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Unprecedented Reactivity of the Bridged Borylene Complexes [μ-BCl{(η^5-C_5H_4Me)$Mn(CO)_2$}$_2$] toward Pyridine

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The reactivity of the bridged chloroborylene complex [μ-BCl{(η^5-C_5H_4Me)$Mn(CO)_2$}$_2$] (**1**) toward pyridine was investigated under various conditions. In the presence of protic reagents such as H[$Co(CO)_4$] or H[BF_4], the formation of the aminoborylene complex [1-(μ-B)-4-H-(NC_5H_5){(C_5H_4Me)$Mn(CO)_2$}$_2$] (**2**) was observed. Compound **2** represents the product of an unprecedented formal 1,4-hydroboration of pyridine. Corresponding reactions of **1** with pyridine and Tl[PF_6] afforded **2** in similar yields, thus providing evidence that the abstraction of the boron bound chloride initiates the observed reaction. Complex **2** was fully characterized in solution and in the crystal.

In the course of our investigations on transition metal complexes of boron,[1] we reported on a variety of both bridged[2] and terminal borylene complexes[3] over the past few years. Although this class of compounds attracted already considerable interest from both experimental[4] and theoretical points of view,[5] their reactivity and chemical behavior is virtually unexplored. There are only very few reports which are concerned with substitution reactions at bridging borylene moieties,[6] metallaborane formation,[7] and photochemically induced borylene transfer.[3c,8] In the present paper, we report on first results of the novel and highly unusual reactivity of the bridged chloroborylene complex [μ-BCl{(η^5-C_5H_4Me)-$Mn(CO)_2$}$_2$] (**1**) toward pyridine under various conditions.

The boron center of chloroborylene complex **1** can be expected to exhibit an increased Lewis acidity in comparison with corresponding aminoborylene complexes of the type [μ-BNR_2{(η^5-C_5H_4Me)$Mn(CO)_2$}$_2$] (R = various ligands), since the chloride ligand provides less effective π-back-bonding.[2a,b,e] Reactions with pyridine and related N-donors, however, failed to afford a base-stabilized borylene complex of the type L_xM-BCl(D)-ML_x (D = donor) which were reported for the bridging BH[2f] and one particular terminal BNH(R) ligand.[3d] In the presence of various protic reagents HX (X = $Co(CO)_4^-$, BF_4^-, HS^-), however, a reaction of **1** with 2 equiv of pyridine is observed, affording the aminoborylene complex in yields up to 36% together with insoluble [HNC_5H_5]Cl according to eq 1. Compound **2** was isolated as a dark red crystalline material and characterized in solution by IR and multinuclear NMR spectroscopy. The spectroscopic data are unobtrusive and like the ^{11}B NMR signal at δ = 111.9 match those of corresponding bridged aminoborylene manganese complexes,[2a,b,6] in particular those of the closely related piperidino derivative [(μ-BNC_5H_{10}){(C_5H_4-Me)$Mn(CO)_2$}$_2$].[2e]

Complex **2** as such is only a further example in an existing series of aminoborylene complexes; its formation, however, is of some interest. Compound **2** represents the product of a formal hydroboration of pyridine, affording selectively the

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(1) For reviews on transition metal complexes of boron see: (a) Braunschweig, H. *Angew. Chem.* **1998**, *110*, 1882; *Angew. Chem., Int. Ed.* **1998**, *37*, 1786. (b) Irvine, G. I.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685. (c) Smith, M. R., III. *Progress in Inorganic Chemistry*; Wiley: New York, 1999. (d) Braunschweig, H.; Colling. M. *Coord. Chem. Rev.* **2001**, *223*, 1.

