DOI: 10.1002/chem.200801136

Reactions of 16e CpCo Half-Sandwich Complexes Containing a Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolate Ligand with Ethynylferrocene and Dimethyl Acetylenedicarboxylate**

Bao-Hua Xu, Xu-Qing Peng, Yi-Zhi Li, and Hong Yan*[a]

Abstract: The reaction of the 16e half-sandwich complex [CpCo($S_2C_2B_{10}H_{10}$)] (**1S**; Cp: cyclopentadienyl) with ethynylferrocene in CH_2Cl_2 at ambient temperature leads to [CpCo($S_2C_2B_{10}H_9$)(CH_2CFc)] (**2S**; Fc: ferrocenyl) and 1,2,4-triferrocenylbenzene. In **2S**, B substitution occurs at the carborane cage in the position B(3)/B(6) with the formation of a C−B bond. In the presence of the protic solvent MeOH, **2S** loses a CpCo fragment to generate [(CH_2CFc)($S_2C_2B_{10}H_9$)] (**3S**). On the other hand, **2S** can take a free CpCo fragment to form [$(CpCo)_2$($S_2C_2B_9H_8$)(CHCFc)] (**4S**) containing a *nido*-C_2B_9 unit. In sharp contrast, [CpCo($Se_2C_2B_{10}H_{10}$)] (**1Se**) does not react with the alkyne in CH_2Cl_2, but in MeOH [(CHCFc)($Se_2C_2B_{10}H_{10}$)] (**5Se**) is generated without the presence of a CpCo unit. The reaction of **1** with dimethyl acetylenedicarboxylate at ambient temperature leads to insertion compounds [CpCo($E_2C_2B_{10}H_{10}$){(MeO_2C)C=C(CO_2Me)}] (**6S**, E=S; **6Se**, E=Se). Upon heating, **6S** rearranges to two geometrical isomers [CpCo($S_2C_2B_{10}H_9$){(MeO_2C)C=CH(CO_2Me)}] (**7S**) and [CpCo($S_2C_2B_{10}H_9$){(MeO_2C)CHC(CO_2Me)}] (**8S**). In both, B−H functionalization takes place at the carborane cage in the position B(3)/B(6), but **7S** is a 16e complex with an olefinic unit in a *Z* configuration, and **8S** is an 18e complex containing an alkyl B−CH group. Further treatment of **7S** with dimethyl acetylenedicarboxylate at ambient temperature affords two B-disubstituted complexes at the carborane cage in the positions of the B(3) and B(6) sites, that is, [CpCo($S_2C_2B_{10}H_8$){(MeO_2C)C=CH(CO_2Me)}$_2$] (**9S**) and [CpCo($S_2C_2B_{10}H_8$){(MeO_2C)CHC(CO_2Me)}{(MeO_2C)C=CH(CO_2Me)}] (**10S**). Compound **9S** is a 16e complex with two olefinic units in *E*/*E* configurations, whereas **10S** is an 18e species containing both an olefinic substituent and an alkyl B−CH unit. The reaction of **7S** with methyl acetylenemonocarboxylate at ambient temperature leads to the sole 16e compound [CpCo($S_2C_2B_{10}H_8$){CH=CH(CO_2Me)}{(MeO_2C)C=CH(CO_2Me)}] (**11S**). In contrast, **6Se** does not rearrange. All new complexes **2S**–**4S**, **5Se**, **6Se**, and **7S**–**11S** were characterized by NMR spectroscopy (^{1}H, ^{11}B, ^{13}C) and X-ray structural analyses were performed for **2S**–**4S**, **5Se**, **6Se**, and **7S**–**9S**.

Keywords: carboranes • chalcogens • cobalt • cyclotrimerization • sandwich complexes

Introduction

Ever since the discovery of 1,2-dicarba-*closo*-dodecaborane in the 1960s, 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] boron-substitution chemistry, in particular the selective synthesis of B-substituted derivatives, proved to be rather difficult.[2] In the last decade, the development of B−H activation of *o*-carborane based on 16e half-sandwich complexes [Cp*M($E_2C_2B_{10}H_{10}$)] (Cp* = pentamethylcyclopentadienyl; M = Rh, Ir; E = S, Se) and [(arene)M($E_2C_2B_{10}H_{10}$)] (M = Ru, Os) has provided convenient access to selective substitution of the carborane cage at the position B(3)/B(6).[3] The availability of this route creates the possibility of investigating the systematic reaction chemistry of the 16e complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand because the metal center, chalcogen element, organic substrates, and reaction conditions strongly influence the reactivity.

It is well documented that 16e complexes of the type [Cp*M($E_2C_2B_{10}H_{10}$)] (M = Rh, Ir; E = S, Se) and [(*p*-cy-

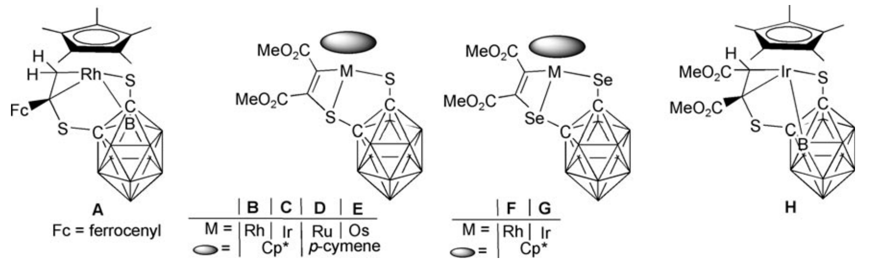
---

[a] Dr. B.-H. Xu, X.-Q. Peng, Prof. Y.-Z. Li, Prof. H. Yan
State Key Laboratory of Coordination Chemistry
School of Chemistry and Chemical Engineering
The Joint Laboratory of Metal Chemistry
Nanjing University–Jin Chuan Group Ltd.
Nanjing University, Nanjing, Jiangsu 210093 (China)
Fax: (+86) 25-83314502
E-mail: hyan1965@nju.edu.cn

[**] Cp: cyclopentadienyl

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

mene)M($S_2C_2B_{10}H_{10}$)] (M = Ru, Os) react with alkynes to generate numerous novel complexes, which results from the insertion of an alkyne into M–E bonds, followed by B–H activation, M–B bond formation, and further transformations.[3–6] However, in the case of ethynylferrocene, HC≡C–Fc, only the reaction with 16e complexes [Cp*Rh($E_2C_2B_{10}H_{10}$)] (E = S, Se) has been described.[4] [Cp*Rh($S_2C_2B_{10}H_{10}$)] reacted with HC≡C–Fc to generate compound **A** (Scheme 1) bearing an M–B bond. In comparison, [Cp*Rh($Se_2C_2B_{10}H_{10}$)]-mediated dimerization of ethynylferrocene in boiling chloroform led to (*E*)- and (*Z*)-1,4-diferrocenylbuten-3-ynes. As for the internal alkyne dimethyl acetylenedicarboxylate, $MeO_2C–C≡C–CO_2Me$, only insertion compounds of the type **B**–**G** (Scheme 1) were isolated at ambient temperature,[3b,5] and they showed high thermal stability with regard to further rearrangement. For instance, the conversion of **C** to **H** was roughly detected by the characteristic ^{11}B signal after a three-day treatment in boiling toluene.[5]



Scheme 1. Some reported examples of **A**,[4] **B**,[3b] **C**–**H**[5] containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand.

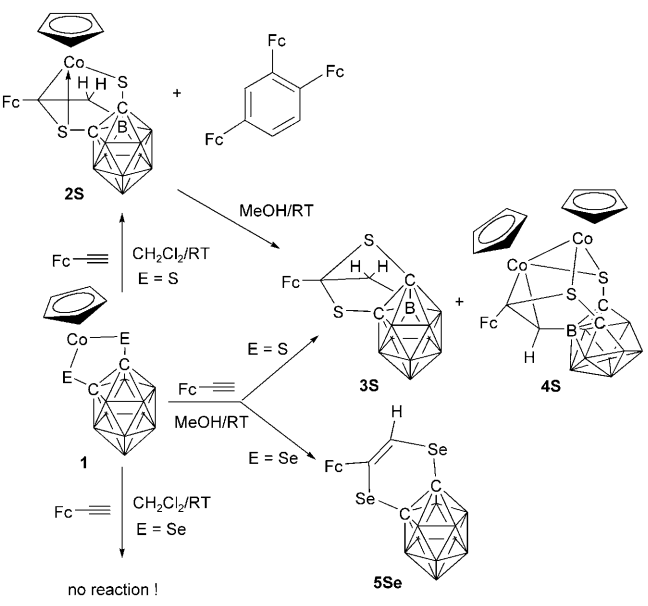
Our preliminary results showed that the 16e complexes [CpCo($E_2C_2B_{10}H_{10}$)] (Cp = cyclopentadienyl; **1S**, E = S; **1Se**, E = Se) are more reactive than their analogous rhodium and iridium species, and thus have the potential to be used for different transformations.[7] In our continuous and systematic study of the role of metal in the reaction chemistry of the 16e complexes [CpCo($E_2C_2B_{10}H_{10}$)] and [Cp*M($E_2C_2B_{10}H_{10}$)] (M = Rh, Ir; E = S, Se), we examined the reactivity of the cobalt species **1S** and **1Se** with two alkynes: HC≡C–Fc and $MeO_2C–C≡C–CO_2Me$. Herein, we report ten new complexes: **2S**–**4S**, **5Se**, **6Se**, and **7S**–**11S**.

