should then only differ slightly. For P3 as a "separated" μ_3-P ligand, a much stronger low-field shift would be expected than the observed value of $\delta = 501.6$.[2] The coupling constant of -190.7 Hz must also be considered as further support for a P2–P3 bond (2.456(3) Å in the σ,σ,π,π ligand P_2O); this value is comparable to that found in **5** (ca. 180 Hz)[8] as well as in compounds in which the *cyclo*-P_5 ligand is additionally *side-on* coordinated (d(P–P) ≈ 2.35 Å, J(P,P) ≈ −200 Hz).[2]

The Co_3FeP_5 framework can also be formally derived from the molecular structure of the complex $[\{Cp^*Co\}_3(\mu\text{-}\eta^2{:}\eta^2{:}\text{-}P_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}P_2)_2]$ (**6**),[11a] by replacement of the μ-η^2:η^2-P_2 ligand by a {Cp*FeP(O)} fragment and by oxidation of one of the μ_3-η^1:η^2:η^1-P_2 ligands to P_2O. This could then form the μ_4-η^1:η^2:η^2:η^1-P_2O ligand of **3** by additional *side-on* coordination of the Cp*Fe fragment.

Stable N_2O complexes are rare. A linear, terminal N_2O ligand has been proposed in complexes of the type $[Ru(NH_3)_5(N_2O)]X_2$ (X = Br, I, BF_4, PF_6), which can be stored at −5 °C.[13] No details can be given as yet about the formation of **3** from **2** by the extension of the cluster skeleton by a Cp″Co fragment.

Experimental Section

3: [{Cp*Fe}{Cp″Co}$_2$(P_4)(P)] (**2**)[2] (180 mg, 0.22 mmol) was dissolved in dichloromethane (40 mL) and stirred for 1 min at room temperature in air (open reaction vessel) (longer exposure to air results in complete decomposition) and then stirred in a closed reaction vessel for 18 h (monitored by ^{31}P NMR spectroscopy). After removal of the solvent, the brown residue was dissolved in dichloromethane (ca. 5 mL), treated with silylated silica gel (ca. 2 g) and dried under an oil pump vacuum until a pouring consistency was obtained. Column chromatography (column: 8 × 1.0 cm, silylated silica gel, petroleum ether, water cooled; petroleum ether/diethyl ether (2/1)) yielded **3** (52 mg; 22% relative to **2**) as a dark brown fraction. The large amount of brown residue retained on the column material could not be eluted by any common solvent.

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[3] Spectroscopic data of **3**: ^{1}H NMR (200.14 MHz, C_6D_5H of the solvent C_6D_6 as internal standard), ^{31}P NMR (81.02 MHz, 85% H_3PO_4 extern.). ^{1}H NMR: $\delta = 5.79$ (s, 1H), 5.66 (s, 1H), 5.51 (s, 1H), 5.32 (s, 1H), 5.02 (s, 1H), 4.88 (s, 1H), 4.78 (s, 1H), 4.71 (s, 1H), 4.15 (s, 1H), 1.86 (s, 15H), 1.75 (s, 9H), 1.74 (s, 9H), 1.70 (s, 9H), 1.53 (s, 9H), 1.33 (s, 9H), 1.22 (s, 9H); ^{31}P NMR: ABMXY spin system (P_A = P1, P_B = P3, P_M = P2, P_X = P5, P_Y = P4), $\delta = 558.8$ (s, P_A), 501.6 (dd, P_B), 265.1 (dd, P_M), 120.9 (dd, P_X), 99.7 (dd, P_Y), $^1J(P_BP_M) = -190.7$, $^1J(P_XP_Y) = -289.9$, $^nJ(P_BP_Y) = 91.6$, $^nJ(P_MP_X) = 137.3$ Hz (n is probably 2); IR (pentane): $\tilde{\nu}$(PO) [cm^{-1}] = 1182 (m, br), 1163 (m, br).

