Convenient synthesis of K[(C₅H₄MeMnH(CO) ₂] and reactions with Cl₂B[N(SiMe₃) ₂] and B₂R₂Cl₂ (R = Me₂N, Me₃C)

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Abstract

A new convenient synthesis for the anionic manganese complex $[(C_5H_4Me)MnH(CO)_2]^-$ (**1b**), from $[(C_5H_4Me)MnH(SiMePh_2)(CO)_2]$ and $K[BEt_3H]$ is described. Compound **1b** which can be isolated on a 15g scale, serves as starting material for the improved syntheses of the borylene complexes $[\{(C_5H_4Me)Mn(CO)_2\}_2BR]$ (**2a**, **b**; $R = Me_2N$, Me_3C), which are formed in a stiochiometric reaction in good yields. In addition, we report on the synthesis and structure of the salt like compound $[\{(Me_3Si)_2N\}BH(tmeda)]$ $[\{(C_5H_4Me)Mn(CO)_2\}_2H]$ (**3**) showing a Mn–H–Mn unit in solution and in the crystal, which was obtained from the reaction of **1b** with $[(Me_3Si)_2N]BCl_2$. © 1997 Elsevier Science S.A.

1. Introduction

$[(C_5H_5)Mn(CO)_3]$ is the parent compound for various anionic manganese complexes. Such species include the dianions $[(C_5H_4R)Mn(CO)_2]^{2-}$ (**4a**, **b**; $R = H$, Me) [1,2], as well as the mono- and dinuclear hydride complexes $[(C_5H_4R)MnH(CO)_2]^-$ (**1a**, **b**; $R = H$, Me) [1,2], and $[\{(C_5H_4R)Mn(CO)_2\}_2H]^-$ (**5a**, **b**; $R = H$, Me) [2–4], respectively. Besides, several anionic complexes of the type $[(C_5H_4R)Mn(ER'_3)(CO)_2]^-$ ($R = H$, Me; $E = $ Si, Ge, Sn, Pb; $R' = $ various ligands) showing silyl- [5,6], germyl- [7], stannyl- [7], or plumbyl ligands [1] are known. The chemistry of the dianionic complexes **4a**, **b** is closely related to the corresponding monoanions **1a**, **b**, because the latter may be either obtained by simply protonating the dianions or they are formed as byproducts during the preparation of **4a**, **b** [1,2]. A number of novel complexes exhibiting bonds between manganese and main group elements derives from these compounds mentioned above. Examples include the formation of $[\{(C_5H_4Me)Mn(CO)_2\}_2GeI]^-$ (**6**) from **5b** and GeI_2 [8], $[\{(C_5H_4Me)Mn(CO)_2\}_2SnMe_2]$ (**7**) from **4b** and Me_2SnCl_2 [2], and $[(C_5H_4Me)Mn(CO)_2C_3Ph_2]$

(**8**) from $Na[(C_5H_4Me)Mn(SiMePh_2)(CO)_2]$ (**9**) and 3,3-dichloro-1,2-diphenylchloropropene [7] (Fig. 1). The last example illustrates the use of **9** and the corresponding germyl-, stannyl-, and plumbylderivatives as synthetic equivalents to dianionic metal complexes [6]. Such compounds may react with an element dihalide under formation of an element-manganese double bond, being achieved by elimination of NaCl and the corresponding silicon-, germanium-, tin-, or leadchloride.