Results and Discussion

Reactions of 1 with HC≡C–Fc: The reactions of [CpCo($E_2C_2B_{10}H_{10}$)] (**1S**, **1Se**) with HC≡C–Fc were explored in two different solvents, and the products isolated by chromatography were characterized by using spectroscopic data and X-ray crystal structure determinations. Connections between products in CH_2Cl_2 and MeOH were defined by treatment of the isolated product in CH_2Cl_2 with MeOH.

In CH_2Cl_2: The reaction of **1S** with HC≡C–Fc in CH_2Cl_2 at ambient temperature led to **2S** and 1,2,4-triferrocenylbenzene (Scheme 2). In comparison, **1Se** does not react.

Compound **2S** was isolated in a yield of 80%. The solid-state structure, as shown in Figure 1[8] and Table 1, indicates the presence of a B–C bond (1.542 Å), rather than an M–B bond as observed in species **A** (Scheme 1) in the analogous rhodium reaction system.[4] The triple bond in HC≡C–Fc has been extended to a typical C–C single bond (1.540 Å) in **2S**, and the C-C-C angle at C(4) (177.7° in HC≡C–Fc) is reduced to 117.9° in **2S**. The newly generated five-membered ring C(3)B(3)C(1)S(1)C(4) is almost planar, whereas the five-membered ring S(1)Co(1)S(2)C(2)C(1) is non-planar. The distance of C(1)–C(2) (1.696 Å) is in the typical range of *o*-carborane derivatives.[2] A similar structural type has been observed in the reactions of 16e rhodium analogues with phenylacetylene and methyl propiolate.[6,7]



Scheme 2. Reaction of **1S** and **1Se** with HC≡C–Fc.

Spectroscopic analysis of **2S** confirms that the relevant features of its solid-state structure are retained in solution. A large value (16 Hz) for the geminal coupling constant in the ^1H NMR spectrum is assigned typically to diastereotopic ^1H nuclei of an alkyl group (B–CH_2). The ^{11}B NMR spectroscopic signal of the boron atom linked to the CH_2 group is readily assigned as 4.4 ppm by comparison of ^1H-coupled and ^1H-decoupled ^{11}B NMR spectra, in contrast to the other

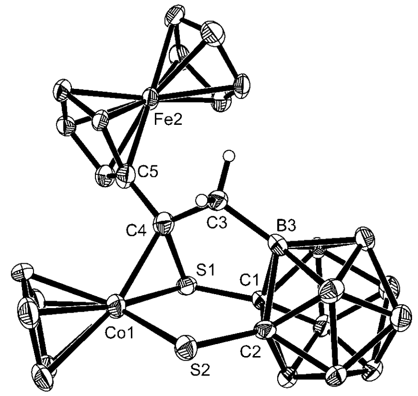


Figure 1. Molecular structure of **2S**; ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co(1)−ring centroid 1.706, C(1)−C(2) 1.696(4), C(2)−B(3) 1.774(4), C(1)−B(3) 1.725(5), Co(1)−S(1) 2.1738(11), Co(1)−S(2) 2.2324(13), Co(1)−C(4) 2.019(3), C(3)−C(4) 1.540(5), C(3)−B(3) 1.542(5), C(4)−C(5) 1.475(5), S(1)−C(4) 1.822(3), S(1)−C(1) 1.795(3), S(2)−C(2) 1.766(3); S(1)-Co(1)-S(2) 96.20(4), S(1)-C(4)-C(3) 114.7(2), C(4)-C(3)-B(3) 110.63, C(3)-C(4)-C(5) 117.9(3), Co(1)-C(4)-C(5) 114.2(2), Co(1)-S(2)-C(2)/C(2)-C(1)-S(1)-Co(1) 171.7.

Table 1. Crystallographic data and structure refinement information for **2S**–**4S** and **5Se**.

	2S	**3S**	**4S**	**5Se**
formula	$C_{19}H_{25}B_{10}CoFeS_2$	$C_{14}H_{20}B_{10}FeS_2$	$2(C_{24}H_{26}B_9Co_2FeS_2),H_2O$	$C_{14}H_{20}B_{10}FeSe_2$
M_w	540.41	416.39	1317.19	510.17
color	purple	yellow	green	yellow
size [mm^3]	0.24×0.26×0.30	0.24×0.26×0.32	0.24×0.26×0.30	0.24×0.26×0.30
crystal system	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	C/c	$P21/c$	$Pbcn$
a [Å]	9.330(3)	24.720(3)	10.3216(14)	16.413(2)
b [Å]	10.212(4)	7.2357(7)	14.753(2)	16.413(3)
c [Å]	13.312(4)	11.8447(11)	20.888(3)	14.818(3)
α [°]	80.733(4)	90	90	90
β [°]	70.911(3)	114.097(4)	115.432(6)	90
γ [°]	83.755(5)	90	90	90
V [Å^3]	1175.0(7)	1934.0(4)	2827.5(7)	3991.8(12)
Z	2	4	2	8
θ range [°]	2.0–26.0	1.8–26.0	1.8–26.0	1.8–26.0
ρ_{calcd} [g cm^{-3}]	1.528	1.430	1.523	1.698
μ [mm^{-1}]	1.509	0.991	1.802	4.399
min, max trans	0.6403, 0.7034	0.7414, 0.7935	0.6014, 0.6505	0.2615, 0.3540
data/restraints/parameters	4530/0/298	2453/0/244	5640/0/352	3928/0/244
F(000)	548	848	1328	1984
no. reflns collected	6386	5114	15547	20723
no. unique reflns [R_{int}]	4530 (0.023)	2453 (0.043)	5640 (0.036)	3928 (0.041)
GOF	1.06	1.11	1.05	1.07
R indices [$I > 2\sigma$(I)]	$R_1 = 0.0494$	$R_1 = 0.0566$	$R_1 = 0.0456$	$R_1 = 0.0387$
	$wR_2 = 0.0823$	$wR_2 = 0.1229$	$wR_2 = 0.1003$	$wR_2 = 0.931$
R indices (all data)	$R_1 = 0.0730$	$R_1 = 0.0621$	$R_1 = 0.0597$	$R_1 = 0.0510$
	$wR_2 = 0.0848$	$wR_2 = 0.1247$	$wR_2 = 0.1045$	$wR_2 = 0.0974$
largest diff. peak and hole [e Å^{-3}]	0.558, −0.974	0.353, −0.450	0.283, −0.300	0.336, −0.400

overlapping signals in negative values. In this reaction system, an analogous species of **A** (Scheme 1) with an M−B bond was not detected even by NMR monitoring at ambient temperature, which demonstrates that the 16e cobalt starting material is more reactive than its rhodium analogue because complex **A** is thermally stable and hard to convert to a species like **2S**.

More interestingly, **1S**-catalyzed alkyne cyclotrimerization occurs in a competitive pathway that leads only to 1,2,4-triferrocenylbenzene, identified by comparison of its spectroscopic data with those reported in the literature.[9] The yield only accounts for 10% of the added alkyne, because the formation of **2S** is rather competitive even at ambient temperature as monitored by NMR spectroscopy. In spite of the importance of ferrocenylarenes, few reports dealt with the cyclotrimerization of HC≡C−Fc[10] because of the bulky ferrocenyl group. Three effective catalysts are [$Co_2(CO)_8$],[11] $TaCl_5$,[12] and cobaltocene;[9] however, they result in a mixture of 1,3,5- and 1,2,4-triferrocenylbenzenes. Note that their separation was only realized by preparative HPLC, and full characterization was completed recently.[9] Thus, the 16e cobalt complex represents perfect selectivity.

In MeOH: In the protic solvent MeOH, the reaction of **1** with excess HC≡C−Fc at ambient temperature led to different products **3S**, **4S**, and **5Se** (Scheme 2).