[4] Crystal structure data for **3**: $C_{49}H_{78}Co_3FeO_2P_5$, $M_r = 1086.60$, monoclinic, space group $P2_1/n$, $a = 10.5809(16)$, $b = 21.0882(17)$, $c = 24.391(4)$ Å, $\beta = 101.825(18)°$, $V = 5326.8(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.355$ Mg m^{-3}, $T = 293(2)$ K, Θ range: 1.96–23.95°, measured reflections: 51646, independent reflections: 8096 ($R_{int} = 0.1456$), R values: final R value ($I > 2\sigma(I)$): $R1 = 0.0639$, $wR2 = 0.1289$, all data: $R1 = 0.1549$, $wR2 = 0.1481$. Diffractometer: Stoe IPDS, structure solution: direct methods, program: SHELXS-97, refinement: full-matrix least-squares against F^2. Program for refinement: SHELXL-97, data/parameters: 8096/688. One of the Cp″ ligands is rotationally disordered. Crystallographic data (excluding structure factors) for the structure reported in this publication have been deposited as supplementary publication no. CCDC-120672 with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge from: CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Rhodium-Induced Selective B(3)/B(6)-Disubstitution of *ortho*-Carborane-1,2-dithiolate**

Max Herberhold,* Hong Yan, Wolfgang Milius, and Bernd Wrackmeyer*

Dedicated to Professor Hubert Schmidbaur on the occasion of his 65th birthday

Ever since the discovery of 1,2-dicarba-*closo*-dodecaborane(12), the chemistry of this exceptionally stable carborane and its 1,7- and 1,12-isomers has aroused considerable interest. Although C-functionalization had readily been accomplished from the beginning,[1] and more recently the complete substitution at all boron positions has been achieved,[2] the selective synthesis of B-substituted derivatives proved to be rather difficult.[3] We have recently reported on the synthesis of the 16e rhodium complex $[Cp^*Rh\{S_2C_2(B_{10}H_{10})\}]$ (**1**),[4] and suggested that this species may be promising for further transformations owing to its electron deficiency at the rhodium center, the reactivity of the rhodium–sulfur bonds, and the potential activation of B–H

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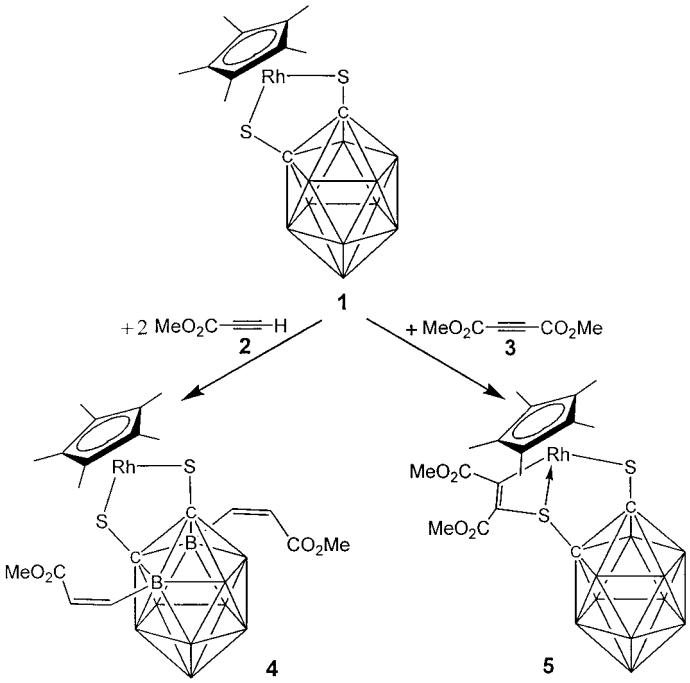
bonds of the carborane cage[5] at sites close to the rhodium atom. In this context, we have studied the reaction of **1** with acetylene methyl carboxylate **2** and acetylene dimethyl dicarboxylate **3** (Scheme 1).



Scheme 1. Reaction of **1** to give **4** and **5**.

In the case of **2**, the B(3)/(6)-disubstituted 16e complex **4** was isolated and characterized.[6] In contrast, the reaction of **1** with **3** gave the 18e complex **5** as the sole product.[7] In a rhodium-catalyzed reaction, a CpRh-dithiolene complex, formed as an intermediate, also reacts with **3**, to give the adduct analogous to **5**.[8] Recently, the 16e complex $[CpCo\{S_2C_2(B_{10}H_{10})\}]$, comparable with **1**, has been reported.[9] The reactions of this CpCo complex with **3** and terminal alkynes have afforded adducts (with molecular structures similar to **5**), which – like **5** – do not undergo further rearrangements. Thus, the molecular structure of **5** is suggested to be typical of an intermediate which remained undetected in the reaction of **1** with the monosubstituted acetylene **2**.

