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16- and 18-Electron Cp*Rh complexes with 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolato ligands, as studied by multinuclear magnetic resonance

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Dedicated to professor Dr Reinhard Schmutzler on the occasion of his 65th birthday.

Abstract

The reaction of $[Cp^*RhCl_2]_2$ **1** with dilithium 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dithiolate (**a**) and -diselenolate (**b**) afforded the 16-electron rhodium(III) half-sandwich complexes $Cp^*Rh[E_2C_2(B_{10}H_{10})]$ [E = S (**3a**), Se (**3b**)]. The 18-electron trimethylphosphane rhodium(III) half-sandwiches $Cp^*Rh(PMe_3)[E_2C_2(B_{10}H_{10})]$ **4a–c** were prepared from the reaction of $Cp^*RhCl_2(PMe_3)$ **2** with the same dichalcogenolates, including the ditelluride (**c**). The complexes **4a**,**b** could also be obtained from the reaction of **3a**,**b** with trimethylphosphane. The molecular geometry of **4b** was determined by X-ray structural analysis. The 16-electron complexes **3** are monomeric in solution as shown by multinuclear magnetic resonance (^{1}H-, ^{11}B-, ^{13}C-, ^{31}P-, ^{77}Se-, ^{103}Rh-, ^{125}Te-NMR), also in comparison with the data for the trimethylphosphane analogues **4a–c** and for **6a** in which the rhodium bears the η^5-1,3-C_5H_3 ^{t}Bu$_2$ ligand. The ^{103}Rh nuclear shielding is reduced by 831 ppm (**3a**) and 1114 ppm (**3b**) with respect to the 18-electron complexes **4a**,**b**. Similarly, the ^{77}Se nuclear shielding in **3b** is reduced by 676.4 ppm with respect to that in **4b**.

Keywords: Rhodium; Half-sandwich complexes; Carboranes; NMR; ^{77}Se; ^{125}Te; ^{103}Rh; X-ray

1. Introduction

We have recently reported on the X-ray structural and NMR spectroscopic characterization of two pentamethylcyclopentadienyl-iridium (Cp*Ir) complexes with the 1,2-dicarba-*closo*-dodecaborane(12)-1,2-diselenolato ligand [1]. As expected, the ^{77}Se nuclear shielding is strongly influenced by the presence or absence of an additional donor ligand such as trimethylphosphane, PMe_3, which converts the 16-electron diselenolene complex $Cp^*Ir[Se_2C_2(B_{10}H_{10})]$ into the coordinatively saturated 18-electron diselenolate derivative, $Cp^*Ir(PMe_3)[Se_2C_2(B_{10}H_{10})]$. The 16-electron complexes are of considerable interest with respect to further transformations. Examples are addition reactions which take place directly at the site of the metal, or insertion reactions by which the reactivity of the metal–chalcogen bonds can be exploited with the expectation of inducing further processes in which also the carborane ligand may participate owing to B–H activation. In order to gain further insight into the bonding situation in such 16-electron complexes, we have now prepared and studied analogous rhodium compounds where the ^{103}Rh-NMR parameters can be used as an additional probe.

2. Results and discussion

2.1. Syntheses

The synthetic approach to the Cp*Rh half-sandwich complexes **3a**,**b** and **4a–c** is outlined in Scheme 1. The