(2) (a) Braunschweig, H.; Wagner, T. *Angew. Chem.* **1995**, *107*, 904; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 825. (b) Braunschweig, H.; Ganter, B. *J. Organomet. Chem.* **1997**, *545*, 163. (c) Braunschweig, H.; Kollann, C.; Englert, U. *Eur. J. Inorg. Chem.* **1998**, 465. (d) Braunschweig, H.; Kollann, C.; Klinkhammer, K. W. *Eur. J. Inorg. Chem.* **1999**, 1523. (e) Braunschweig, H.; Koster, M. *J. Organomet. Chem.* **1999**, *588*, 231. For further reports on bridged borylene complexes see: (f) Shimoi, M.; Ikubo, S.; Kawano, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4222. (g) Aldridge, S.; Coombs, D. L.; Jones, C. *Chem. Commun.* **2002**, 856.

(3) (a) Braunschweig, H.; Kollann, C.; Englert, U. *Angew. Chem.* **1998**, *110*, 3355; *Angew. Chem., Int. Ed.* **1998**, *37*, 3179. (b) Braunschweig, H.; Colling, M.; Kollann, C.; Merz, K. *Angew. Chem.* **2001**, *113*, 4327; *Angew. Chem., Int. Ed.* **2001**, *38*, 4198. (c) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem.*, in press. For further contributions on terminal borylene complexes see: (d) Cowley, A. H.; Lomelí, V.; Voigt, A. *J. Am. Chem. Soc.* **1998**, *120*, 6401. (e) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem.* **2000**, *112*, 978; *Angew. Chem., Int. Ed.* **2000**, *39*, 948.

(4) (a) Wrackmeyer, B. *Angew. Chem.* **1999**, *111*, 817; *Angew. Chem., Int. Ed.* **1999**, *38*, 771. (b) Braunschweig, H.; Colling, M. *J. Organomet. Chem.* **2000**, *614*, 18. (c) Braunschweig, H. *Inorganic Chemical Highlights*; Wiley-VCH: Weinheim, 2001. (d) Braunschweig, H.; Colling, M. *Eur. J. Inorg. Chem.*, in press.

(5) Boehme, C.; Uddin, J.; Frenking, G. *Coord. Chem. Rev.* **2000**, *197*, 249 and references therein.

(6) Braunschweig, H.; Müller, M. *Chem. Ber.* **1997**, *130*, 1295.

(7) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem.* **2002**, *114*, 1359; *Angew. Chem., Int. Ed.* **2002**, *39*, 1415.

(8) Braunschweig, H.; Colling, M.; Kollann, C.; Stammler, H.-G. *Angew. Chem.* **2001**, *113*, 2298; *Angew. Chem., Int. Ed.* **2001**, *38*, 2229.

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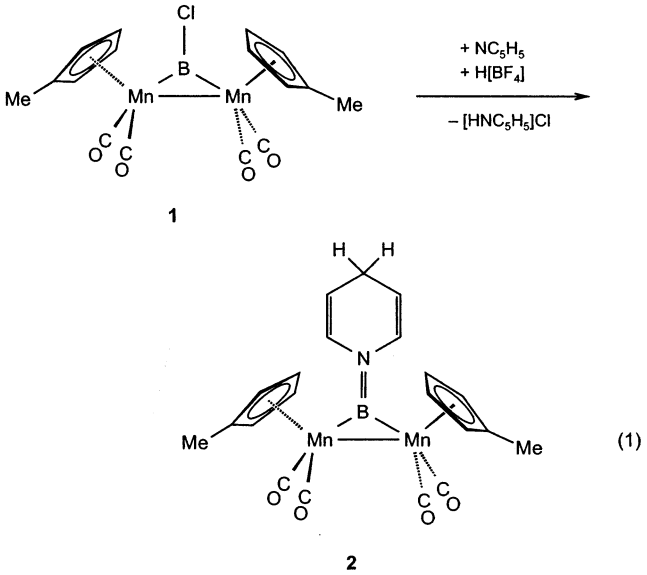

(1)

thermodynamically favored 1,4-isomer.[9] Mainly due to their biochemical relevance, considerable effort was put into the synthesis of dihydropyridines and their derivatives for some decades.[10] Selected syntheses include the catalytic hydrosilylation[11] and the stoichiometric hydroalumination;[12] a corresponding hydroboration of free pyridine, however, was not reported previously.