We reported the formation and structure of the first bridging borylene complexes **2a**, **b** obtained from the nonstoichiometric reaction of **9** with the diborane(4) derivatives $B_2(NMe_2)_2Cl_2$ and $B_2(CMe_3)_2Cl_2$, respectively, in yields less than 46% [9]. Such elementdiyl complexes of boron and aluminium are exceptionally rare. In the case of boron, compounds **2a**, **b** are still the only known representatives and just two structurally characterized bridging alanediyl complexes are known: (1) $[(CpNi)_2\{(C_5Me_5)Al\}_2]$ [10], showing a tetrahedral Ni_2Al_2 core with two bridging alanediyl moieties, was obtained by the reaction of $\{(C_5Me_5)Al\}_4$ with $[Cp_2Ni]$ and (2) $ArAl[CpFe(CO)_2]_2$ (Ar = 2-[(dimethylamino)methyl]phenyl) [11], which consists of two $[CpFe(CO)_2]$ units being bridged by the alanediyl ligand, was isolated under NaCl elimination from the
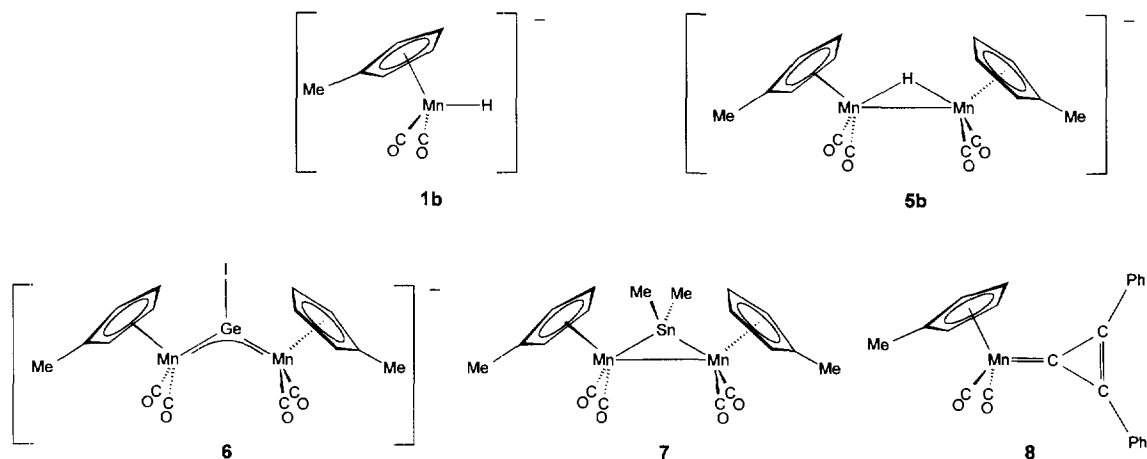
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Fig. 1.

reaction of $AlCl_2$ with two equivalents of $Na[CpFe(CO)_2]$.

Two more types of reactions between diborane(4) derivatives and transition metal complexes, leading to compounds with metal boron bonds, are known. Firstly, the oxidative addition of a diborane to a suitable metal center under cleavage of the boron boron bond and formation of bisboryl complexes [12–14], and, secondly, the reactions of $Na[CpM(CO)_n]$ ($M = W$, $n = 3$; $M = Fe$, $n = 2$) with $B_2(NMe_2)_2Cl_2$ giving the corresponding diborane(4)yl complexes $[Cl(Me_2N)B-B(NMe_2)M(Cp)(CO)_n]$ [15]. The latter are rare examples for compounds with a transition metal–boron bond, which show not the catecholgroup (catechol = 1,2-$O_2C_6H_4$) as ligand to boron [16–24].

2. Results and discussion

The reaction of $[(C_5H_4Me)MnH(SiMePh_2)(CO)_2]$ with $K[BEt_3H]$ gives the anionic hydride complex $[(C_5H_4Me)MnH(CO)_2]^-$ (**1b**); the corresponding potas-

sium salt was isolated as a yellow solid in yields > 80% (Scheme 1). The compound shows in solution ν_{CO} bands at 1863 and 1774 cm^{-1}, and a characteristic high field shifted ^{1}H-NMR signal at $\delta = -12.38$ for the manganese bonded proton. These data correspond to earlier findings, describing the preparation of **1b** in situ [1,2]. The silane $HSiMePh_2$, being formed during the reaction, can be isolated almost quantitively from the filtrate by destillation and is characterized by NMR methods.

A displacement of the manganese moiety under formation of silanes was formerly achieved by treating the complexes $[(C_5H_4Me)MnH(Si RR'R'')(CO)_2]$ (R, R', $R'' = $ various ligands) with nucleophiles such as water or methanol. Reactions with the strong bases NaH, $Li[AlH_4]$ or LiC_6H_5, however, gave the deprotonated products $M[(C_5H_4Me)Mn(Si RR'R'')(CO)_2]$ ($M = $ Li, Na) [5]. In our case the strong nucleophilic character [25] rather than the basicity of $K[BEt_3H]$ seems to be responsible for the course of the reaction.