Compound **3S** was isolated in a yield of 40%. Its X-ray structure (Figure 2 and Table 1) displays a tripod with a B−CH_2 unit, but lacks a CpCo moiety compared to **2S**.[8] Obviously, a symmetric structure was achieved in **3S** as revealed by its spectroscopic data. For example, a singlet at $\delta = 2.28$ ppm in the ^{1}H NMR spectrum was assigned to the two magnetically equivalent protons of the B−CH_2 unit, in contrast to two doublets ($J = 16$ Hz) separated by 1.1 ppm in **2S**. Additionally, the ^{13}C NMR spectrum shows one slightly broadened signal at $\delta = 90.1$ ppm assigned to the two equal carbon atoms of the carborane cage. A lower-field ^{11}B signal at 0.6 ppm for the substituted boron atom was observed relative to the negative values for the other boron signals.

Complex **5** is novel. We are unaware of any previous generation of compounds arising by loss of a *p*-cymene/Cp*-metal fragment from transition-metal half-sandwich complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand. The reaction provides a facile route for the incorporation of ethynylferrocene into an *o*-carborane dithiolate to generate ferrocene–carborane conjugates.

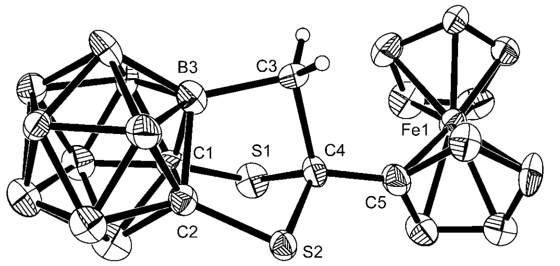


Figure 2. Molecular structure of **3S**; ellipsoids show 30 % probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.637(9), C(1)–B(3) 1.680(12), C(2)–B(3) 1.713(11), C(3)–B(3) 1.734(10), S(2)–C(2) 1.788(7), S(1)–C(1) 1.732(8), S(1)–C(4) 1.735(7), S(2)–C(4) 1.848(7), C(3)–C(4) 1.783(9), C(4)–C(5) 1.466(9); S(1)-C(4)-S(2) 107.0(3), S(1)-C(4)-C(5) 116.0(5), S(2)-C(4)-C(5) 112.0(5), C(1)-S(1)-C(4) 91.3(3), C(2)-S(2)-C(4) 88.1(3), S(2)-C(4)-C(3) 103.2(4), S(1)-C(4)-C(3) 105.2(4), C(5)-C(4)-C(3) 112.3(5), C(4)-C(3)-B(3) 93.2(5).

Compound **4S** was isolated as a minor product. Interestingly, it contains an open C_2B_9 cluster rather than a *closo*-C_2B_{10} cage, as shown by X-ray analysis (Figure 3 and Table 1). The characteristic well-separated ^{11}B signals in a larger range from 11 to −33 ppm present a sharp contrast with those of *closo*-*o*-carborane derivatives.[3–7] The generation of a *nido*-C_2B_9 unit is attributed to the protic solvent MeOH.[13] Note that a basic environment or an alcoholic solvent can readily lead to loss of an apex BH close to the two C atoms of *o*-carborane since B(3)/B(6)–H are more acidic.[2,14] The broader singlet at $\delta = 1.69$ ppm in the ^{1}H NMR spectrum corresponds to the alkyl B–CH moiety. The generation of a metal–metal bond leads to each cobalt atom being electronically saturated.

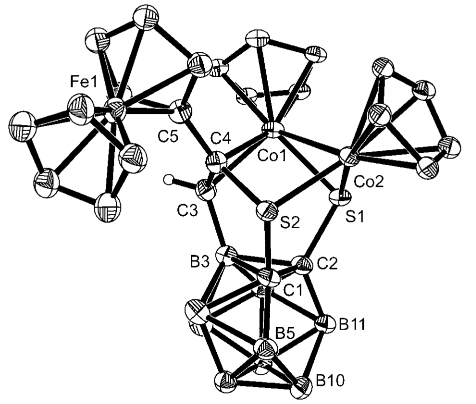


Figure 3. Molecular structure of **4S**; ellipsoids show 30 % probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co(1)–ring centroid 1.696, Co(2)–ring centroid 1.697, Co(1)–Co(2) 2.5603(7), C(1)–C(2) 1.572(5), C(1)–B(3) 1.741(6), C(2)–B(3) 1.711(5), S(1)–C(2) 1.772(4), S(2)–C(1) 1.794(4), C(3)–B(3) 1.567(5), Co(2)–S(1) 2.1537(10), Co(2)–S(2) 2.1886(10), Co(1)–C(4) 2.079(3), Co(1)–C(3) 2.051(3), S(2)–C(4) 1.813(4), C(4)–C(5) 1.463(5); C(3)-C(4)-C(5) 128.3(3), Co(1)-C(4)-C(5) 111.9(2), S(2)-C(4)-C(5) 116.7(3), Co(2)-S(2)-C(4) 91.18(12), Co(1)-C(4)-S(2) 105.00(16), Co(1)-C(3)-B(3) 113.5(2), S(1)-Co(1)-C(3) 92.95(11), Co(1)-S(1)-C(2) 105.20(12), Co(2)-S(1)-C(2) 106.24(12), S(1)-Co(2)-S(2) 90.96(4).

Attempts to synthesize the selenium analogues of **3S** and **4S** from **1Se** and HC≡C–Fc in MeOH were unsuccessful. However, a new compound **5Se** was generated. Its X-ray crystal structure (Figure 4 and Table 1) shows an addition product of the alkyne to the 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand at the selenium sites with extrusion of the CpCo unit. The newly generated six-membered ring is bent at the Se(1)···Se(2) vector at an angle of 126.7°. The C(3)–C(4) bond length (1.327 Å) falls in the range of a C=C bond.

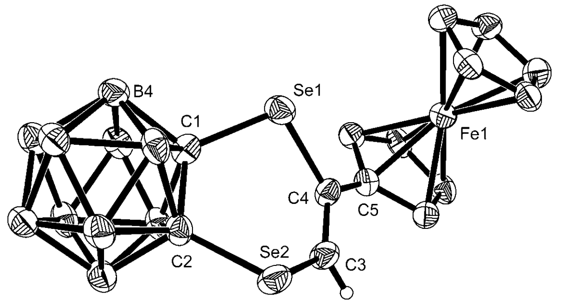
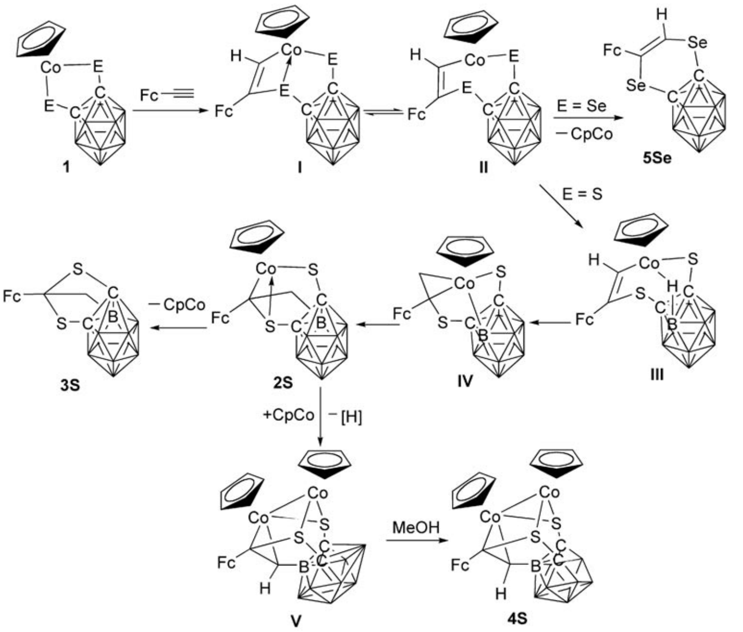


Figure 4. Molecular structure of **5Se**; ellipsoids show 30 % probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.634(5), Se(1)–C(1) 1.916(4), Se(2)–C(2) 1.934(4), Se(2)–C(3) 1.911(4), Se(1)–C(4) 1.894(4), C(3)–C(4) 1.327(5), C(4)–C(5) 1.461(5); C(1)-Se(1)-C(4) 101.33(16), C(2)-Se(2)-C(3) 99.45(16), Se(2)-C(3)-C(4) 126.3(3), Se(1)-C(4)-C(3) 121.0(3), Se(1)-C(4)-C(5) 116.2(3), C(3)-C(4)-C(5) 122.8(3), C(1)-C(2)-Se(1)-Se(2)/C(3)-C(4)-Se(1)-Se(2) 53.3.