The formation of **2** is obviously the result of a rather complex process. In a first step the proton obviously facilitates the cleavage of the B−Cl bond and, thus, the attack of the pyridine to the boron center. Further experiments employing Tl[PF_6] as a strong chloride acceptor afforded **2** in similar yields, thus proving that the observed reaction is initiated by chloride abstraction. A cationic pyridine stabilized borylene complex of the type [(μ-BNC_5H_5){(C_5H_4Me)-Mn$(CO)_2$}$_2$]$^+$ in which the pyridine is activated by a highly Lewis acidic boron center and, thus, is susceptible to addition of hydride in 4-position appears to be a reasonable intermediate. Attempts to isolate or spectroscopically characterize this proposed cationic species, however, failed as yet. To identify the source for the hydride, the addition of which finally leads to the neutral product **2**, further experiments were conducted employing deuterated solvents and reagents. All reactions using d_{14}-hexane or d_{12}-cyclohexane as solvents and d_5-pyridine afforded exclusively the protonated species **2**. Hence, it must be concluded that the C_5H_4Me ligands act as a source for the hydride, thus accounting for the yield being always lower than 50%.

An X-ray structure analysis for **2** was performed with single crystals being obtained from Et_2O solutions at −30 °C (Figure 1, Table 1).[13] The compound crystallizes in the space group $P2_1/c$, and the molecule adopts approximate C_2-symmetry. The central Mn_2B moiety forms an isosceles triangle with B−Mn (202.3(5) and 200.7(5) pm) and Mn−Mn (280.83(10) pm) distances similar to those being reported for related bridged manganese borylene complexes. The B−N distance of 141.8(6) pm indicates a corresponding double bond considering the slight twisting of about 11° of the 1,4-dihydropyridine ring with respect to the central dimetallacyclopropane skeleton. The presence of a saturated carbon center in 4-position of the former is indicated by C−C distances of 149.5(7) and 148.5(6) pm, respectively.

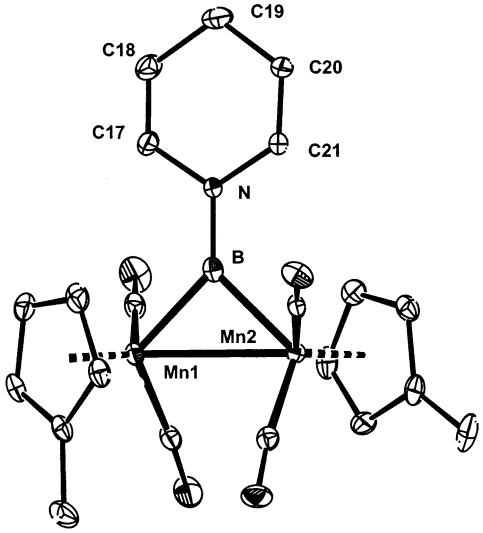

Figure 1. Structure of **2** in the crystal; selected distances (pm) and angles (deg): Mn(1)−Mn(2) 280.83(10), Mn(1)−B 202.3(5), Mn(2)−B 200.7(5), B−N 141.8(6), C(17)−C(18) 131.4(6), C(18)−C(19) 149.5(7), C(19)−C(20) 148.5(6), C(20)−C(21) 132.3(6); B−Mn(1)−Mn(2) 45.60(14), B−Mn(2)−Mn(1) 46.05(15), Mn(2)−B−Mn(1) 88.4(2).

Table 1. Crystallographic Data for **2**

formula	$C_{21}H_{20}BMn_2NO_4$	μ, mm^{-1}	1.305
fw	471.08	scan range, θ, deg	2.36−25.97
a, Å	14.7942(15)	wavelength, Å	0.71073
b, Å	10.644(2)	scan mode	$\omega/2\theta$
c, Å	12.634(3)	measured reflns	7648
β, deg	96.55(3)	indep reflns	3799
V, Å^3	1976.5(7)	obsd reflns [$I > 2\sigma(I)$]	2362
T, K	213	variables refined	262
space group	$P2_1/c$ (No. 14)	R^a	0.0480
Z	4	$R_w{}^b$	0.0983
D_{calcd}, g·cm^{-3}	1.583	GOF	0.920

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0367P)^2$ ($P = F_o^2 + 2F_c^2$)/3.

