Boryl and Bridged Borylene Complexes of Iron and Ruthenium

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Keywords: Boron / Iron / Ruthenium / Boryl Complexes / Borylene Complexes

The reactivity of aminodihaloboranes R_2NBX_2 (R = Me, $SiMe_3$; X = Cl, Br) towards transition metal complexes of the type $Na[(\eta^5\text{-}C_5R'_5)M(CO)_2)]$ (M = Fe, Ru; R′ = H, Me) was investigated. In the case of Me_2NBBr_2 and M = Fe the borylcomplexes $[(\eta^5\text{-}C_5R'_5)(CO)_2Fe\{BBr(NMe_2)\}]$ ($C_5R'_5$ = C_5H_5 **9a**; $C_5R'_5$ = C_5H_4Me **9b**; $C_5R'_5$ = C_5Me_5 **10**) were obtained. The compounds **9a** and **9b** were formed together with the corresponding bridged borylene complexes $[\mu\text{-}BNMe_2(\mu\text{-}CO)\{(\eta^5\text{-}C_5R'_5)Fe(CO)\}_2]$ ($C_5R'_5$ = C_5H_5 **11a**; $C_5R'_5$ = C_5H_4Me **11b**) in a 1:1 ratio, the latter, however, could be isolated from these mixtures as pure materials. In addition the novel boryl and borylene ruthenium complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Ru\{BX(NMe_2)\}]$ (X = Cl **12a**; X = Br **12b**), $[(\eta^5\text{-}C_5H_5)(CO)_2Ru\{BCl\{NSiMe_3\{BClN(SiMe_3)_2\}\}\}]$ (**13**) and $[\mu\text{-}BN(SiMe_3)_2(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_5)Ru(CO)\}_2]$ (**14**) were obtained by similar methods. All compounds were characterized by multinuclear NMR and IR spectroscopy. The structure of **13** in the solid state was determined by a single-crystal X-ray diffraction study.

Introduction

Transition metal complexes of boron, especially boryl and borylene complexes, have attracted considerable interest over the last decade.[1][2] The synthesis of boryl complexes, which are known to be versatile compounds for the functionalization of hydrocarbons,[3a−3c,4] is achieved mainly by the use of 1,2-dioxobenzo- or catecholborane and its derivatives.[5a−5j] More recently, however, nitrogen-substituted boranes have also proved to be well suited for the synthesis of such compounds. Examples include aminoboryl complexes,[6a,6b] diborane(4)yl complexes[7a,7b] and η^1-borazine complexes.[8]

In contrast to numerous reports on boryl complexes, only very few bridged[9−11] and terminal[12][13] borylene complexes are known. The first compounds of this class, bridged borylene complexes of the type $[\mu\text{-}BR\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2]$ (R = NMe_2 **1a**; R = *t*Bu **1b**), were obtained by an unprecedented reaction of diboranes(4) with cleavage of the boron boron bond[9a,9b] and, recently, the corresponding dinuclear cobalt complex $[\mu\text{-}BH(PMe_3)(\mu\text{-}CO)\{Co(CO)_3\}_2]$ (**2**) was obtained by a similar cleavage reaction of 1,2-bis(trimethylphosphane)diborane(4) (Scheme 1).[10] In the case of compounds **1** the range of bridged borylene complexes was broadened by utilizing substitution reactions at the metal-coordinated boron with preservation of the central Mn_2B core.[11] Both synthetic methods, however, are very specific and are restricted to the examples mentioned above. In order to open a more general access to bridged borylene complexes we investigated the reactions of aminodihaloboranes with anionic transition metal complexes. The compounds $[\mu\text{-}BN(SiMe_3)_2(\mu\text{-}CO)\{(\eta^5\text{-}C_5R'_5)Fe(CO)\}_2]$ ($C_5R'_5$ = C_5H_5 **3a**; $C_5R'_5$ = C_5H_4Me **3b**) represent the first borylene complexes obtained by this method (Scheme 1).[6b]

In the first part of the present paper we describe the synthesis of boryl and bridged borylene complexes from the reaction of Me_2NBBr_2 with $Na[(\eta^5\text{-}C_5R_5)Fe(CO)_2)]$ (R = H, Me) and point out some differences with respect to the corresponding reactions of Me_2NBCl_2.[6b]

The second part of the paper reports on novel ruthenium complexes of boron, including the synthesis and spectroscopic characterization of the first bridged borylene complex of this transition metal.

Results and Discussion

Iron Complexes

A number of iron complexes of boron were obtained by salt elimination reactions employing the strongly nucleophilic compound $Na[(\eta^5\text{-}C_5R_5)Fe(CO)_2)]$ (R = H, Me) and suitable haloboranes. Examples include boryl complexes such as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2)BCat]$ (Cat = 1,2-$O_2C_6H_4$) (**4**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2)BPh_2]$ (**5**)[5a], the diborane(4)yl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2)\{B(NMe_2)BCl(NMe_2)\}]$ (**6**)[7a] and the η^1-borazine complexes $[\{(C_5R_5)(CO)_2Fe\}_n\text{-}Cl_{3-n}B_3N_3H_3]$ (n = 1, C_5R_5 = C_5Me_5 **7a**; n = 2, C_5R_5 = C_5H_4Me **7b**; n = 3, C_5R_5 = C_5H_5 **7c**).[8] In the case of aminodichloroboranes, corresponding reactions with the sterically less demanding Me_2NBCl_2 always resulted in the formation of monosubstituted boryl complexes $[(\eta^5\text{-}C_5R_5)(CO)_2Fe\{BCl(NMe_2)\}]$ (C_5R_5 = C_5Me_5 **8a**; C_5R_5 = C_5H_4Me **8b**; C_5R_5 = C_5H_5 **8c**) regardless of the iron to boron ratio.[6b] The more bulky, albeit more electrophilic $(Me_3Si)_2NBCl_2$, however, reacts with substitution of both the chloride ligands yielding the bridged borylene complexes $[\mu\text{-}BN(SiMe_3)_2(\mu\text{-}CO)\{(\eta^5\text{-}C_5R'_5)Fe(CO)\}_2]$ ($C_5R'_5$ = C_5H_5 **3a**; $C_5R'_5$ = C_5H_4Me **3b**).[6b]