The NMR data of **5Se** are in agreement with its solid-state structure. A characteristic feature in the ^{1}H NMR spectrum includes a singlet at $\delta = 7.19$ ppm assigned to the olefinic proton. 2D ^{13}C/^{1}H heteronuclear correlation (HETCOR; HMBC and HMQC) experiments based on coupling constants $^nJ(^{13}C, ^1H)$ $(n = 1, 2)$ were performed to allow complete assignment of ^{13}C NMR spectroscopic signals. As a result, the ^{13}C signal of the =CH unit of the six-membered ring is identified at $\delta = 113.5$ ppm. The carbon atom linked to the ferrocenyl group (=C–Fc) was assigned at $\delta = 130.1$ ppm. A similar structure was observed for (FcCCH)[$(Ge(Me)_2)_2(C_2B_{10}H_{10})$] resulting from the reaction of the cyclic nickel complex $(Me_3P)_2$Ni[$(Ge(Me)_2)_2$-$(C_2B_{10}H_{10})$] with HC≡C–Fc.[15]

Transformation of 2S in MeOH at ambient temperature: Upon treatment in MeOH at ambient temperature for three days, **2S** converts to **3S** and **4S** in yields of 60 and 20 %, respectively (Scheme 2). In practice, in the presence of silica gel the conversion of **2S** to **3S** in CH_2Cl_2 at ambient temperature is immediate; upon reaction in boiling toluene for three days the conversion is also quantitative. Therefore, it can be safely assumed that **2S** is the intermediate of the reaction of **1S** and HC≡C–Fc in MeOH, thus connecting **1S** and the isolated products **3S** and **4S**.



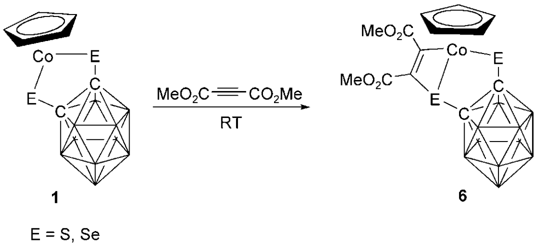
Scheme 3. Mechanism proposed for the reaction of **1** with HC≡C−Fc in MeOH.

Mechanistic implications: The two starting materials (**1S** and **1Se**) reacted with HC≡C−Fc in MeOH to yield markedly different final products. Mechanistic suggestions for the generation of **2S**–**4S** and **5Se** are shown in Scheme 3. The pathway from **1S** to **2S** via **I**–**IV** has been well documented in our previous work.[3–7] In the case of selenium, reductive elimination of the cobalt fragment from **II** leads to **5Se**. The formation of **3S** most likely arises from an initial nucleophilic attack of MeOH on the cobalt center in **2S**, followed by reductive elimination of a CpCo fragment. The released CpCo fragment can be captured by **2S** itself to generate **V**. But the introduction of an extra CpCo moiety alters the electronic environment of the "pseudo" aromatic system that may facilitate loss of a BH vertex in the protic MeOH to give **4S**. Note that one hydrogen atom is extruded from the alkyl B−CH_2 unit in the conversion of **2S** to **4S**. Hence, the generation of **3S**–**5S** provides a relatively unexplored facet of the chemical interactions between the metal complex and the organic substrate.

Reactions of 1 with MeO_2C−C≡C−CO_2Me: The reactions of **1S** and **1Se** with MeO_2C−C≡C−CO_2Me in CH_2Cl_2 at ambient temperature led to **6S** and **6Se**, respectively (Scheme 4). The solid-state structure of **6S** was described by Kang's research group.[16] In the present work, its ^{11}B and ^{13}C NMR data were first reported for comparison with the selenium analogue.

Compound **6Se** was isolated in a yield of 80%. The crystal structure and data (Figure 5 and Table 2) indicate the addition of one alkyne to a Co−Se bond to give a four-membered ring, as observed in **6S**.[8] The ^{13}C data of the carborane ($\delta = 067.5$ and 70.7 ppm) shift to a high field relative to **6S** (79.2 and 98.6 ppm) owing to the heavy-atom effect exerted by replacement of S with Se. However, the chemical shifts of the two olefinic carbon atoms are similar in both **6S** and **6Se**.

Transformation of 6 at a higher temperature: The insertion complexes of the type **B**–**G** (Scheme 1)[3b,5] could be considered as intermediates connecting the 16e half-sandwich complexes to the isolated products, such as *ortho*-metalation or boron-substitution compounds, in spite of not being isolated from the reactions with other alkynes, that is, HC≡C−CO_2Me, HC≡C−Ph, HC≡C−Fc, HC≡CH, HC≡C−Me, and HC≡C−CH_2OMe. However, it is well document-



Scheme 4. Reactions of **1S** and **1Se** with MeO_2C−C≡C−CO_2Me.

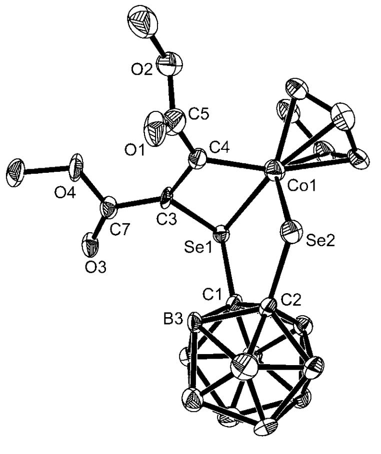


Figure 5. Molecular structure of **6Se**; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co(1)−ring centroid 1.692, C(1)−C(2) 1.672(8), Se(1)−Co(1) 2.3626(10), Se(2)−Co(1) 2.3557(11), C(3)−C(4) 1.371(8), Co(1)−C(4) 1.908(6), Se(1)−C(3) 1.922(6); Se(1)-C(3)-C(4)-Co(1) −2.4(5), Se(1)-Co(1)-Se(2)/Se(2)-C(2)-C(1)-Se(1) 163.7.

Table 2. Crystallographic data and structure refinement information for **6Se** and **7S–9S**.

	6Se	**7S**	**8S**	**9S**
formula	$4(C_{13}H_{21}B_{10}CoO_4Se_2),H_2O$	$C_{27}H_{44}B_{20}Cl_2Co_2O_8S_4$	$C_{13}H_{21}B_{10}CoO_4S_2$	$C_{19}H_{27}B_{10}CoO_8S_2$
M_w	2283.01	1029.86	472.47	614.56
color	red	red	blue	red
size [mm^3]	0.22×0.24×0.30	0.24×0.26×0.30	0.24×0.26×0.30	0.24×0.26×0.30
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pbcn*	*P*21/*c*	*C*2/*c*
a [Å]	11.9366(13)	18.3927(16)	10.9122(12)	12.1832(14)
b [Å]	14.6959(16)	11.7460(11)	9.9909(11)	18.753(2)
c [Å]	15.0536(16)	21.2801(19)	19.728(2)	12.903(2)
α [°]	62.5130(10)	90	90	90
β [°]	75.200(2)	90	90.212(3)	112.670(1)
γ [°]	83.032(2)	90	90	90
V [Å^3)]	2264.9(4)	4597.4(7)	2150.8(4)	2720.2(6)
Z	1	4	4	4
θ range [°]	1.6–26.0	1.9–26.0	1.9–26.0	2.1–26.0
ρ_{calcd} [g cm^{-3}]	1.674	1.488	1.459	1.501
μ [mm^{-1}]	3.991	1.064	1.010	0.829
min, max trans	0.3313, 0.4224	0.7407, 0.7842	0.7514, 0.7935	0.783, 0.821
data/restraints/parameters	8758/0/553	4522/0/300	4229/0/273	2670/0/206
$F(000)$	1114	2088	960	1256
no. reflns collected	12 587	23 620	11 445	7345
no. unique reflns (R_{int})	8758 (0.032)	4522 (0.037)	4229 (0.045)	2670 (0.040)
GOF	1.03	1.04	0.99	1.08
R indices ($I>2\sigma(I)$)	$R_1=0.0586$ $wR_2=0.1226$	$R_1=0.0431$ $wR_2=0.1050$	$R_1=0.0554$ $wR_2=0.1065$	$R_1=0.0494$ $wR_2=0.1132$
R indices (all data)	$R_1=0.0820$ $wR_2=0.1277$	$R_1=0.0547$ $wR_2=0.1086$	$R_1=0.0752$ $wR_2=0.1096$	$R_1=0.0646$ $wR_2=0.1160$
largest diff. peak and hole (e Å^{-3})	0.441, −0.806	0.614, −0.987	0.394, −0.724	0.472, −0.289