All manipulations were carried out in dry nitrogen atmosphere in Schlenk glassware. Solvents were dried by standard procedures, distilled, and stored under nitrogen and molecular sieves. [μ-BCl{(η^5-C_5H_4Me)Mn$(CO)_2$}$_2$][6] was synthesized according to known procedures The NMR is described as the following: Varian Unity 500 at 499.843 (^{1}H, standard TMS internal), 150.364 (^{11}B, standard BF_3·OEt_2 in C_6D_6 external), 125.639 MHz (^{13}C{^{1}H}, APT, standard TMS internal). Elemental analyses (C, H, N) were performed using a Carlo-Erba elemental analyzer, model 1106, and IR spectra were obtained in hexane using a Perkin-Elmer FT-IR 1720 x.

(9) Multinuclear NMR experiments proved the absence of the kinetically favored 1,2-isomer [1-(μ-B)-2-H-(NC_5H_5){(C_5H_4Me)Mn$(CO)_2$}$_2$] which was independently prepared and characterized.

(10) Lavilla, R. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1141 and references therein.

(11) (a) Cook, N. C.; Lyons, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 3396. (b) Hao, L.; Harrod, J. F.; Lebuis, A.-M.; Mu, Y.; Shu, R.; Samuel, E.; Woo, H.-G. *Angew. Chem.* **1998**, *110*, 3314.

(12) Tanner, D. D.; Yang, C.-M. *J. Org. Chem.* **1993**, *58*, 1840.

(13) Details of the crystal structure determination are available on request from the Cambridge Crystallographic Data Centre.

Preparation of [1-(μ−B)-4-H-(NC_5H_5){(C_5H_4Me)Mn(CO)$_2$}$_2$] (2). [μ-BCl{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**1**) (0.44 g, 1.03 mmol) was dissolved in 30 mL of hexane at −78 °C and treated with pyridine (0.16 g, 2.02 mmol) and H[BF_4] (1.70 mL of a 0.61 molar solution in Et_2O). The dark red mixture was warmed to ambient temperature over 2 h and stirred for 1 day. The mixture was cooled to −78 °C, and further amounts of pyridine (0.08 g, 1.01 mmol) and H[BF_4] dissolved in Et_2O (1.70 mL) were added. The mixture was stirred for 16 h at ambient temperature, all volatiles were removed in high vacuum, and the remaining solid was treated with 40 mL of hexane and filtered. The filtrate was concentrated in high vacuum to 20 mL and stored at −30 °C. After 1 day, a small amount of [(η^5-C_5H_4Me)Mn(CO)$_2$(NC_5H_5)] was isolated as a byproduct. Further concentration of the solution to 10 mL and cooling to −30 °C afforded, after 1day, 0.12 g (25.2%) of [1-(μ-B)-4-H-(NC_5H_5){(C_5H_4Me)Mn(CO)$_2$}$_2$] (**2**) as dark red crystals, mp 121 °C. ^{1}H NMR: δ = 1.80 (s, 6H, Me), 2.84 (m, 2H, CH_2), 4.00−4.11 (m, 8H, C_5H_4), 4.78 (m, 2H, NC_5H_6), 6.87 (m, 2H, NC_5H_6). ^{11}B NMR: δ = 111.9. ^{13}C NMR: δ = 13.24 (Me), 23.47 (CH_2), 82.61, 84.32, 85.78, 87.85, 101.76 (C_5H_4), 105.01, 132.75 (NC_5H_6), 229.35, 232.81 (CO). IR(toluene): ν = 1961.9, 1923.8, 1893.3, 1879.7 cm^{-1} (CO). $C_{21}H_{20}BMn_2NO_4$ (471.08) Calcd: C 53.54, H 4.28, N 2.97. Found: C 53.12, H 4.23, N 2.88.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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