We have started to investigate the reactivity of **1b** towards halogenated monoboranes and diborane(4)
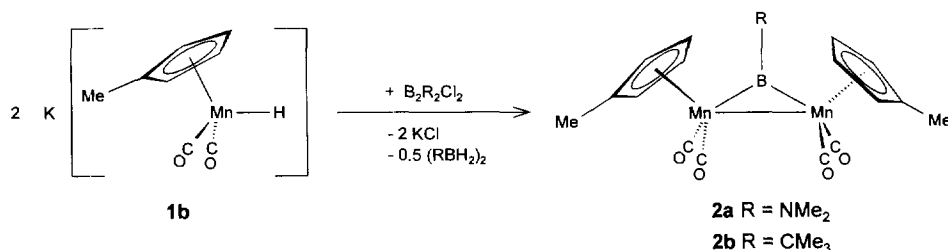
Scheme 1.
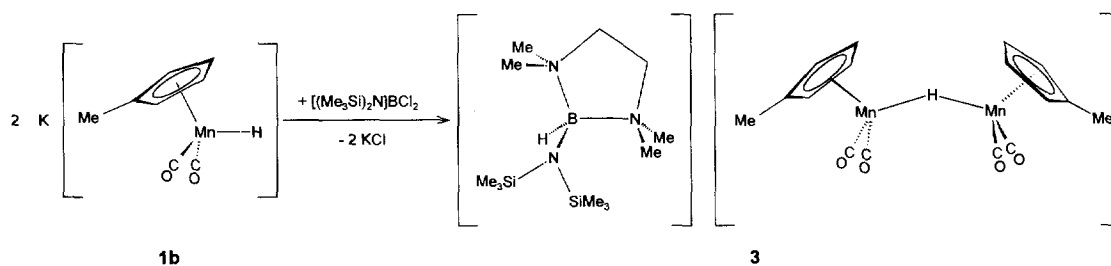
Scheme 2.

derivatives and improved the synthesis [1] of the bridging borylene complexes [{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$BR], (2a, b; R = Me$_2$N, Me$_3$C) [5,6] (Scheme 2). The borylene complexes are formed under cleavage of the boron boron bond and formation of stoichiometric amounts of the corresponding diborane(6) derivatives (RBH$_2$)$_2$, which were isolated from the reaction mixture and characterized by NMR methods. Obviously, a hydrogen transfer from manganese to boron occurres, since reactions in deuterated solvents yield the same products. 2a, b were isolated as red crystalline solids in good yields between 60% and 70% and their spectroscopical properties correspond to our earlier findings [5,6].

The cleavage of the boron boron bond in the starting diborane(4) decisively contributes to the formation of the borylene complex, since reactions of 1b with the boranes RR'NBCl$_2$ (R, R' = Me; R = CMe$_3$, R' = SiMe$_3$; R, R' = SiMe$_3$) under the same conditions always led to various boron containing products with uncharacteristic ^{11}B-NMR signals in the range of δ = 30–35 ppm. The reaction of 1b with [(Me$_3$Si)$_2$N]BCl$_2$ in the presence of tmeda, however, gives the salt like compound [{(Me$_3$Si)$_2$N}BH(tmeda)][{(C$_5$H$_4$Me)-Mn(CO)$_2$}$_2$H] (3) in 48% yield as dark red brown crystals (Scheme 3). Again, a hydrogen transfer from manganese to boron occurres, and a binuclear mangenese complex, now with a bridging hydrogen atom, is formed. The constitution of 3 in solution is derived from the NMR and IR spectra. The boronium ion shows a characteristic highfield shifted doublet in the ^{11}B-NMR spectrum at δ = 9.94 and a ν_{BH} band in the IR spectrum at 2017 cm^{-1}. The anion is characterized by a highfield shifted ^{1}H-NMR signal for the bridging hydrogen atom at δ = −27.48 and four ν_{CO} bands in the IR spectrum at 1902, 1869, 1823, and 1800 cm^{-1}. These results bear a strong resemblance to the corresponding data of the anionic species [{(C$_5$H$_4$$R$)Mn(CO)$_2$}$_2$H]$^-$ (5a, b; R = H, Me), which were characterized with Li, Na, K, NEt$_4$ [2], Na(2,2,2-crypt) [2] [3,4], and Na(2,1,1-

crypt) [26] as counterions in solution. In the crystal both the boronium ion and the dinuclear anion of 3 adopt a C_1 symmetry. Large displacement parameters are found for the MeCp-ring (C11–C16) bonded to Mn2. Due to its incorporation into a five membered ring, boron shows a greater deviation from the tetrahedral coordination as such boronium ions without bridging amine ligands [27]. The dinuclear anion, however, exhibits a remarkable structural difference to related compounds with respect to the Mn–Mn distance (Table 1). [{(C$_5$H$_5$)Mn(CO)$_2$}$_2$H]$^-$ (5a) and [{(C$_5$H$_4$Me)Mn(CO)$_2$}$_2$H]$^-$ (5b), which were structurally characterized with the counterions Na(2,2,2-crypt) [3,4], and Na(2,1,1-crypt) [26], respectively, show Mn–Mn distances of 298.3(1) pm and 296.6(3) pm, respectively. For 3, however, a significantly longer distance of 3.099(1) pm was found. The extension of the intermetallic distance is paralleled by a flatening of the Mn–H–Mn angle from 128(7)° for 5b to 152(4)° for 3, while the Mn–H distances in both compounds are in the range of 160 pm. Secondary effects such as crystal packing or the influence of the various cations appear to be feasible explanations for the deviation of these structural features.