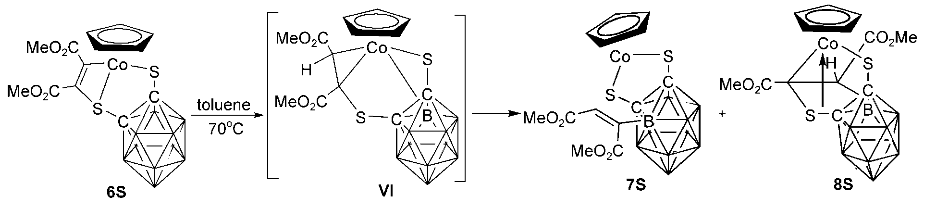
ed that these complexes are rather stable with respect to further rearrangements. For example, after heating in boiling toluene for three days, little rearrangement of **C** to *ortho*-metalation compound **H** (Scheme 1) could be detected by ^{11}B NMR spectroscopy on the basis of a high-field shift of the ^{11}B signal of a B–Ir bond.[5] Hence, the further transformation of this type of product plays a crucial role in supporting the mechanism we proposed for metal-induced B–H activation and B functionalization of the *o*-carborane cage.[3]

Upon heating at 70 °C, **6S** rearranges to **7S** and **8S** in an approximate ratio of 1:1 (Scheme 5). Both are geometrical isomers with B substitution at the carborane cage. Compound **7S** was isolated in a yield of 40 %. The solid-state structure (Figure 6 and Table 2) shows a 16e complex containing an olefinic substituent at the B(3)/B(6) site in a *cis* arrangement.[8] The generation of **7S** follows well-established procedures through metal-induced B–H activation and M–B formation.[3–6] The intermediate **VI** (Scheme 5) rearranges in two ways leading to **7S** and **8S**, respectively. In **7S**, the five-membered ring Co(1)S(1)C(1)C(2)S(2) is planar as in **1S**. The ^1H NMR spectrum shows a signal at $\delta=6.84$ ppm for the vinyl proton of the =CH moiety. The broad ^{13}C resonance at $\delta=143.7$ ppm for the carbon atom linked to B(3)/B(6) is indicative. One carbon signal of the carborane is recognized at $\delta=97.1$ ppm owing to a symmetric structure of **7S**.

The X-ray structure of **8S** (Figure 7 and Table 2) displays the formation of an alkyl B–CH unit,[8] analogous to **2S**. The C=C double bond (1.340 Å) in **6S** has been extended to the range of a single bond (1.528 Å) in **8S**. In solution, broad signals at $\delta=2.86$ for ^1H and 46.7 ppm for ^{13}C for the B–CH group in **8S** were observed. In comparison, **6Se** does not convert under the same conditions. However, heating to 110 °C leads to decomposition to $[(CpCo)_2(Se_2C_2B_{10}H_{10})]$.

At present, **6S** is the only 18e alkyne addition complex that can convert under mild conditions and generate two different final products with B substitution at the B(3)/B(6) positions. The cause arises from the symmetric internal alkyne that determines the sole intermediate **VI**, further leading to two equal rearrangements to **7S** and **8S**. Previous observations led to a structural type of either **7S** or **8S**.[3] The sequence shown in Scheme 5 provides direct evidence for our mechanistic proposal on metal-induced B–H activation and B–H functionalization of the *o*-carborane cage.[3]

Reactions of 7S with R-C≡C−CO$_2$Me (R = H or CO$_2$Me): Owing to electron deficiency at the metal center, **7S** is promising for use as an electron acceptor. A subsequent reaction with $MeO_2C-C\equiv C-CO_2Me$ at ambient temperature led to **9S** and **10S** (Scheme 6). Compound **9S** was isolated in a yield of 60 %. Single-crystal X-ray diffraction reveals (Figure 8 and Table 2) a symmetric molecule with a 16e metal center and B disubstitution at the B(3) and B(6) sites of the carborane cage.[9] Unexpectedly, the configurations of



Scheme 5. Rearrangement of **6S** to **7S** and **8S**.

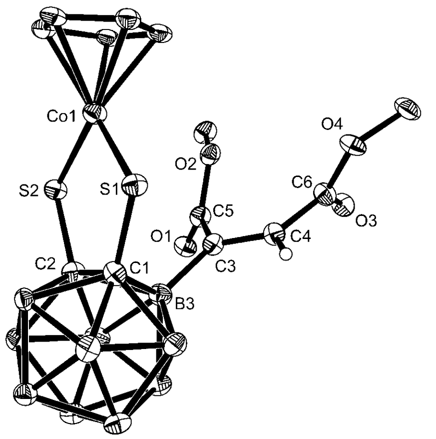


Figure 6. Molecular structure of **7S**; ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co(1)–ring centroid 1.636, Co(1)–S(1) 2.1318(8), Co(1)–S(2) 2.1396(8), C(1)–C(2) 1.632(4), S(1)–C(1) 1.793(3), S(2)–C(2) 1.800(3), C(3)–C(4) 1.330(4), C(3)–B(3) 1.580(4); C(5)-C(3)-C(4)-C(6) 2.5(4), S(1)-C(1)-C(2)-S(2)/S(2)-Co(1)-S(1) 2.

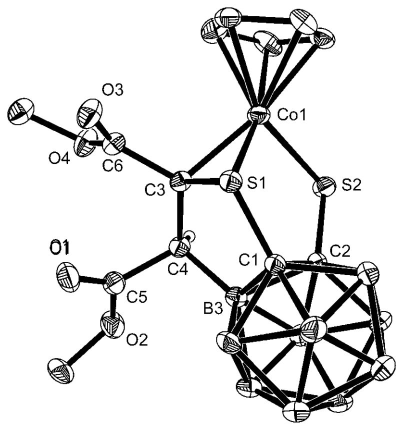
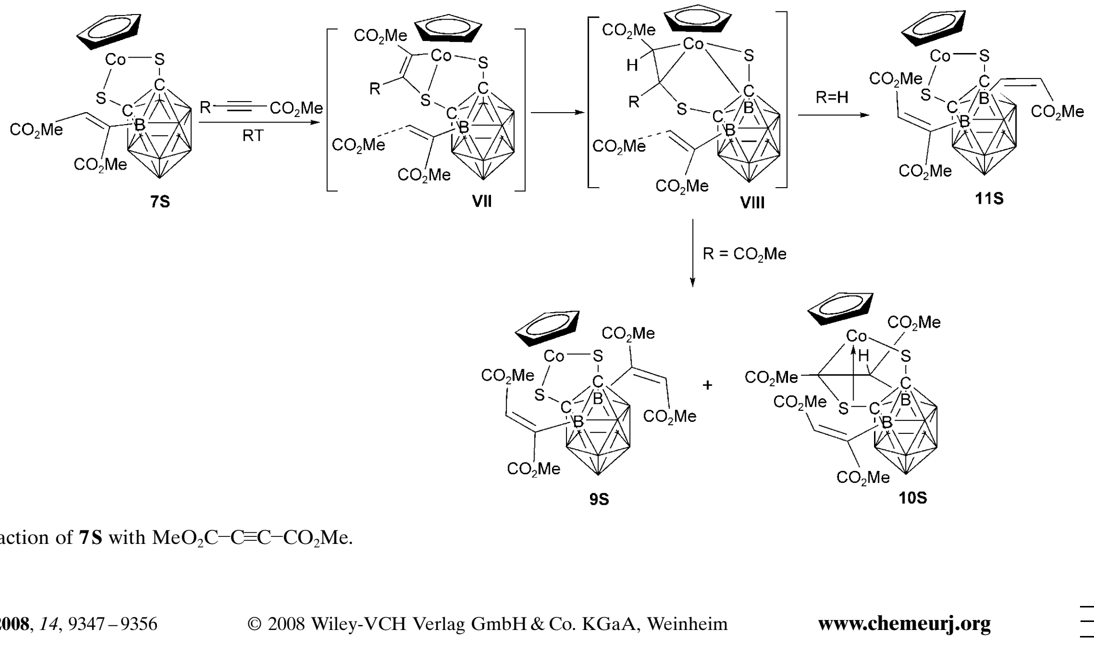


Figure 7. Molecular structure of **8S**; ellipsoids show 30% probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co(1)–ring centroid 1.681, C(1)–C(2) 1.690(4), S(1)–C(3) 1.786(3), C(3)–C(4) 1.528(4), C(4)–B(3) 1.597(5), C(1)–B(3) 1.704(5), C(2)–B(3) 1.728(5), S(1)–C(1) 1.789(3), S(2)–C(2) 1.756(3), Co(1)–S(1) 2.1599(9), Co(1)–S(2) 2.2276(9); C(6)-C(3)-C(4)-C(5) −30.3(4), C(4)-B(3)-C(1)-S(1)/C(4)-C(3)-S(1) 165.9, S(1)-C(1)-C(2)-S(2)/S(1)-Co(1)-S(2) 175.3.

the two olefinic substituents are both in the *trans* (*E*) arrangement, in contrast to the *cis* (*Z*) configuration in **7S**. The easy conversion at ambient temperature reflects the low barrier energy between the two configurations in this specific system. In the ^{1}H NMR spectrum one singlet at $\delta=6.70$ ppm corresponds to the C=CH unit, in contrast to $\delta=6.84$ ppm in **7S**. The sharp ^{13}C signal at $\delta=141.9$ ppm and the broad one at $\delta=134.8$ ppm of the carbon nuclei linked directly to B(3)/B(6) are indicative of the B–C=CH unit, in contrast to $\delta=141.3$ and 143.7 ppm in **7S**.