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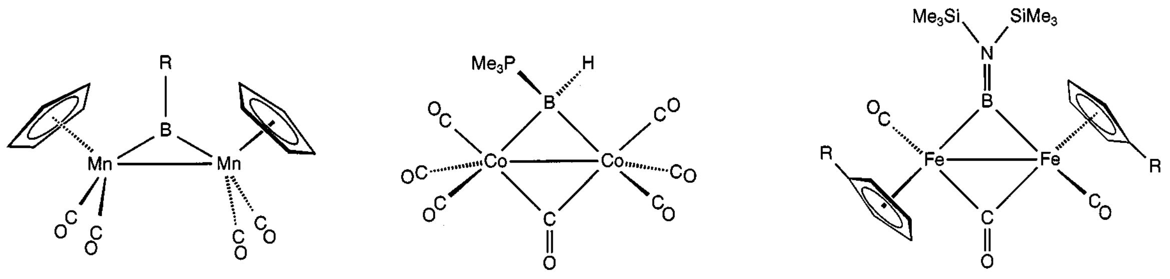


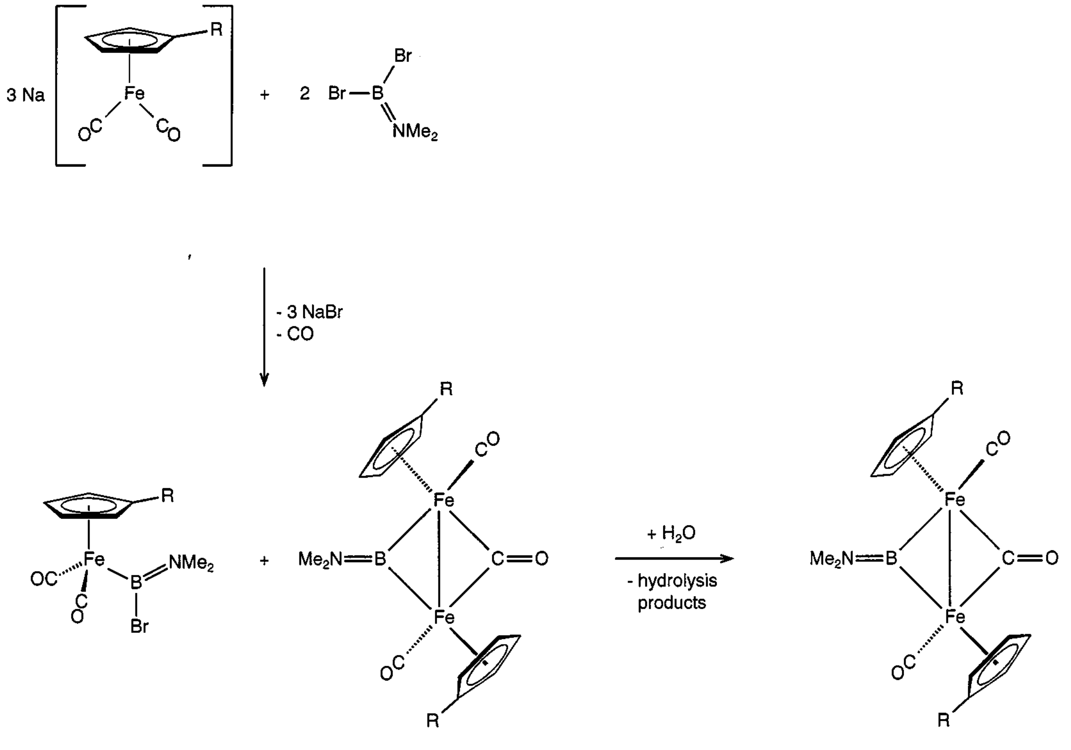
1a, R = NMe$_2$
1b, R = *t*Bu

2

3a, R = H
3b, R = Me

Scheme 1. Examples for bridged borylene complexes

Due to the weaker boron halide bonds,[14a,14b] Me$_2$NBBr$_2$ proves to be more reactive than the corresponding aminodichloroborane and reacts with Na[(η^5-C$_5$R$_5$)Fe(CO)$_2$)] in benzene at ambient temperature to form a 1:1 mixture of the boryl complexes [(η^5-C$_5$R'$_5$)(CO)$_2$Fe{BBr(NMe$_2$)}] (C$_5$R'$_5$ = C$_5$H$_5$ **9a**; C$_5$R'$_5$ = C$_5$H$_4$Me **9b**) and the corresponding bridged borylene complexes [μ-BNMe$_2$(μ-CO){(η^5-C$_5$R'$_5$)Fe(CO)}$_2$] (C$_5$R'$_5$ = C$_5$H$_5$ **11a**; C$_5$R'$_5$ = C$_5$H$_4$Me **11b**) according to Scheme 2. These mixtures were obtained as dark red solids from hexane at −30°C and attempts to seperate the boryl and borylene complexes by crystallisation or sublimation failed. The multinuclear NMR spectra of these mixtures, however, show no significant impurities and it was possible to assign all signals by comparison with the related compounds **8b**, **c** and **3a**, **b**, respectively. The boryl complexes **9a**, **b** are characterized by low-field-shifted signals in the ^{11}B-NMR spectra at δ = 54.5 (**9a**) and 55.0 (**9b**), and show the expected double sets of signals for the Me$_2$N groups in both ^{1}H- and ^{13}C-NMR spectra, indicating a hindered rotation of this group with respect to the boron nitrogen double bond. Interestingly, treatment of the obtained mixtures with water in diethyl ether under air (Scheme 2) resulted in a selective hydrolysis of the boryl complexes and the borylene complexes **11a**, **b** could subsequently be isolated as dark red crystals. The stability of **11a**, **b** towards air and water is in sharp contrast

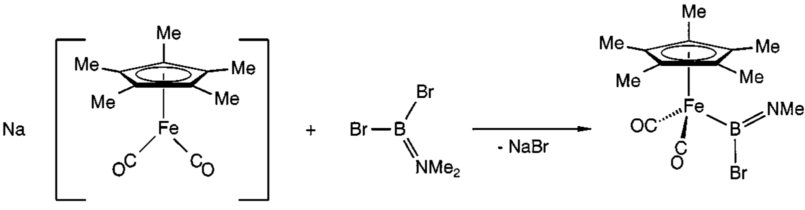


9a, R = H
9b, R = Me

11a, R = H
11b, R = Me

11a, R = H
11b, R = Me

Scheme 2. Syntheses of the bridged borylene complexes **11a**, **b**