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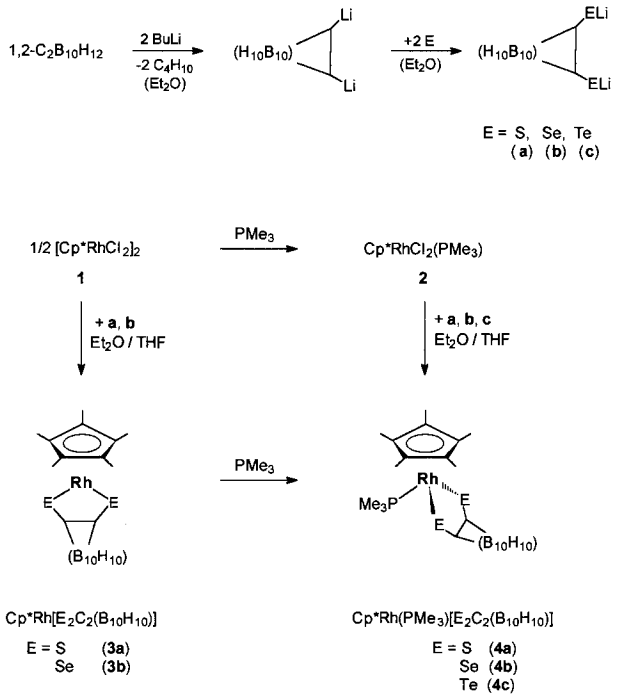
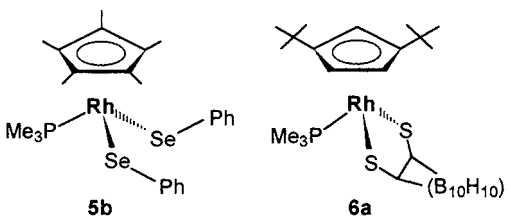


Scheme 1.

1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolato ligands were obtained by insertion of chalcogen into the two carbon–lithium bonds of the dilithiated carborane cluster in diethylether solution. The yellow dilithium 1,2-dichalcogenolates $(B_{10}H_{10})C_2(ELi)_2$ (E = S (**a**), Se (**b**) [1] and Te (**c**)) can be used in situ.

Whereas the dilithium dithiolate and diselenolate solutions (**a**,**b**) cleanly split the chloro-bridged dimer $Cp^*_2Rh_2Cl_2(\mu\text{-}Cl)_2$ (**1**) to give the green 16-electron dithiolene and diselenolene complexes **3a**,**b**, the corresponding ditellurolene complex could not be isolated from the reaction of **1** with a dilithium ditellurolate solution (**c**) at room temperature. However, the complete series of the 18-electron dichalcogenolate derivatives **4a**–**c** is accessible via the mononuclear precursor $Cp^*RhCl_2(PMe_3)$ (**2**). The crystalline, red complexes **4a**–**c** are air-stable, the solutions in organic solvents are orange to red; **4a**,**b** has also been prepared by addition of PMe_3 to **3a** and **3b**, respectively. Other phosphanes such as PPh_3 can be added similarly. For the purpose of comparison, two similar complexes (**5b** [2] and **6a**) were included in the present study.



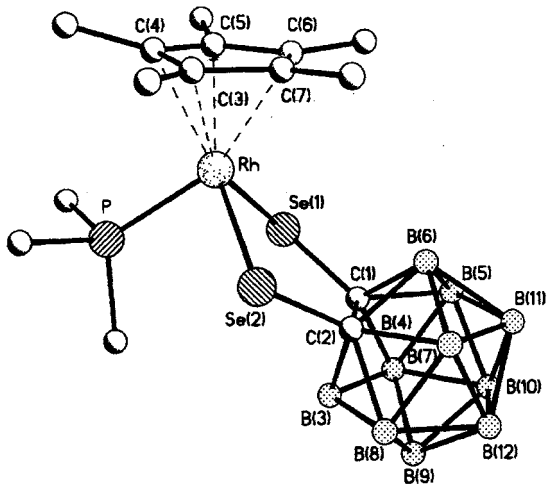


Fig. 1. Molecular structure of $Cp^*Rh(PMe_3)\{[Se_2C_2(B_{10}H_{10}]$ (**4b**).

2.2. Molecular structure of $Cp^*Rh(PMe_3)[Se_2C_2(B_{10}H_{10})]$ (4b)

The Cp*Rh complex **4b** crystallizes in the form of red prisms in the monoclinic space group $C2/c$ with eight molecules in the unit cell. Its molecular structure is isotypic to that of the analogous Cp*Ir complex, $Cp^*Ir(PMe_3)[Se_2C_2(B_{10}H_{10})]$ (**4b**–Ir) [1], and similar to $Cp^*Rh(PMe_3)(SePh)_2$ (**5b**) [2]. The molecular structure of **4b** is shown in Fig. 1; important bond distances and angles are given in Table 1. The metal–selenium bond lengths in **4b** (246.4 pm av.) and **4b**–Ir (247.0 pm av.) are slightly shorter than in **5b** (249.5 pm av.), and the Se(1)–metal–Se(2) bond angles (90.5° in **4b**, 90.2° in **4b**–Ir) are reduced (92.2° in **5b**). As expected, the angles at the selenium atoms (103.2° av. in **4b**, 103.5 in **4b**–Ir) are distinctly smaller in the rigid 1,2-dicarbaborane-diselenolate complexes than in **5b** (111.0 and 114.8°) where the two phenylselenolato ligands are able to avoid each other. The dihedral angles along the Se ···· Se vector are almost identical in **4b** (155.1°) and **4b**–Ir (156.1°), whereas it is 180° in the phosphane-free diselenolene complex $Cp^*Ir[Se_2C_2(B_{10}H_{10})]$ [1].

