Diboran(4)yl Groups as Ligands to Transition Metals

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Received April 3, 1996

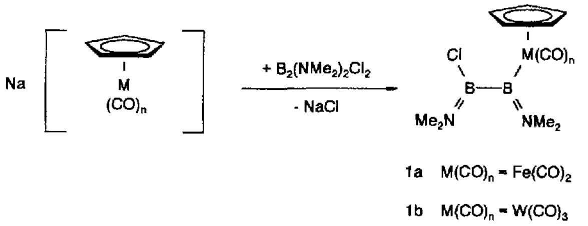
Key Words: Diboranes / Transition-metal boryl complexes

Reaction of Na[(Cp)Fe(CO)$_2$] and Na[(Cp)W(CO)$_3$] with $B_2(NMe_2)_2Cl_2$ yields the first transition metal-substituted diboranes [Cl(Me$_2$N)B−B(NMe$_2$)M(Cp)(CO)$_n$] [M(Cp)(CO)$_n$ = Fe(Cp)(CO)$_2$, W(Cp)(CO)$_3$] (**1a**, **b**). The compounds were characterized in solution by NMR methods and in the crystal by X-ray structural determination.

Recently, several transition metal boryl compounds were characterized, most of them containing the 1,2-phenylenedioxy group (1,2-$O_2C_6H_4$ = cat) as ligand to boron[1]. In general, these compounds had been obtained by oxidative addition of (cat)BH to complexes of late transition metals or by salt elimination from (cat)BCl and anionic transition metal complexes. Corresponding reactions with diborane(4) derivatives proceed with cleavage of the boron-boron bond and addition of the boron-containing fragments to the metal center, again yielding boryl complexes[2]. In the case of the reaction of several 1,2-dichlorodiboranes with K[(η^5-C_5H_4Me)Mn(SiMePh$_2$)(CO)$_2$] a different reaction was found. The diboranes reacted with formation of binuclear manganese complexes with a bridging borylene group BR (R = NMe$_2$, *t*Bu), and (RBH$_2$)$_2$ was found as boron-containing byproduct[3]. In this paper we report on the syntheses and structures of the first transition metal-substituted diborane(4) compounds.

Results and Discussion

Reaction of Na[M(Cp)(CO)$_n$] [M(Cp)(CO)$_n$ = Fe(Cp)(CO)$_2$, W(Cp)(CO)$_3$] with $B_2(NMe_2)_2Cl_2$ yields the transition metal diboranyl complexes **1a**, **b** according to Eq. (1).



(1)

These compounds were isolated as brown or dark yellow crystals, which can be handled in air for short periods and can be stored under nitrogen at room temperature. In solution both complexes **1a**, **b** show two characteristic ^{11}B-NMR shifts δ = 39.0 and 69.5 and δ = 40.3 and 62.7, respectively. The signals at higher field are in the same region as the shift of the starting material at δ = 37.5[4], the signals of the transition metal-substituted boron atoms, however, exhibit the expected low-field shift of 20−30 ppm. The four methyl groups of both compounds bound to nitrogen show four signals in the ^{1}H- and ^{13}C-NMR spectra, respectively, which is due to a restricted rotation with respect to the B−N bond.

The X-ray structure analyses reveal that both molecules adopt a C_1 symmetry in the crystal. The boron and nitrogen atoms are trigonal-planar-coordinated and both boryl groups are almost perpendicular to each other (dihedral angle for **1a**, **b**: 92.4 and 92.3°, resp.). The B−N distances are in a range of 137.6(3) and 138(1) pm and the B−B distances amount to 168.3(3) and 169(1) pm, respectively. Hence, the geometry of **1a**, **b** is comparable to other structurally characterized diborane(4) derivatives having two dimethylamino groups[5]. The metal boron distances are 209.0(3) and 237.0(8) pm, respectively, thus being 13 and 18 pm longer as for known boryl complexes of iron and tungsten[1].