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to the known reactivity of [μ-BN$(SiMe_3)_2$(μ-CO){(η^5-$C_5R'_5$)Fe(CO)}$_2$] ($C_5R'_5$ = C_5H_5 **3a**; $C_5R'_5$ = C_5H_4Me **3b**),[6b] which decompose under these conditions, whereas the related dimethylaminoborylene complex [μ-$BNMe_2${(η^5-C_5H_5)Mn$(CO)_2$}$_2$] (**1a**)[9a,9b] exhibits a very similar stability. One might expect the electron-withdrawing effect of the nitrogen bound $SiMe_3$ groups and, hence, the enhanced electrophilicity of the boron atom in **3a**, **b** to be responsible for this different reactivity. The molecular structure of **11a**, **b** in solution can be deduced from the NMR and IR spectra. Due to the formation of two iron boron bonds these borylene complexes show highly deshielded signals in their ^{11}B-NMR spectra at δ = 103.5 (**11a**) and 104.5 (**11b**). The presence of a bridging carbonyl group, which has already been found for **3a**, **b** is established by ^{13}C-NMR and IR spectroscopic data (**11a,** δ = 275.8, ṽ = 1942 cm^{-1}, 1776 cm^{-1}; **11b,** δ = 277.0, ṽ = 1946 cm^{-1}, 1778 cm^{-1}).

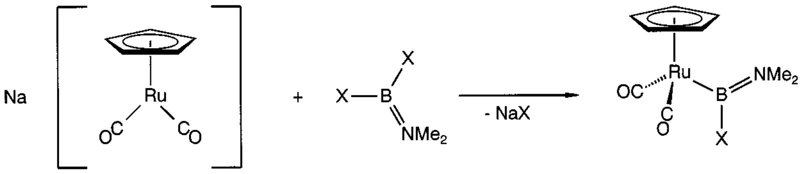
Similar reactions of Me_2NBBr_2 with the sterically demanding Na[(η^5-C_5Me_5)Fe$(CO)_2$)] result in the selective substitution of only one bromide and formation of the boryl complex [(η^5-C_5Me_5)$(CO)_2$Fe{BBr(NMe_2)}] (**10**), which is isolated as a brown crystalline solid in 34% yield after recrystallization from hexane (Equation 1). The structure of **10** in solution is derived from the NMR and IR spectra, which resemble those of the related compounds **8a−c** and **9a**, **b**, e.g. the signal in the ^{11}B-NMR spectrum at δ = 57.2 and the characteristic double sets of signals for the Me_2N group in both ^{1}H- and ^{13}C-NMR spectra. The CO stretching frequencies in the IR spectrum at 1991 cm^{-1} and 1933 cm^{-1} give no evidence for any iron-boron π-backbonding in solution, which corresponds to the findings for other nitrogen-substituted boryl complexes of iron.[6b,7a,8]

Ruthenium Complexes

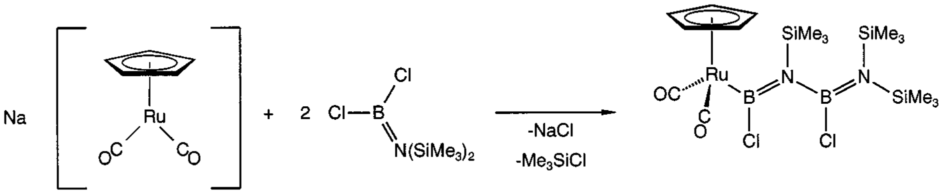
Ruthenium complexes of boron, which are characterized by two-centre, two-electron bonds between ruthenium and boron are extremely rare. The few examples known, include the boryl complexes [(η^5-C_5Me_5)Ru$(CO)_2$){B(1,2-O_2-3,5-$Me_2C_6H_2$)}][4] and [Ru(BR_2)Cl(CO)$(PPh)_3$] (R = various ligands),[15] as well as the diborane(4)yl complex [(η^5-C_5H_5)Ru$(CO)_2$){B(NMe_2)BCl(NMe_2)}].[7b] The latter represents the only structurally characterized compound of this type.

