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Synthesis, Reactivity, and Crystal and Molecular Structures of $Nb(L)(\eta^6\text{-}C_6H_{5-n}X_n)_2B(C_6H_{5-n}X_n)_2$, a Class of Mononuclear Metal Compounds Containing the 12-Electron-Donor Tetraarylborato Ligand

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The one-electron oxidation of $Nb(mes)_2$ (mes = 1,3,5-trimethylbenzene) with ferrocenium tetraarylborate, produces the 16-electron $[Nb(mes)_2]^+$ cation, which adds disubstituted symmetrical alkynes to give the ionic compounds $[Nb(mes)_2)(alkyne)][Y]$ (alkyne = MeC_2Me, Y = BPh_4 (**1a**), Y = $B(p\text{-}FC_6H_4)_4$ (**1b**), Y = $B[3,5\text{-}(CF_3)_2C_6H_3]_4$ (**1c**); alkyne = PhC_2Ph, Y = BPh_4 (**2a**), Y = $B(p\text{-}FC_6H_4)_4$ (**2b**)). **2b** crystallizes in space group *C*2/*c* (No. 15) with four formula units in cells of dimensions a = 17.640(3) Å, b = 16.8386(8) Å, c = 19.616(2) Å, and β = 97.230(9)°; the $[Nb(mes)_2(PhC_2Ph)]^+$ cation contains bent η^6-mesitylene ligands, a coordination position being occupied by PhC_2Ph as a formal two-electron donor. The alkyne in **1a–c** is displaced by CO at room temperature and at atmospheric pressure to give the carbonyl derivatives $[Nb(mes)_2CO][Y]$ (**3a–c**). Thermal treatment of **1a**,**b** and **2a** in toluene gave mesitylene displacement and formation of the neutral covalent compounds containing the uninegative tetraarylborato ligand of formula $[Nb(RC_2R)(\eta^6\text{-}C_6H_4X)_2B(C_6H_4X)_2]$ (R = Me, X = H (**4a**), X = *p*-F (**4b**); R = Ph, X = H (**5a**)). **4a** crystallizes in space group $P\bar{4}2_1m$ (No. 113), with two formula units in cells of dimensions a = 9.734(1) Å and c = 11.6333(9) Å; **4b** crystallizes in space group $P2_12_12_1$ (No. 19) with eight formula units in cells of dimensions a = 11.776(3) Å, b = 15.666(3) Å, and c = 28.042(5) Å. **4a**,**b** both contain the novel bonding arrangement of the tetraarylborato ligand with two interannularly niobium-bridged aryl rings. This new type of bonding is not restricted to the methyl-substituted (**4a**) or phenyl-substituted (**4b**) acetylenic derivatives: CO is also compatible with the new bonding arrangement. Alkyne displacement by CO gives the neutral covalent complex $[Nb(CO)(\eta^6\text{-}C_6H_4X)_2B(C_6H_4X)_2]$ (X = H (**6a**), *p*-F (**6b**)). An X-ray diffractometric experiment on **6a** has confirmed the novel bonding arrangement of the tetraarylborato ligand for this compound, which crystallizes in space group $P2_12_12_1$ (No. 19) with four formula units in cells of dimensions a = 10.495(2) Å, b = 14.586(1) Å, and c = 17.174(3) Å.

Introduction

Bis(arene)metal complexes represent an important area of inorganic chemistry. The chromium(0) derivatives were originally synthesized by Hein[1] by the reaction of the phenyl Grignard reagent with anhydrous chromium(III) chloride, followed by a hydrolytic treatment. The true nature of these compounds was later recognized by Fischer and co-workers,[2] who introduced a new synthetic procedure for η^6-arene complexes consisting of treating an anhydrous metal halide with Al/AlX_3 in the parent hydrocarbon as medium. Recent work from these laboratories on early transition metals has established that the primary products of the reduction are $[V(\eta^6\text{-arene})_2]^+$ for vanadium[3] and complexes of general formula $[M(\eta^6\text{-arene})][AlX_4]_2$ for niobium(II)[4] and for zirconium(II) and hafnium(II).[5] Moreover, the bis(mesitylene)niobium(I) cation,[4] $[Nb(mes)_2]^+$, is known: this is a 16-electron species and, accordingly, a rather unstable compound. It has already been noted[6] that systems containing two arene ligands *per* metal atom in a bent conformation are rare in coordination chemistry. We have found[4] such an example in the complex $[Nb(mes)_2L]^+$ (L = CO), which has an angle of tilt between the arene ligands of 147.7°; the PMe_3 derivative $[Nb(\eta^6\text{-toluene})_2PMe_3]^+$ has been reported[7] to have an angle of tilt of 142.3°. We therefore reckoned that the class of the bis(mesitylene)niobium(I) cationic complexes could be extended to other ligands L. Moreover, the result obtained by Elschenbroich and co-workers on $Si(C_6H_5)_4$, which was found[6] to act as an uncharged 12-electron-donor system for vanadium(0) or chromium(0),

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prompted us to attempt the preparation of tetraarylborato complexes of niobium(I) with a similar, still unknown type of bonding, using $[Nb(mes)_2L][BAr_4]$ as precursor. The negative charge on the tetraarylborato ligand was anticipated to confer a specific stability to the system, since displacement by uncharged ligands could not occur without modifying the nature of the product completely. Appropriately modified bent bis(arene) systems are of considerable interest as precursors to asymmetric catalytic systems for stereoselective olefin polymerization.[8]

We recently succeeded[9] in preparing the new tetraphenylborato complexes $[Nb(L)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (L = MeC_2Me, PhC_2Ph), and we described the X-ray structure of the but-2-yne derivative in a preliminary form. We have now found that the new bonding arrangement is stable over a wide range of tetraarylborato derivatives of niobium(I) and with CO as a ligand as well. We report in this paper the syntheses and the X-ray structures of these compounds together with the chemical and structural properties of their ionic precursors. NMR evidence of the tetraphenylborato group being involved in coordination to lanthanum(III) with two phenyl rings of unknown hapticity has been reported.[10]

Experimental Section

General Methods. Unless otherwise stated, all operations were carried out under an atmosphere of prepurified argon. The reaction vessels were oven-dried before use. Solvents were dried by conventional methods.

Infrared spectra were recorded with a Perkin-Elmer Model FT1725X instrument on solutions or Nujol mulls of the compounds prepared under rigorous exclusion of moisture and oxygen. The ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectra were measured at room temperature with a Varian Gemini 200 spectrometer operating at 200 MHz for ^1H, 50.3 MHz for ^{13}C, 188.1 MHz for ^{19}F, and 64.2 MHz for ^{11}B. ^1H and ^{13}C, ^{19}F, and ^{11}B NMR spectra are referred to TMS, $CFCl_3$, and $BF_3 \cdot Et_2O$ as external standards, respectively. Gas-chromatographic analyses were performed with a Dani Model 8400 instrument equipped with a Carbowax 20 M column.

Bis(1,3,5-trimethylbenzene)niobium(0) ($Nb(mes)_2$),[4] $[Nb(mes)_2][BPh_4]$,[4] ferrocenium tetraphenylborate ($[FeCp_2][BPh_4]$,[11] and the sodium salts Na[Y] (Y = $B(p\text{-}FC_6H_4)_4$,[12] $B(p\text{-}CF_3C_6H_4)_4$,[13] $B[3,5\text{-}(CF_3)_2C_6H_3)]_4$[14]) were prepared according to the literature.

Preparation of $[FeCp_2][Y]$ (Y = $B(p\text{-}FC_6H_4)_4$, $B(p\text{-}CF_3C_6H_4)_4$, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$). Only the preparation of $[FeCp_2][B(p\text{-}FC_6H_4)_4]$ is described in detail. By operating in air, a solution of $[FeCp_2][HSO_4]$ in water, obtained from $FeCp_2$ (4.62 g, 24.8 mmol) and 96% H_2SO_4 (40 mL), was treated at room temperature with a solution of $Na[B(p\text{-}FC_6H_4)_4]$ (12 g, 29.0 mmol) in water (100 mL). Immediate precipitation of a blue solid was observed, which was filtered, washed with ethanol (5 × 50 mL) and Et_2O (5 × 50 mL), and dried overnight over P_4O_{10}, affording $[FeCp_2][B(p\text{-}FC_6H_4)_4]$: 11.2 g, 78.2% yield. Anal. Calcd for $C_{34}H_{26}BF_4Fe$: C, 70.7; H, 4.5. Found: C, 69.5; H, 4.4.

$[FeCp_2][B(p\text{-}CF_3C_6H_4)_4]$: 50% yield. Anal. Calcd for $C_{38}H_{26}BF_{12}Fe$: C, 58.7; H, 3.4. Found: C, 59.2; H, 3.7.

$[FeCp_2][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$: 83% yield. Anal. Calcd for $C_{42}H_{22}BF_{24}Fe$: C, 48.1; H, 2.1. Found: C, 47.9; H, 2.0.

Preparation of $[Nb(mes)_2][Y]$ (Y = $B(p\text{-}FC_6H_4)_4$, $B(p\text{-}CF_3C_6H_4)_4$, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$). Only the preparation of $[Nb(mes)_2][B(p\text{-}FC_6H_4)_4]$ is described in detail. A suspension of $FeCp_2[B(p\text{-}FC_6H_4)_4]$ (2.66 g, 4.6 mmol) in toluene (50 mL) was treated with $Nb(mes)_2$ (1.51 g, 4.5 mmol). After about 36 h of stirring at room temperature, a brown solid in an orange solution was obtained, which was filtered, washed with toluene (5 × 5 mL), and dried *in vacuo*, affording 2.88 g (89% yield) of $[Nb(mes)_2][B(p\text{-}FC_6H_4)_4]$ in the form of a pyrophoric brown solid.[15] This solid was found to absorb CO in toluene at 22.4 °C up to a CO/Nb molar ratio of 0.98 to give $[Nb(mes)_2(CO)][B(p\text{-}FC_6H_4)_4]$ (**3b**) characterized[4] by its IR spectrum in THF solution ($\tilde{\nu}_{CO}$ = 1990 cm^{-1}).