The Cp* ligand in **4b** is unsymmetrically coordinated in a form approaching a cyclic π-allyl (C(3)–C(5))/monoolefin (C(6)–C(7)) system; the 'olefinic' bond C(6)–C(7) (139.0(8) pm) connecting the carbon atoms with the largest Rh–C distances (228.1(5) pm av.) is definitely shorter than both the adjacent bonds C(6)–C(5) and C(7)–C(3) (143.9(8) pm av.) and the 'allylic' bonds C(3)–C(4) and C(4)–C(5) (142.3(8) pm av.). An analogous distortion of the Cp* ligand is observed in the Cp*Ir analogue **4b**–Ir [1].

2.3. NMR spectroscopic results

^{1}H- and ^{13}C-NMR data (see Section 4 and Table 2) support the proposed structure of the complexes **3**, **4**

Table 1
Selected bond distances and angles for Cp*Rh(PMe$_3$)[Se$_2$C$_2$B$_{10}$H$_{10}$)] (**4b**)

Distances (pm)			
Rh–P	228.3(2)	Rh–Cp*(Z) [a]	188.1
Rh–Se(1)	247.0(1)	Rh–C(3)	220.4(5)
Rh–Se(2)	245.8(1)	Rh–C(4)	221.4(5)
Se(1)–C(1)	194.1(6)	Rh–C(5)	220.2(5)
Se(2)–C(2)	195.1(5)	Rh–C(6)	228.6(5)
C(1)–C(2)	166.0(8)	Rh–C(7)	227.6(5)
C(1)–B(3)	172.8(8)	C(3)–C(4)	142.1(8)
C(1)–B(4)	171.5(9)	C(4)–C(5)	142.5(8)
C(1)–B(5)	171.9(9)	C(5)–C(6)	144.1(8)
C(1)–B(6)	172.1(9)	C(6)–C(7)	139.0(8)
C(2)–B(3)	172.5(9)	C(7)–C(3)	143.7(8)
C(2)–B(6)	170.8(8)	P–C(13)	180.8(7)
C(2)–B(7)	171.8(8)	P–C(14)	181.1(6)
C(2)–B(8)	171.0(8)	P–C(15)	182.4(7)
Se(1)···Se(2)	349.9(8)		
Angles (°)			
Se(1)–Rh–Se(2)	90.46(2)	Rh–Se(1)–C(1)	103.0(2)
Se(1)–Rh–P	89.14(4)	Rh–Se(2)–C(2)	103.4(2)
Se(2)–Rh–P	88.79(4)	Se(1)–C(1)–C(2)	118.8(3)
		Se(2)–C(2)–C(1)	117.6(3)
Se(1)–Rh–Se(2)/Se(1)–C(1)–C(2)–Se(2)			155.1 [b]

[a] Z is the center of the Cp* ring.
[b] Dihedral angle along the Se···Se vector.