The anionic ruthenium moiety [(η^5-C_5H_5)Ru$(CO)_2$)]$^-$ was reported to be less nucleophilic than the corresponding iron anion [(η^5-C_5H_5)Fe$(CO)_2$)]$^-$ and hence one might expect a reduced, and probably more selective, reactivity with respect to salt eliminations.[16] Indeed, the reaction of Na[(η^5-C_5H_5)Ru$(CO)_2$)] with Me_2NBX_2 (X = Cl, Br) results in the selective formation of the borylcomplexes [(η^5-C_5H_5)$(CO)_2$Ru{BX(NMe_2)}] (X = Cl **12a**; X = Br **12b**) with substitution of only one halide according to Equation 2. Both compounds can be isolated as dark yellow crystalline materials from hexane in yields of 77% (**12a**) and 41% (**12b**), respectively. These boryl complexes are stable at ambient temperature in hydrocarbon solution under nitrogen but decompose rapidly on contact with air or water. The structure of **12a, b** in solution is derived from multinuclear-NMR and IR spectroscopy. The signals in the ^{11}B-NMR spectra at δ = 50.3 (**12a**) and 48.1 (**12b**) are considerably shifted to lower field with respect to the signals of the starting aminoboranes (δ ≈ 30),[17] thus appearing in the expected region for aminoboryl complexes. The double sets of signals for the Me_2N groups in the NMR spectra are again consistent with a hindered rotation of this group with respect to the boron nitrogen double bond. A variable temperature ^{1}H-NMR spectroscopic study of **12a** shows a coalescence of the two resonances at 98 °C from which a value of $\Delta G^{\neq}$ = 75.4 kJ/mol for the rotation barrier can be calculated. This figure is in agreement with a value of $\Delta G^{\neq}$ = 72.3 kJ/mol for the related iron complex [(η^5-C_5R_5)$(CO)_2$Fe{BCl(NMe_2)}] (C_5R_5 = C_5H_4Me **8b**).[6b] The IR spectra of both compounds show no evidence for a metal boron π-interaction, since the CO stretching frequencies (**12a**, 2019 cm^{-1}, 1956 cm^{-1}; **12b**, 2022 cm^{-1}, 1960 cm^{-1}) closely resemble those of the corresponding methyl ruthenium complex (2028 cm^{-1}, 1960 cm^{-1}).[18]

The compound Na[(η^5-C_5H_5)Ru$(CO)_2$)] exhibits a markedly different reactivity towards $(Me_3Si)_2NBCl_2$ and the nature of the reaction products depends on the reaction conditions and stoichiometry employed. According to Equation 3, Na[(η^5-C_5H_5)Ru$(CO)_2$)] reacts with two equivalents of $(Me_3Si)_2NBCl_2$ to form the boryl complex **13**, which can be isolated in 30% yield as a yellow crystalline material. This compound contains the unusual boryl ligand −BCl($NSiMe_3$)−BCl[N$(SiMe_3)_2$], which was formed by an intramolecular elimination of $ClSiMe_3$. The solution spectroscopic data indicate a structure for compound **13** similar to the ruthenium boryl complexes **12a**, **b**. This is indicated by a lowfield-shifted signal in the ^{11}B-NMR spectrum at δ = 60.3 for the metal-coordinated boron atom (δ = 35.0 for NBN) and the CO stretching frequencies at 2018 cm^{-1} and 1955 cm^{-1} in the IR spectrum. Crystals of **13** suitable



12a, X = Cl
12b, X = Br



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for an X-ray structure analysis were obtained after several days from hexane solutions at −30 °C (Scheme 1). The complex crystallizes in the spacegroup $P\bar{1}$ and the molecule adopts C_1 symmetry in the crystal. The ruthenium-boron distance of 211.5(2) pm is 6 pm shorter than in the compound $[(\eta^5\text{-}C_5H_5)Ru(CO)_2)\{B(NMe_2)BCl(NMe_2)\}$,[7b] but still exceeds the sum of the covalent radii of both elements, thus giving no evidence for a ruthenium-boron π-interaction in the solid state. In the BNBN chain, two short boron-nitrogen distances of 141.5(2) pm (B1−N4) and 140.5(3) pm (B2−N5) are found, together with a significantly longer distance of 147.0(2) pm (B2−N4). These values, together with the dihedral angles between the bonding planes of B1/N4 (17.5°), B2/N4 (96.2°) and B2/N5 (17.7°), indicate boron nitrogen double bonds between B1 and N4, and between B2 and N5, and a single bond between B2 and N4.