Compound **10S** was isolated in a yield of 10%. Unfortunately, attempts to grow suitable single crystals for structural determination failed. However, spectroscopic data support the structure proposed in Scheme 6. The NMR spectroscopic data demonstrate that the second B substitution has occurred with an alkyl B–CH unit, as shown by a broader ^{1}H singlet at $\delta=2.85$ ppm and a broader ^{13}C signal at $\delta=29.4$ ppm for the B–CH unit. Additionally, the ^{11}B signal at $\delta=0.5$ ppm is attributed to the characteristic boron atom linked to the alkyl unit, in contrast to the negative values of other boron signals. In the B-substituted olefinic unit, the ^{1}H spectroscopic signal of the =CH unit appears at $\delta=7.45$ ppm, compared to $\delta=6.84$ ppm in **7S**. A mass spectrometric measurement displays a molecular peak. Note that an *E* configuration for the olefinic unit in **10S** is assumed on the basis of the facile configuration conversion from **7S** to **9S**.

Notably, the reaction of **7S** with $MeO_2C{-}C{\equiv}C{-}CO_2Me$ to generate **9S** and **10S** is not a simple repetition of the one from **1S** to **7S** and **8S**. The predicted intermediate **VII**, an analogue of **6S**, is not isolated, and **9S** and **10S** are the final products at ambient temperature. The experimental results reveal that the presence of one B substitution can accelerate



Scheme 6. Reaction of **7S** with $MeO_2C{-}C{\equiv}C{-}CO_2Me$.

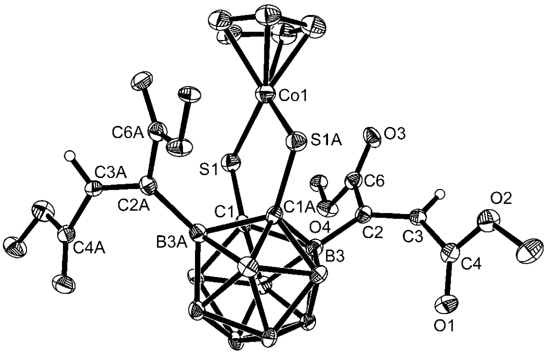


Figure 8. Molecular structure of **9S**; ellipsoids show 30 % probability levels, and some of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co(1)–ring centroid 1.634, Co(1)–S(1) 2.1408(9), S(1)–C(1) 1.778(3), C(1)–C(1A) 1.645(3), C(2)–B(3) 1.596(5), C(2)–C(3) 1.328(4); C(1)-S(1)-Co(1)-S(1A)/C(1)-C(1A)-S(1A) 4.7.

the reactivity of the 16e metal center. This finding is attributed to the "pseudo" aromatic properties of both the carborane cage and the five-membered ring of S(1)Co(1)S(2)C(2)C(1). In comparison, the generation of **10S** is less favored than **9S**, which indicates that the rearrangement of **VIII** to **10S** is less favored due to the electronic effect of the CO_2Me unit.

If a second alkyne $HC{\equiv}C{-}CO_2Me$ was used for further reaction with **7S**, only **11S**, an analogue of **9S**, was isolated in a yield of 80 %. Good-quality single crystals for X-ray measurement were not obtained; however, the spectroscopic data support the proposed B-disubstituted structure (Scheme 6). The doublets at $\delta = 5.18$ and 6.23 ppm with a coupling constant of $J = 15$ Hz suggest an olefinic unit in a *Z* configuration, as observed in the analogous Co, Rh, and Ir complexes. The singlet at $\delta = 6.72$ ppm is assigned to the vinyl proton of the $B{-}C{=}CH{-}CO_2Me$ unit. The ^{13}C NMR spectrum displays one sharp resonance at $\delta = 134.6$ ppm ($B{-}CH{=}CH$), a broad signal at $\delta = 135.2$ ppm ($B{-}CH{=}CH$), and a sharp signal at $\delta = 141.7$ ppm ($B{-}C{=}CH{-}CO_2Me$), as confirmed by 2D $^{13}C/^{1}H$ HETCOR (HMQC) experiment. Similarly, a configuration change of the first olefinic unit from *Z* to *E* was assumed from **7S** to **11S** as occurred from **7S** to **9S**. Moreover, it appears that the number of the electron-withdrawing CO_2Me groups affects the product type, that is, from **7S** to **11S** or to **9S** and **10S**. In practice, the electronic effect influences the rearrangement selectivity of the species **VIII**, further leading to different types of products.

Conclusion

The reaction of $[CpCo(S_2C_2B_{10}H_{10})]$ (**1S**) with $HC{\equiv}C{-}Fc$ affords **2S** with a C–B bond instead of an M–B bond. This finding demonstrates that the 16e cobalt compound is more reactive than its analogous 16e rhodium and iridium complexes. The protic solvent MeOH induces conversion of **2S** to the interesting structures of **3S** and **4S**. In addition, a competitive pathway of **1S**-catalyzed cyclotrimerization of $HC{\equiv}C{-}Fc$ is present that leads to more congested 1,2,4-triferrocenylbenzene as a sole product. This was not observed in the rhodium and iridium systems. In the reaction of **1S** with $MeO_2C{-}C{\equiv}C{-}CO_2Me$, the rearrangement of the alkyne insertion complex **6S** further verifies our previously proposed mechanism on metal-induced B–H activation. The B-substituted 16e species **7S** is more reactive than **1S**, which reflects a "pseudo" aromatic system. Additionally, the cobalt complexes with selenium show less reactivity than the sulfur analogues. This parallels the observations in related Rh and Ir complexes.

Experimental Section

General: *n*BuLi (2.0 M in hexanes, Aldrich), *o*-carborane (Katchem, Czech Republic), methyl acetylenemonocarboxylate (Alfa Aesar), and dimethyl acetylenedicarboxylate (Aldrich) were used as supplied. Ethynylferrocenyl,[17] $[CpCo(CO)I_2]$,[18] and 16e complex $[CpCo(E_2C_2B_{10}H_{10})]$ (E = S, Se)[19] were prepared by modified literature procedures. All reactions were carried out under argon by using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use. Diethyl ether, THF, petroleum ether, and toluene were heated to reflux and distilled over sodium/benzophenone ketyl under nitrogen. CH_2Cl_2 was heated to reflux and distilled over CaH_2 under nitrogen. The NMR measurements were performed on a Bruker DRX 500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ ($\delta(^1H) = 7.24$, $^{13}C = 77.0$ ppm), $CDHCl_2/CD_2Cl_2$ ($\delta(^1H) = 5.33$; $^{13}C = 53.8$ ppm), and external $Et_2O{\cdot}BF_3$ ($\delta(^{11}B) = 0$ ppm). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the region of 4000–400 cm^{-1}. The C and H microanalyses were carried out with an Elemetar Vario EL III elemental analyzer. Mass spectra were recorded in a Micromass GC-TOF for EIMS (70 eV).

Synthesis of 2S: A mixture of **1** (66.0 mg, 0.2 mmol) and $HC{\equiv}C{-}Fc$ (105 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was stirred for 6 h at ambient temperature. The color turned gradually from red to deep purple. After removal of solvent, the residue was subjected to chromatography on neutral alumina, and elution with petroleum ether/CH_2Cl_2 (2:1) gave **2S** (86.4 mg, 80 %). Purple solid; m.p. 161 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 1.82$ (d, $^2J(H,H) = 16$ Hz, 1H; $B{-}CH_2$), 2.91 (d, $^2J(H,H) = 16$ Hz, 1H; $B{-}CH_2$), 3.60 (s, 1H; Fc), 4.30 (s, 1H; Fc), 4.40 (s, 5H; Fc), 4.43 (s, 1H; Fc), 4.57 (s, 1H; Fc), 4.49 ppm (s, 5H; Cp); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 33.5$ (br, $B{-}CH_2$), 67.5, 68.3, 69.5, 69.6, 89.9, 102.3 (Fc), 83.3 (Fc–C–S), 86.1 (Cp), 95.4, 98.5 ppm (carborane); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = -11.4$ (1B), −7.6 (1B), −6.6 (5B), −6.1 (1B), −4.8 (1B), 4.4 (1B, $B{-}CH_2$); IR (KBr): $\tilde{\nu} = 2572$ cm^{-1} (B–H); MS (70 eV): m/z (%): 416.1 (100) [M^+]; elemental analysis calcd (%) for $C_{19}H_{25}B_{10}CoFeS_2$: C 42.23, H 4.66; found: C 41.78, H 4.89.

