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The reaction of ethynylferrocene with Cp*Rh half-sandwich complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolato ligand, $Cp^*Rh[E_2C_2(B_{10}H_{10})]$, E = S, Se

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Abstract

Dimerisation of ethynylferrocene (**2**) to give a mixture of (*E*)- and (*Z*)-1,4-diferrocenylbuten-3-yne (ratio = 1:1) takes place in boiling chloroform if the 16e half-sandwich complex $Cp^*Rh[Se_2C_2(B_{10}H_{10})]$ (**1Se**) is present. Under these conditions cyclo-trimerisation was not observed. In contrast, $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ (**1S**) reacts with **2** in a 1:1 ratio by insertion into one of the Rh–S bonds, followed by B–H activation, transfer of a hydrogen atom to carbon via rhodium and formation of a Rh–B bond to give **7S** which was characterised by an X-ray structural analysis.

Keywords: Alkynes; B–H Activation; Carborane; Catalysis; Ferrocene; Rhodium; Selenium; Sulfur

1. Introduction

Transition metal complexes containing sterically demanding dichalcogenolato ligands such as ferrocene-1,1′-dichalcogenolate, $[Fe(C_5H_4E)_2]^{2-}$ [1,2], or *ortho*-carborane-1,2-dichalcogenolate, $[(B_{10}H_{10})C_2E_2]^{2-}$ [3–10] (E = S, Se), have recently attracted interest, also with respect to catalytic reactions. Depending on the reaction conditions, the analogous complexes of either sulfur or selenium might behave differently [10].

We have shown that the 16e half-sandwich rhodium complexes, $Cp^*Rh[E_2C_2(B_{10}H_{10})]$ (E = S, **1S** and E = Se, **1Se** [9]), react readily with alkynes such as methyl acetylene carboxylates ($MeO_2C–C{\equiv}CH$ and $MeO_2C–C{\equiv}C–CO_2Me$) and phenylacetylene to give numerous different complexes which result from addition and insertion into one of the Rh–E bonds, followed by B–H activation, M–B bond formation and further transformations [8,11–13]. It was also observed that the complexes **1S** and **1Se** both catalyse the cyclotrimerisation of $MeO_2C–C{\equiv}CH$ or $Ph–C{\equiv}CH$ to give mixtures of the respective 1,3,5- and 1,2,4-trisubstituted benzenes [13]. However, there are some reactions in which the sulfur complex **1S** and the selenium complex **1Se** lead to different products [10]. In this context, ferrocenylacetylene, $Fc–C{\equiv}CH$ (**2**), appeared to be an attractive alkyne for studying the reactivity towards **1S** and **1Se**, with respect to both metal-induced B–H activation and potential oligomerisation reactions. Cyclo-trimers of $Fc–C{\equiv}CH$ are known [14], cyclo-tetramers are unknown, and the non-cyclic dimers, the (*E*)- and (*Z*)-1,4-di(ferrocenyl)buten-3-ynes **3**, were obtained previously in moderate yield (< 50%) from the reaction of formylferrocene, either with (bromomethyl)triphenylphosphonium bromide [15] (1:10 ratio of the (*E*)- and (*Z*)-isomers) or with the corresponding chloro derivative [16] (1:1 ratio of the (*E*)- and (*Z*)-isomers) in the presence of potassium *tert*-butanolate.