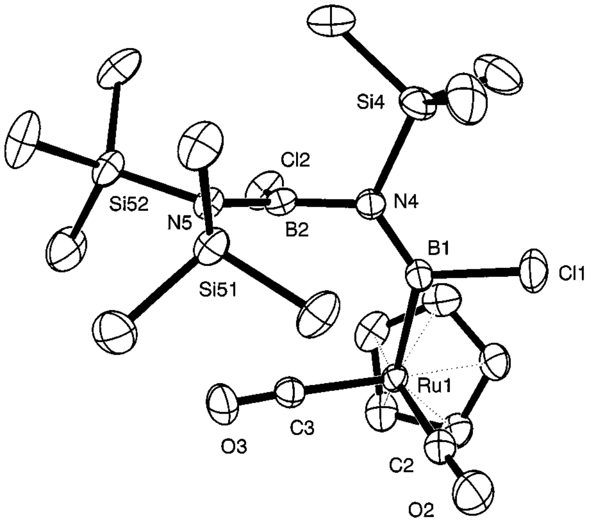


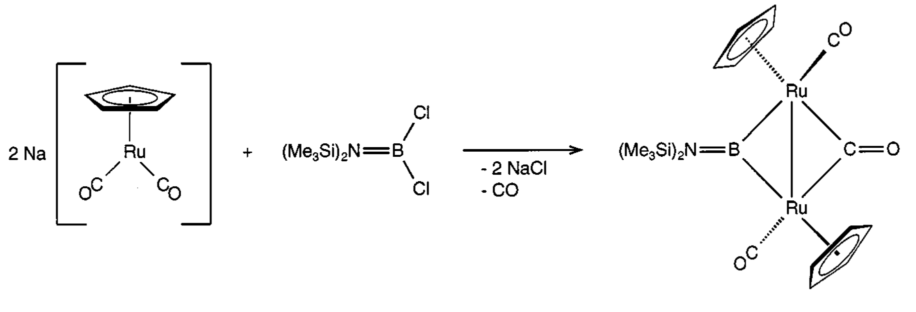
Figure 1. X-ray crystal structure of **13**. Selected bond lengths (pm) and angles (deg): Ru1−B1 211.5(2); B1−N4 141.5(2); B1−Cl1 185.4(2); N4−B2 147.0(2); B2−Cl2 182.2(2); B2−N5 140.5(2); Ru1−B1−Cl1 112.54(9); Ru1−B1−N4 133.29(12); Cl1−B1−N4 114.01(12); B1−N4−B2 120.90(14); N4−B2−Cl2 114.18(12); Cl2−B2−N5 118.76(13); N4−B2−N5 126.97(15).

The bridged borylene ruthenium complex $[\mu\text{-}BN(SiMe_3)_2(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_5)Ru(CO)\}_2]$ (**14**) can be obtained from the reaction of $(Me_3Si)_2NBCl_2$ with two equivalents of $Na[(\eta^5\text{-}C_5H_5)Ru(CO)_2)]$, according to Equation 4, with elimination of one CO group. In order to prevent the formation of **13** as a by-product, the aminodichloroborane has to be added very slowly to a suspension of an excess of the anionic ruthenium complex. The borylene complex **14** can be isolated as a moderately air- and water-sensitive yellow amorphous solid from hexane at −30 °C in 20% yield. The molecular structure of **14** in solution can be deduced from NMR and IR spectroscopic data and resembles that for the analogous iron compounds. The strongly deshielded signal at δ = 105.9 in the ^{11}B-NMR spectrum is in the expected region for aminobridged borylene complexes and the presence of a bridging CO group is established by the characteristic signal at δ = 250.2 in the ^{13}C-NMR spectrum and by a CO stretching frequency of 1776 cm^{-1} in the IR spectrum.

Conclusion

This study provides some insight into the reactivity of transition metal complexes of the type $Na[(\eta^5\text{-}C_5R_5)M(CO)_2)]$ (M = Fe, Ru) towards aminodihaloboranes. In the case of the strong nucleophiles $[(\eta^5\text{-}C_5R_5)Fe(CO)_2)]^-$ ($C_5R_5 = C_5H_5$, C_5H_4Me) the formation of bridged borylene complexes may be achieved not only by the use of electrophilic aminoboranes, such as $(Me_3Si)_2NBCl_2$, but also by employing dibromoboranes, which contain a more reactive boron halide bond. This is illustrated by the formation of $[\mu\text{-}BNMe_2(\mu\text{-}CO)\{(\eta^5\text{-}C_5R_5)Fe(CO)\}_2]$ ($C_5R_5 = C_5H_5$ **11a**; $C_5R_5 = C_5H_4Me$ **11b**) from Me_2NBr_2. The reaction of Me_2NBr_2 with the very bulky $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2)]$, however, results in the substitution of only one bromide and formation of the boryl complex $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\{Br(NMe_2)\}]$ (**10**).

The less nucleophilic ruthenium analogue $[(\eta^5\text{-}C_5H_5)Ru(CO)_2)]^-$ reacts with both Me_2NBCl_2 and Me_2NBBr_2 with selective substitution of only one halide



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and formation of the boryl complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Ru\{BX(NMe_2)\}]$ (X = Cl **12**a; X = Br **12b**). The first bridged borylene complex of ruthenium $[\mu\text{-}BN(SiMe_3)_2(\mu\text{-}CO)\{(\eta^5\text{-}C_5H_5)Ru(CO)\}_2]$ (**14**) was obtained from the reaction of $(Me_3Si)_2NBCl_2$ with two equivalents of $Na[(\eta^5\text{-}C_5H_5)Ru(CO)_2)]$.