and **6** in solution. This is also true for the ^{11}B, ^{31}P, ^{77}Se, ^{103}Rh, and ^{125}Te NMR data (Table 2), of which the ^{77}Se and ^{103}Rh chemical shifts were of particular interest with regard to the 16 or 18 electron count (vide infra) of the complexes **3** and **4**, respectively. Although the ^{11}B(carborane) resonances were only partially resolved; the patterns due to partial overlap fit to C_{2v} symmetry of **3** (four signals expected) and C_s symmetry of **4** and **6** in solution (seven signals expected). A single ^{13}C(carborane) resonance signal is found for all complexes **3**, **4** and **6**, typically broadened as a result of scalar relaxation of the second kind owing to partially relaxed ^{13}C–^{11}B scalar coupling [4]. At the field strength of 11.5 T, the ^{77}Se resonance signals, and even more so the ^{125}Te-NMR signals, are also broad, and this has already been traced [2] to efficient nuclear spin relaxation via the chemical shift anisotropy (CSA) mechanism. All ^{103}Rh-NMR signals were detected indirectly either from ^{31}P- or ^{1}H-NMR spectra by selective heteronuclear ^{31}P{^{1}H,^{103}Rh} triple resonance or ^{1}H{^{103}Rh} double resonance experiments [5]. The former experiments were fairly straightforward [2], whereas the latter were rather demanding with respect to highly resolved ^{1}H-NMR spectra because of the small magnitude of the coupling constants $\left| {}^{3}J(^{103}\mathrm{Rh},^{1}\mathrm{H}_{\mathrm{Cp}^*}) \right|$. This splitting is frequently not resolved in routine ^{1}H-NMR spectra, and attempts at inverse 2D ^{1}H/^{103}Rh experiments based on these small coupling constants have failed so far. The large intensity of the ^{1}H(Cp*)-NMR signal (even for fairly diluted samples) is apt to cause radiation damping [6], which leads to signal broadening. Slight detuning of the ^{1}H coil [6] helped to obtain sharper signals with better resolution. The irradiaton power of the ^{103}Rh frequency had to be carefully adjusted to a low level in order to maintain the required high resolution and to provide sufficient energy for disturbing the relevant transitions at the same time (sharpening of the ^{1}H(Cp*) NMR signal as shown by an increase in the signal height of ca. 30%). To the best of our knowledge, this is the first time that these particular experiments have been adapted to high-field PFT spectrometers.

The positions of the ^{13}C(carborane) signals reflect mainly the influence of the neighbourhood of the

Table 2
NMR spectroscopic data [a] of the rhodium complexes **3**–**6**

Complex	δ^{103}Rh	δ^{31}P	δ^{77}Se δ^{125}Te	1,2-$C_2B_{10}H_{10}$	
				δ^{13}C(1,2)	δ^{11}B
3a Cp*Rh[$S_2C_2(B_{10}H_{10})$] [b]	+1165 ± 5	–	–	94.1	−10.7, −8.7, −7.3; −5.2 ratio 2:2:4:2
3b Cp*Rh[$Se_2C_2(B_{10}H_{10})$] [b]	+1150 ± 5	–	+1102.0 [138 ± 5]	73.2	−8.7, −7.0,−5.3 ratio 2:6:2
4a Cp*Rh(PMe_3)[$S_2C_2(B_{10}H_{10})$] [c]	+334 ± 1	11.8 [149.6]	–	93.5	−10.7, −9.6, −5.7, −2.0 ratio 2:4:3:1
4b Cp*Rh(PMe_3)[$Se_2C_2(B_{10}H_{10})$] [c]	+36 ± 1	7.8 [147.7]	+ 425.6 [26 ± 4]	69.0	−9.8, −8.0, −5.9, −4.7, −2.7 ratio 2:4:2:1:1
4c Cp*Rh(PMe_3)[$Te_2C_2(B_{10}H_{10})$] [c]	−523 ± 1	2.0 [146.2]	+ 970 [45 ± 5]	25.6	−7.9, −5.2, −3.2, −1.6 ratio 2:6:1:1
5b Cp*Rh(PMe_3)($SePh)_2$ [2]	+201.5 ± 0.3	0.4 [148.5], (18.3)	+134.1 [53.2], (18.3)	–	–
6a ($C_5H_3^tBu_2$)Rh(PMe_3)[$S_2C_2(B_{10}H_{10})$] [c]	+460 ± 2	12.3 [143.7]	–	93.7 [b]	−11.1, −10.3, −9.6, −5.7, +0.4 ratio 2:2:2:3:1

[a] Coupling constants $^{1}J(^{103}$Rh, ^{31}P) and $^{1}J(^{103}$Rh, E) in square brackets, $^{2}J(^{31}$P, E) in parentheses.
[b] CD_2Cl_2.
[c] $CDCl_3$.

chalcogen atoms (heavy atom effect [3,7]), and there is only a slight deshielding in going from the 18-electron (**4a**,**b**) to the 16-electron complexes (**3a**,**b**).