Syntheses of 3S and 4S

Method A: A mixture of **1** (66.0 mg, 0.2 mmol) and $HC{\equiv}C{-}Fc$ (105 mg, 0.5 mmol) in MeOH (20 mL) was stirred for 72 h at ambient temperature. The color turned gradually from red to deep brown. After removal of solvent, the residue was subjected to chromatography on silica and elution with petroleum ether gave **3S** (33.3 mg, 40 %), followed by **4S** (13.1 mg, 10 %) with 1:1 petroleum ether/CH_2Cl_2.

Method B: A purple solution of **2S** (108.0 mg, 0.2 mmol) in MeOH (15 mL) was stirred at room temperature for 72 h. The color changed gradually to brown. After removal of solvent, the residue was subjected to chromatography on silica to give **3S** (49.9 mg, 60 %) and **4S** (13.0 mg, 20 %).

*Compound **3S***: Yellow solid; m.p. 165 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 2.28$ (brs, 2H; $B{-}CH_2$), 4.28 (s, 5H; Fc), 4.30 (s, 2H; Fc), 4.49 ppm (s, 2H; Fc); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 39.3$ (br, B−CH_2), 67.8, 69.1, 69.8, 105.2 (Fc), 81.8 (Fc−C−S), 90.1 ppm (carborane); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = -13.0$ (1 B), −11.1 (1 B), −5.9 (5 B), −3.2 (1 B), −0.6 (1 B), 0.6 ppm (1 B; B-CH_2); IR (KBr): $\tilde{\nu} = 2593$ cm^{-1} (B−H); MS (70 eV): *m*/*z* (%): 416.0 (100) [M^+]; elemental analysis calcd (%) for $C_{14}H_{20}B_{10}Fe_1S_2$: C 40.38, H 4.84; found: C 40.06, H 5.02.

*Compound **4S***: Green solid; m.p. 190 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 1.69$ (br s, 1 H; B−CH), 4.28, 4.32, 4.31, 4.46, 4.63 (9 H, 1:5:1:1:1; Fc), 4.81, 5.31 ppm (10 H, 1:1; CpCo); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = -32.4$ (1 B), −24.2 (1 B), −18.7 (1 B), −12.9 (1 B), −12.3 (1 B), −3.9 (1 B), −1.2 (1 B), −0.05 (1 B), 10.7 ppm (1 B); IR (KBr): $\tilde{\nu} = 2542$ cm^{-1} (B−H); MS: (70 eV): *m*/*z* (%): 650.9 (58) [M^+]; elemental analysis calcd (%) for $C_{24}H_{30}B_9Co_2Fe_1S_2{\cdot}0.5\,H_2O$: C 43.77, H 4.11; found: C 43.35, H 4.89.

Synthesis of 5Se: A mixture of **1Se** (85.0 mg, 0.2 mmol) and $HC\equiv C{-}Fc$ (105 mg, 0.5 mmol) in MeOH (20 mL) was stirred for 48 h at ambient temperature. The color turned gradually from red to dark brown. After removal of the solvent in vacuo, the residue was subjected to chromatography on silica gel with petroleum ether/CH_2Cl_2 (5:1) and gave a yellow zone of **5Se** (40.8 mg, 40 %). Yellow solid; m.p. 163 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 4.20$ (s, 5 H; Cp), 4.42 (m, 2 H; Fc), 4.49 (m, 2 H; Fc), 7.19 ppm (s, 1 H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta =$ 67.0, 68.8, 69.6, 74.2 (Fc), 76.2, 113.5 (carborane), 113.0 (CH=), 130.1 ppm (=C−Fc); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = -5.7$ (8 B), −0.7 ppm (2 B); IR (KBr): $\tilde{\nu} = 2585$ cm^{-1} (B−H); MS (70 eV): *m*/*z* (%): 510.1 (47) [M^+]; elemental analysis calcd (%) for $C_{14}H_{20}B_{10}Fe_1Se_2$: C 32.96, H 3.95; found: C 32.27, H 4.37.

Syntheses of 6S and 6Se: $MeO_2C{-}C\equiv C{-}CO_2Me$ (0.25 mL, 2.0 mmol) was added to a red solution of **1S** (66.0 mg, 0.2 mmol) or a suspension of **1Se** (85.0 mg, 0.2 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 24 h and the color changed gradually to dark red. After removal of the solvent, the residue was subjected to chromatography on silica gel. Elution with CH_2Cl_2 gave **6S** (76 mg, 80 %) and **6Se** (90 mg, 80 %) as a deep red color.

*Compound **6S***: Red solid; ; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 3.77$ (s, 3 H; OMe), 3.94 (s, 3 H; OMe), 5.24 ppm (s, 5 H; Cp); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 52.6$, 52.7 (OMe), 79.2, 98.6 (carborane), 86.7 (Cp), 118.8 (S−C=), 155.2, 177.9 (C=O), 178.8 ppm (Co−C=); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = -8.30$ (3 B), −4.62 (2 B), −2.11 (5 B).

*Compound **6Se***: Red solid; m.p. 179 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 3.78$ (s, 3 H; OMe), 3.94 (s, 3 H; OMe), 5.20 ppm (s, 5 H; Cp); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 52.7$, 52.8 (OMe), 67.5, 70.7 (carborane), 85.6 (Cp), 118.9 (Se−C=), 153.6, 171.5 (C=O), 178.0 ppm (Co-C=); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = -7.6$ (3 B), −6.7 (1 B), −4.8 (2 B), −3.2 (3 B), −1.5 ppm (1 B); IR (KBr): $\tilde{\nu} = 1708$ cm^{-1} (C=O), 2575 cm^{-1} (B−H); MS (70 eV): *m*/*z* (%): 566 (21) [M^+]; elemental analysis calcd (%) for $C_{13}H_{21}B_{10}Co_1O_4Se_2{\cdot}0.25\,H_2O$: C 27.36, H 3.80; found: C 26.73, H 4.29.

Syntheses of 7S and 8S: A red solution of **6S** (0.2 mmol, 95.0 mg) in toluene was heated to 70 °C for 12 h. The color changed to yellow. After the solvent was removed in vacuo, the residue was subjected to chromatography on silica gel and elution with CH_2Cl_2 gave **7S** (28.0 mg, 30 %) and **8S** (28.0 mg, 30 %).

*Compound **7S***: Red solid; m.p. 201 °C; ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 3.82$ (s, 3 H; OMe), 3.89 (s, 3 H; OMe), 5.41 (s, 5 H; Cp), 6.84 ppm (s, 1 H; =CH); ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): $\delta = 51.8$, 52.3 (OMe), 97.1 (carborane), 81.7 (Cp), 141.3 (=CH), 143.7 (br; C−B), 167.0, 171.1 ppm (C=O); ^{11}B NMR (160 MHz, CD_2Cl_2, 25 °C): $\delta = -7.7$ (2 B), −6.8 (3 B), −6.1 (2 B), −4.9 (2 B), −4.0 ppm (1 B); IR (KBr): $\tilde{\nu} =$ 1709 cm^{-1} (C=O), 2566 cm^{-1} (B−H); MS (70 eV): *m*/*z* (%): 472 (12) [M^+]; elemental analysis calcd (%) for $C_{13}H_{21}B_{10}Co_1O_4S_2$: C 33.05, H 4.48; found: C 32.48, H 4.79.

*Compound **8S***: Blue solid; m.p. 194 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 2.86$ (br s, 1 H; B−CH), 3.82 (s, 3 H; OMe), 3.83 (s, 3 H; OMe), 4.95 ppm (s, 5 H; Cp); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 46.7$ (br; B−CH), 52.5, 52.7 (OMe), 86.1 (Cp), 95.3 (S−C), 97.1, 113.9 (carborane), 171.5, 176.3 ppm (C=O); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = -11.4$ (1 B), −5.9 (4 B), −5.2 (4 B), 2.4 ppm (1 B); IR (KBr): $\tilde{\nu} = 1733$, 1704 cm^{-1} (C=O), 2589 cm^{-1} (B−H); MS (70 eV): *m*/*z* (%): 472 (6) [M^+]; elemental analysis calcd (%) for $C_{13}H_{21}B_{10}Co_1O_4S_2$: C 33.05, H 4.48; found: C 32.66, H 4.23.

Syntheses of 9S and 10S: $MeO_2C{-}C\equiv C{-}CO_2Me$ (0.25 mL, 2.0 mmol) was added to a red solution of **7S** (94.0 mg, 0.2 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 24 h at ambient temperature to give a brown-red solution. After removal of solvent, the residue was subjected to TLC and elution with CH_2Cl_2 gave **9S** (72.0 mg, 60 %) and **10S** (12.0 mg, 10 %).