The reactivity of aminobridged borylene complexes of the type $[\mu\text{-}BNR_2\{ML_x\}_2]$ with respect to hydrolysis and oxidation depends on the electronic nature of the amino-group NR_2 and, to a lesser extent, on steric factors or on the transition metal. In the case where $NR_2 = N(SiMe_3)_2$, the electron-withdrawing effect of the silyl groups enhances the reactivity of the borylene complexes. The sterically less demanding, albeit stronger electron donating, Me_2N group, however, makes the corresponding borylene complexes rather unreactive towards air and/or water.

Experimental Section

All manipulations were carried out under dry nitrogen using standard Schlenk techniques, unless otherwise stated. Solvents and reagents were dried by standard procedures, distilled and stored under nitrogen over molecular sieves. Me_2NBCl_2,[19] Me_2NBBr_2,[19] $(Me_3Si)_2NBCl_2$,[20] $Na[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$[21] and $Na[(\eta^5\text{-}C_5H_5)Ru(CO)_2]$[22] were synthesized according to literature procedures. – NMR: Varian Unity 500 at 499.843 MHz (^{1}H, standard TMS internal), 150.364 MHz (^{11}B, standard $BF_3 \cdot OEt_2$ in C_6D_6 external), 125.639 MHz ($^{13}C\{^1H\}$, APT, standard TMS internal); all NMR spectra were recorded in C_6D_6 as solvent. – Mass spectra were recorded on a Finnigan MAT 95 (70 eV) and elemental analyses (C, H, N) were obtained from a Carlo–Erba elemental analyzer, model 1106. – IR: Perkin–Elmer FT-IR 1720x.

Reaction of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with Me_2NBBr_2: $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (0.80 g, 4.00 mmol) was suspended in 25 mL of benzene and Me_2NBBr_2 (0.43 g, 2.00 mmol) was added dropwise at ambient temperature. After stirring for 15 min, all volatiles were removed in vacuo and the residue was treated with 20 mL of hexane, filtered and the remaining solid rinsed with 5 mL of hexane. The dark red filtrate was concentrated in vacuo to 15 mL and stored at −30°C for a period of 7 d. The dark red precipitate thus formed was found to be a 1:1 mixture of the boryl complex **9a** and the bridged borylene complex **11a**. – ^{1}H NMR: δ = 2.72 (s, 3 H, NMe, **9a**), 2.87 (s, 3 H, NMe, **9a**), 2.98 (s, 6 H, NMe_2, **11a**), 4.10 (s, 5 H, C_5H_5, **9a**), 4.39 (s, 10 H, C_5H_5, **11a**). – ^{11}B NMR: δ = 54.5 (s, 1 B, Fe–B–Br, **9a**), 103.5 (s, 1 B, Fe–B–Fe, **11a**). – ^{13}C NMR: δ = 35.3 (NMe, **9a**), 37.9 (NMe, **9a**), 43.1 (NMe_2, **11a**), 83.1 (C_5H_5, **9a**), 87.0 (C_5H_5, **11a**), 213.6 (CO, **11a**), 216.9 (CO, **9a**), 275.8 (μ-CO, **11a**).

Isolation of μ-Carbonyl-[μ-(dimethylamino)boranediyl]bis[carbonyl-(η^5-cyclopentadienyl)iron](*Fe*–*Fe*) (11a): The mixture of **9a/11a** was dissolved in 15 mL of raw diethyl ether and 10 mL of water were added without employing an inert gas atmosphere. After vigorously shaking the mixture for 3 min, the red organic layer was separated from the turbid, brownish aqueous phase and evaporated to dryness. The remaining red solid was recrystallized from 10 mL of hexane, yielding pure **11a** (0.08 g, 10.5%) as a dark red, crystalline solid. – ^{1}H NMR: δ = 2.98 (s, 6 H, NMe_2), 4.39 (s, 10 H, C_5H_5). – ^{11}B NMR: δ = 103.5 (s). – ^{13}C NMR: δ = 43.1 (NMe_2), 87.0 (C_5H_5), 213.6 (CO), 275.8 (μ-CO). – IR (toluene): $\tilde{\nu}$ = 1942 cm^{-1}, 1776 (CO). – $C_{15}H_{16}BFe_2NO_3$ (380.79): calcd. C 47.31, H 4.24; N 3.68; found C 46.85; H 4.39; N 3.80.

Reaction of $Na[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]$ with Me_2NBBr_2: This compound was prepared as described above, using $Na[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]$ (2.42 g, 11.31 mmol) and Me_2NBBr_2 (0.97 g, 4.53 mmol). The dark red solid obtained is a 1: 1 mixture of the boryl complex **9b** and the bridged borylene complex **11b**. – ^{1}H NMR: δ = 1.79 (s, 3 H, C_5H_4Me, **9b**), 1.86 (s, 6 H, C_5H_4Me, **11b**), 2.68 (s, 3 H, NMe, **9b**), 2.76 (s, 3 H, NMe, **9b**), 3.06 (s, 6 H, NMe_2, **11b**), 3.95–4.03 (m, 4 H, C_5H_4Me, **9b**), 4.08–4.48 (m, 8 H, C_5H_4Me, **11b**). – ^{11}B NMR: δ = 55.0 (s, 1 B, Fe–B–Br, **9b**), 104.5 (s, 1 B, Fe–B–Fe, **11b**). – ^{13}C NMR. δ = 12.9 (C_5H_4Me, **11b**), 13.1 (C_5H_4Me, **9b**), 34.7 (NMe, **9b**), 37.5 (NMe, **9b**), 43.2 (NMe_2, **11b**), 83.1, 85.2 (C_5H_4Me, **9b**), 83.7, 84.7, 86.2, 90.2 (C_5H_4Me, **11b**), 102.4 (*ipso*-C, C_5H_4Me, **9b**), 103.8 (*ipso*-C, C_5H_4Me, **11b**), 214.0 (CO, **11b**), 218.5 (CO, **9b**), 277.0 (μ-CO, **11b**).