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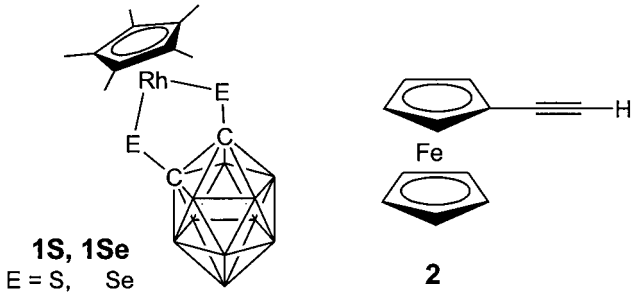
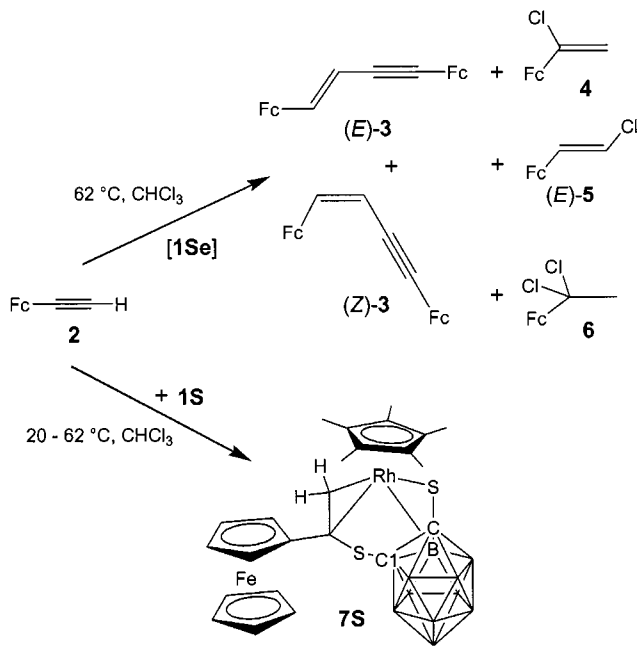


2. Results and discussion

2.1. Synthesis

The new reactions of ethynylferrocene (**2**) are summarised in Scheme 1. Heating of **2** in the presence of catalytic amounts of the rhodium complexes **1S** or **1Se** in toluene (70–110°C), conditions under which phenylacetylene readily trimerises [13], did not lead to a defined reaction. The higher boiling chlorinated hydrocarbon 1,1,2,2-tetrachloroethane induced decomposition of **2**. However, in boiling chloroform, in the presence of **1Se**, dimerisation of **2** took place to give a mixture (1:1) of (*E*)- and (*Z*)-1,4-di(ferrocenyl)buten-3-ynes **3** in yields varying from $< 5\%$ up to 65%, in addition to the ferrocene derivatives **4**, (*E*)-**5** and **6**, and **1Se** could be recovered (Scheme 1). There was no reaction of **2** in boiling chloroform in the absence of **1Se**. The presence of **4**, **5** and **6** indicates that chloroform also takes part in this reaction, and this points towards a radical mechanism. A future study of this reaction should include radical initiators or inhibitors in order to gain further insight. At present, it appears that small amounts of unidentified impurities in the chloroform influence the efficiency and reproducibility of the catalytic processes in an unpredictable manner.



Scheme 1.