The RhE_2C_2-cyclic structure causes reduced shielding of the ^{31}P nuclei in the Me_3P complexes **4a**–**c** in comparison with their noncyclic bis(phenylchalcogenolato) congeners [2], although the trend is analogous. In the latter compounds, the magnitude of $|{}^1J(^{103}Rh,^{31}P)|$ increases in the series with E = S, Se, Te, whereas the opposite trend is observed here for **4a**–**c** which again may be due to the cyclic structure.

As a result of their wide range, $\delta^{77}Se$ data are useful for qualitative descriptions of the bonding situation [8]. The ^{77}Se-NMR signal in the 16-electron complex **3b** is shifted by 676.4 ppm to higher frequency with respect to that in the 18-electron complex **4b**. The magnitude of deshielding is similar to that observed for the analogous pair of iridium complexes [1]. This indicates that the selenium atoms in **3b** are incorporated in a ring system with increased delocalisation of electron density, as is usually observed for heteroaromatic compounds containing selenium [9]. The $\delta^{125}Te$ value for **4c** (+970) is in the expected range, considering the linear relationship between $\delta^{77}Se$ and $\delta^{125}Te$ data [10].

The ^{103}Rh nuclear shielding [11] should sensitively reflect changes in the electronic structure of the complexes **3**–**6**. Indeed, there is a marked deshielding of the ^{103}Rh nuclei in the 16-electron complexes **3a**,**b** with respect to the 18-electron complexes **4a**,**b**, the difference in shielding being larger for the pair **3b**/**4b** (1114 ppm) than for **3a**/**4a** (831 ppm). The ^{103}Rh chemical shifts depend in a complex way on the energies of d–d transitions as a result of the ligand field splitting and the coordination number. Therefore, a straightforward relationship of $\delta^{103}Rh$ with the structure of the respective rhodium complex cannot be expected. However, the large shift difference observed here for 18-electron and 16-electron Rh(III) complexes will stimulate the search for similar examples. Apparently, the nature of the cyclopentadienyl group has a considerable influence on ^{103}Rh chemical shifts, as shown by comparison of the data for **4a** (δ +334) and **6a** (δ +460). This had also been noted for noncyclic Rh(III) complexes by comparing the influence of Cp and Cp* [2]. The heavy atom effect [7] is clearly evident by inspecting the change of −857 ppm in the $\delta^{103}Rh$ data in the series **4a**–**c**.

3. Conclusions

The 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolate ligand can be used to stabilize the reactive monomeric 16-electron complexes of the Cp*Rh fragment in solution, as shown by multinuclear magnetic resonance data. The ^{77}Se- and ^{103}Rh-NMR data are particularly indicative of changes in the electronic structure. The successful determination of ^{103}Rh chemical shifts (in the absence of a Rh–P bond) via selective heteronuclear $^1H\{^{103}Rh\}$ double resonance experiments using the $^1H(Cp^*)$ resonance is promising for further studies of Cp*Rh complexes, and can now also be used in the investigation of the multifaceted chemistry of the 16-electron complexes.

4. Experimental

All manipulations were routinely carried out in standard Schlenck vessels under argon. The solvents were kept free of traces of water and oxygen, and distilled in a stream of argon before use. The *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, is commercially available. The starting complexes $[Cp^*RhCl_2]_2$ **1** [12] and $Cp^*RhCl_2(PMe_3)$ **2** [13] were prepared according to literature methods starting from $RhCl_3 \cdot 3H_2O$. The 1,3-di(*tert*-butyl)-cyclopentadienyl analogues, $[(C_5H_3^tBu_2)RhCl_2]_2$ and $(C_5H_3^tBu_2)RhCl_2(PMe_3)$, were obtained similarly using di(*tert*-butyl)cyclopentadiene (isomer mixture) as the precursor of the η^5-$C_5H_3^tBu_2$-1,3 ring ligand.