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. Heraeus TQ 150, and TQ 718 high pressure mercury lamps, respectively, were used for irradiations. [(Me$_3$Si)$_2$N]BCl$_2$ [28], B$_2$(Me$_2$N)$_2$Cl$_2$ [29], and B$_2$(Me$_3$C)$_2$Cl$_2$ [30] 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 BF$_3$ · OEt$_2$

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[1] The reaction was merely successful if isolated 1b was used as a starting material, all attempts with the same compound prepared in situ in thf solution (see Ref. [1,2]) gave no comparable results.

[2] 2,1,1-crypt = C$_{14}$H$_{28}$N$_2$O$_4$; 2,2,2-crypt = C$_{18}$H$_{36}$N$_2$O$_6$.
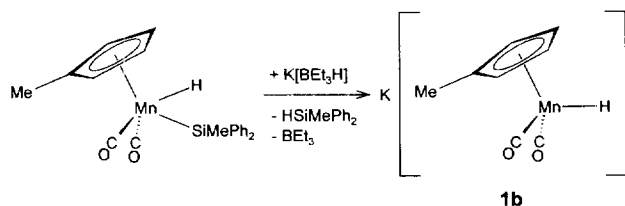
Scheme 3.

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, Modell 1106.

3.1. Synthesis of $K[(C_5H_4Me)MnH(CO)_2]$ (1b)

A solution of 25.00 g (114.63 mmol) $[(C_5H_4Me)Mn(CO)_3]$ and 15.15 g (76.39 mmol) $HSiMePh_2$ in 1000 ml hexane is irradiated for 12 h at $-30°C$. An equimolar amount of $K[BEt_3H]$ (1 M solution in THF) is added dropwise to the solution and immediately a yellow precipitate is formed. The mixture is stirred for 2 h at room temperature and the precipitate is filtered, washed thoroughly with several portions of hexane, and dried in high vacuum. Yield: 15.35 g (87.33%). Surplus $[(C_5H_4Me)Mn(CO)_3]$ and the $HSiMePh_2$ which is formed on the addition of $K[BEt_3H]$ may be recovered in very high yields from the filtrate by destillation. ^1H-NMR (C_4D_8O): $\delta = -12.38$ (s, 1H, MnH), 1.86 (s, 3H, Me), 4.08 (br, 4H, C_5H_4). ^{13}C-NMR: $\delta = 15.58$ (Me), 77.68, 79.03, 96.41 (C_5H_4), 240.87 (CO). IR (C_4H_8O): ν_{CO} 1863 (s), 1774 (s).

3.2. Improved syntheses of $[\{(C_5H_4Me)Mn(CO)_2\}_2 B(NMe_2)\}(Mn-Mn)]$ (2a) and $[\{(C_5H_4Me)Mn(CO)_2\}_2 B(CMe_3)\}(Mn-Mn)]$ (2b)

In a typical experiment 5.10 g (22.17 mmol) $K[(C_5H_4Me)MnH(CO)_2]$ are suspended in 70 ml benzene and 11.08 mmol of the diborane(4) are added dropwise at room temperature. The mixture is stirred for 1 d at room temperature while the colour changes from

orange to dark red. The solvent is pumped off and the residue is treated with 100 mL hexane. After filtration and cooling to $-30°C$, the product is obtained as dark red crystals. Yields range from 60% to 70%.

3.3. Synthesis of $[\{(Me_3Si)_2N\}BH(tmeda)]$ $[\{(C_5H_4Me)Mn(CO)_2\}_2H]$ (3)

A suspension of 2.82 g (12.25 mmol) 1b and 0.71 g (6.13 mmol) tmeda in 50 ml benzene is stirred for 10 min at room temperature. 1.48 g (6.13 mmol) $[(Me_3Si)_2N]BCl_2$ are added dropwise and the suspension turns dark brown immediately. The mixture is stirred for 2 h, evaporated to dryness, and the resulting solid is treated with 35 ml hexane and 15 ml toluene. The solution is filtered and dark red brown crystals are collected from the filtrate at $-30°C$ after several days. Yield: 1.98 g (48.23%). ^1H-NMR (C_6D_6): $\delta = -27.48$ (s, 1H, MnH), 0.02, 0.11 (2s, 18H, Me_3Si), 2.21, 2.23 (2s, 18H, NCH_3), 2.33 (s, 6H, MeC_5H_4), 3.19 (s, 4H, NCH_2), 4.48, 4.64 (2s, 8H, C_5H_4). ^{11}B-NMR: $\delta = 9.94$ (d, $^1J_{BH} = 109.6$ Hz). ^{13}C-NMR: $\delta = 3.69, 5.01$ (SiMe$_3$), 15.29 (MeC_5H_4), 48.18, 54.08 (NMe), 57.56 (NCH_2), 80.01, 81.48, 96.85 (C_5H_4), 240.79 (CO). IR (C_4H_8O): ν_{BH} 2017 (w); ν_{CO} 1902 (s), 1869 (vs), 1823 (vs), 1800 (sh).