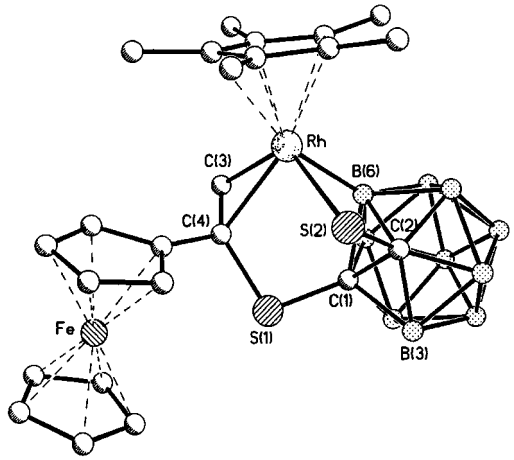


Fig. 1. Molecular structure of the Cp*Rh complex **7S**. Selected bond lengths (pm) and angles (°): Rh–centroid(Cp*) 191.7, Fe–centroid(Cp) 165.9, Fe–centroid(C_5H_4) 165.4, Rh–B(6) 209.0(3), Rh–C(3) 215.9(3), Rh–C(4) 221.6(3), Rh–S(2) 241.37(8), S(1)–C(1) 176.9(3), S(1)–C(4) 180.2(3), S(2)–C(2) 176.8(3), C(1)–C(2) 172.9(4), C(3)–C(4) 140.0(4); B(6)RhC(3) 86.53(12), B(6)RhC(4) 88.10(11), C(3)RhC(4) 37.31(11), B(6)RhS(2) 72.21(9), C(3)RhS(2) 120.19(8), C(1)S(1)C(4) 102.87(13), C(2)S(2)Rh 87.73(9), C(1)C(2)S(2) 111.72(18), C(2)B(6)Rh 100.31(17), C(1)B(6)Rh 110.34(18), C(4)C(3)Rh 73.55(16), C(3)C(4)S(1) 120.0(2), C(3)C(4)Rh 69.14(16); planes C(4)C(3)Rh/C(4)RhB(3) 86.8, C(4)C(3)B(6)/B(6)RhS(2) 121.9, C(4)RhB(6)/B(6)RhS(2) 85.9.

It is remarkable that **1S** behaves rather differently, i.e. it does not catalyse the dimerisation of ethynylferrocene **2**; only traces of **3** and no chlorinated species such as **4**, **5** or **6** were found. In contrast to **1Se**, the sulfur analogue **1S** reacts with **2** in chloroform at room temperature or at 62°C to give **7S** in high yield. The complex **7S** contains a Rh–B bond as the result of a reaction sequence including initial insertion [17] of **2** into one of the Rh–S bonds, Rh-induced B–H activation [8,11–13], and final hydrogen transfer [18] from boron via the rhodium to the terminal carbon atom of the inserted ethynylferrocene unit.

2.2. X-ray structural analysis of 7S

The molecular structure of **7S** is shown in Fig. 1, and selected bond lengths and angles are given in the legend to Fig. 1. The insertion of the sterically hindered triple bond of the alkyne **2** into one of the Rh–S bonds of **1S**, followed by the shift of a hydrogen atom from the carborane cage to the carbon atom C-3, causes the expected structural changes as compared to the known molecular structure of **2** [15,19–21]. In particular, the

former triple bond (116.4(7) pm in **2**) has been extended into the range of a Rh-coordinated double bond (140.0(4) pm in **7S**), the CCC angle at the α-carbon C4 (177.7(5)° in **2**) is reduced (123.4(3)° in **7S**), and the almost ecliptic arrangement of the cyclopentadienyl rings ($\tau = 3.8°$ in **2**) has become more staggered ($\tau = 27.4°$ in **7S**). The four-membered ring RhS(2)C(2)B(6) is almost planar (mean deviation 1.3 pm), whereas the five-membered ring RhC(4)S(1)C(1)B(6) is non-planar, folded at the line C(4)–B(6) (154.4°). The structure of the carborane cage is only slightly distorted, as shown by the length of the C(1)–C(2) bond (172.9(4) pm) which is just outside of the typical range known for *ortho*-carborane derivatives (162–170 pm [22]). These and most other structural parameters determined for **7S** are very similar to those of a related complex in which the ferrocenyl is replaced by a phenyl substituent [12].

3. Experimental

3.1. General

The 16e complexes Cp*Rh[$E_2C_2(B_{10}H_{10})$] (**1S** and **1Se**) [9] and ethynylferrocene (**2**) [15,16,23] were prepared as described previously. NMR measurements: Bruker ARX 250 (^{1}H, ^{13}C-NMR) and DRX 500 spectrometers (^{11}B, ^{103}Rh-NMR); chemical shifts are given with respect to $CHCl_3/CDCl_3$ ($\delta^1H = 7.24$; $\delta^{13}C = 77.0$) or $CDHCl_2$ ($\delta^1H = 5.33$, $\delta^{13}C = 53.8$); BF_3–OEt_2 ($\delta^{11}B = 0$) and $\Xi(^{103}Rh) = 3.14$ MHz. Mass spectra: Varian MAT CH7, EI-MS (70 eV), direct inlet. IR spectra: Perkin–Elmer 983 G.