4.1. Syntheses

$Li_2E_2C_2(B_{10}H_{10})$ (E = S (**a**), Se (**b**) or Te (**c**)): A solution of 2 mmol (0.29 g) *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, in 40 ml of diethylether was lithiated by addition of 2.75 ml of a 1.6 M solution of butyllithium (4.4 mmol) in hexane. The corresponding amount (4.4 mmol) of the elemental chalcogen (E = S, Se, Te) was added and the solution stirred for 1–6 h (depending on the chalcogen E = S (1 h), Se (3 h), Te (6 h)) at ambient temperature to give the corresponding 1,2-carborane-1,2-dichalcogenolates, $Li_2E_2C_2(B_{10}H_{10})$ (E = S (**a**), Se (**b**) or Te (**c**)) in almost quantitative yield, as judged from the reactions with metal complexes. The solutions of **a**–**c** can be directly used for further reactions.

$Cp^*Rh[E_2C_2(B_{10}H_{10})]$ (E = S (**3a**) and Se (**3b**)): A solution of either **a** or **b** (1 mmol in 30 ml of Et_2O) was added to the solution of 0.5 mmol (0.31 g) $[Cp^*RhCl_2]_2$ **1** in 100 ml of tetrahydrofuran. The reaction mixture was stirred 4–5 h at room temperature, then the solvents were evaporated under reduced pressure. The residue was redissolved in CH_2Cl_2 and the product purified by column chromatography on silica. Elution with CH_2Cl_2–hexane (3:1) gave a dark-green zone of **3a** or a green zone of **3b**, respectively. The compounds do not melt up to 300°C but slowly decompose in the presence of air above 200°C; in the case of the thermally less stable selenium complex, a white product ($C_2B_{10}H_{12}$) was generated.

3a: yield 0.38 g (85%); EI–MS: $m/e = 445$ (100%, M^+); IR (KBr): ν(B–H) 2590, 2561 cm^{-1}. ^1H-NMR

(CD_2Cl_2): δ(Cp*) 1.76(s); ^{13}C-NMR (CD_2Cl_2): 10.6 and 99.3 (Cp*), 94.1 ($C_2B_{10}H_{10}$).

3b: yield 0.30 g (56%); low solubility in organic solvents; EI–MS: $m/e = 539$ (100%, M^+), 398 (50%, $Cp^*RhSe_2^+$); IR (KBr): ν(B–H) 2584, 2559 cm^{-1}. ^{1}H-NMR (CD_2Cl_2): δ(Cp*) = 1.70(s); ^{13}C-NMR (CD_2Cl_2): $\delta = 10.9$ and 98.5 (Cp*), 73.2 ($C_2B_{10}H_{10}$).

Cp*Rh(PMe_3)[$E_2C_2(B_{10}H_{10})$] (E = S (**4a**), Se (**4b**) and Te (**4c**)): A solution of 1 mmol **a**, **b** or **c** in 30 ml of Et_2O was combined with a solution of 0.39 g (1 mmol) $Cp^*RhCl_2(PMe_3)$ **2** in 50 ml of THF. The solvents were removed under reduced pressure, and the residue taken up in CH_2Cl_2. Filtration gave a red CH_2Cl_2 solution. Crystallization from CH_2Cl_2 by slow diffusion of hexane into the concentrated solution afforded crystals of **4a** (red), **4b** (red) or **4c** (brown–red).

4a: red crystals, yield 0.40 g (91%). EI–MS: $m/e = 520$ (1%, M^+), 444 (100%, M^+-PMe_3); IR (CsI): ν(B-H) 2576, 2559 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 1.71$ (d, Cp*, 15H, J(P,H) 3.1 Hz), 1.57 (d, PMe_3, 9H, J(P,H) 10.9 Hz); ^{13}C-NMR ($CDCl_3$): $\delta = 9.6$ (d, Cp*(Me), J(P,C) 1.45 Hz), 16.9 (dd, PMe_3, J(P,C) 35.3 Hz, J(Rh,C) 0.9 Hz), 93.5 (C_2-carborane), 102.3 (dd, Cp*, J(P,C) 4.8 Hz, J(Rh,C) 3.2 Hz).