Isolation of μ-Carbonyl-[μ-(dimethylamino)boranediyl]bis[carbonyl-(η^5-methylcyclopentadienyl)iron](*Fe*–*Fe*) (11b): The mixture of **9b/11b** was treated in the same way as described above. After recrystallisation from hexane, pure **11b** (0.19 g, 12.0%) was recovered at −30°C as a red, crystalline solid. – ^{1}H NMR: δ = 1.86 (s, 6 H, C_5H_4Me), 3.06 (s, 6 H, NMe_2), 4.08–4.48 (m, 8 H, C_5H_4Me). – ^{11}B NMR: δ = 104.5 (s). – ^{13}C NMR: δ = 12.9 (C_5H_4Me), 43.2 (NMe_2), 83.7, 84.7, 86.2, 90.2 (C_5H_4Me), 103.8 (*ipso*-C, C_5H_4Me), 214.0 (CO, **11b**), 277.0 (μ-CO). – IR (toluene): $\tilde{\nu}$ = 1946 cm^{-1}, 1778 (CO). – $C_{17}H_{20}BFe_2NO_3$ (408.84): calcd. C 49.94, H 4.93; N 3.43; found C 49.79; H 4.99; N 3.51.

[Bromo(dimethylamino)boryl]dicarbonyl(η^5-pentamethylcyclopentadienyl)iron (10): $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ (1.64 g, 6.07 mmol) was suspended in 30 mL of benzene and Me_2NBBr_2 (1.29 g,5.92 mmol) was added dropwise from a syringe at ambient temperature. After stirring for 15 min, all volatiles were removed in vacuo and the dark brown, solid residue was treated with 20 mL of hexane, filtered and the remaining solid rinsed with 10 mL of hexane. The dark red filtrate was concentrated in vacuo to 15 mL and stored at −30°C overnight. Compound **10** (0.77 g, 33.7%) was obtained as red-brown needles. − ^{1}H NMR: δ = 1.52 (s, 15 H, C_5Me_5), 2.87 (s, 3 H, NMe), 3.06 (s, 3 H, NMe). − ^{11}B NMR: δ = 57.2. − ^{13}C NMR δ = 9.8 (C_5Me_5), 44.4 (NMe), 44.8 (NMe), 95.5 (C_5Me_5), 217.4 (CO). − IR (toluene): $\tilde{\nu}$ = 1991 cm^{-1}, 1933 (CO). − $C_{14}H_{21}BBrFeNO_2$ (381.89): calcd. C 44.03, H 5.54, N 3.67; found C 43.97, H 5.82, N 3.60.

[Chloro(dimethylamino)boryl]dicarbonyl(η^5-cyclopentadienyl)-ruthenium (12a): As described for **10**, Na[(η^5-C_5H_5)Ru(CO)$_2$] (0.65 g, 2.65 mmol) was treated with Me_2NBCl_2 (0.33 g, 2.65 mmol). Compound **12a** (0.64 g, 77.4%) was obtained as a brown-yellow, crystalline solid. − ^{1}H NMR: δ = 2.70 (s, 3 H, NMe), 2.91 (s, 3 H, NMe), 4.61 (s, 5 H, C_5H_5). − ^{11}B NMR: δ = 50.3. − ^{13}C NMR: δ = 40.7 (NMe), 44.4 (NMe), 87.4 (C_5H_5), 201.9 (CO). − IR (toluene): $\tilde{\nu}$ = 2019 cm^{-1}, 1956 (CO). − $C_9H_{11}BClNO_2Ru$ (312.51): calcd. C 34.59; H 3.55, N 4.48; found C 34.03, H 3.59, N 4.30.

[Bromo(dimethylamino)boryl]dicarbonyl(η^5-cyclopentadienyl)-ruthenium (12b): As described for **10**, 1.86 g (7.65 mmol) of Na[(η^5-C_5H_5)Ru(CO)$_2$] was treated with 1.64 g (7.65 mmol) Me_2NBBr_2. Compound **12b** (1.12 g, 40.1%) was obtained as brown-yellow crystals. − ^{1}H NMR: δ = 2.72 (s, 3 H, NMe), 2.99 (s, 3 H, NMe), 4.59 (s, 5 H, C_5H_5). − ^{11}B NMR: δ = 48.1. − ^{13}C NMR: δ = 43.5 (NMe), 45.0 (NMe), 87.8 (C_5H_5), 201.9 (CO). − IR (toluene): $\tilde{\nu}$ = 2022 cm^{-1}, 1960 (CO). − $C_9H_{11}BBrNO_2Ru$ (356.96): calcd. C 30.28; H 3.11, N 3.92; found C 30.19, H 3.34, N 4.08.