$[Nb(mes)_2][B(p\text{-}CF_3C_6H_4)_4]$: 82% yield; pyrophoric brown solid[15] which absorbed CO in toluene at 22.4 °C up to a CO/Nb molar ratio of 1.00 to give $[Nb(mes)_2(CO)][B(p\text{-}CF_3C_6H_4)_4]$ ($\tilde{\nu}_{CO}$ = 1991 cm^{-1}, THF).

$[Nb(mes)_2][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$: the reaction of $Nb(mes)_2$ with $[FeCp_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ afforded a biphasic system consisting of an upper orange layer and a dark brown lower layer. After the upper layer was eliminated and the lower one was washed with toluene and heptane, a brown pyrophoric solid[15] was obtained in 74% yield after evaporation to dryness. The solid absorbed CO in toluene at 22.4 °C up to a CO/Nb molar ratio of 0.99 to give $[Nb(mes)_2(CO)][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ (**3c**) (IR spectrum in THF solution: 1990 cm^{-1}).

Preparation of $[Nb(mes)_2(MeC_2Me)[Y]$ (Y = BPh_4, 1a;[9] Y = $B(p\text{-}FC_6H_4)_4$, 1b; Y = $B[3,5\text{-}(CF_3)_2C_6H_3]_4$, 1c). A suspension of $[Nb(mes)_2][BPh_4]$ in toluene (50 mL), obtained by reacting $Nb(mes)_2$ (0.515 g, 1.54 mmol) with $[FeCp_2][BPh_4]$ (0.74 g, 1.47 mmol), was treated at about 15 °C with but-2-yne (0.2 ml, 2.55 mmol); a red precipitate formed. The reaction mixture was stirred at about 15 °C for 12 h, and the solid was filtered and dried *in vacuo* at room temperature, affording $[Nb(mes)_2(MeC_2Me)][BPh_4]$ (**1a**; 0.82 g, 78.5% yield) in the form of a brick red, moisture- and oxygen-sensitive and thermally unstable compound. Anal. Calcd for $C_{46}H_{50}BNb$: C, 78.2; H, 7.1. Found: C, 76.8; H, 7.0. IR spectrum (poly(chlorotrifluoroethylene) mull): 3051 m, 3029 m, 2998 m, 2983 m, 2964 m, 2923 m, 1818 w, 1608 m, 1593 m, 1580 m, 1539 m, 1525 m, 1479 s, 1451 s, 1436 s, 1376 s cm^{-1}. ^1H NMR (THF-d_8): 6.67–7.20 (m, 26 H), 2.19 (s, 18 H), 1.55 (s, 6 H) ppm.

$[Nb(mes)_2(MeC_2Me)][B(p\text{-}FC_6H_4)_4]$ (**1b**) was obtained in 94% yield. This compound is stable in air for short periods of time; under an inert atmosphere, it starts to decompose at about 50 °C. Anal. Calcd for $C_{46}H_{46}BF_4Nb$: C, 71.0; H, 6.0. Found: C, 69.9; H, 5.5. IR spectrum (Nujol mull): 1817 w, 1581 s, 1491 s, 1205 s, 1156 s, 1093 w, 1085 m, 1015 m, 934 w, 897 m, 813 s, 779 m, 552 s cm^{-1}.

$[Nb(mes)_2(MeC_2Me)][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ (**1c**) was obtained in 75% yield. It is stable in air for short periods of time; no decomposition was observed under an inert atmosphere up to 100 °C. Anal. Calcd for $C_{54}H_{42}BF_{24}Nb$: C, 51.9; H, 3.4. Found: C, 51.0; H, 3.0. IR spectrum (Nujol mull): 1832 w, 1792 w, 1611 m, 1540 w, 1354 s, 1279 vs, 1228 m, 1168 vs, 1138 vs, 1030 m, 896 m, 840 m, 713 s, 683 s cm^{-1}.

Preparation of $[Nb(mes)_2(PhC_2Ph)][Y]$ (Y = BPh_4, 2a;[9] Y = $B(p\text{-}FC_6H_4)_4$, 2b). A suspension of $[Nb(mes)_2][BPh_4]$ in toluene (50 mL), obtained from $Nb(mes)_2$ (0.44 g, 1.3 mmol) and $[FeCp_2][BPh_4]$ (0.67 g, 1.3 mmol), was treated with PhC_2Ph (0.23 g, 1.3 mmol); a brick red solid quickly formed. After 12 h of

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[15] No satisfactory analytical data were obtained on these products due to their extreme sensitivity to air. They were characterized by their subsequent reaction with CO and with substituted acetylenes (*vide infra*).

stirring at room temperature, the reaction mixture was filtered and the solid was washed with toluene (2 × 5 mL) and dried *in vacuo* at room temperature, affording $[Nb(mes)_2(PhC_2Ph)][BPh_4]$ (**2a**; 0.60 g, 56% yield) as a brick red microcrystalline solid extremely sensitive to moisture and oxygen. Anal. Calcd for $C_{56}H_{54}BNb$: C, 81.0; H, 6.5. Found: C, 79.9; H, 6.4. IR spectrum (poly(chlorotrifluoroethylene) mull): 3057 m, 3023 m, 3001 m, 2981 m, 2915 m, 1959 m, 1767 m, 1592 w, 1579 m, 1569 w, 1544 w, 1522 m, 1484 s, 1451 m, 1440 s, 1427 s, 1380 s, 1373 m cm^{-1}. ^1H NMR (THF-d_8): 6.74–7.30 (m, 36 H), 1.94 (s, 18 H) ppm.

The brick red $[Nb(mes)_2(PhC_2Ph)][B(p\text{-}FC_6H_4)_4]$ (**2b**), stable in air for short periods of time, was obtained (91% yield) in a similar way. Anal. Calcd for $C_{56}H_{50}BF_4Nb$: C, 74.5; H, 5.6. Found: C, 74.7; H, 5.8. IR spectrum (poly(chlorotrifluoroethylene) mull): 3073 w, 3057 w, 3023 w, 2960 w, 2926 w, 2862 w, 1770 w, 1579 s, 1544 m, 1488 s, 1451 m, 1440 m, 1377 m cm^{-1}.

Reaction of $[Nb(mes)_2(MeC_2Me)][Y]$ (Y = BPh_4, $B(p\text{-}FC_6H_4)_4$, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$) with CO. Synthesis of 3a–c. Only the reaction of **1a** to give **3a** is described in detail. A suspension of $[Nb(mes)_2(MeC_2Me)][BPh_4]$ (0.087 g, 0.12 mmol) in toluene (3 mL) was treated with CO at atmospheric pressure. Formation of a green solid was observed after 2 h. A gas-chromatographic analysis of the liquid phase showed the presence of but-2-yne. The reaction mixture was evaporated to dryness at room temperature, and the residue was dissolved in THF (3 mL). The infrared spectrum of the green solution in the carbonyl stretching region showed the absorption at 1990 cm^{-1} typical[4] of the $[Nb(mes)_2CO]^+$ cation. In a gas-volumetric experiment, 0.98 mmol of CO/mol of Nb was found to be absorbed at room temperature.

Thermal Treatment of $[Nb(mes)_2(MeC_2Me)][Y]$ (Y = BPh_4, $B(p\text{-}FC_6H_4)_4$): Preparation of $[Nb(MeC_2Me)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (4a)[9] and $[Nb(MeC_2Me)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}FC_6H_4)_2]$ (4b). A suspension of $[Nb(mes)_2(MeC_2Me)][BPh_4]$ (1.49 g, 2.1 mmol) in toluene (100 mL) containing but-2-yne (2 mL, 25.2 mmol) was heated at 100 °C for 30 min and filtered. The red-orange filtrate, after evaporation to 50 mL and cooling at about −30 °C, gave red-orange crystals of **4a** (0.07 g). The solution, after reduction of the volume of the solvent to 25 mL *in vacuo* at room temperature and treatment with heptane (50 mL), gave a second crop of product in the form of red-orange microcrystals (0.095 g). Anal. Calcd for $C_{28}H_{26}BNb$: C, 72.1; H, 5.6; Nb, 19.9. Found: C, 71.9; H, 5.7; Nb, 18.9. IR spectrum (Nujol and poly(chlorotrifluoroethylene) mulls): 3067 w, 3047 m, 2963 m, 1919 m, 1591 s, 1481 m, 1425 s, 1347 w, 1276 w, 1261 m, 1159 m, 1148 m, 1089 m, 1015 m, 803 m, 752 s, 709 s, 589 m cm^{-1}. ^1H NMR spectrum (benzene-d_6): 7.70 (d, 4 H), 7.10 (m, 6 H), 5.3 (t, 4 H, J_{HH} = 7 Hz), 5.15 (m, 6 H), 2.40 (s, 6 H) ppm.

The primary orange solid (1.09 g) was extracted with hot toluene (100 mL) under reduced pressure (*ca.* 400 mmHg) for 5 h; the resulting red-orange solution, after removal of about 50 mL of toluene and cooling at about −30 °C, gave a third crop of orange microcrystals of $[Nb(MeC_2Me)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (0.228 g) for a total yield of 40%. No hexamethylbenzene was found either in the solutions or in the solid.

The preparation of **4b** was performed in a similar way except for the heating time, which was 1 h at 110 °C. The yield was 70%. Anal. Calcd for $[Nb(MeC_2Me)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}FC_6H_4)_2]$, $C_{28}H_{22}BF_4Nb$: C, 62.5; H, 4.1. Found: C, 63.0; H, 4.3. IR spectrum (Nujol and poly(chlorotrifluoroethylene) mulls): 3078 w, 3012 w, 2962 w, 2928 w, 1889 w, 1593 s, 1508 m, 1496 s, 1432 m, 1376 m, 1261 s, 1231 m, 1211 m, 1159 m, 1095 s, 1016 s, 973 m, 802 s, 594 m cm^{-1}. ^1H NMR spectrum (benzene-d_6): 7.42 (dd, 4 H, J_{HH} = 8 Hz, J_{HF} = 6.6 Hz), 7.10 (dd, 4 H, J_{HH} = 8.6 Hz, J_{HF} = 17.5 Hz), 5.13 (t, 4 H, $J_{HH} = J_{HF}$ = 7.2 Hz), 4.66 (dd, 4 H, J_{HH} = 7.2 Hz, J_{HF} = 4.5 Hz), 2.29 (s, 6 H) ppm. ^{13}C NMR spectrum (benzene-d_6): 162.34 (d, *C*–F, J_{CF} = 256 Hz; 139.55 (d, *C*–F, η^6 ring, J_{CF} = 167 Hz), 135.04 (d, C_{ortho}, J_{CF} = 7 Hz), 115.02 (d, C_{meta}, J_{CF} = 19 Hz), 100.49 (s, *C*–Me), 95.73 (s, br, C_{ortho}, η^6 ring), 91.32 (s, br, C_{meta}, η^6 ring), 23.05 (s, CH_3) ppm. ^{19}F NMR spectrum (benzene-d_6): −113.6 (s, br, 1 F), −119.5 (quintet, 1 F, J_{FH} = 7.5 Hz, η^6 ring) ppm. ^{11}B NMR (benzene-d_6): −7.37 ppm.

