0.96 g (40.42 %); m.p. 105°C. ^{1}H-NMR ($CDCl_3$): $\delta = 1.42$ (m, 4H, $NCH_2\mathit{CH_2}$), 1.60 (m, 2H, $NCH_2CH_2\mathit{CH_2}$), 1.90 (s, 6H, Me) 3.41–3.56 (m, 4H, NCH_2), 4.03–4.26 (m, 4H, C_5H_4). ^{11}B-NMR ($CDCl_3$): $\delta = 101.1$. ^{13}C-NMR ($CDCl_3$): $\delta = 13.51$ (Me), 24.99, 27.40 ($NCH_2\mathit{CH_2CH_2}$), 54.15 (NCH_2), 81.84, 83.87, 85.97, 87.55, 100.96 (C_5H_4), 230.39, 233.85 (CO). IR (hexane) $\nu_{CO} = 1955$ (m), 1917 (m), 1887 (m). Anal. Calc. for $C_{21}H_{24}BMn_2NO_4$ (475.11): C, 53.09; H, 5.09; N, 2.95. Found: C, 52.75; H, 5.09; N, 2.91.

Acknowledgements

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References

[1] H. Braunschweig, Angew. Chem. 110 (1998) 1882; Angew. Chem. Int. Ed. Engl. 37 (1998) 1786.

[2] G.I. Irvine, M.J.G. Lesley, T.B. Marder, N.C. Norman, C.R. Rice, E.G. Robins, W.R. Roper, G.R. Whittell, L.J. Wright, Chem. Rev. 98 (1998) 2685.

[3] J.F. Hartwig, Xiaoming He, Angew. Chem. 108 (1996) 352; Angew. Chem. Int. Ed. Engl. 35 (1996) 315 (for further examples see Refs. [1,2]).

[4] A. Kerr, T.B. Marder, N.C. Norman, A.G. Orpen, M.J. Quayle, C.R. Rice, P.L. Timms, G.R. Whittell, Chem. Commun. (Cambridge) (1998) 319.

[5] H. Braunschweig, B. Ganter, M. Koster, T. Wagner, Chem. Ber. 129 (1996) 1099.

[6] H. Braunschweig, M. Koster, R. Wang, Inorg. Chem. 38 (1999) 415.

[7] H. Braunschweig, T. Wagner, Angew. Chem. 107 (1995) 904; Angew. Chem. Int. Ed. Engl. 34 (1995) 825.

[8] H. Braunschweig, M. Müller, Chem. Ber. 130 (1997) 1295.

[9] H. Braunschweig, B. Ganter, J. Organomet. Chem. 545 (1997) 163.

[10] H. Nöth, M. Wagner, Chem. Ber. 124 (1991) 1963.

[11] H. Nöth, H. Schick, W. Meister, J. Organomet. Chem. 1 (1964) 401.

[12] K. Folting, J.C. Huffman, L.N. Lewis, K.G. Caulton, Inorg. Chem. 18 (1979) 3483.

[13] D. Loderer, H. Nöth, H. Pommerening, W. Rattay, H. Schick, Chem. Ber. 127 (1994) 1605.

[14] D.L. Reger, D.J. Fauth, M.D. Dukes, Syn. React. Inorg. Metal-Org. Chem. 7 (1977) 151.