The molecular structures of **4**[10] and **5**[10] are shown in Figure 1 and Figure 2, respectively. A planar rhodadithiolene five-membered ring is present in **4**, as expected for a 16e species.[9, 11, 12] This electron count is also in agreement with the magnetic deshielding of the ^{103}Rh nucleus ($\delta(^{103}Rh) = +1210 \pm 5$, close to that of **1** with $\delta(^{103}Rh) = +1165 \pm 5$).[4] The structure of **5** indicates that an addition of **3** to one of the Rh–S bonds has taken place to give a four-membered ring containing a C=C bond, a Rh–C σ bond, and a coordinative S→Rh bond.

The *Z* configuration at the C=C bonds in **4** rules out the possibility that **4** has been formed by way of direct 1,2-hydroboration. We therefore suggest an alternative mechanism briefly outlined in Scheme 2. Complex **5** (Scheme 1) is apparently a type of 18e complex which is frequently formed when an alkyne is added to a M–S bond in metalladithiolenes.[8, 9] Therefore, it can be safely assumed that complex **7** (analogous to **5** in Scheme 1), generated by rearrangement of the η^2-alkyne complex **6**, is an intermediate in the reaction of **1** with **2** (Scheme 2). An equilibrium between the 18e complex **7** and its 16e isomer **8** (formed by opening of the coordinative S→Rh bond), enables the rhodium atom to approach the sites of either B(3)–H or B(6)–H with the result of B–H activation.[5] These agostic interactions are the prerequisite for hydride transfer from the boron atom to the rhodium atom accompanied by formation of a Rh–B bond in **9**,[5, 13] and further transfer of the hydride from rhodium to the adjacent olefinic carbon atom in **10**.[13] The next step includes cleavage of the Rh–B bond and formation of the boron-substituted

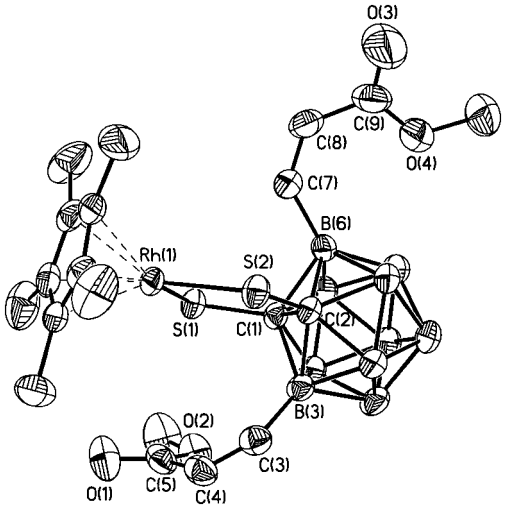


Figure 1. ORTEP plot of the molecular structure of **4**. Selected bond lengths [pm] and angles [°]: Rh(1)–Z 178.2, Rh(1)–S(1) 227.94(10), Rh(1)–S(2) 227.31(10), S(1)–C(1) 178.3(4), S(2)–C(1) 178.2(4), C(1)–C(2) 164.3(5), B(3)–C(3) 157.1(6), B(6)–C(7) 155.8(6), C(3)–C(4) 131.7(5), C(7)–C(8) 133.8(6); S(1)Rh(1)S(2) 92.42(4), S(1)Rh(1)S(2)/S(1)C(1)C(2)S(2) 179.1, B(3)C(3)C(4)/C(3)C(4)C(5) 5.2, B(6)C(7)C(8)/C(7)C(8)C(9) 1.6.