Thermal Treatment of $[Nb(mes)_2(PhC_2Ph)][BPh_4]$: Synthesis of $[Nb(PhC_2Ph)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (5a).[9] A suspension of $[Nb(mes)_2(PhC_2Ph)][BPh_4]$, obtained from $[Nb(mes)_2][BPh_4]$ (1.20 g, 1.84 mmol) and PhC_2Ph (0.375 g, 2.1 mmol) in toluene (100 mL), was heated at 100 °C for 30 min and filtered when hot. The volume of the red filtrate was reduced to about 10 mL and cooled at about −30 °C. The red crystalline $[Nb(PhC_2Ph)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (0.170 g, 16% yield) was collected by filtration and dried *in vacuo*. Found: C, 76.9; H, 5.5. Anal. Calcd for $C_{38}H_{30}BNb$: C, 77.3; H, 5.1. IR spectrum (poly(chlorotrifluoroethylene) mull): 3058 w, 2939 w, 1776 m, 1588 w, 1495 w, 1482 m, 1439 m, 1431 m, 1377 m cm^{-1}. ^1H NMR spectrum (benzene-d_6): 7–8 (m, 20 H), 5.52 (t, 4 H, *J* = 6.9 Hz), 5.25 (dd, 4 H, $J_{H_{ortho}H_{meta}}$ = 6.9 Hz, $J_{H_{ortho}H_{para}}$ = 1.5 Hz), 3.21 (tt, 2 H, $J_{H_{para}H_{meta}}$ = 6.8 Hz, $J_{H_{para}H_{ortho}}$ = 1.5 Hz) ppm. ^{13}C NMR spectrum (benzene-d_6): 141.4 (s, C_{ipso}), 136.4 (s, C_{ipso}, η^6 ring), 134.0 (s, C_{ortho}), 131.0 (s, C_{meta}), 124.7 (s, C_{para}), 107.0 (s, C_{para}, η^6 ring), 102.6 (s, C_{ortho}, η^6 ring), 99.7 (s, C_{meta}, η^6 ring) ppm.

Reaction of $[Nb(MeC_2Me)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ with CO: Synthesis of $[Nb(CO)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (6a). A red solution of $[Nb(MeC_2Me)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (0.29 g, 0.62 mmol) in toluene (50 mL) was treated with CO at room temperature to give a brown solution ($\tilde{\nu}_{CO}$ = 1992 cm^{-1}). The reaction mixture was dried *in vacuo* at room temperature, affording 0.140 g (51.6% yield) of $[Nb(CO)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ as a brown microcrystalline solid slightly sensitive to air and moisture. The compound was recrystallized from toluene at about −30 °C. Anal. Calcd for $C_{25}H_{20}BNbO$: C, 68.2; H, 4.6. Found: C, 69.0; H, 4.7. IR spectrum: 1992 (toluene), 1995 (Nujol) cm^{-1}. ^1H NMR spectrum (benzene-d_6): 7.80 (d, 4 H, $J_{H_{ortho}H_{meta}}$ = 7 Hz), 7.12 (m, 6 H), 5.25 (t, 4 H, *J* = 7 Hz), 5.10 (m, 6 H) ppm.

Reaction of $[Nb(MeC_2Me)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}FC_6H_4)_2]$ with CO: Synthesis of $[Nb(CO)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}FC_6H_4)_2]$ (6b). A solution of $[Nb(MeC_2Me)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}FC_6H_4)_2]$ (0.15 g, 0.28 mmol) in toluene (10 mL) was exposed to CO at atmospheric pressure. The mixture was stirred at room temperature for 12 h; an IR spectrum of the solution did not reveal any absorption in the carbonyl stretching region. When the temperature was raised to about 60 °C for 4 h, the color of the solution changed from red to brown. After evaporation to dryness, 0.105 g (74% yield) of $[Nb(CO)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}FC_6H_4)_2]$ was obtained. The compound was recrystallized from toluene at about −30 °C. Anal. Calcd for $C_{25}H_{16}BF_4NbO$: C, 58.6; H, 3.1. Found: C, 58.8; H, 3.0. IR spectrum: 2039 (toluene), 2038 (Nujol) cm^{-1}. ^1H NMR spectrum (benzene-d_6): 7.40 (dd, 4 H, J_{HH} = 9 Hz, J_{HF} = 7 Hz), 7.10 (dd, 4 H, J_{HH} = 9 Hz, J_{HF} = 13 Hz), 5.0 (t, 4 H, $J_{HH} = J_{HF}$ = 7 Hz), 4.50 (dd, 4 H, J_{HH} = 7.2 Hz, J_{HF} = 4.0 Hz) ppm.

Structure Solution and Refinement of 2b, 4a,b, and 6a. $[Nb(mes)_2(PhC_2Ph)][B(p\text{-}FC_6H_4)_4]$ (**2b**) crystals were obtained by slowly cooling a saturated (50 °C) toluene solution to room temperature. $[Nb(MeC_2Me)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (**4a**) crystals were obtained by slowly cooling a toluene solution to about −30 °C. $[Nb(MeC_2Me)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}FC_6H_4)_2]$ (**4b**) crystals were grown from heptane after dissolution at 60 °C and slow cooling of the solution to about −30 °C. $[Nb(CO)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (**6a**) crystals were grown from toluene at about −30 °C.

The X-ray data were collected with an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Calculations were performed on a VAX station 3100 using the SHELXS[16] and SDP[17] programs. Crystal data and data collection parameters are reported in Table 1. The unit cell constants were

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Table 1. Lattice Constants and Parameters of the Structure Determination of $[Nb(mes)_2(PhC_2Ph)][B(p\text{-}F\text{-}C_6H_4)_4]\cdot 2C_7H_8$ (2b), $[Nb(MeC_2Me)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$ (4a), $[Nb(MeC_2Me)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}F\text{-}C_6H_4)_2]$ (4b), and $[Nb(CO)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]\cdot C_7H_8$ (6a)

	2b	**4a**	**4b**	**6a**
formula	$C_{56}H_{50}BF_4Nb\cdot 2C_7H_8$	$C_{28}H_{26}BNb$	$C_{28}H_{22}BF_4Nb$	$C_{25}H_{20}BNbO\cdot C_7H_8$
mol wt	1087.0	466.2	538.2	532.3
cryst dimens (mm)	0.4 × 0.4 × 0.3	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.3	0.12 × 0.12 × 0.16
space group	$C2/c$ (No. 15)	$P\bar{4}2_1m$ (No. 113)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
cell constants				
a (Å)	17.640(3)	9.734(1)	11.776(3)	10.495(2)
b (Å)	16.8386(8)	9.734(1)	15.666(3)	14.586(1)
c (Å)	19.616(2)	11.6333(9)	28.042(5)	17.174(3)
β (deg)	97.230(9)			
V (Å^3)	5780(2)	1102.3(3)	5173(3)	2629(1)
Z	4	2	8	4
D_{calc} (g cm^{-3})	1.143	1.405	1.382	1.345
T (K)	293	293	293	243
radiation (λ, Å)	Cu Kα (1.5418)	Mo Kα (0.7093)	Mo Kα (0.7093)	Mo Kα (0.7093)
μ (cm^{-1})	21.0	5.33	4.85	4.58
F(000)	2272	480	2176	1096
scan range	ω	ω	$\omega/2\theta$	ω
range of data collection (θ, deg)	5–70	3–29	3–30	3–27
no. of meas rflns	6919	6183	11 200	3181
abs cor	PSI-SCAN[18]	PSi-SCAN[18]	DIFABS[19]	
no. of indep rflns in refinement	4686 ($I > 3\sigma(I)$)	1444 ($I > 3\sigma(I)$)	4192 ($I > 3\sigma(I)$)	1967 ($I > \sigma(I)$)
no. of refined params	363	81	392	287
residual peak (e/Å^3)	0.29	0.4	0.61	0.7
extinction coeff	2.5 × 10^{-6}	not refined	1.3 × 10^{-7}	7 × 10^{-9}
R^a	0.031	0.022	0.053	0.060
$R_w{}^b$	0.046	0.031	0.066	0.058
GOF	1.643	1.115	1.905	1.510

[a] $R = \sum|\Delta F|/\sum|F_o|$. [b] $R_w = [\sum w(\Delta F)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2|F_o|$.