4b: red crystals, yield 0.44 g (83%). EI–MS: $m/e = 614$ (9%, M^+), 538 (100%, M^+–PMe_3); IR (CsI): ν(B–H) 2584, 2563 and 2550 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 1.78$ (d, Cp*, 15H, J(P,H) 3.1 Hz), 1.64 (d, PMe_3, 9H, J(P,H) 10.6 Hz); ^{13}C-NMR ($CDCl_3$): $\delta = 9.9$ (d, Cp*(Me), J(P,C) 2.4 Hz), 18.2 (dd, PMe_3, J(P,C) 36.6 Hz, J(Rh,C) 0.8 Hz), 69.0 (C_2-carborane), 101.8 (dd, Cp*, J(P,C) 4.8 Hz, J(Rh,C) 3.1 Hz).

4c: red–brown crystals, yield 0.25 g (40%). EI–MS: $m/e = 711$ (2%, M^+), 635 (91%, M^+–PMe_3), 494 (100%, $Cp^*RhTe_2^+$); IR (CsI): ν(B–H) 2573 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 1.98$ (d, Cp*, 15H, J(P,H) 3.0 Hz), 1.80 (dd, PMe_3, 9H, J(P,H) 10.0 Hz, J(Rh,C) 0.8 Hz); ^{13}C-NMR ($CDCl_3$): $\delta = 10.9$ (d, Cp*(Me), J(P,C) 1.4 Hz), 21.7 (dd, PMe_3, J(P,C) 38.6 Hz, J(Rh,C) 0.9 Hz), 25.6 (C_2-carborane), 102.4 (dd, Cp*, J(P,C) 4.3 Hz, J(Rh,C) 3.3 Hz).

($C_5H_3^tBu_2$)Rh(PMe_3)[$S_2C_2(B_{10}H_{10})$] (**6a**): the complex was prepared in analogy to **4a** by consecutive addition of PMe_3 and $Li_2S_2C_2(B_{10}H_{10})$ (**a**) (or vice versa) to [($C_5H_3^tBu_2$)$RhCl_2$]$_2$ in THF solution. Red crystals, yield ca. 80%.

6a: EI–MS: $m/e = 563$ (5%, M^+), 487 (100%, M^+–PMe_3); IR (CsI): ν(B–H) 2624, 2566 cm^{-1}. ^{1}H-NMR (CD_2Cl_2): $\delta = 1.27$ (s, ^{t}Bu, 18H), 1.63 (dd, PMe_3, 9H, J(P,H) 11.3 Hz, J(Rh,H) 0.8 Hz), 4.48 (d, 2H, J(H,H) 1.5 Hz) and 5.63 (d(t), 1H, J(Rh,H) 6.9, J(H,H) = 1.5 Hz); ^{13}C-NMR (CD_2Cl_2): $\delta = 19.2$ (d, PMe_3, J(P,C) 36.7 Hz), 29.9 (s, ^{t}Bu(Me)), 33.1 (s, CMe_3) 75.7 (d, $C_5H_3^tBu_2$ (CH-4 and CH-5), J(Rh,C) 5.8 Hz); 85.5 (d, $C_5H_3^tBu_2$ (CH-2), J(Rh,C) 15.9 Hz), 93.7 (s, $S_2C_2(B_{10}H_{10})$), 134.5 (d, $C_5H_3^tBu_2$ (C-1 and C-3) J(Rh,C) 3.3 Hz).

4.2. Instrumentation

NMR measurements were carried out using Bruker ARX 250 and DRX 500 spectrometers (chemical shifts are given with respect to $CHCl_3/CDCl_3$ ($\delta^1H = 7.24$; $\delta^{13}C = 77.0$), $CHDCl_2/CD_2Cl_2$ ($\delta^1H = 5.33$; $\delta^{13}C = 53.8$), external Et_2O–BF_3 ($\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz), external H_3PO_4 aqueous, 85% ($\delta^{31}P = 0$ for $\Xi(^{31}P) = 40.480747$ MHz), external Me_2Se ($\delta^{77}Se = 0$ for $\Xi(^{77}Se) = 19.071523$ MHz), $\delta^{103}Rh = 0$ for $\Xi(^{103}Rh) = 3.16$ MHz, external $MeTe_2$ ($\delta^{125}Te = 0$ for $\Xi(^{125}Te) = 26.169773$ MHz). A triple resonance probe head (tunable to ^{1}H, ^{31}P, and ^{103}Rh) served for the indirect ^{103}Rh-NMR measurements, using the Bruker DRX 500 spectrometer. Mass spectra: Varian MAT CH7, EI–MS (70 eV), direct inlet. IR spectra: Perkin–Elmer 983 G.