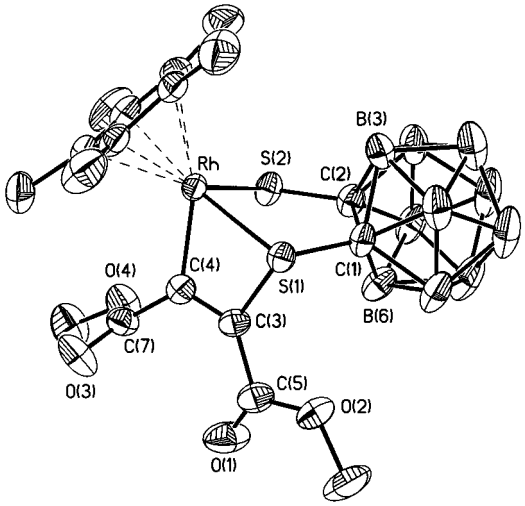


Figure 2. ORTEP plot of the molecular structure of **5**. Selected bond lengths [pm] and angles [°]: Rh–Z 183.8, Rh–S(1) 239.66(9), Rh–S(2) 238.04(9), Rh–C(4) 202.2(4), S(1)–C(1) 180.6(3), S(2)–C(2) 177.7(4), S(1)–C(3) 178.8(3), C(1)–C(2) 167.8(5), C(3)–C(4) 133.5(5); S(1)RhS(2) 87.88(3); S(1)RhC(4) 67.93(10), S(1)C(3)C(4) 104.8(2), S(1)RhS(2)/S(1)C(1)C(2) 154.3, S(1)RhC(4)/S(1)C(3)C(4) 170.5

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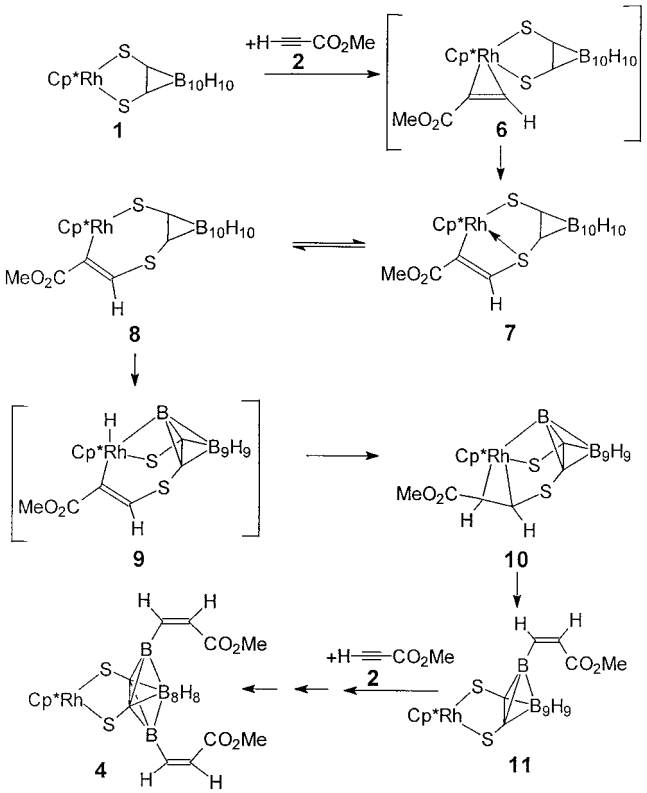

Scheme 2. Proposed mechanism for the reaction of **1** with **2** to give **4**.

carborane **11** as a 16e complex. Repetition of the whole sequence starting from **11** leads to the B(3)/B(6)-disubstituted final product **4**.

In conclusion, addition of an alkyne to a 16e rhodium complex, followed by insertion into the flexible Rh–S bond, starts a fascinating interplay between 16e and 18e complexes and makes use of all reactive sites. In the present example this provides a straightforward route to a selectively B(3)/B(6)-disubstituted *ortho*-carborane.