Table 2. Atomic Coordinates of $[Nb(mes)_2(PhC_2Ph)][B(p\text{-}F\text{-}C_6H_4)_4]\cdot 2C_7H_8$ (2b)[a]

atom	x	y	z	B(eq)[b] (Å^2)	atom	x	y	z	B(eq)[b] (Å^2)
Nb1	0.000	0.17791(1)	0.250	3.397(4)	C23	0.0889(1)	0.1285(1)	0.6414(1)	4.81(5)
F1	0.0502(1)	0.07432(9)	0.53180(8)	7.29(4)	C24	0.0382(2)	0.1269(1)	0.5829(1)	5.02(5)
F2	0.2460(1)	0.5197(1)	0.8207(1)	10.08(6)	C25	−0.0248(2)	0.1750(1)	0.5738(1)	5.14(5)
C1	−0.0042(1)	0.3023(1)	0.2821(1)	3.93(4)	C26	−0.0357(1)	0.2283(1)	0.6253(1)	4.49(5)
C2	−0.0207(1)	0.3493(1)	0.3405(1)	4.11(4)	C31	0.0735(1)	0.3534(1)	0.7700(1)	4.06(4)
C3	−0.0086(2)	0.3189(1)	0.4075(1)	5.38(6)	C32	0.1367(1)	0.3590(2)	0.7344(1)	5.12(5)
C4	−0.0280(2)	0.3617(2)	0.4621(1)	6.41(7)	C33	0.1947(1)	0.4146(2)	0.7505(2)	6.48(7)
C5	−0.0610(2)	0.4358(2)	0.4516(2)	6.29(6)	C34	0.1891(1)	0.4646(2)	0.8051(2)	6.83(7)
C6	−0.0734(2)	0.4669(2)	0.3865(1)	6.05(6)	C35	0.1293(2)	0.4633(2)	0.8420(2)	6.10(6)
C7	−0.0530(1)	0.4251(1)	0.3311(1)	4.96(5)	C36	0.0720(1)	0.4077(1)	0.8244(1)	4.97(5)
C11	−0.1377(1)	0.2124(1)	0.2133(1)	4.68(5)	C41	0.2695(4)	0.2045(5)	0.4905(3)	8.7(2)
C12	−0.1144(1)	0.1548(1)	0.1682(1)	4.80(5)	C42	0.1986(2)	0.2158(3)	0.5192(2)	9.4(1)
C13	−0.0935(1)	0.0785(1)	0.1936(1)	4.64(5)	C43	0.2726(5)	0.3504(6)	0.4932(4)	10.2(2)
C14	−0.0840(1)	0.0659(1)	0.2642(1)	4.46(4)	C44	0.2986(3)	0.1363(4)	0.4759(3)	12.9(2)
C15	−0.0973(1)	0.1259(1)	0.3121(1)	4.40(4)	C45	0.1708(4)	0.2768(6)	0.5332(4)	9.0(2)
C16	−0.1275(1)	0.1976(1)	0.2839(1)	4.54(5)	C51	0.2534(3)	0.7078(4)	0.5607(4)	17.4(2)
C17	−0.1724(2)	0.2894(2)	0.1860(2)	6.61(7)	C52	0.2386(3)	0.6640(4)	0.4973(4)	18.7(2)
C18	−0.0844(2)	0.0115(2)	0.1445(2)	6.76(7)	C53	0.2659(2)	0.7861(3)	0.5603(3)	17.7(2)
C19	−0.0974(2)	0.1076(2)	0.3875(1)	6.12(6)	C54	0.2573(6)	0.6608(7)	0.6070(8)	17.4(5)
C21	0.0137(1)	0.2346(1)	0.6865(1)	3.76(4)	B	0.000	0.2940(2)	0.750	3.75(6)
C22	0.0754(1)	0.1820(1)	0.6926(1)	4.39(4)					

[a] Estimated standard deviations in parentheses refer to the least significant digit. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos\beta)\beta_{13}]$.

obtained from a least-squares refinement of 25 accurately centered reflections. In the case of **6a** a very small crystal was used and no absorption correction was applied. In all other cases an empirical absorption correction was applied before averaging symmetrically equivalent reflections. The structures were solved by Patterson and difference Fourier methods. In the final full-matrix refinement hydrogen atoms were included in structure factor calculations and statistical weights were used for observed reflections. The atomic coordinates are reported in Tables 2–5.

Reaction of $[Nb(mes)_2][BPh_4]$ with Acetylene. (a) In Toluene. A suspension of $[Nb(mes)_2][BPh_4]$, obtained from $Nb(mes)_2$ (0.34 g, 1.02 mmol) and $[FeCp_2][BPh_4]$ (0.49 g, 0.97 mmol) in toluene (50 mL), was treated with acetylene at room temperature. Gas absorption and formation of a black solid was observed. The mixture was stirred at room temperature for 24 h and filtered, and the solid was washed with toluene and dried *in vacuo*, affording 1.02 g of polyacetylene[20] (monomer/Nb molar ratio 38.5). The ratio between the areas of the two absorptions at 1014 and 741 cm^{-1} indicated that the polymer was a 20:1 mixture of *trans* and *cis* polyacetylene. The solution contained 18.5 mmol of benzene (by gas chromatography) for a benzene/Nb molar ratio of 18.

(b) In THF. A solution of $[Nb(mes)_2(THF)][BPh_4]$[4] (0.07 g, 0.1 mmol) in THF (100 mL) was saturated with acetylene at room temperature. An exothermic reaction took place with formation of black polyacetylene. After 24 h of stirring at room temperature, the polymer was filtered, washed with THF, and dried *in vacuo* (0.07 g; monomer/Nb molar ratio 28). The solution contained 39.8 mmol of benzene (by gas chromatography) for a benzene/Nb molar ratio of 412.

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Table 3. Atomic Coordinates of [Nb(MeC$_2$Me)(η^6-C$_6$H$_5$)$_2$B(C$_6$H$_5$)$_2$] (4a)^a

atom	*x*	*y*	*z*	B^b (Å^2)	atom	*x*	*y*	*z*	B^b (Å^2)
Nb	0.000	0.500	0.05748(2)	2.286(3)	C6	–0.2286(2)	0.5561(2)	–0.3315(2)	3.68(4)
C1	0.0865(2)	0.5865	–0.1185(2)	2.62(3)	C7	–0.3135(3)	0.6413(3)	–0.3975(2)	4.37(5)
C2	0.1981(2)	0.5199(2)	–0.0603(2)	2.94(3)	C8	–0.2709(2)	0.7709	–0.4290(3)	4.47(4)
C3	0.2404(2)	0.5629(2)	0.0511(2)	3.47(4)	C9	0.0444(3)	0.4556	0.2453(3)	4.44(4)
C4	0.1711(2)	0.6711	0.1049(3)	3.80(4)	C10	0.1376(4)	0.3624	0.3071(5)	9.13(8)
C5	–0.0981(2)	0.5981	–0.2954(2)	2.96(3)	B	0.000	0.500	–0.2169(3)	2.65(4)

^{a} Estimated standard deviations in parentheses refer to the least significant digit. ^{b} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33}]$.

Table 4. Atomic Coordinates of the two Independent Molecules of [Nb(McC$_2$Me)(η^6-*p*-FC$_6$H$_4$)$_2$B(*p*-F-C$_6$H$_4$)$_2$] (4b)^a

atom	*x*	*y*	*z*	B(eq)^b (Å^2)	atom	*x*	*y*	*z*	B(eq)^b (Å^2)
Nb1	0.34550(9)	0.74354(7)	0.76050(4)	3.56(2)	C42	0.278(1)	0.410(1)	0.8860(5)	7.3(4)*
Nb2	0.73064(9)	0.55981(7)	0.53598(4)	3.27(2)	C43	0.296(1)	0.438(1)	0.9293(5)	7.0(4)*
F1	0.4295(7)	0.6764(5)	0.6497(3)	7.4(2)	C44	0.279(1)	0.515(1)	0.9471(6)	7.9(4)*
F2	0.4262(7)	0.9427(5)	0.7959(3)	7.7(2)	C45	0.250(1)	0.5786(9)	0.9119(5)	6.4(4)*
F3	–0.3033(7)	0.6234(6)	0.8306(4)	9.9(3)	C50	0.8181(9)	0.5416(7)	0.6102(4)	3.1(2)*
F4	0.3272(8)	0.3735(6)	0.9606(3)	10.6(3)	C51	0.7114(9)	0.5814(7)	0.6169(4)	3.1(2)*
F5	0.5199(6)	0.4227(5)	0.5679(3)	6.2(2)	C52	0.609(1)	0.5380(7)	0.6041(4)	3.8(3)*
F6	0.7288(7)	0.6410(5)	0.4229(2)	6.5(2)	C53	0.6176(9)	0.4586(7)	0.5829(4)	3.9(3)*
F7	1.3433(7)	0.4130(6)	0.6438(3)	9.9(3)	C54	0.718(1)	0.4181(8)	0.5718(4)	4.3(3)*
F8	0.9882(7)	0.8787(5)	0.7377(3)	6.7(2)	C55	0.8167(9)	0.4594(7)	0.5882(4)	3.7(3)*
C1	0.399(1)	0.897(1)	0.6720(5)	8.6(5)	C60	0.9074(9)	0.6267(7)	0.5503(4)	3.2(2)*
C2	0.429(1)	0.8320(9)	0.7095(4)	4.7(3)	C61	0.8213(9)	0.6904(7)	0.5419(4)	3.6(2)*
C3	0.508(1)	0.7966(8)	0.7307(5)	5.5(3)	C62	0.763(1)	0.6977(7)	0.4984(4)	3.9(2)*
C4	0.631(1)	0.783(1)	0.7418(5)	7.6(4)	C63	0.789(1)	0.6365(8)	0.4652(5)	5.2(3)*
C5	0.470(1)	0.653(1)	0.5145(5)	7.5(5)	C64	0.864(1)	0.5714(8)	0.4700(4)	4.5(3)*
C6	0.561(1)	0.5895(9)	0.5066(5)	5.8(4)	C65	0.925(1)	0.5673(8)	0.5134(4)	3.9(3)*
C7	0.595(1)	0.5266(9)	0.4840(5)	5.5(4)	C70	1.0454(8)	0.5464(7)	0.6127(4)	2.8(2)*
C8	0.576(2)	0.461(1)	0.4473(5)	10.2(5)	C71	1.144(1)	0.5556(8)	0.5854(4)	4.4(3)*
C10	0.244(1)	0.6167(7)	0.7729(4)	4.2(3)*	C72	1.246(1)	0.5125(8)	0.5947(5)	5.5(3)*
C11	0.361(1)	0.5960(8)	0.7707(5)	5.1(3)*	C73	1.246(1)	0.4588(8)	0.6327(5)	5.6(3)*
C12	0.419(1)	0.6136(9)	0.7273(5)	6.3(4)*	C74	1.154(1)	0.4422(9)	0.6615(5)	5.8(3)*
C13	0.369(1)	0.6541(8)	0.6886(4)	4.8(3)*	C75	1.055(1)	0.4868(8)	0.6499(4)	4.5(3)*
C14	0.254(1)	0.6781(8)	0.6905(4)	4.8(3)*	C80	0.9373(9)	0.6816(7)	0.6399(4)	3.4(2)*
C15	0.195(1)	0.6581(8)	0.7309(4)	4.5(3)*	C81	0.897(1)	0.6786(7)	0.6877(4)	3.7(3)*
C20	0.244(1)	0.7254(7)	0.8318(4)	3.7(2)*	C82	0.9125(9)	0.7443(8)	0.7199(4)	3.9(2)*
C21	0.361(1)	0.7340(8)	0.8442(4)	4.4(3)*	C83	0.968(1)	0.8138(8)	0.7039(4)	4.3(3)*
C22	0.423(1)	0.8076(8)	0.8333(4)	5.1(3)*	C84	1.012(1)	0.8226(8)	0.6590(4)	4.6(3)*
C23	0.369(1)	0.8694(8)	0.8098(4)	4.9(3)*	C85	0.9939(9)	0.7571(8)	0.6277(4)	4.0(2)*
C24	0.256(1)	0.8675(8)	0.7951(4)	4.7(3)*	C92	0.377(4)	0.224(3)	0.538(2)	13(1)*
C25	0.194(1)	0.7944(7)	0.8080(4)	3.6(3)*	C97	0.469(5)	0.187(3)	0.520(2)	15(2)*
C30	0.050(1)	0.6315(8)	0.8269(4)	4.2(3)*	C91	0.583(4)	0.740(4)	–0.996(2)	13(1)*
C31	–0.013(1)	0.6902(8)	0.8513(4)	4.7(3)*	C96	0.488(5)	0.706(3)	0.004(2)	17(2)*
C32	–0.133(1)	0.6892(9)	0.8553(5)	5.8(3)*	C94	0.189(3)	0.269(3)	0.518(1)	12(1)*
C33	–0.185(1)	0.629(1)	0.8302(5)	6.8(4)*	C93	0.193(3)	0.722(3)	0.029(1)	11(1)*
C34	–0.130(1)	0.5684(9)	0.8042(5)	6.3(3)*	C95	0.406(4)	0.686(3)	0.023(2)	14(2)*
C35	–0.012(1)	0.5705(9)	0.8010(4)	5.2(3)*	B1	0.187(1)	0.6300(9)	0.8266(5)	4.0(3)*
C40	0.231(1)	0.5594(9)	0.8638(4)	5.2(3)*	B2	0.931(1)	0.6006(9)	0.6057(5)	3.4(3)*
C41	0.245(1)	0.4744(9)	0.8512(5)	6.7(4)*					