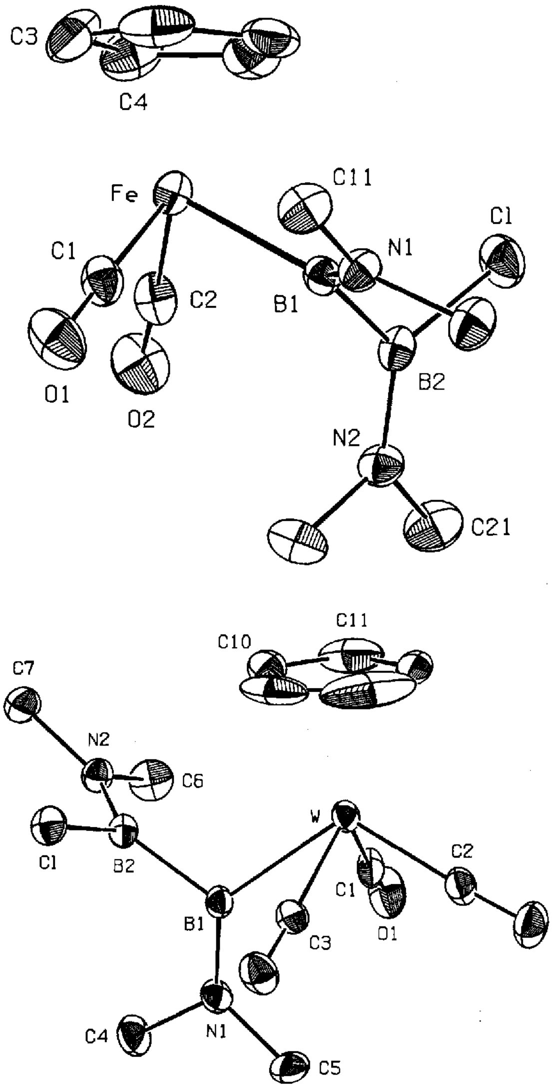
The substitution of one chloro ligand by the [M(Cp)(CO)$_n$] group according to Eq. (1) proceeds under mild conditions in good yields. Exchange of the second chlorine, however, fails even in refluxing toluene, obviously for steric reasons.

The described compounds are the first examples for diboran(4)yl groups as boron-bound ligands to transition metals. The absence of the catechol group as stabilizing ligand for such boryl complexes opens up the perspectives of investigating the reaction behaviour of metal-coordinated boron which is yet unknown. Possible reactions which are worth to be examined are for example the exchange of the boron-bound amino ligands or the cleavage of the boron-boron bond.

Experimental

All manipulations were carried out under dry nitrogen in Schlenk glassware. Solvents were dried by standard procedures, distilled and stored under nitrogen and molecular sieves. $B_2(NMe_2)_2Cl_2$[4], Na[Fe(Cp)(CO)$_2$][6], and Na[W(Cp)(CO)$_3$][7] were synthesized as described in the literature. − NMR: Varian Unity 500 at 499.843 (^{1}H, standard TMS intern), 150.364 (^{11}B, standard $BF_3 \cdot OEt_2$ in C_6D_6 extern), 125.639 MHz (^{13}C{^{1}H}, APT, stand-

Figure 1. Molecular structures of **1a**, **b** (thermal ellipsoids scaled to 30% probability). Selected bond lengths [pm] and angles [°]; **1a**: Fe–B1 209.0(3), N1–B1 137.6(3), N2–B2 137.7(3), B1–B2 168.3(3); Fe–B1–B2 111.2(2); **1b**: W–B1 237.0(8), N1–B1 138(1), N2–B2 137(1), B1–B2 169(1); W–B1–B2 109.7(5)



ard TMS intern). – Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, model 1106. – IR: Perkin-Elmer FT-IR 1720 x.

2-Chloro-1-[dicarbonyl(η^5-cyclopentadienyl)iron]-1,2-bis(dimethylamino)diborane(4) (**1a**): Neat $B_2(NMe_2)_2Cl_2$ (0.93 g, 5.1 mmol) was added to a suspension of Na[(Cp)Fe(CO)$_2$] (1.02 g, 5.1 mmol) in benzene (20 ml) at ambient temp. The reaction mixture was stirred for 24 h. After removal of the solvent in high vacuo, the solid residue was extracted with 30 ml of hexane. After filtration and cooling to −30°C, 0.86 g (52%) of pure **1a** was obtained as brown crystals, m.p. 92°C. – ^{1}H NMR: δ = 2.51, 2.77, 2.82, and 2.84 (4 s, 3 H each, NMe$_2$), 4.35 (s, 5 H, C_5H_5). – ^{11}B NMR: δ = 39.0 (BCl), 69.5 (BFe). – ^{13}C NMR: δ = 37.01, 40.96, 44.06, and 47.68 (NMe$_2$), 83.64 (C_5H_5), 217.15 and 217.32 (CO). – IR (KBr): $\tilde{\nu}$ = 1988 (m), and 1932 (m) cm^{-1} (C=O). – $C_{11}H_{17}B_2ClFeN_2O_2$ (322.2): calcd. C 41.01, H 5.32, N 8.69; found C 40.71, H 5.39, N 8.51.