4.3. X-ray structure analysis of *4b*

4.3.1. Crystal

$C_{15}H_{34}B_{10}PSe_2Rh$; $M_r = 614.3$, containing 0.5 CH_2Cl_2, red prism of dimensions $0.32 \times 0.20 \times 0.15$ mm, monoclinic, space group $C2/c$ with lattice parameters $a = 2494.92(15)$, $b = 1766.93(12)$, $c = 1488.69$ (11) pm, $\beta = 123.030(5)°$, $V = 5502.0(6) \times 10^6$ pm^3, $Z = 8$, absorption coefficient $\mu = 3.523$ mm^{-1}, $F(000) = 2688$.

4.3.2. Data collection

Siemens P4 diffractometer, Mo–K_α radiation, $\lambda = 71.073$ pm (graphite monochromator), 296 K, crystal sealed under argon into glass capillary; 2θ range 3–55°, ω scan type, 7127 reflections collected, 6269 independent, semi-empirical absorption correction, min./max. transmission factors: 0.2218/0.4182.

4.3.3. Strucure solution and refinement

Direct methods (SHELXTL V 5.4), refinement of 276 parameters with full-matrix least-squares on F^2, all non-hydrogen atoms were refined with anisotropic temperature factors, the hydrogen atoms were described on calculated positions with fixed isotropic temperature factors applying the riding model; the refinement converged at final R indices [$I > 2\sigma(I)$] $wR_2 = 0.1269$, and $R_1 = 0.0453$, max./min. residual difference electron density $1.703/-1.283$ e $\times 10^{-6}$ pm^{-3}.

5. Supplementary information

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120668. Copies of these data can be obtained free of charge on application to The Director,

CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@chemcrys-cam.ac.uk).

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References

[1] M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, Eur. J. Inorg. Chem. (1999) 873.
[2] M. Herberhold, T. Daniel, D. Daschner, W. Milius, B. Wrackmeyer, J. Organomet. Chem. (1999) in press.
[3] M. Herberhold, G.-X. Jin, A.L. Rheingold, G.F. Sheats, Z. Naturforsch. Teil B 47 (1992) 1091.
[4] B. Wrackmeyer, Progr. NMR Spectrosc. 12 (1979) 227.
[5] (a) W. McFarlane, Annu. Rep. NMR Spectrosc. 1 (1968) 135. (b) W. McFarlane, Annu. Rep. NMR Spectrosc. A 5 (1972) 353.
[6] R. Freeman, in: A Handbook of Nuclear Magnetic Resonance, Longman Scientific Technical, Essex, UK, 1988, pp. 177–179.
[7] J. Mason, Adv. Inorg. Chem. Radiochem. 22 (1979) 199.
[8] T.M. Klapötke, M. Broschag, Compilation of Reported ^{77}Se NMR Chemical Shifts, Wiley, Chichester, 1996.
[9] (a) I. Johannsen, H. Eggert, J. Am. Chem. Soc. 106 (1984) 1240. (b) H. Poleschner, R. Radeglia, H. Meyer, Org. Magn. Reson. 22 (1984) 480. (c) H. Poleschner, R. Radeglia, J. Fuchs, J. Organomet. Chem. 427 (1992) 213. (d) B. Olk, R.-M. Olk, Z. Anorg. Allg. Chem. 600 (1991) 89. (e) R.A. Fischer, H.-J. Kneuper, W. A. Herrmann, J. Organomet. Chem. 300 (1987) 365. (f) T. Klapötke, Spectrochim. Acta Part A 44 (1988) 461.
[10] H.C.E. McFarlane, W. McFarlane, in: J. Mason (Ed.), Multinuclear NMR, Plenum Press, New York, 1987 (Chapter 15).
[11] B. Mann, in: S. Pregosin (Ed.), Transition Metal Nuclear Magnetic Resonance Spectroscopy, Elsevier, Amsterdam 1991, pp. 177–215.
[12] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228.
[13] K. Isobe, P.M. Bailey, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1981) 2003.