^{a} Estimated standard deviations in parentheses refer to the least significant digit. ^{b} Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}]$.

Results and Discussion

Tetraarylborates of the Bis(mesitylene)niobium(I) Cation. As the ionic alkyne derivatives of the bis(mesitylene)niobium(I) cation are the precursors to the uncharged tetraarylborato complexes, these compounds are described first.

The one-electron oxidation of Nb(mes)$_2$ with the ferrocenium cations [FeCp$_2$][Y][21] (see eq 1) affords the 16-electron bis(mesitylene)niobium(I) cations [Nb(mes)$_2$][Y], which are expected to add a 2-electron-donor ligand to give the corresponding 18-electron species. As a matter of fact, when toluene suspensions of [Nb(mes)$_2$][Y] (Y = BPh$_4$, B(*p*-FC$_6$H$_4$)$_4$, B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$) are treated with an excess of RC$_2$R, orange to red solids of general formula [Nb(mes)$_2$(RC$_2$R)][Y] have been obtained according to eq 2. Due to the low solubility of the starting materials, reactions 2 required a few hours to go to completion.

$$\mathrm{Nb(mes)_2} + [\mathrm{FeCp_2}][\mathrm{Y}] \rightarrow [\mathrm{Nb(mes)_2}][\mathrm{Y}] + \mathrm{FeCp_2} \quad (1)$$

$$\mathrm{Y} = \mathrm{BPh_4},\ \mathrm{B}(p\text{-}\mathrm{FC_6H_4})_4,\ \mathrm{B}(p\text{-}\mathrm{CF_3C_6H_3})_4,\ \mathrm{B}[3,5\text{-}(\mathrm{CF_3})_2\mathrm{C_6H_3}]_4$$

$$[\mathrm{Nb(mes)_2}][\mathrm{Y}] + \mathrm{RC_2R} \rightarrow \underset{\textbf{1a–c, 2a,b}}{[\mathrm{Nb(mes)_2(RC_2R)}][\mathrm{Y}]} \quad (2)$$

$$\mathrm{R} = \mathrm{CH_3},\ \mathrm{Y} = \mathrm{BPh_4}\ (\textbf{1a}),\ \mathrm{B}(p\text{-}\mathrm{FC_6H_4})_4\ (\textbf{1b}),\ \mathrm{B}[3,5\text{-}(\mathrm{CF_3})_2\mathrm{C_6H_3}]_4\ (\textbf{1c});\ \mathrm{R} = \mathrm{Ph},\ \mathrm{Y} = \mathrm{BPh_4}\ (\textbf{2a}),\ \mathrm{B}(p\text{-}\mathrm{FC_6H_4})_4\ (\textbf{2b})$$

The preparation of **1a** should be performed at low temperature in order to prevent the thermal rearrangement to the uncharged tetraphenylborato compound (*vide*

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[21] The ferrocenium derivatives [FeCp$_2$][Y] with Y = B(*p*-FC$_6$H$_4$)$_4$, B(*p*-CF$_3$C$_6$H$_4$)$_4$, and B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$ are new compounds.

Table 5. Atomic Coordinates of $[Nb(CO)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]\cdot C_7H_8$ (6a)[a]

atom	*x*	*y*	*z*	*B*[b] (Å^2)
Nb	0.75656(8)	0.82955(5)	0.70640(4)	3.69(1)
O	0.788(1)	0.7430(7)	0.5334(5)	20.9(4)
C	0.771(1)	0.7761(7)	0.5925(5)	10.9(3)
C10	0.7827(7)	0.9541(5)	0.7894(4)	3.6(2)
C11	0.6818(9)	0.9768(6)	0.7363(4)	3.9(2)
C12	0.7036(9)	0.9782(6)	0.6563(4)	5.1(2)
C13	0.8255(9)	0.9564(6)	0.6264(5)	4.5(2)
C14	0.9278(9)	0.9321(7)	0.6769(5)	4.5(2)
C15	0.9051(8)	0.9304(6)	0.7562(5)	3.8(2)
C20	0.7137(8)	0.8113(5)	0.8393(4)	3.7(2)
C21	0.8196(9)	0.7521(6)	0.8191(5)	4.1(2)
C22	0.806(1)	0.6841(6)	0.7626(5)	5.0(2)
C23	0.6898(9)	0.6740(7)	0.7230(4)	5.1(2)
C24	0.5824(9)	0.7290(7)	0.7402(5)	4.8(2)
C25	0.5957(8)	0.7980(6)	0.7977(5)	3.5(2)
C30	0.8653(8)	0.9131(6)	0.9366(5)	3.6(2)
C31	0.8733(9)	0.8427(6)	0.9925(5)	4.6(2)
C32	0.967(1)	0.8417(8)	1.0475(6)	6.2(3)
C33	1.055(1)	0.9072(8)	1.0496(6)	7.0(3)
C34	1.0515(9)	0.9783(9)	0.9977(6)	7.0(3)
C35	0.9512(9)	0.9805(8)	0.9404(6)	5.3(3)
C40	0.6242(8)	0.9619(6)	0.9149(5)	3.8(2)
C41	0.5980(8)	1.0552(6)	0.9083(5)	3.8(2)
C42	0.4991(9)	1.0984(7)	0.9456(5)	5.2(2)
C43	0.4141(9)	1.0451(8)	0.9897(5)	5.6(3)
C44	0.434(1)	0.9569(7)	0.9991(6)	5.6(3)
C45	0.5366(9)	0.9147(7)	0.9615(5)	4.5(2)
C50	0.741(2)	0.355(1)	0.7674(8)	11.0(4)*
C51	0.749(1)	0.3761(8)	0.6857(6)	8.6(3)*
C52	0.795(1)	0.308(1)	0.6450(8)	10.6(4)*
C53	0.835(1)	0.221(1)	0.6677(9)	10.3(4)*
C54	0.821(2)	0.213(1)	0.7522(9)	11.4(5)*
C55	0.769(1)	0.2762(8)	0.8005(7)	8.5(3)*
C56	0.681(1)	0.424(1)	0.802(1)	17.3(6)
B	0.742(1)	0.9145(6)	0.8762(5)	3.2(2)

[a] Estimated standard deviations in parentheses refer to the least significant digit. [b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}]$.

infra). Electron-withdrawing groups on the phenyl rings of the borate anion stabilize the compounds: for example, pure **1a** was obtained only at low temperature, while **1b** is stable up to 50 °C and **1c** does not decompose even at 100 °C and is stable in air for short periods of time. This is in agreement with the known[14,22] suppression of the electrophilic attack by proton on the phenyl-ring carbon ipso to boron by introducing electron-withdrawing substituents on the ring. Moreover, it is known that substituents such as $-F$ and $-CF_3$ on the tetraarylborato anion strongly influence the catalytic[23] and electronic[14] properties of the cationic moiety. The higher stability of the ring-substituted borate derivatives should be attributed to a number of factors, such as the lower polarization due to the lower charge density on the anion, the lower tendency to undergo the arene-exchange reaction (*vide infra*), and the reluctance of the ring-substituted fragments to undergo both nucleophilic and electrophilic attacks.

The diphenylacetylene compounds **2a** and **2b** are more thermally stable than the but-2-yne derivatives: in the case of **2b**, no rearrangement (*vide infra*) was observed even at temperatures as high as 100 °C.

Compounds **1** and **2** have been characterized by IR spectroscopy in the solid state. The IR spectra show the absorption due to $\tilde{\nu}_{CC}$ of the alkyne triple bond in the range 1832–1767 cm^{-1}, as expected for an alkyne coordinated to a transition metal.[24] The observed values, which are shifted by about 350–400 cm^{-1} to lower wavenumbers with respect to the free alkyne values (2223 cm^{-1} for C_2Ph_2 and 2233 cm^{-1} for C_2Me_2[25]), are in agreement with a *considerable back-donation from the metal to the empty* π^* orbitals of the alkyne ligand, as shown by the bending away of the phenyl groups of the diphenylacetylene ligand in the structure of compound **2b** (*vide infra*).