2-Chloro-1-[tricarbonyl(η^5-cyclopentadienyl)tungsten]-1,2-bis(dimethylamino)diborane(4) (**1b**): $B_2(NMe_2)_2Cl_2$ (0.46 g, 2.6 mmol) was added to a suspension of Na[(Cp)W(CO)$_3$] (0.91 g, 2.6 mmol) in benzene (20 ml) at ambient temp. The reaction mixture was stirred for 24 h. After removal of the solvent in high vacuo, the solid residue was extracted with 30 ml of hexane. After filtration and cooling to −30°C, 0.49 g (40%) of pure **1b** was obtained as yellow crystals, m.p. 104°C. – ^{1}H NMR: δ = 2.40, 2.54, 2.67, and 2.88 (4 s, 3 H each, NMe$_2$), 4.94 (s, 5 H, C_5H_5). – ^{11}B NMR: δ = 40.3 (BCl), 62.7 (BW). – ^{13}C NMR: δ = 36.76, 41.12, 42.95, and 48.07 (NMe$_2$), 92.34 (C_5H_5), 216.26, 219.16, and 222.98 (CO). – IR (KBr): $\tilde{\nu}$ = 1988 (m), 1908 (m), and 1892 (m) cm^{-1} (C=O). – $C_{12}H_{17}B_2ClN_2O_3W$ (478.2): calcd. C 30.14, N 5.86, H 3.58; found C 30.04, N 5.80, N 3.67.

Crystal Structure Analysis of **1a** *and* **1b**: For both structures geometry and intensity data were collected on an Enraf-Nonius CAD4 diffractometer (Mo-K_α radiation, λ = 0.7107 Å). Structure solution and refinement with SDP[8] for **1a** and with MolEN[9] for **1b**. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were treated as riding [d_{C-H} = 0.98 Å, $B_{iso}(H) = 1.3 \cdot B_{iso}(C)$]. A weighting scheme $w = 1/\sigma^2(F_o)$ was applied to all reflections.

1a: Temperature −10°C; crystal dimensions 0.20 × 0.25 × 0.25 mm^3, formula $C_{11}H_{17}B_2ClFeN_2O_2$, molecular mass 322.19 g · mol^{-1}; cell constants a = 9.579(6), b = 9.897(3), c = 8.929(6) Å, α = 99.08(4), β = 114.96(5), γ = 86.38(4)°; V = 758(2) Å^3; space group triclinic $P\bar{1}$ (no. 2), Z = 2, $D_{calcd.}$ = 1.412 g · cm^{-3}, μ = 11.67 cm^{-1}, $F(000)$ = 332.0; 2829 reflections measured in the range $3 \leqslant \Theta \leqslant 25°$ (ω scan), 2376 of which with $I > 3\sigma(I)$, 2338 independent reflections with $I > 1\sigma(I)$ for 173 parameters; no correction for absorption, sec. extinction coefficient $E = 1.43 \cdot 10^{-6}$[10], $R(F)$ = 0.036, $R_w(F)$ = 0.055, GOF = 1.917; residual electron density 0.329 e/Å^3.

1b: Temperature −70°C; crystal dimensions 0.10 × 0.15 × 0.50 mm^3, formula $C_{12}H_{17}B_2ClN_2O_3W$; molecular mass 478.21 g · mol^{-1}; cell constants a = 21.918(3), b = 10.247(1), c = 7.398(2) Å, V = 1661.4(8) Å^3; space group orthorhombic $Pna2_1$ (no. 33), Z = 4, $D_{calcd.}$ = 1.912 g · cm^{-3}, μ = 72.71 cm^{-1}, $F(000)$ = 912.0; 5105 reflections measured in the range $3 \leqslant \Theta \leqslant 30°$ (ω scan), 3562 of which with $I > 3\sigma(I)$, 3610 independent reflections with $I > 1\sigma(I)$ for 189 parameters; emp. absorption correction by PSI scans[11] (max. transmission 1.00, min. 0.84), no correction for extinction, $R(F)$ = 0.032, $R_w(F)$ = 0.037, GOF = 1.166; residual electron density 1.85 e$^-$/Å^3 (0.77 Å from W)[12].

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[12] Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-405252 (**1a**) and CSD-405330 (**1b**).

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