Anal. calcd. for $C_{28}H_{50}BN_3O_4Si_2Mn_2$: C, 50.22; H, 7.52; N, 6.27. Found: C, 50.55; H, 7.45; N, 6.22.

Table 1
Selected bond distances (Å) and angles (deg) for 3

Distances (Å)		Angles (deg)	
B–N1	1.487(6)	N1–B–N2	117.1(3)
B–N2	1.669(7)	N2–B–N3	99.3(4)
B–N3	1.667(7)	N1–B–N3	119.4(4)
B–H2	1.16(4)	N2–B–H2	101(2)
Mn1–Mn2	3.099(1)	Mn1–H1–Mn2	152(4)
Mn1–H1	1.61(6)	C1–Mn1–H1	102(2)
Mn2–H1	1.59(6)	C1–Mn1–C2	93.3(2)
Mn1–C1	1.751(5)	C3–Mn2–H1	101(2)
Mn2–C3	1.755(5)	C3–Mn2–C4	93.2(3)

Table 2
Summary of X-ray crystallographic data for 3

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Empirical formula	$Mn_2SiO_4N_3C_{28}BH_{48}$
fw	639.49
Cryst. syst.	triclinic
Space group	$P\bar{1}$ (No 2)
a/Å	10.694(2)
b/Å	12.469(2)
c/Å	13.099(2)
α/deg	93.92(1)
β/deg	97.92(2)
γ/deg	101.95(2)
V/Å^3	1684(1)
d_{calcd}/g cm^{-3}	1.261
Z	2
F (000)	676
μ (Mo Kα)/cm^{-1}	7.87
T/K	203
Scan mode	Ω
Scan range/°	$3 \leq \Theta \leq 30$
Total No. of data	10630
No. of unique observed data $I > 1.0\sigma(I)$	4981
No. of variables	369
R, R_w	0.080, 0.064
Weighting factor, w	$w = 1/\sigma^2(Fo)$
GOF	1.360
Max resid. density/eÅ^{-3}	0.34
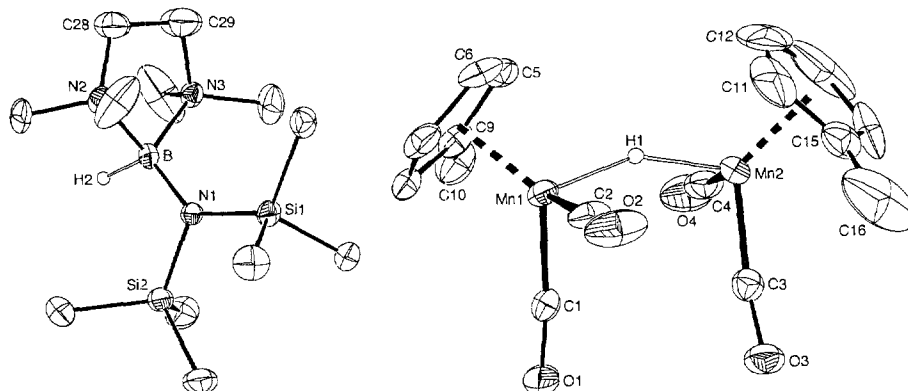
Fig. 2.

3.4. Structure determination of 3

A crystal with approx. dimensions of 0.1 × 0.3 × 0.4 mm was studied on an Enraf–Nonius CAD4 diffractometer with graphite-monochromized Mo Kα radiation (λ = 0.71073 Å). Crystal data and parameters of data collection and structure refinement are compiled in Table 2. The structure was solved by direct methods using SHELXS-86 [31] and refinement with MolEN [32]. In the final least squares full-matrix refinement, all non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were included as riding atoms with an idealized geometry (C–H = 0.98 Å, $B_H = 1.3B_C$, except H1 (bonded to Mn) and H2 (bonded to B) which are refined isotropically.

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