Table 6. Selected Bond Distances (Å) and Angles (deg) in $[Nb(mes)_2(PhC_2Ph)][B(p\text{-}FC_6H_4)_4]\cdot 2C_7H_8$ (2b)[a]

Nb1–C1	2.190(2)	C31–B	1.645(2)
C21–B	1.640(2)	F2–C34	1.372(2)
F1–C24	1.373(2)	C1–C2	1.452(2)
C1–C1′	1.286(4)		
C1–Nb1–C1′	34.14(9)	C1–C1′–C2	146.3(1)
C1–C2–C3	121.3(2)	C1–C2–C7	120.8(2)
C21–B–C21′	104.8(2)	C21–B–C31	111.45(9)
C21′–B–C31	112.11(8)	C31–B–C31′	105.1(2)

[a] Estimated standard deviations in parentheses refer to the least significant digit.

Compounds **1** and **2** are soluble in ethereal solvent (in the case of **1a** it has been shown by ^1H NMR spectroscopy that THF readily displaces the alkyne ligand), and the solubility in aromatic hydrocarbons varies with both the alkyne ligand (the diphenylacetylene derivatives are more soluble than the but-2-yne analogues) and the anion (the solubility increases with increasing ring substitution in the tetraarylborate anion[23b]). In the case of **2b**, the solubility in toluene has allowed crystals to be grown and a structural study to be performed.

The molecular structures of the cationic and anionic parts of $[Nb(mes)_2(PhC_2Ph)][B(p\text{-}FC_6H_4)_4]$ are reported in Figure 1. Table 6 lists a selection of bonding distances and angles. We note that the $[B(p\text{-}FC_6H_4)_4]^-$ anion of compound **2b** has not been structurally characterized before. The structure consists of $[Nb(mes)_2(PhC_2Ph)]^+$ cations and $[B(p\text{-}FC_6H_4)_4]^-$ anions: the anionic part of the compound shows a slightly distorted tetrahedral *arrangement of the four fluoro-substituted aromatic rings* around the boron atom with two angles smaller (C21–B–C21′ = 104.8(2)° and C31–B–C31′ = 105.1(2)°) and two angles larger than 109.5° (C21–B–C31 = 111.45(9)° and C21–B–C31 = 112.11(8)°). The phenyl rings are substantially planar, with a maximum deviation from the least-squares plane of 0.009 Å, while the angle between the planes of the rings is 70.2° (average deviation 9.2°), a value which can be compared with those reported[26] for the phenyl rings of the tetraphenylborate anion (70.9°, average deviation 6.1°).

The cationic part of **2b** represents another example of a bent bis(arene) derivative of niobium(I), the others being $[Nb(mes)_2(CO)]^+$ [4] and $[Nb(\eta^6\text{-toluene})_2(PMe_3)]^+$.[7] The $[Nb(mes)_2(PhC_2Ph)]^+$ species presents a larger bending of the aromatic rings with respect to the carbonyl derivative (147.7 *vs* 142.3°, respectively) and longer Nb–ring centroid distances (2.016 Å *vs* 1.923 Å, mean value), in agreement with the increased steric hindrance of the diphenylacety-

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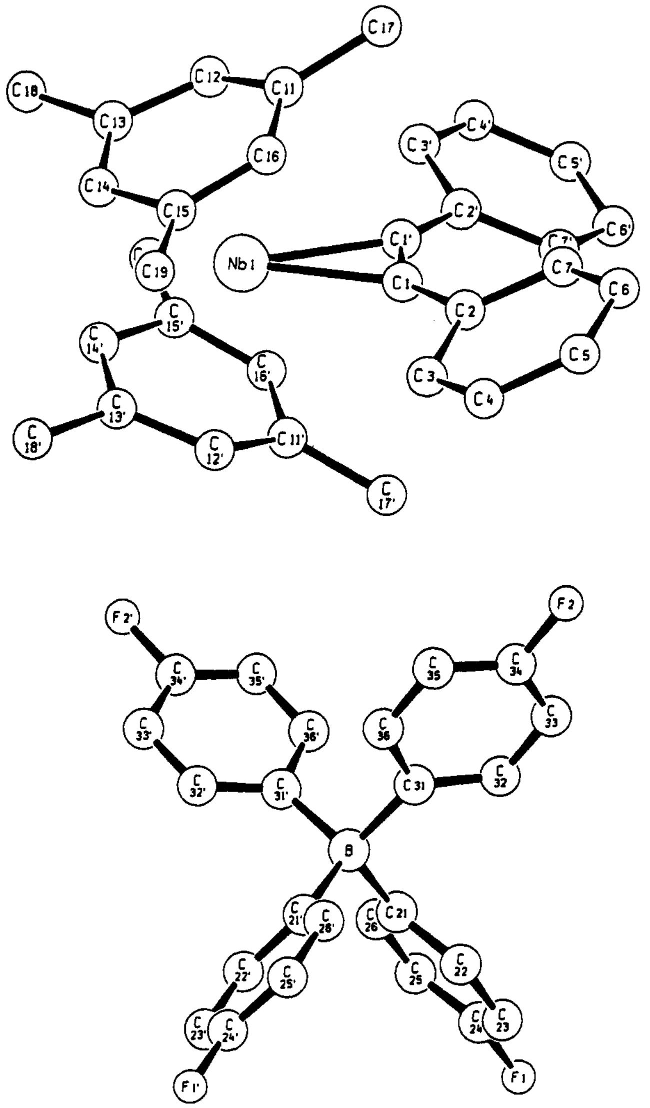

Figure 1. SCHAKAL view of the $[Nb(mes)_2(PhC_2Ph)]^+$ cation and of the $[B(p\text{-}FC_6H_4)_4]^-$ anion in $[Nb(mes)_2(PhC_2Ph)][B(p\text{-}FC_6H_4)_4]\cdot 2C_7H_8$ (**2b**).

lene ligand. Moreover, it is worth noting that the mesitylene rings are not eclipsed, as observed in the other structurally characterized derivatives of niobium(I)[4,27] and niobium(0),[27] but rotated by about 37°.

As far as the Nb–alkyne fragment is concerned, the Nb–C1 distance is 2.190(2) Å; the C1–C1′ distance (1.286(4) Å) is longer than in free acetylenes (*ca.* 1.21 Å),[28] and the C2–C1–C1′ angle (146.3(1)°) deviates considerably from 180°. When comparison is made with the data reported in Table 7, which collects the relevant parameters for some structurally characterized niobium(I) and tantalum(I) alkyne derivatives, it appears that, in agreement with the 18-electron rule, the alkyne behaves as a two-electron donor in **2b**.

The acetylenic derivatives of niobium(I) have been reacted with CO at atmospheric pressure in toluene: but-2-yne is promptly displaced by carbon monoxide according to eq 3. In one case (**3a**), the CO absorption was measured

$$\underset{\mathbf{1}}{[Nb(mes)_2(MeC_2Me)][Y]} + CO \rightarrow \underset{\mathbf{3a\text{–}c}}{[Nb(mes)_2(CO)][Y]} + MeC_2Me \quad (3)$$

$$Y = BPh_4\ (\mathbf{3a}),\ B(p\text{-}FC_6H_4)_4\ (\mathbf{3b}),\ B[3,5\text{-}(CF_3)_2C_6H_3]_4\ (\mathbf{3c})$$

and found to correspond to 1 mol of CO/mol of Nb complex and the displaced but-2-yne was found by gas chromatography. The green carbonyl products are moderately soluble in THF; these solutions show one IR carbonyl stretching vibration at about 1990 cm^{-1}, substantially independent of the nature of the counteranion. Compounds **3a–c** were found spectroscopically to be identical with the carbonylation products of the unstable, ionic $[Nb(mes)_2][Y]$.

On the other hand, compounds **2** do not react with CO, suggesting a stronger interaction between diphenylacetylene and niobium. This is in agreement with the CC stretching vibrations of **2**, which are at lower wavenumbers (mean value 1770 cm^{-1}) than for compounds **1** (mean value 1820 cm^{-1}).

Niobium(I) Complexes Containing the 12-Electron-Donor Tetraarylborato Ligand. As noted earlier in this paper, some of the cationic alkyne complexes containing the tetraarylborato counteranion undergo a thermal rearrangement in toluene solution. The derivatives **1a,b** and **2a**, when heated at temperatures as high as 70 °C, produce red to orange solutions which upon filtration and cooling at about −30 °C afford red to orange crystals of $[Nb(RC_2R)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2]$, according to eq 4.

$$[Nb(mes)_2(RC_2R)][B(XC_6H_4)_4] \xrightarrow{\text{toluene}} \underset{\mathbf{4a,b,\ 5a}}{[Nb(RC_2R)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2]} + 2\ mes \quad (4)$$

$$R = Me,\ X = H\ (\mathbf{4a},\ p\text{-}F\ (\mathbf{4b}));\ R = Ph,\ X = H\ (\mathbf{5a})$$

The yields of reactions 4 varied from 16% for **5a** to about 70% for **4b**. In the case of compounds 4, an excess of but-2-yne during the thermal treatment is beneficial to the yield of the reaction; on the other hand, no reaction is observed for R = Ph and X = *p*-F, the starting material being recovered unchanged after the thermal treatment. Moreover, we note that the thermal treatment of $[Nb(mes)_2][BPh_4]$ in the absence of any additional ligand (CO or an alkyne) led to complete decomposition to unidentified pyrophoric black materials by operating under the same experimental conditions as for the preparation of compounds 4 and 5.