3.2. Catalytic transformations of ethynylferrocene (2) in the presence of Cp*Rh[$Se_2C_2(B_{10}H_{10})$] (1Se)

The mixture of **1Se** (53.8 mg, 0.1 mmol) and ethynylferrocene (**2**) (105 mg, 0.5 mmol) in $CHCl_3$ (30 ml) was stirred for 3 days at 62°C. The colour turned to deep brown–red. After removal of the solvent the residue was chromatographed on silica gel. Elution with hexane–CH_2Cl_2 (3:1) first gave a yellow zone containing Fc–C(Cl)=CH_2 (**4**) and Fc–CH=CHCl ((*E*)-**5**) (25 mg; 20%) in a 1:1 ratio (they can be separated by careful chromatography), then an orange–red zone containing (*E*)-**3** and (*Z*)-**3** (68 mg; 65%) in a 1:1 ratio (they can also be separated by chromatography over silica [16]). Elution with hexane–CH_2Cl_2 (1:3) gave back **1Se** (48 mg). Final elution with acetone gave Fc–CCl_2–CH_3 (**6**) (14 mg, 10%) as a brick-red product which was absorbed on the silica column. In repeated experiments using different samples of chloroform (Merck or Aldrich; used without purification, or traces of HCl/H_2O were added, or $CHCl_3$ was dried over P_2O_5 and distilled), the yields of **3** varied in an non-reproducible way and occasionally fell below 5%.

(*Z*)-**3**: ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 4.17$ (s, 5H, Cp), 4.26 (m, 2H), 4.27 (s, 5H, Cp), 4.32 (m, 2H), 4.51 (m, 2H), 4.86 (m, 2H), 5.57 (d, ^3J(H,H) = 11.4 Hz, 1H, FcCH =), 6.43 (d, ^3J(H,H) = 11.4 Hz, 1H, =CH–C≡C). (*E*)-**3**: ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 4.14$ (s, 5H, Cp), 4.20 (m, 2H), 4.22 (s, 5H, Cp), 4.26 (m, 2H), 4.36 (m, 2H), 4.42 (m, 2H), 5.86 (d, ^3J(H,H) = 16.0 Hz, 1H, FcCH=), 6.72 (d, ^3J(H,H) = 16.0 Hz, 1H, =CH–C≡C). EI-MS (for the 1:1 mixture of (*Z*)-**3** and (*E*)-**3**): $m/z =$ 420 (100%, M^+).

4, Fc–C(Cl)=CH_2: ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta =$ 4.20 (s, 5H, Cp), 4.28 (m, 2H, H3, H4), 4.52 (m, 2H, H2, H5), 5.23 (d, ^2J(H,H) = 1.4 Hz, 1H, =CH_2), 5.44 (d, ^2J(H,H) = 1.4 Hz, 1H, =CH_2). ^{13}C{^{1}H}-NMR (62.9 MHz, $CDCl_3$): $\delta = 66.5$ (C2, C5), 68.9 (C3, C4), 69.2 (Cp), 80.4 (C1), 108.5 (=CH_2), 139.0 (FcC(Cl)=).

(*E*)-**5**, Fc–CH=CHCl: ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 4.14$ (s, 5H, Cp), 4.23 (m, 2H), 4.27 (m, 2H), 6.20 (d, ^3J(H,H) = 13.5 Hz, 1H, =CHCl), 6.55 (d, ^3J(H,H) = 13.5 Hz, 1H, FcCH=). ^{13}C{^{1}H}-NMR (62.9 MHz, $CDCl_3$): $\delta = 67.3$ and 69.4 (C2–C5), 69.8 (Cp), 83.3 (C1), 113.9 (FcCH=), 130.9 (=CHCl). EI-MS (70 eV) (for the 1:1 mixture of **4** and (*E*)-**5**): $m/z = 246$ (100%, M^+), 210 (30%, $M^+ - HCl$).