Dicarbonyl(chloro{chlorobis(trimethylsilylamino)boryl](trimethylsilyl)amino}boryl)(η^5-cyclopentadienyl)ruthenium (13): Na[(η^5-C_5H_5)Ru(CO)$_2$] (0.87 g, 3.55 mmol) was suspended in 25 mL of benzene and $(Me_3Si)_2NBCl_2$ (1.72 g, 7.10 mmol) was added all at once at ambient temperature. After stirring for 20 min, all volatiles were removed in vacuo and the brown, solid residue was treated with 25 mL of hexane, filtered and the remaining solid was rinsed with hexane (2 × 5 mL). The brown filtrate was concentrated in vacuo to 15 mL and stored at −30°C. After 72 h, **13** (0.60 g, 30.1%) was obtained as dark yellow crystals. − ^{1}H NMR: δ = 0.44 [s, 18 H, N(SiMe$_3$)$_2$], 0.49 (s, 9 H, NSiMe$_3$), 4.80 (s, 5 H, C_5H_5). − ^{11}B NMR: δ = 35.0 (s, 1 B, NBN), 60.3 (s, 1 B, NBRu). − ^{13}C NMR: δ = 3.8 [N(SiMe$_3$)$_2$], 5.3 (NSiMe$_3$), 89.3 (C_5H_5), 202.3 (CO). − IR (toluene): $\tilde{\nu}$ = 2018 cm^{-1}, 1955 (CO). − MS; *m/z* (%): 547 (5) [M$^+$ − Me], 534 (4) [M$^+$ − CO], 439 (6) [M$^+$ − Me − ClSiMe$_3$], 339 (40) [M$^+$ − (C_5H_5)Ru(CO)$_2$], 231 (100) [M$^+$ − ClSiMe$_3$ − (C_5H_5)Ru(CO)$_2$], 98 (75) [BNSiMe$_3$$^+$], 73 (90) [SiMe$_3$$^+$]. − $C_{16}H_{32}B_2Cl_2N_2O_2RuSi_3$ (562.29): calcd. C 34.17; H 5.74; N 4.98; found C 34.26; H 5.89; N 4.93.

{μ-[Bis(trimethylsilyl)amino]boranediyl}-μ-carbonylbis[carbonyl-(η^5-cyclopentadienyl)ruthenium](*Ru*−*Ru*) (14): A solution of $(Me_3Si)_2NBCl_2$ (0.38 g, 1.58 mmol) in 5 mL of benzene was added dropwise over a period of 10 min to a suspension of Na[(η^5-C_5H_5)Ru(CO)$_2$] (1.55 g, 6.32 mmol) in 20 mL of benzene at ambient temperature. The colour of the reaction mixture turned from dark yellow to brown during the addition. After stirring the mixture for another 10 min, all volatiles were removed in vacuo. The light brown residue was suspended in 20 mL of hexane and filtered. Compound **14** (0.18 g, 19.6%) was recovered from the filtrate at −30°C as an orange, amorphous solid. − ^{1}H NMR: δ = 0.29 (s, 18 H, SiMe$_3$), 4.90 (s, 10 H, C_5H_5). − ^{11}B NMR: δ = 105.9. − ^{13}C NMR: δ = 5.0 (SiMe$_3$), 90.2 (C_5H_5), 203.6 (CO), 250.2 (μ-CO). − IR (toluene): $\tilde{\nu}$ = 1932 cm^{-1}, 1776 (CO). − $C_{19}H_{28}BNO_3Ru_2Si_2$ (587.55): calcd. C 38.84, H 4.80; N 2.38; found C 38.26, H 4.58, N 2.08.

Crystal Structure Data Determination of 13: X-ray-quality crystals were removed from a Schlenk tube and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected, attached to a glass fiber and instantly placed in a low-temperature N_2 stream of a P2$_1$ four-circle diffractometer (Siemens). M_r = 562.30, triclinic, space group $P\bar{1}$, a = 911.6(2), b = 1133.7(2), c = 1465.4(3), α = 103.09(2), β = 102.72(2), γ = 111.000(15)°, V = 1.2994(5) mm^3, Z = 2, $\rho_{calc.}$ = 1.437 M gm^{-3}, $F(000)$ = 576, λ = 71.073 pm, T = 173 K, μ(MoK_α) = 0.962 mm^{-1}, crystal size: 0.4 × 0.4 × 0.3 mm, 3.02° < 2θ < 60°; of the 8516 reflections collected 7562 were unique and 7561 were used for refinement of 263 parameters; max./min. difference electron density: −866/744 e nm^{-3}. $R1$ = 0.027 [$F > 4\sigma(F)$] and wR_2 = 0.075 (all data) with $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{0.5}$. Calculations were carried out with the SHELXTL PC 5.03[23] and SHELXL-97[24] program system installed on a local PC. The phase problem was solved by direct methods and the structures were refined on F_o^2 by full-matrix least-squares refinement. An extinction correction was applied, extinction coefficient: 0.0115(7). Anisotropic thermal parameters were included for all non-hydrogen atoms. H atoms were placed geometrically and refined using a riding model, including free rotation of methyl groups. Their isotropic thermal parameters were constrained to 1.2 (cyclopentadienyl H) or 1.5 (methyl groups) times U_{eq} of the bonded carbon. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116235. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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Received March 12, 1999
[I99098]