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Table 7. Structural Parameters for Niobium(I) and Tantalum(I) Alkyne Complexes

complex	M–C (Å)	C–C (Å)	R–C–C (deg)	alkyne donor no.[a]	ref
$\mathrm{NbI(CO)_2(C_2Me_2)(PEt_3)_2}$	2.094(8)	1.30(1)	136.0(9)	4	29
$\mathrm{TaI(CO)_2(C_2Ph_2)(PMe_3)_2}$	2.06(6)	1.33(1)	135(3)	4	30
$\mathrm{NbCl(dmpe)_2(Me_3SiOC_2OSiMe_3)}$	2.074(3)	1.310(6)	133.4(2)	4	31
$\mathrm{TaCl(dmpe)_2(Me_3SiOC_2OSiMe_3)}$	2.065(5)	1.339(9)	132.3(3)	4	31
$\mathrm{Ta(OSO_2CF_3)(dmpe)_2(Me_3SiOC_2OSiMe_3)}$	2.07(1)	1.36(1)	135(1)	4	31
$\mathrm{TaCl(dmpe)_2(Me_3SiOC_2OSiPr^i{}_3)}$	2.110(5)	1.322(7)	131.2(5)	4	32
$\mathrm{NbCp(CO)(C_2Ph_2)_2}$	2.19	1.35(2)	138	3	33
$\mathrm{NbCp(CO)(PhC_2GePh_3)_2}$	2.18	1.30	141	3	34
$\mathrm{NbCp(CO)(C_2Ph_2)(\eta^4\text{-}C_4Ph_4)}$	2.25(4)	1.26(4)	141(3)	2	35
$\mathrm{[Nb(mes)_2(C_2Ph_2)][B(\mathit{p}\text{-}FC_6H_4)_4]}$	2.190(2)	1.286(4)	146.3(1)	2	this work
$\mathrm{[Nb(C_2Me_2)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]}$	2.269(3)	1.2195(8)	150.8(3)	2	this work
$\mathrm{[Nb(C_2Me_2)(\eta^6\text{-}\mathit{p}\text{-}C_6H_4F)_2B(\mathit{p}\text{-}C_6H_4F)_2]}$	2.23(1)	1.23(1)	147(1)	2	this work

[a] Number of electrons assumed to be involved in the bonding.

The structures of compounds **4** and **5** were assigned on the basis of IR and NMR spectra and were confirmed *via* X-ray diffraction studies on single crystals of **4a,b**.

The IR spectra of compounds **4** and **5** show an absorption of medium intensity in the range 1700–1900 cm^{-1} which is assigned to the stretching vibration of the carbon–carbon bond of the coordinated alkyne. As may be seen from the data differences up to 100 cm^{-1} are observed in the case of **4a** with respect to the ionic bis(mesitylene)precursor **1a**, thus suggesting that the alkyne ligand interacts less strongly with the niobium atom in the neutral compounds **4** and **5** than in the ionic species **1** and **2**.

compd	$\tilde{\nu}_{CC}$ (cm^{-1})	compd	$\tilde{\nu}_{CC}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})
1a	1818	**4a**	1919	101
1b	1817	**4b**	1889	72
2a	1767	**5a**	1776	9

The ^{1}H NMR spectrum of **4b** containing the *p*-fluoro-substituted tetraarylborato ligand shows two sets of aromatic ligands equally contributing to the intensity of the resonances: one of them has been assigned to the aromatic rings not coordinated to the transition metal (7.42 and 7.10 ppm) and the other to the niobium-bonded aromatic rings (5.13 and 4.66 ppm). The upfield shift on coordination is a well-documented phenomenon.[36] Also, the spectrum of **5a**, containing the tetraphenylborato ligand, shows two sets of signals with the multiplet due to the *para* proton displaying an exceedingly high upfield shift (3.21 ppm).

The ^{13}C NMR spectrum of **4b** shows a singlet at 100.49 ppm attributed to the carbon atoms of the alkyne triple bond. According to the empirical correlation between the alkyne π back-donation and the ^{13}C chemical shift observed by Templeton,[37] a resonance in the range 100–120 ppm is considered to be typical of an alkyne ligand behaving as a two-electron donor. Moreover, the ^{13}C NMR spectra of both **4b** and **5a** show the presence of two sets of signals for the aromatic carbons, one of which is shifted upfield,[38] the other being located in a range of frequencies typical of the aromatic carbon atoms.

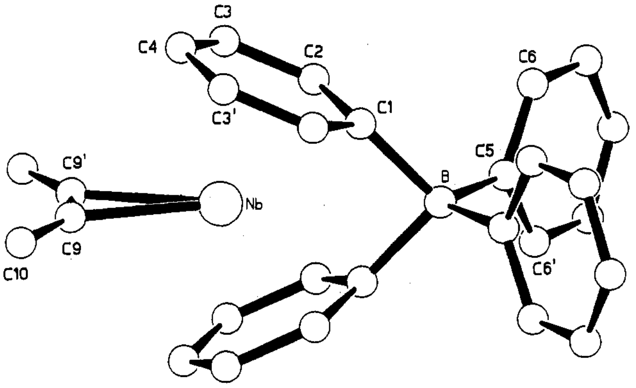

Figure 2. SCHAKAL plot of $\mathrm{[Nb(MeC_2Me)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]}$ (**4a**) with the numbering scheme used. Estimated standard deviations in parentheses refer to the least significant digit.

Table 8. Selected Bond Distances (Å) and Angles (deg) in $\mathrm{[Nb(CH_3C_2CH_3)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]}$ (4a)[a]

C1–B	1.653(3)	C5–B	1.631(3)
Nb–C9	2.269(3)	C9–C9′	1.2195(8)
C9–C10	1.472(4)		
C9–Nb–C9′	31.18(5)	C2–C1–B	118.84(9)
C9′–C9–C10	150.8(3)	C1–B–C1′	92.3(2)
C1–B–C5	112.81(7)	C1–B–C5′	112.82(7)
C5–B–C5′	112.0(3)		

[a] Estimated standard deviations given in parentheses refer to the least significant digit.

The spectroscopic data could be explained by assuming that two of the aryl rings of the tetraarylborato moiety interact with the niobium center, most presumably *via* an interannular boron-bridged system. This structural assignment has been confirmed by the X-ray study performed on single crystals of both **4a** and **4b**.

The structure of **4a** (see Figure 2) is described first. Table 8 gives a selection of bond distances and angles. The molecule is highly symmetric and contains a niobium atom bonded to two of the four aromatic rings of the tetraphenylborato ligand in a bent fashion: the angle at niobium between the perpendiculars of the aryl rings is 131.6°, a value which is well below those found[4,7] in other niobium(I) bis(arene) derivatives (147.7° in $\mathrm{[Nb(mes)_2(CO)]^+}$ and 142.3° in $\mathrm{[Nb(\eta^6\text{-}toluene)_2(PMe_3)]^+}$). The bonding of the two aromatic rings around the niobium atom is the result of the particular nature of the arene ligands which are held together by the boron atom, a bonding situation which is hardly comparable with any of the existing bis(arene)niobium(I) cations. In this case, interatomic repulsions must be minimized, and in this connection the angle at niobium also depends on the B–C1 bond distance (1.653(3) Å) and the C1–B–C1′ angle (92.3(5)°).

4a represents the first example of a compound containing the tetraphenylborate anion interacting through *two* η^6-

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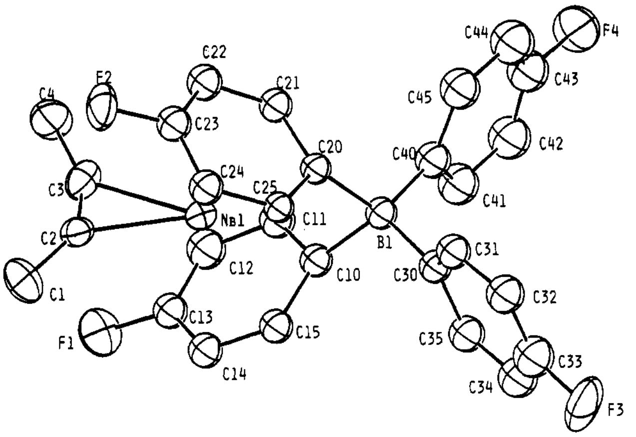

Figure 3. ORTEP plot of [Nb(MeC$_2$Me)(η^6-p-FC$_6$H$_4$)$_2$B(p-F-C$_6$H$_4$)$_2$] (**4b**) with the numbering scheme used. The ellipsoids are drawn at 30% probability.

bonded aromatic rings with *one* transition-metal center. A similar bonding situation was observed by Elschenbroich *et al.*[6] in the case of Cr(η^6-C$_6$H$_5$)$_2$Si(C$_6$H$_5$)$_2$. In this compound the bite angle of the two chromium-bonded aromatic rings is 165.5° and the C–Si–C angle is 95.9°; the larger values with respect to those of **4a** are presumably due to the larger covalent radius of silicon with respect to that of boron. In the case of our niobium(I) compound, the removal of the arene moieties by neutral ligands can only lead to ionic products of the type [Nb(L)$_n$][BAr$_4$] unless a reduction step to niobium(0) is simultaneously carried out. In view of the low stability of zerovalent niobium complexes[39] in general, this reaction pathway does not appear to be a favorable one. On the other hand, the large size of both BAr$_4^-$ and [Nb(L)$_n$]$^+$, and the correspondingly relatively small lattice and solvation energies involved, should not favor the formation of the ionic products. Thus, a relatively high stability of these neutral tetraarylborates of niobium(I) is anticipated. This is confirmed by the properties of the new compounds, as explained later on in this paper.

The mean niobium–ring centroid distance in **4a** is 1.931 Å, intermediate between those observed[4,7] in [Nb(mes)$_2$(CO)]$^+$ (1.912 Å) and [Nb(η^6-toluene)$_2$(PMe$_3$)]$^+$ (1.998 Å). The phenyl rings are substantially planar, but the C–C bond distances within the coordinated rings (mean value 1.419(3) Å) are longer than those observed in the other two rings (mean value 1.392(3) Å). Similar findings have been reported for tetraphenylborates η^6-bonded to a transition metal.[40]

The interaction between niobium(I) and but-2-yne is characterized by the following parameters (see Table 8): Nb–C9, 2.269(3) Å; C9–C9′, 1.2195(8) Å; C10–C9–C9′, 150.8(3)°. This is consistent with the alkyne behaving as a two-electron donor.[29–35]

The molecular structure of [Nb(MeC$_2$Me)(η^6-p-FC$_6$H$_4$)$_2$B(p-FC$_6$H$_4$)$_2$] (**4b**) is reported in Figure 3, and some relevant bond distances and angles are listed in Table 9. There are two independent molecules in the unit cell, and each molecule consists of a B(p-FC$_6$H$_5$)$_4$ group coordinated to the niobium atom *via* two p-fluorophenyl rings, a but-2-yne moiety completing the coordination sphere of the central atom. The metal is encapsulated within the two aromatic rings in an acentric position: the projection onto the ring planes is closer to C10 and C20 (2.346(9) and 2.348(9) Å, respectively) than to the other carbon atoms (mean value 2.40(1) Å). The two η^6-bonded rings are bent at an angle of 129.1°. The parameters describing the interaction of niobium with the but-2-yne ligand are as follows: the average niobium–carbon distance is 2.23(1) Å, the average C–C distance is 1.23(1) Å, and the average C–C–C angle is 149(1)°. In comparison with the values observed for **4a**, it appears that in **4b** the Nb–butyne-2 interaction is stronger and the C–C multiple bond is weaker, consistent with the infrared results, which show that the $\tilde{\nu}_{CC}$ vibration is at lower wavenumbers for **4b** than for **4a** (*vide supra*).

Table 9. Selected Bond Distances (Å) and Angles (deg) in [Nb(CH$_3$C$_2$CH$_3$)(η^6-p-FC$_6$H$_4$)$_2$B(p-F-C$_6$H$_4$)$_2$] (4b)[a]

Nb1–C2	2.22(1)	Nb2–C6	2.21(1)
Nb1–C3	2.25(1)	Nb2–C7	2.22(1)
C1–C2	1.50(2)	C5–C6	1.48(2)
C2–C3	1.23(1)	C6–C7	1.24(2)
C3–C4	1.50(2)	C7–C8	1.47(2)
C10–B1	1.66(1)	C50–B2	1.63(1)
C20–B2	1.64(1)	C60–B2	1.63(1)
C30–B1	1.61(2)	C70–B2	1.60(1)
C40–B1	1.61(2)	C80–B2	1.59(1)
C2–Nb1–C3	32.0(4)	C6–Nb2–C7	32.4(4)
Nb1–C2–C1	139.9(9)	Nb2–C6–C5	138(1)
Nb1–C2–C3	75.0(8)	Nb2–C6–C7	74.4(8)
Nb1–C3–C2	73.0(8)	Nb2–C7–C6	73.2(8)
C1–C2–C3	145(1)	C5–C6–C7	148(1)
Nb1–C3–C4	133.7(9)	Nb2–C7–C8	137(1)
C2–C3–C4	153(1)	C6–C7–C8	150(1)
C10–B1–C20	91.7(7)	C50–B2–C60	94.3(7)
C10–B1–C30	114.3(9)	C50–B2–C70	112.1(8)
C10–B1–C40	111.7(8)	C50–B2–C80	116.3(8)
C20–B1–C30	113.3(9)	C60–B2–C70	113.3(8)
C20–B1–C40	115.7(9)	C60–B2–C80	112.4(8)
C30–B1–C40	109.3(9)	C70–B2–C80	108.1(8)

[a] Estimated standard deviations given in parentheses refer to the least significant digit.

It is worth noting that compound **4b** crystallizes in the enantiomeric space group $P2_12_12_1$: this is presumably due to a molecular asymmetry resulting from the orientation of the aryl groups.

The formation of compounds 4 and 5 should be commented upon. Two mesitylene groups are lost during the thermal treatment (see eq 4). Moreover, it should be considered that the thermal treatment is carried out in toluene and yet the product does not retain toluene or mesitylene. It is reasonable to suggest that reaction 4 is favorably driven by entropy. We believe that the enthalpic contribution is small in this case, although the different bonding situation as one goes from the ionic to the covalent compound of eq 4 is difficult to assess.

The existence of the Nb(L)(η^6-C$_6$H$_{5-n}$X$_n$)$_2$B(C$_6$H$_{5-n}$X$_n$)$_2$ complexes is not restricted to but-2-yne (compounds **4a,b**) and diphenylacetylene (compound **5a**) as ancillary ligands.[41] As a matter of fact, carbon monoxide has the appropriate electronic properties to stabilize this new bonding arrangement. Compounds 4 react with CO according to eq 5. With **4a**, but-2-yne is easily substituted

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$$[\mathrm{Nb(MeC_2Me)}][(\eta^6\text{-}\mathrm{XC_6H_4})_2\mathrm{B}(\mathrm{XC_6H_4})_2] + \mathrm{CO} \rightarrow [\mathrm{Nb(CO)}(\eta^6\text{-}\mathrm{XC_6H_4})_2\mathrm{B}(\mathrm{XC_6H_4})_2] + \mathrm{MeC_2Me} \quad (5)$$

6a,b

X = H (**6a**), 25 °C, 40 min; X = *p*-F (**6b**), 60 °C, 4 h

$$[\mathrm{Nb(mes)_2(CO)}][\mathrm{BPh_4}] \not\twoheadrightarrow [\mathrm{Nb(CO)}(\eta^6\text{-}\mathrm{C_6H_5})_2\mathrm{B}(\mathrm{C_6H_5})_2] + 2\ \mathrm{mes} \quad (6)$$

6a

by CO at room temperature to give the new carbonyl derivative ($\tilde{\nu}_{CO}$, 1995 cm^{-1}). It is noteworthy that all attempts to convert $[\mathrm{Nb(mes)_2(CO)}]\mathrm{BPh_4}$ into **6a** by thermal treatment in toluene (eq 6) failed and the starting material was recovered unchanged. On the other hand, the formation of **6b** does not take place at room temperature; prolonged heating to about 60 °C is necessary for the reaction. The red-orange product is characterized by a carbonyl stretching vibration at 2038 cm^{-1}. The relatively high wavenumber value may be related to a reduction of π back-donation from niobium to carbon monoxide due to the presence of the fluorine atoms on the aromatic rings.

Compound **6a** has been characterized by X-ray diffraction methods, and the molecular structure is shown in Figure 4; Table 10 lists some relevant bond distances and angles. The C20–B–C10 angle is slightly reduced (91.1(5)°) with respect to **4a** (92.3(5)°), thus allowing the bonding angle at niobium to increase to 137.0° and the niobium to the ring centroid distance to decrease from 1.931 Å in **4a** to 1.895 Å (mean value) in **6a**.

The carbonyl ligand is slightly bent (Nb–C–O angle 174.0(1)°) with Nb–C (2.111(9) Å) and C–O (1.14(1) Å) distances in the range generally observed for niobium(I) carbonyl complexes.[43]

Conclusions

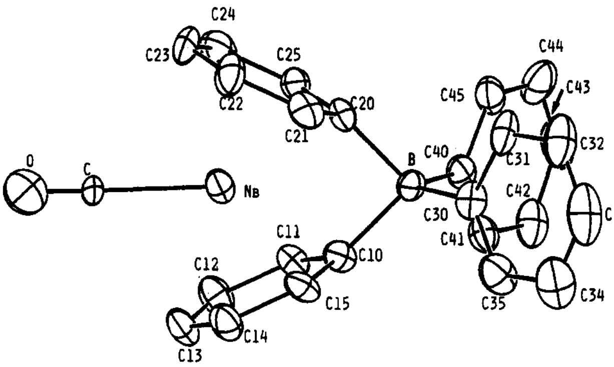

Figure 4. ORTEP plot of $[\mathrm{Nb(CO)}(\eta^6\text{-}\mathrm{C_6H_5})_2\mathrm{B}(\mathrm{C_6H_5})_2]\cdot\mathrm{C_7H_8}$ (**6a**) with the numbering scheme used. The ellipsoids are drawn at 30% probability.

Table 10. Bond Distances (Å) and Angles (deg) in $[\mathrm{Nb(CO)}(\eta^6\text{-}\mathrm{C_6H_5})_2\mathrm{B}(\mathrm{C_6H_5})_2]\text{-}\mathrm{C_7H_8}$[a]

Nb–C	2.111(9)	C–O	1.14(1)
C10–B	1.66(1)	C20–B	1.66(1)
C30–B	1.66(1)	C40–B	1.56(1)
Nb–C–O	174(1)	C15–C10–B	120.1(7)
C10–B–C20	91.1(5)	C10–B–C30	111.4(8)
C10–B–C40	115.6(7)	C20–B–C30	111.5(7)
C20–B–C40	115.0(7)	C30–B–C40	110.9(7)

[a] Estimated standard deviations given in parentheses refer to the least significant digit.

This paper has established that the tetraarylborato group can function as a 12-electron donor with respect to *one* metal atom; these compounds can be prepared for niobium(I) provided that CO or substituted acetylenes are present around the metal as ancillary ligands.

Experiments are planned with the aim of synthesizing tetraarylborato complexes of group 4 metals (Ti, Zr, Hf) in the newly discovered bonding arrangement.

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Supplementary Material Available: Tables of positional parameters of hydrogen atoms (S-IH), all bond distances and angles (S-II), and thermal parameters (*B*'s, S-IIIA; *U*'s, S-IIIB; β's (S-IIIC)), for **2b**, positional parameters of hydrogen atoms (S-V), all bond distances and angles (S-VI), and thermal parameters (*U*'s, S-VII) for **4a**, positional parameters of hydrogen atoms (S-IXH), all bond distances and angles (S-X), and thermal parameters (*B*'s, S-XIA; *U*'s, S-XIB; β's S-XIC)) for **4b**, and positional parameters of hydrogen atoms (S-XIIIH), all bond distances and angles (S-XIV), and thermal parameters (*U*'s, S-XV) for **6a** (28 pages). Ordering information is given on any current masthead page.

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(41) The bis(mesitylene)niobium(I) compound $[\mathrm{Nb(mes)_2}]\mathrm{BPh_4}$ in a toluene suspension with acetylene at room temperature, after displaying a transient red color, gave *trans*-polyacetylene mainly. The reaction is catalytic, and about 38 mol of monomer/mol of niobium was converted into the polymer, and benzene (18.5 mol/mol of niobium) was also formed by trimerization of acetylene. The catalytic performance of the niobium(I) cation is higher in THF solution containing the $[\mathrm{Nb(mes)_2(THF)}]^+$ cation.[4] Under these conditions, 27 mol of monomer/mol of niobium(I) was converted into the polymer and benzene was obtained for a benzene/niobium molar ratio of 412, corresponding to a conversion of about 1200 mol of acetylene/mol of niobium. These results are in line with the known[42] catalytic activity of several transition-metal systems in the poly- or oligomerization of acetylenes.

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