6, Fc–CCl_2–CH_3: ^{1}H-NMR ($CDCl_3$): $\delta = 2.37$ (s, 3H, CH_3), 4.17 (s, 5H, Cp), 4.47 (m, 2H), 4.74 (m, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 27.6$ (CH_3), 67.8 (CCl_2), 69.6 and 72.4 (C2–C5), 69.9 (Cp), 79.2 (C1). EI-MS: $m/z = 282$ (100%, M^+).

3.3. Synthesis of 7S

A mixture of the complex **1S** (88.8 mg; 0.2 mmol) and FcC≡CH (2) (160 mg; 0.76 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature. The colour changed gradually to dark-red within several hours. After removal of the solvent the residue was chromatographed. Elution with hexane–CH_2Cl_2 (3:1) gave back the excess of FcC≡CH, and elution with hexane–CH_2Cl_2 (1:2) produced a deep-red zone containing 7S (117 mg, 90%). Recrystallisation from CH_2Cl_2 at −10°C afforded red crystals (m.p. = 162°C (dec.)).

^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.53$ (s, 15H, Cp*), 3.04 (dd, ^2J(H,H) = ^2J(Rh,H) = 2.1 Hz, 1H, CH_2), 3.14(dd, ^2J(H,H) = ^2J(Rh,H) = 2.1 Hz, 1H, CH_2), 4.11 (m, 1H, Fc), 4.13 (m, 1H, Fc), 4.18 (m, 1H, Fc), 4.28 (s, 5H, Cp), 5.08 (m, 1H, Fc). ^{13}C{^{1}H}-NMR (62.9 MHz, $CDCl_3$): $\delta = 9.4$ (Cp*), 47.1 (d, ^1J(Rh,C) = 10.1 Hz, Rh-CH_2), 65.1, 68.9, 69.8, 70.2, 102.3 (Fc), 87.2, 94.1 (C_2-$B_{10}H_{10}$), 96.9 (d, ^1J(Rh,C) = 7.6 Hz, Rh–C), 104.7 (d, ^1J(Rh,C) = 3.5 Hz, Cp*). ^{11}B{^{1}H}-NMR (160.5 MHz, $CDCl_3$): $\delta = -14.8$ (Rh–B), −13.3, −12.8, −9.9, −6.5, −5.3, −4.3 (1:2:1:1:1:3:1). ^{103}Rh-NMR (15.7 MHz, $CDCl_3$): $\delta = -32 \pm 1$. IR(KBr): 2561, 2578(ν_{B-H}). FD-MS: 655 (100%, M^+), 444 (37%, $M^+ - (FcC{\equiv}CH)$).

3.4. Crystal structure of **7S**

Intensity data collection was carried out on a Siemens P4 diffractometer with Mo–K_α radiation (λ = 71.073 pm, graphite monochromator) at room temperature. The hydrogen atoms of the carborane cage were located via difference Fourier syntheses. The remaining hydrogens are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

7S: $C_{24}H_{35}B_{10}S_2FeRh{\cdot}CHCl_3$, orange prism of dimensions 0.18 × 0.14 × 0.12 mm, crystallises in the triclinic space group ; $a = 1132.59(6)$, $b = 1153.72(8)$, $c = 1434.92(12)$ pm, $\alpha = 81.622(6)$, $\beta = 71.038(4)$, $\gamma = 68.835(4)°$, $Z = 2$, $\mu = 1.326$ mm^{-1}; 6749 reflections collected in the range 2°–25° in θ, 5782 reflections independent, 5254 reflections assigned to be observed ($I > 2\sigma(I)$); full matrix least squares refinement with 407 parameters, R_1/wR_2 values 0.0271/0.0723, absorption correction (ψ-scans), minimum/maximum transmission factors 0.4840/0.6054; maximum/minimum residual electron density 0.714/−0.651 e 10^{-6} pm^{-3}.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure of **7S** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153351. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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