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[6] Preparation of **4**: To the green solution of **1** (0.2 g, 0.45 mmol) in $CHCl_3$ (30 mL) **2** (0. 38 mL; 4.5 mmol) was added in one portion. The mixture was heated at reflux for three days; the color changed first to red and then gradually to green. After removal of the solvent, the residue was chromatographed on silica gel (Merck, Kieselgel 60). Elution with CH_2Cl_2 gave **4** as a deep green zone. Recrystallization from CH_2Cl_2/hexane afforded air-stable dark red crystals. Correct elemental analysis; yield 80%; m. p. 202 °C (decomp). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.83$ (s,15H; Cp*), 3.73 (s, 6H; MeO), 5.80 (d, ^3J(H,H) = 15.2 Hz, 2H; =CH–B)), 6.27 (d, ^3J(H,H) = 15.2 Hz, 2H; =CH–C(O)); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.3$ (Cp*), 51.0 (MeO), 94.4 ($S_2C_2B_{10}H_{10}$), 99.5 ($J(^{103}Rh,^{13}C) = 7.4$ Hz), 132.6 (=CH), 138.2 (b, =CH–B), 167.1 (CO); ^{11}B NMR (160.5 MHz; CD_2Cl_2, 25 °C, Et_2O–BF_3): $\delta = -6.5$ (3,6), −8.0, −8.5, −11.0 (in the ratio 2:2:4:2); ^{103}Rh NMR (15.8 MHz, $CDCl_3$, 20 °C, $\Xi(^{103}Rh) = 3.16$ MHz): $\delta = 1210 \pm 5$; EI MS (70 eV): *m*/*z*: 612 (100) [M^+].
[7] Preparation of **5**: The reaction of **1** with **3** was carried out in the same way as described in reference [6]. The color turned red immediately after addition of **3**. Evaporation of the solvent left a red residue which gave pure **5** after recrystallization from CH_2Cl_2/hexane [80%; red needles; m. p. 187 °C (decomp)]. ^{1}H NMR (250 MHz, CD_2Cl_2, 25 °C): $\delta = 1.68$ (s, 15H; Cp*), 3.75 (s, 3H; MeO), 3.78 (s, 3H; MeO); ^{13}C NMR (62.9 MHz; CD_2Cl_2, 25 °C, TMS): $\delta = 9.3$ (Cp*), 52.0 and 52.7 (MeO), 77.7 and 97.2 ($C_2B_{10}H_{10}$), 100.3 ($J(^{103}Rh,^{13}C) = 5.8$ Hz; Cp*), 123.0 ($J(^{103}Rh,^{13}C) = 5.9$ Hz; SC=), 158.5 ($J(^{103}Rh,^{13}C) = 2.0$ Hz), 168.5 ($J(^{103}Rh,^{13}C) < 2$ Hz; CO), 182.2 ($J(^{103}Rh,^{13}C) = 28.4$ Hz; Rh–C=); ^{11}B NMR (160.5 MHz; CD_2Cl_2, 25 °C, Et_2O–BF_3): $\delta = -4.0, -5.3, -5.8, -7.8, -9.2, -11.0$ (signals overlap); ^{103}Rh NMR (15.8 MHz, CD_2Cl_2, 20 °C, $\Xi(^{103}Rh) = 3.16$ MHz): $\delta = 1049 \pm 2$.
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[10] Crystal structure determinations: Intensity data collections were carried out on a Siemens P4 diffractometer with $Mo_{K\alpha}$ radiation (λ = 71.073 pm, graphite monochromator) at room temperature. **4**: Dark red prism of dimensions 0.25 × 0.18 × 0.12 mm, triclinic, space group $P\bar{1}$; $a = 1140.2(3)$, $b = 1523.1(2)$, $c = 1693.8(2)$ pm, $\alpha = 82.936(8)$, $\beta = 81.565(9)$, $\gamma = 89.211(9)°$, $Z = 4$, $\mu = 0.762$ mm^{-1}; 15256 reflections collected in the range 2–27.5° in ϑ, 13255 reflections independent, 9464 reflections assigned to be observed ($I > 2\sigma(I)$); full-matrix least-squares refinement with 648 parameters, *R*1/*wR*2 values 0.0464/0.0993, absorption correction (ψ scans), min./max. transmission factors 0.2978/0.3301; max./min. residual electron density 1.13/−0.73 e10^{-6} pm^{-3}. **5**: Red prism of dimensions 0.35 × 0.18 × 0.12 mm, orthorhombic, space group *Pbca*; $a = 1593.78(12)$, $b = 1391.95(18)$, $c = 2469.5(2)$ pm, $Z = 8$, $\mu = 0.800$ mm^{-1}; 9501 reflections collected in the range 2–30° in ϑ, 7982 reflections independent, 5361 reflections assigned to be observed ($I > 2\sigma(I)$); full-matrix least-squares refinement with 316 parameters, *R*1/*wR*2 values 0.0500/0.1115, absorption correction (ψ scans), min./max. transmission factors 0.4013/0.4468; max./min. residual electron density 0.449/−2.095 e10^{-6} pm^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-133225 (**5**) and 133226 (**4**). 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).
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