*Compound **9S***: Red solid; m.p. 187 °C; ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 3.67$ (s, 3 H×2; OMe), 3.77 (s, 3 H×2; OMe), 5.44 (s, 5 H; Cp), 6.70 ppm (s, 1 H×2; =CH); ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): $\delta = 52.1$ (OMe), 52.7 (OMe), 82.4 (Cp), 99.7 (carborane), 134.8 (br; B−C=), 141.9 (C=*C*H), 167.0, 171.1 ppm (C==O); ^{11}B NMR (160 MHz, CD_2Cl_2, 25 °C): $\delta = -12.7$ (3 B), −11.0 (6 B), −9.0 ppm (1 B); IR (KBr): $\tilde{\nu} = 1720$ cm^{-1} (C=O), 2567 cm^{-1} (B−H); MS (70 eV): *m*/*z* (%): 615 (6) [M^+]; elemental analysis calcd (%) for $C_{19}H_{27}B_{10}Co_1O_8S_2$: C 37.13, H 4.43; found: C 36.73, H 4.87.

*Compound **10S***: Blue solid; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 2.85$ (br s, 1 H; B−CH), 3.79 (s, 3 H; OMe), 3.83 (s, 3 H; OMe), 3.86 (s, 3 H; OMe), 3.96 (s, 3 H; OMe), 4.87 (s, 5 H; Cp), 7.45 ppm (s, 1 H; =CH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 29.4$ (br; B−CH), 52.2, 52.5, 52.6, 52.7 (OMe), 85.7, 98.5 (carborane), 86.3 (Cp), 97.0 (S−C), 143.2 (=CH), 166.9, 169.7, 171.5, 176.4 ppm (C=O); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): $\delta = 0.5$ (1 B), −5.0 (1 B), −8.7 (7 B), −13.7 ppm (1 B); IR (KBr): $\tilde{\nu} = 1723$ cm^{-1} (C=O), 2577 cm^{-1} (B−H); MS (70 eV): *m*/*z* (%): 615 (20) [M^+]; elemental analysis calcd (%) for $C_{19}H_{27}B_{10}Co_1O_8S_2$: C 37.13, H 4.43; found: C 36.63, H 4.80.

Synthesis of 11S: $HC\equiv C{-}CO_2Me$ (0.25 mL, 2.0 mmol) was added to a solution of **7S** (94.0 mg, 0.2 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 24 h at ambient temperature to give a brown-red solution. After removal of solvent, the residue was subjected to TLC and elution with CH_2Cl_2 gave **11S** (89.0 mg, 80 %). Red solid; ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 3.64$ (s, 3 H; OMe), 3.68 (s, 3 H; OMe), 3.78 (s, 3 H; OMe), 5.18 (d, ^3J (H,H) = 15 Hz, 1 H; B-CH=C*H*), 5.41 (s, 5 H; Cp), 6.23 (br d, ^3J (H,H) = 15 Hz, 1 H; B-C*H*=CH), 6.72 ppm (s, 1 H; C=CH); ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): $\delta = 51.4$, 52.0, 52.7 (OMe), 82.2 (Cp), 99.1 (carborane), 134.6 (B−CH=*C*H), 135.2 (br; B−*C*H=CH), 141.7 (C=*C*H−C(O)), 167.1, 171.2 ppm (C=O); ^{11}B NMR (160 MHz, CD_2Cl_2, 25 °C): $\delta = -12.9$ (3 B), −11.1 (4 B), −10.1 ppm (3 B); IR (KBr): $\tilde{\nu} = 1711$, 1722 cm^{-1} (C=O), 2566 cm^{-1} (B−H); MS (70 eV): *m*/*z* (%): 556 (37) [M^+]; elemental analysis calcd (%) for $C_{17}H_{25}B_{10}Co_1O_6S_2$: C 36.69, H 4.53; found: C 35.98, H 4.94.

X-ray crystallography: Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in petroleum ether/dichloromethane. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer by means of graphite-monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation at 273 K. During collection of the intensity data, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption by using the SADABS program.[20] The structures were solved by direct methods with the SHELXL-97 program.[21] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in the calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. All calculations were performed by using the Bruker Smart program.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 20471017, 20771055, 90713023, and 20721002), the Major State Basic Research Development Program of China (No. 2006CB806104), the National Basic Research Program of China

(No. 2007CB925101), and the Natural Science Foundation of Jiangsu Province (No. BK2007131).

---

[1] R. N. Grimes, *Carboranes*, Academic Press, New York, **1970**.

[2] V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209–223.

[3] a) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *J. Chem. Soc. Dalton Trans.* **2001**, 1782–1789; b) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Angew. Chem.* **1999**, *111*, 3888–3890; *Angew. Chem. Int. Ed.* **1999**, *38*, 3689–3691.

[4] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **2001**, *623*, 149–152.

[5] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Chem. Eur. J.* **2000**, *6*, 3026–3032.

[6] a) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1627–1633; b) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Chem. Eur. J.* **2002**, *8*, 388–395.

[7] a) B. H. Xu, D. H. Wu, Y. Z. Li, H. Yan, *Organometallics* **2007**, *26*, 6300–6306; b) B. H. Xu, J. C. Tao, Y. Z. Li, S. H. Li, H. Yan, *Organometallics* **2008**, *27*, 334–340.

[8] CCDC-685850 (**2S**), 68585 1 (**3S**), 686359 (**4S**), 689332 (**5Se**), 689333 (**6Se**), 689334 (**7S**), 689335 (**8S**), and 689336 (**9S**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[9] S. Fiorentini, B. Floris, P. Galloni, F. Grepioni, M. Polito, P. Tagliatesta, *Eur. J. Org. Chem.* **2006**, 1726–1732.

[10] a) Y. Yamamoto, H. Kataoka, K. Kinpara, H. Nishiyama, K. Itoh, *Lett. Org. Chem.* **2005**, *2*, 219–221; b) L. Dufková, I. Císařová, P. Štěpnička, M. Kotora, *Eur. J. Org. Chem.* **2003**, 2882–2887.

[11] a) K. Schlögl, H. Soukup, *Tetrahedron Lett.* **1967**, *8*, 1181–1184; b) M. Rosenblum, N. Brawn, B. King, *Tetrahedron Lett.* **1967**, *8*, 4421–4425.

[12] P. Štěpnička, I. Císařová, J. Sedláček, J. Vohlídal, M. Polášek, *Collect. Czech. Chem. Commun.* **1997**, *62*, 1577–1584.

[13] J. J. Schaeck, S. B. Kahl, *Inorg. Chem.* **1999**, *38*, 204–206, and references therein.

[14] J. Q. Wang, M. Herberhold, G. X. Jin, *Organometallics* **2006**, *25*, 3508–3514.

[15] a) J. Lee, T. Lee, S. S. Lee, K. M. Park, S. O. Kang, J. Ko, *Organometallics* **2002**, *21*, 3922–3929; b) Y. Kang, J. Lee, Y. K. Kong, S. O. Kang, J. Ko, *Organometallics* **2000**, *19*, 1722–1728.

[16] a) D. H. Kim, J. Ko, K. Park, S. Cho, S. O. Kang, *Organometallics* **1999**, *18*, 2738–2740; b) J. H. Won, D. H. Kim, B. Y. Kim, S. J. Kim, C. Lee, S. Cho, J. Ko, S. O. Kang, *Organometallics* **2002**, *21*, 1443–1453.

[17] a) K. Wurst, O. Elsner, H. Schottenberger, *Synlett* **1995**, 833–834; b) J. G. Rodriguez, A. Oñate, R. M. Martin-Villamil, I. Fonseca, *J. Organomet. Chem.* **1996**, *513*, 71–76; c) M. Rosenblum, N. Brawn, J. Papenmeier, M. Applebaum, *J. Organomet. Chem.* **1966**, *6*, 173–180.

[18] a) R. B. King, *Inorg. Chem.* **1966**, *5*, 82–87; b) S. A. Frith, J. L. Spencer, *Inorg. Synth.* **1990**, *28*, 273–280.

[19] a) X. F. Hou, X. Wang, J. Q. Wang, G. X. Jin, *J. Organomet. Chem.* **2004**, *689*, 2228–2235; b) M. Murata, S. Habe, S. Araki, K. Namiki, T. Yamada, N. Nakagawa, T. Nankawa, M. Nihei, J. Mizutani, M. Kurihara, H. Nishihara, *Inorg. Chem.* **2006**, *45*, 1108–1116, and references therein.

[20] G. M. Sheldrick, *SADABS*, *A Program for Empirical Absorption Correction*, University of Göttingen, Göttingen (Germany), **1998**.

[21] G. M. Sheldrick, *SHELXL-97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen (Germany), **1997**.

Received: June 10, 2008
Published online: September 2, 2008

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim