Mononuclear half-sandwich rhodium complexes containing phenylchalcogenolato ligands: a multinuclear (^{1}H, ^{13}C, ^{31}P, ^{77}Se, ^{103}Rh, ^{125}Te) magnetic resonance study[☆]

Max Herberhold [1], Thomas Daniel, Daniela Daschner, Wolfgang Milius, Bernd Wrackmeyer *

Laboratorium für Anorganische Chemie der Universität Bayreuth, Universitätstraße 30, D-95440 Bayreuth, Germany

Abstract

Diphenyl dichalcogenides react with CpRh(PMe$_3$)(CO) (**1**) to give the cyclopentadienyl complexes CpRh(PMe$_3$)(EPh)$_2$ (E = S (**2a**), Se (**2b**) and Te (**2c**)) and carbon monoxide. The analogous pentamethylcyclopentadienyl complexes Cp*Rh(PMe$_3$)(EPh)$_2$ (E = S (**4a**), Se (**4b**) and Te (**4c**)) were prepared from Cp*Rh(PMe$_3$)Cl$_2$ (**3**) and the chalcogenolates, NaSPh or LiEPh (E = Se, Te). With 1,2-benzenedithiol in the presence of triethylamine, CpRh(PMe$_3$)(S$_2$C$_6$H$_4$), (**6a**) and Cp*Rh(PMe$_3$)(S$_2$C$_6$H$_4$) (**7a**) could be obtained starting from either CpRh(PMe$_3$)I$_2$ (**5**) or Cp*Rh(PMe$_3$)Cl$_2$ (**3**), respectively. The molecular geometry of Cp*Rh(PMe$_3$)(SePh)$_2$ (**4b**) was determined by a single crystal structure analysis which confirmed a distorted tetrahedral arrangement of the ligands. All compounds were characterised by ^{1}H-, ^{13}C-, ^{31}P-, ^{103}Rh- and, where possible, by ^{77}Se- or ^{125}Te-NMR spectroscopy. A negative sign of $^1J(^{103}$Rh,^{13}C$_{Cp})$ (reduced coupling constant $^1K(^{103}$Rh,^{13}C$_{Cp}) > 0$) was determined by selective ^{13}C{^{1}H,^{31}P} triple resonance experiments for **2a** and **4a**–**4c**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Chalcogens; Half-sandwich complexes; Phenylchalcogenolates; X-ray; NMR

1. Introduction

Although numerous organothiolato complexes of the transition metals have been reported [1], only a limited number of selenolato and tellurolato analogues are available [2]. The systematic classification of the chalcogenolato complexes is further complicated by the fact that even metals in the same group of the periodic table do not necessarily tend to form analogous compounds. Thus, in contrast to the mononuclear half-sandwich cyclopentadienyl iridium compounds with thiolato ligands, CpIr(L)(SR)$_2$ and Cp*Ir(L)(SR)$_2$ [3,4], most of the cyclopentadienyl rhodium thiolato complexes (CpRh and Cp*Rh) possess dinuclear structures [5,6]. However, the synthesis of mononuclear Cp*Rh(L)(SR$_F$)$_2$ (L = CO, PPh$_3$; R$_F$ = C$_6$F$_5$, C$_6$F$_4$H-p) starting from the coordinatively unsaturated educts Cp*Rh(SR$_F$)$_2$ has also been described [7].

In the case of the half-sandwich rhodium complexes, ^{103}Rh-NMR spectroscopy can be applied as an additional tool for structural studies in solution, especially in combination with ^{77}Se- and ^{125}Te-NMR [8]. This paper describes the synthesis of mononuclear phenylchalcogenolato rhodium(III) complexes of the general composition CpRh(PMe$_3$)(EPh)$_2$ and Cp*Rh(PMe$_3$)(EPh)$_2$ (E = S, Se, Te), and of two 1,2-benzenedithiolato compounds, CpRh(PMe$_3$)(S$_2$C$_6$H$_4$) and Cp*Rh(PMe$_3$)(S$_2$C$_6$H$_4$). The new complexes were characterised by ^{1}H-, ^{13}C-, ^{31}P-, ^{77}Se-, ^{103}Rh- and ^{125}Te-NMR spectroscopy.

2. Results and discussion

2.1. Syntheses

When CpRh(PMe₃)(CO) (1) and diphenyl disulphide (1:1) are kept in boiling toluene for 10 h, the complex CpRh(PMe₃)(SPh)₂ (2a) can be isolated in good yield. The analogous complexes CpRh(PMe₃)(SePh)₂ (2b) and CpRh(PMe₃)(TePh)₂ (2c) are obtained similarly when the solution is stirred for one or two days at room temperature (r.t.) (Scheme 1). The yields of 2a–c after recrystallization are in the range 80–90%.

The electron impact (EI) mass spectrum of the green bis(phenyltellurolato) complex 2c contains only the molecular ion and its fragments, whereas the red compounds 2a and 2b show additional species in the higher mass region. The presence of the binuclear ions [CpRh(EPh)]₂⁺ (E = S, Se) indicates easy dimerisation which appears to become less favoured in the order S > Se > Te. [CpRh(SPh)]₂ has been described by Connelly [6].

Although the Cp*Rh(PMe₃)(EPh)₂ (E = S (4a), Se (4b), Te (4c)) can be prepared in a similar way starting from Cp*Rh(PMe₃)CO under CO elimination and formal oxidation of rhodium(I) to rhodium(III), the Cp*Rh complexes 4a–c were more conveniently prepared by substitution of chloro ligands in the rhodium(III) complex Cp*Rh(PMe₃)Cl₂ (3) according to Scheme 2. If a three-fold excess of NaSPh is added to a suspension of the dichloro complex Cp*Rh(PMe₃)Cl₂ (3) in MeOH solution, a dark red precipitate is formed. After extraction and recrystallization, the dithiolato compound Cp*Rh(PMe₃)(SPh)₂ (4a) is isolated as a red solid in about 80% yield.

The red–violet phenylselenolato complex Cp*Rh-(PMe₃)(SePh)₂ (4b) and the green phenyltellurolato compound Cp*Rh(PMe₃)(TePh)₂ (4c) were prepared in THF solution, starting from 3 and LiEPh, which had been generated in situ from a 1:2 mixture of E₂Ph₂ and Li[BHEt₃]. The EI mass spectra of all three Cp*Rh compounds 4a–c contain the molecular ion. In the higher mass region the selenium complex 4b again shows the binuclear ion [Cp*Rh(SePh)]₂⁺, while in the case of 4a, in addition to [Cp*Rh(SPh)]₂⁺, the triply bridged species [Cp*Rh-(SPh)₃RhCp*]⁺ is also observed. Salts of this cation can be prepared either from [Cp*RhCl₂]₂ and NaSPh or from Cp*Rh(CO)₂ and S₂Ph₂.

As expected, the chelate ligand 1,2-benzenedithiolate leads to even more stable mononuclear complexes. The diiodo complex CpRh(PMe₃)I₂ (5), easily accessible from the reaction of CpRh(PMe₃)(CO) (1) with iodine, was reacted with 1,2-benzenedithiol in the presence of triethylamine. After column chromatography, CpRh(PMe₃)-(S₂C₆H₄) (6a) can be isolated as an orange–brown solid (Scheme 3). Under similar conditions, the dichloro complex Cp*Rh(PMe₃)Cl₂ (3) leads to the analogue, Cp*Rh-(PMe₃)(S₂C₆H₄) (7a) in almost quantitative yield.
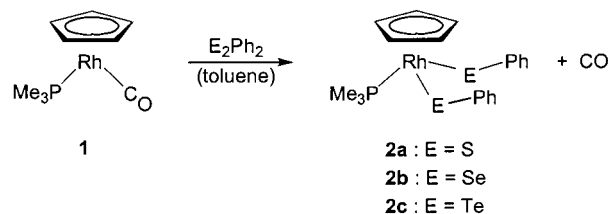
Scheme 1.

The complex Cp*Rh(S₂C₆H₄) without the PMe₃ ligand is known to exist in solution in a monomer–dimer equilibrium, whereas only the dimeric form is found to be present in the solid state [9].

2.2. Molecular structure of Cp*Rh(PMe₃)(SePh)₂ (4b)

Fig. 1 presents the molecular geometry of 4b; selected bond distances and angles are given in Table 1. The arrangement of the ligands around the metal corresponds to a distorted tetrahedron with the Cp* ring occupying one coordination site.

Most of the bond lengths observed for 4b are in good agreement with those of Cp*Rh(PMe₃)[(SC₅H₄)₂Fe] which contains a chelating 1,1′-ferrocenedichalcogenolate ligand [10]. However, the pentamethylcyclopenta2dienyl ligand in 4b is more symmetrically attached to the rhodium atom. The distances between the metal centre and the selenium atoms are consistent with those found in the cation [Cp*Rh(SePh)₃RhCp*]⁺ (Rh — Se = 248–252 pm), while the bond lengths Se–C in 4b (191 pm) are slightly shorter (by 3 pm) [11]. The angles Se(1)–Rh–P (90.7(1)°) and Se(2)–Rh–P (83.8(1)°) are remarkably different due to the different orientation of the selenolato ligands in the molecule. The distance between the two selenium atoms (359.5 pm) indicates that direct bonding interactions are absent, and the half-sandwich compounds

Scheme 2.

Scheme 3.

Table 1
Bond lengths (pm) and bond angles (°) in $Cp*Rh(PMe_3)(SePh)_2$ (**4b**), with estimated S.D. values

Bond lengths

Rh–Se(1)	249.9(1)	Rh–C(3)	223.5(6)
Rh–Se(2)	249.1(1)	Rh–C(4)	224.1(7)
Rh–P	227.7(2)	Rh–C(5)	220.7(6)
Rh–C(1)	224.9(6)	Se(1)–C(11)	191.4(6)
Rh–C(2)	224.7(6)	Se(2)–C(17)	191.6(7)

Bond angles

Se(1)–Rh–Se(2)	92.2(1)	Rh–Se(1)–C(11)	111.0(2)
Se(1)–Rh–P	83.8(1)	Rh–Se(2)–C(17)	114.8(2)
Se(2)–Rh–P	90.7(1)		
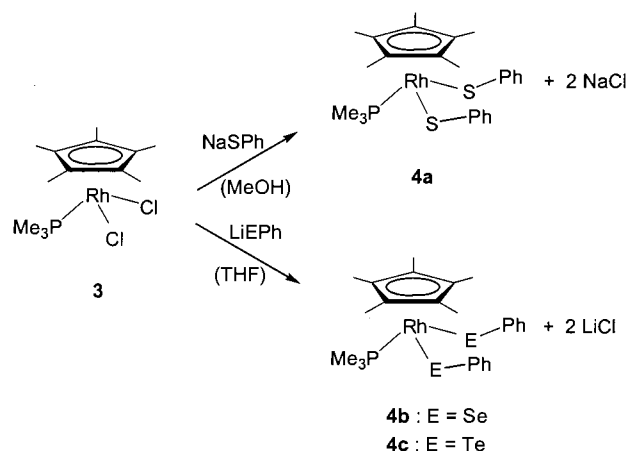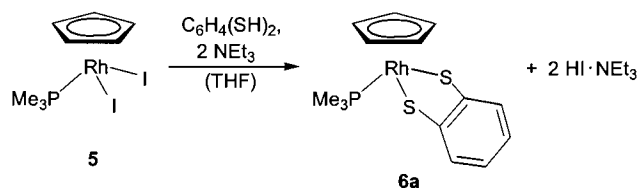
$Cp*Rh(PMe_3)(EPh)_2$ are therefore best described as rhodium(III) complexes.

2.3. NMR spectroscopic characterisation

The [31]P-, [103]Rh-, ^{77}Se-, and [125]Te-NMR data of the phenylchalcogenolato complexes **2a–c** and **4a–c** and of the 1,2-dithiolato complexes **6a** and **7a** are collected in Table 2; the ^{1}H- and ^{13}C-NMR data are given in Section 3. All NMR spectra are in complete agreement with the proposed structures.

There is little variation in the ^{1}H- and ^{13}C-NMR data of the cyclopentadienyl ring and of the PMe_3 ligand. The phenylchalcogenolato ligands show the usual pattern in the ^{1}H- and ^{13}C-NMR spectra. The different chalcogens take only a small influence on δ^1H and δ^{13}C(o, m, p) of the phenyl group, whereas the influence on δ^{13}C(i) is larger, with the typical order [12] of increasing ^{13}C nuclear shielding in the series S < Se < Te. This 'heavy-atom effect' has been observed for similar compounds [10]. In some cases it proved possible to record ^{13}C-NMR spectra with signal-to-noise (S/N) ratio and high resolution sufficient to detect [77]Se or [125]Te satellites (e.g. **4b** and **4c**). The magnitude of the

coupling constants $^1J(^{77}Se,^{13}C) = 123.5$ (**4b**) and $^1J(^{125}Te,^{13}C) = 353.0$ Hz (**4c**) is in the expected range [13]. There are hardly any data in the literature for comparison of the magnitude of the coupling constants between ^{13}C and either [77]Se or [125]Te across more than one bond. In the case of **4b**, $^1J(^{13}C,^{13}C)$ data of the SePh group could be obtained [$^1J(^{13}C_{ipso},^{13}C_{ortho}) = 58.0$, $^1J(^{13}C_{ortho},^{13}C_{meta}) = 54.8$, $^1J(^{13}C_{meta},^{13}C_{para}) = 55.7$ Hz] which are very similar to known values $^1J(^{13}C,^{13}C)$ for PhSeMe [$^1J(^{13}C_{ipso},^{13}C_{ortho}) = 58.3$, $^1J(^{13}C_{meta},^{13}C_{para}) = 56.3$ Hz] [14]. This supports the evidence from δ^{13}C data that the terminal Rh–Se bond has no particular influence on the bonding situation in the phenyl ring.

The complexes **2a** and **4a–4c** were studied by a series of heteronuclear triple resonance experiments of the type $^{13}C\{^1H,^{31}P\}$ with selective irradiation of ^{31}P transitions in order to determine the signs of coupling constants $J(^{103}Rh,^{13}C)$ to the cyclopentadienyl ^{13}C, the phenyl [13]C(i) and the trimethylphosphane ^{13}C nuclei (see Fig. 2 for an example). The ^{13}C and ^{31}P nuclei are the active spins, and the [103]Rh nucleus is the passive spin in all of these experiments, allowing for the comparison of relative signs of coupling constants [15] $J(^{103}Rh,^{13}C)$ and $^1J(^{103}Rh,^{31}P)$. Since the sign of $^1J(^{103}Rh,^{31}P)$ is known to be negative [16], ($\gamma(^{103}Rh) < 0$; the reduced coupling constant $^1K(^{103}Rh,^{31}P)$ is positive), the absolute sign of the coupling constants $J(^{103}Rh,^{13}C)$ for these bonding situations becomes available for the first time. In all four cases [Cp, Cp*, C(i) and Me_3P], the sign of $J(^{103}Rh,^{13}C)$ is negative ($K(^{103}Rh,^{13}C) > 0$).

There is a significant increase in the shielding of ^{31}P nuclei by 10.6 ppm in the series **2a–2c**, which is less pronounced (4 ppm) in the series **4a–4c**. In both series, the magnitude of $^1J(^{103}Rh,^{31}P)$ increases slightly (by 4.5 and 5.4 Hz) on going from E = S to E = Te.

Both [77]Se and [125]Te nuclear shielding are reduced (by about 150 and 260 ppm, respectively) when the Cp ring is replaced by the Cp* ring. Considering the huge range of δ^{77}Se and δ^{125}Te values and the roughly linear
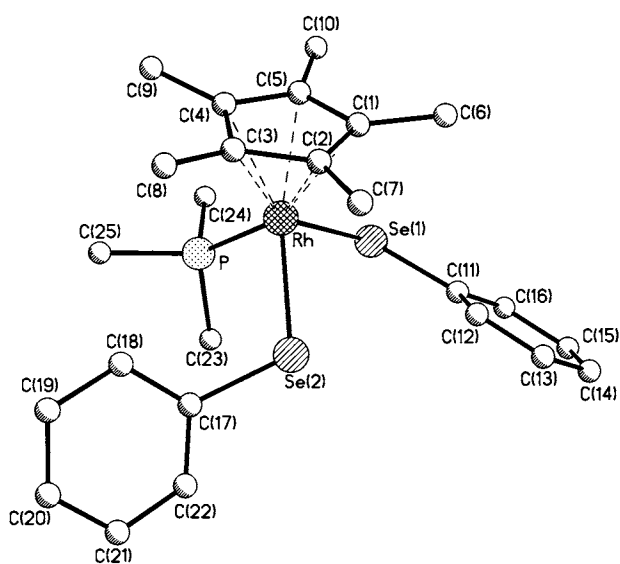

Fig. 1. Molecular structure of $Cp*Rh(PMe_3)(SePh)_2$ (**4b**) (The hydrogen atoms are omitted for clarity). See Table 1 for selected distances and bond angles.

Table 2
^{31}P-, ^{77}Se-, ^{125}Te- and ^{103}Rh-NMR data [a]

	Complex	δ ^{31}P [b]	δ ^{103}Rh	δ ^{77}Se [c]/δ ^{125}Te [d]
2a	CpRh(PMe$_3$)(SPh)$_2$	13.9 (141.7)	388.2 ± 0.2	
2b	CpRh(PMe$_3$)(SePh)$_2$	8.9 (143.1/17.0)	106.5 ± 0.5	−15.0 [56] (17.0)
2c	CpRh(PMe$_3$)(TePh)$_2$	3.3 (146.2/42.0)	−553.0 ± 1	−71.6 {110} (42.0)
4a	Cp*Rh(PMe$_3$)(SPh)$_2$	1.6 (144.1)	461.3 ± 0.2	
4b	Cp*Rh(PMe$_3$)(SePh)$_2$	0.4 (148.5/18.3)	201.5 ± 0.3	134.1 [53] (18.3)
4c	Cp*Rh(PMe$_3$)(TePh)$_2$	−2.4 (150.5/43.9)	−384.0 ± 0.5	188.5 {112} (43.9)
6a	CpRh(PMe$_3$)(S$_2$C$_6$H$_4$)	17.9 (141.6)	52.0 ± 1	
7a	Cp*Rh(PMe$_3$)(S$_2$C$_6$H$_4$)	10.8 (150.4)	−11.0 ± 0.5	

[a] All NMR spectra were measured in CDCl$_3$ solution at r.t.
[b] Coupling constants (± 1 Hz) $^1J(^{103}$Rh^{31}P)/$^2J(^{77}$Se^{31}P) and $^1J(^{103}$Rh^{31}P)/$^2J(^{125}$Te^{31}P) are given in parentheses.
[c] Coupling constants (± 3 Hz) $^1J(^{103}$Rh^{77}Se) are given in square brackets.
[d] Coupling constants (± 3 Hz) $^1J(^{125}$Te^{103}Rh) are given in curly brackets.

relationship between δ ^{77}Se and δ ^{125}Te [13], the data are in the expected range for terminal phenylchalcogenolato ligands (see Ref. [11] for δ ^{77}Se of bridging and terminal PhSe groups linked to rhodium). The values of the coupling constants $^1J(^{103}$Rh,^{77}Se) are similar to known data [11], and the data $^1J(^{125}$Te,^{103}Rh) appear to fit into the pattern known so far [13]. Examples for $^2J(^{77}$Se,^{31}P) and $^2J(^{125}$Te,^{31}P) across a metal centre in such complexes are rare and cannot be discussed at present.

The ^{77}Se- and more so, the ^{125}Te-NMR signals are broad (e.g. 4c: $h_{1/2}(^{125}$Te) = 260 ± 10 Hz). This broadening of the resonance signals can be traced to efficient nuclear spin relaxation by chemical shift anisotropy (CSA). That means that ^{77}Se and ^{125}Te satellites, e.g. in ^{31}P-NMR spectra, must also be broadened. In the case of 4c, the line width of the ^{125}Te satellites in the 202.5 MHz ^{31}P-NMR spectra was found to be 7 ± 0.5 Hz, which is in good agreement with a calculated line width of 7.5 Hz [assuming that the broadening in both ^{125}Te- and ^{31}P-NMR spectra arise from the same origin (CSA)]. With high-field NMR spectrometers, the fairly short relaxation times, $T_1(^{77}$Se) (ca. 10–30 ms) and $T_1(^{125}$Te) (ca. 1–3 ms), for the type of compounds studied offer distinct advantages with respect to instrument time, in particular if diluted solutions are studied. However, in the case of ^{125}Te-NMR, the pronounced broadening of the ^{125}Te-NMR signals may compensate most of the advantage in S/N gained by the short repetition time of consecutive 90° pulses.

The 'heavy-atom effect', already mentioned for δ ^{13}C(i), is also evident, but to a much larger extent, for ^{103}Rh nuclear shielding when sulphur is replaced by selenium and tellurium in the phenylchalcogenolato complexes (e.g. ^{103}Rh nuclear shielding increases by more than 920 ppm from 2a to 2c and by 745 ppm from 4a to 4c). Interestingly, the δ ^{103}Rh values change dramatically (from 388.2 to 52.0 and from 461.3 to −11.0) if the two phenylthiolato groups in 2a or 4a are replaced by the benzenedithiolato group in 6a and 7a.

The chelating benzenedithiolato ligand exerts a large shielding effect on the ^{103}Rh nucleus, and the influence of the Cp versus the Cp* ring ligand is inverted in the metallacyclic compounds. A more thorough discussion must be based on direct structural evidence. However, the δ ^{103}Rh data of 6a and 7a indicate substantial changes in the electronic structure of the metallacycles when compared with analogous non-cyclic derivatives. The ring size of the metallacycles, as well as the annelation of the aromatic system may have a marked influence, since the metallacyclic complex Cp*Rh(PMe$_3$)(S$_2$fc) (fc = 1,1′-ferrocenediyl), for which the molecular structure in the solid state is known [10], gives a ^{103}Rh-NMR signal at δ = 368 ± 1, rather close to that of 4a (δ ^{103}Rh = 461.3 ± 0.2).
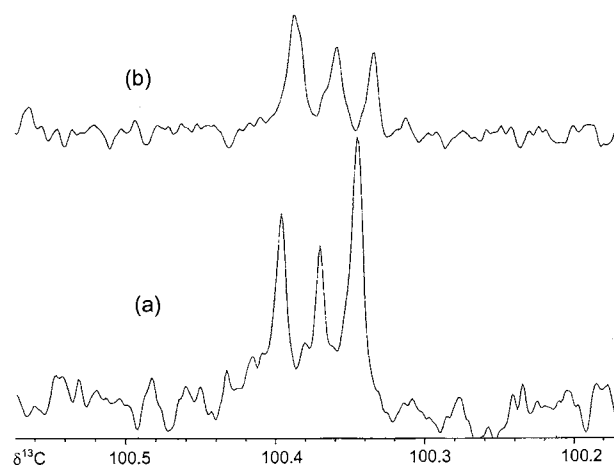
Fig. 2. Heteronuclear triple resonance experiments (125.8 MHz) ^{13}C{^{1}H,^{31}P} with selective irradiation of ^{31}P transitions in the case of Cp*Rh(PMe$_3$)SPh$_2$ (4a); shown is the region of the quaternary ^{13}C(Cp*) resonance (dd, $^1J(^{103}$Rh,^{13}C) = 4.9, $^2J(^{31}$P,^{13}C) = 3.3 Hz). (a) Irradiation of the low frequency part of the ^{31}P resonance of the ^{31}P–^{103}Rh–^{13}C isotopomer, showing the effect on the low-frequency doublet, and (b) the analogous effect on the high-frequency doublet by selective irradiation of the respective high-frequency ^{31}P transitions. This proves that the signs of $^1J(^{103}$Rh,^{13}C$_{Cp*}$) and $^1J(^{103}$Rh,^{31}P) are alike.

3. Experimental

3.1. General and physical methods

All reactions were carried out under an atmosphere of argon and in carefully dried solvents. The starting materials $CpRh(PMe_3)(CO)$ (**1**) [17], $Cp*Rh(PMe_3)Cl_2$ (**3**) [18] and $CpRh(PMe_3)I_2$ (**5**) [19] were prepared according to published methods.

NMR: Jeol FX 90 Q, Bruker ARX 250, Jeol EX 270, Bruker AC 300 ($\delta\,^1H$ ($CHCl_3/CDCl_3$) = 7.24; $\delta\,^{13}C(CDCl_3) = 77.0$; $\delta\,^{31}P = 0$ for external H_3PO_4, 85% aq.), and Bruker DRX 500 [^{77}Se-NMR ($\delta\,^{77}Se = 0$ for Me_2Se with $\Xi(^{77}Se) = 19.071523$ MHz); ^{125}Te-NMR ($\delta\,^{125}Te = 0$ for Me_2Te with $\Xi(^{125}Te) = 31.549802$ MHz). Triple resonance experiments $^{31}P\{^1H,^{103}Rh\}$ for the determination of $\delta\,^{103}Rh$ (with respect to $\Xi(^{103}Rh) = 3.16$ MHz), $^{13}C\{^1H,^{31}P\}$ for determination of coupling signs]. The power for irradiation of ^{31}P transitions was carefully selected (< 55 db) in order to achieve the desired differential effects, in particular for the $^{13}C(PMe_3)$ and $^{13}C(i)$-signals where the effect of spin tickling [20] had to be observed since $|J(^{31}P,^{13}C)| \gg |J(^{103}Rh,^{13}C)|$. EI MS: Varian Mat CH7; the m/e data refer to the isotopes ^{32}S, ^{80}Se and ^{128}Te; the experimental isotope patterns correspond to the natural distribution of the chalcogen isotopes. Decomposition points were determined using a Büchi 510 melting point apparatus.

3.2. CpRh(PMe₃)(SPh)₂ (2a)

A solution of **1** (110 mg, 0.40 mmol) in 20 ml of toluene was treated with S_2Ph_2 (88 mg, 0.40 mmol) and the mixture was heated at 110°C (reflux) for 10 h. The dark red solution was evaporated, the red residue washed with 20 ml of pentane and recrystallized from toluene:pentane to give a red solid (192 mg (87%), m.p. (dec.) 135°C). EI MS: m/e (relative intensity %): 554 (6, $[CpRh(SPh)]_2^+$), 462 (7, $CpRh(PMe_3)(SPh)_2^+$), 353 (80, $CpRh(PMe_3)(SPh)^+$), 277 (100, $CpRh(SPh)^+$), 244 (13, $CpRh(PMe_3)^+$). ^1H-NMR ($CDCl_3$, 250 MHz): 7.50 (d, $J(HH) = 7.2$ Hz, 4H, H(2)/H(6)), 7.05 (dd, $J(HH) = 7.2$ and 7.0 Hz, 4H, H(3)/H(5)), 6.95 (t, $J(HH) = 7.0$ Hz, 2H, H(4)), 5.29 (d, $J(PH) = 1.3$ Hz, 5H, C_5H_5), 1.54 (d, $J(PH) = 11.3$ Hz, 9H, PMe_3). ^{13}C-NMR ($CDCl_3$, 126 MHz): 145.8 (dd, $J(RhC) = 3.7$ Hz, $J(PC) = 0.9$ Hz, C(1)), 133.0 (d, $J(RhC) = 0.9$ Hz, C(2)/C(6)), 127.7 (C(3)/C(5)), 123.4 (C(4)), 91.7 (dd, $J(RhC) = 4.1$ Hz, $J(PC) = 3.4$ Hz, C_5H_5), 18.2 (dd, $J(RhC) = 0.7$ Hz, $J(PC) = 35.8$ Hz, PMe_3).

3.3. CpRh(PMe₃)(SePh)₂ (2b)

A solution of **1** (83 mg, 0.31 mmol) in 20 ml of toluene was treated with Se_2Ph_2 (96 mg, 0.31 mmol)

and the mixture was stirred for one day at r.t. A dark red solution was formed which was taken to dryness under vacuum. The residue was recrystallized from toluene:pentane to give an orange–red solid (153 mg (89%), m.p. (dec.) 109°C). EI MS: m/e (relative intensity %): 650 (4, $[CpRh(SePh)]_2^+$), 558 (8, $CpRh(PMe_3)(SePh)_2^+$), 401 (100, $CpRh(PMe_3)$-$(SePh)^+$), 325 (98, $CpRh(SePh)^+$), 244 (11, $CpRh(PMe_3)^+$). ^1H-NMR ($CDCl_3$, 250 MHz): 7.64 (d, $J(HH) = 7.2$ Hz, 4H, H(2)/H(6)), 7.05 (m, 6H, H(3)/H(4)/H(5)), 5.22 (d, $J(PH) = 1.7$ Hz, 5H, C_5H_5), 1.61 (d, $J(PH) = 11.0$ Hz, 9H, PMe_3). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 135.9 (C(1)), 135.4 (C(2)/C(6)), 127.9 (s, C(3)/C(5)), 124.8 (C(4)), 91.0 (dd, $J(RhC) = 3.7$ Hz, $J(PC) = 3.7$ Hz, C_5H_5), 19.7 (d, $J(PC) = 36.1$ Hz, PMe_3).

3.4. CpRh(PMe₃)(TePh)₂ (2c)

A solution of **1** (117 mg, 0.43 mmol) in 20 ml of toluene was treated with Te_2Ph_2 (176 mg, 0.43 mmol) and the mixture was stirred for two days at r.t. The solvent was removed from the resulting green solution under vacuum, 20 ml of THF were added to the residue and the suspension filtered through cellulose. The filtrate was concentrated to about 5 ml in vacuum, 40 ml of pentane was added and the solution cooled to $-30°C$. After several hours a green microcrystalline solid precipitated which was removed by filtration and dried under high vacuum (223 mg (79%), m.p. (dec.) 121°C). EI MS: m/e (relative intensity %): 654 (25, $CpRh(PMe_3)(TePh)_2^+$), 449 (100, $CpRh(PMe_3)$-$(TePh)^+$), 373 (91, $CpRh(TePh)^+$), 244 (90, $CpRh(PMe_3)^+$). ^1H-NMR ($CDCl_3$, 250 MHz): 7.79 (dd, $J(HH) = 8.0$ Hz, 4H, H(2)/H(6)), 7.14 (dd, $J(HH) = 8.0$ and 7.0 Hz, 4H, H(3)/H(5)), 6.99 (t, $J(HH) = 7.0$ Hz, 2H, H(4)), 5.23 (d, $J(PH) = 1.7$ Hz, 5H, C_5H_5), 1.70 (dd, $J(RhH) = 0.7$ Hz, $J(PH) = 10.4$ Hz, 9H, PMe_3). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 140.3 (C(2)/C(6)), 128.1 (C(3)/C(5)), 126.2 (C(4)), 110.5 (C(1)), 90.6 (dd, $J(RhC) = 3.7$ Hz, $J(PC) = 3.7$ Hz, C_5H_5), 22.9 (d, $J(PC) = 36.7$ Hz, PMe_3).

3.5. Cp*Rh(PMe₃)(SPh)₂ (4a)

A suspension of **3** (300 mg, 0.78 mmol) in 30 ml of MeOH was treated with NaSPh (305 mg, 2.31 mmol) and the mixture was stirred for 3 h at r.t. A dark red suspension was formed which was taken to dryness under vacuum. The residue was extracted three times with 10 ml of CH_2Cl_2:pentane (1:1), and the combined extracts were reduced in volume to ca. 10 ml. Then 50 ml of pentane was added and the solution cooled to $-78°C$. After several hours a red microcrystalline solid precipitated. The supernatant was decanted, the precipitate washed twice with portions (10 ml) of cold pen-

tane and dried under high vacuum to give a red microcrystalline powder (326 mg (79%), m.p. (dec.) 131°C). EI MS: m/e (relative intensity %): 803 (1, $[Cp*Rh]_2(SPh)_3^+$), 694 (2, $[Cp*Rh(SPh)]_2^+$), 532 (1, $Cp*Rh(PMe_3)(SPh)_2^+$), 456 (2, $Cp*Rh(SPh)_2^+$), 423 (6, $Cp*Rh(PMe_3)(SPh)^+$), 347 (28, $Cp*Rh(SPh)^+$), 314 (1, $Cp*Rh(PMe_3)^+$), 238 (9, $Cp*Rh^+$), 76 (74, PMe_3^+), 61 (100, PMe_2^+). ^{1}H-NMR (CDCl$_3$, 270 MHz): 7.37 (d, $J(HH) = 7.9$ Hz, 4H, H(2)/H(6)), 6.96 (dd, $J(HH) = 7.9$ and 7.3 Hz, 4H, H(3)/H(5)), 6.87 (t, $J(HH) = 7.3$ Hz, 2H, H(4)), 1.66 (d, $J(PH) = 3.1$ Hz, 15H, C_5Me_5), 1.45 (d, $J(PH) = 10.4$ Hz, 9H, PMe$_3$). ^{13}C-NMR (CDCl$_3$, 126 MHz): 144.2 (dd, $J(RhC) = 0.8$ Hz, $J(PC) = 4.4$ Hz, C(1)), 133.1 (d, $J(PC) = 0.8$ Hz, C(2)/C(6)), 127.1 (C(3)/C(5)), 122.47 (C(4)), 100.0 (dd, $J(RhC) = 4.9$ Hz, $J(PC) = 3.3$ Hz, C_5Me_5), 15.3 (dd, $J(RhC) = 0.5$ Hz, $J(PC) = 33.5$ Hz, PMe$_3$), 9.5 (d, $J(PC) = 1.4$ Hz, C_5Me_5).

3.6. Cp*Rh(PMe$_3$)(SePh)$_2$ (4b)

A solution of Se$_2$Ph$_2$ (233 mg, 0.75 mmol) in 10 ml of THF was slowly treated with 1.5 ml of a 1 M solution of Li[BHEt$_3$] in THF and the mixture was stirred for 15 min at r.t. A pale yellow solution was formed which was added to a suspension of **3** (220 mg, 0.57 mmol) in 10 ml of THF. After 3 h stirring at r.t. the solvent from the resulting dark red solution was removed under vacuum, and then the residue filtered through cellulose using 20 ml of CH$_2$Cl$_2$:pentane (1:10). The filtrate was concentrated to about 5 ml in volume, 30 ml of pentane was added and the solution cooled to −30°C. After several hours a red–violet crystalline solid started to precipitate. The supernatant solution was decanted and the precipitate dried under high vacuum to produce red–violet crystals (273 mg (76%), m.p. (dec.) 119°C). EI MS: m/e (relative intensity %): 790 (1, $[Cp*Rh(SePh)]_2^+$), 628 (2, $Cp*Rh(PMe_3)(SePh)_2^+$), 552 (3, $Cp*Rh(SePh)_2^+$), 471 (18, $Cp*Rh(PMe_3)(SePh)^+$), 552 (3, $Cp*Rh(SePh)_2^+$), 471 (18, $Cp*Rh(PMe_3)(SePh)^+$), 395 (100, $Cp*Rh(SePh)^+$), 314 (5, $Cp*Rh(PMe_3)^+$), 76 (47, PMe_3^+), 61 (64, PMe_2^+). ^{1}H-NMR (CDCl$_3$, 500 MHz): 7.57 (d, $J(HH) = 7.9$ Hz, 4H, H(2)/H(6)), 7.01 (m, 6H, H(3)/H(4)/H(5)), 1.76 (d, $J(PH) = 3.2$ Hz, 15H, C_5Me_5), 1.58 (d, $J(PH) = 10.3$ Hz, 9H, PMe$_3$). ^{13}C-NMR (CDCl$_3$, 126 MHz): 135.6 ($J(SeC) = 7.8$ Hz, $J(C(1)C(2)) = 58.0$ Hz, $J(C(2)C(3)) = 54.8$ Hz, C(2)/C(6)), 133.8 (dd, $J(RhC) = 0.7$ Hz, $J(SeC) = 123.5$ Hz, $J(PC) = 3.9$ Hz, $J(C(1)C(2)) = 58.0$ Hz, C(1)), 127.3 ($J(C(3)C(4)) = 55.7$ Hz, C(3)/C(5)), 124.10 ($J(C(3)C(4)) = 55.7$ Hz, C(4)), 99.4 (dd, $J(RhC) = 5.2$ Hz, $J(SeC) = 2.9$ Hz, $J(PC) = 3.2$ Hz, C_5Me_5), 17.2 (dd, $J(RhC) = 1.0$ Hz, $J(SeC) = 3.2$ Hz, $J(PC) = 34.3$ Hz, PMe$_3$), 9.8 (d, $J(PC) = 1.3$ Hz, C_5Me_5).

3.7. Cp*Rh(PMe$_3$)(TePh)$_2$ (4c)

A solution of Te$_2$Ph$_2$ (279 mg, 0.68 mmol) in 10 ml of THF was slowly treated with 1.4 ml of a 1 M solution of Li[BHEt$_3$] in THF, and the mixture was stirred for 15 min at r.t. The dark red solution thus formed was added to a suspension of **3** (219 mg, 0.57 mmol) in 10 ml of THF. After 3 h stirring at r.t. the solvent was removed from the resulting dark green solution under vacuum and the residue chromatographed on Al$_2$O$_3$V. With pentane an orange–yellow band of Te$_2$Ph$_2$ was eluated. Subsequent eluation with toluene gave a green zone that was taken to dryness under vacuum. The oily residue was stirred in 10 ml of pentane for 30 min at r.t. and then cooled to −78°C. After several hours the supernatant liquid was decanted and the green microcrystalline solid dried under high vacuum (250 mg (61%), m.p. (dec.) 103°C).). EI MS: m/e (relative intensity %): 724 (7, $Cp*Rh(PMe_3)(TePh)_2^+$), 519 (21, $Cp*Rh(PMe_3)(TePh)^+$), 443 (47, $Cp*Rh(TePh)^+$), 366 (15, $Cp*RhTe^+$), 314 (12, $Cp*Rh(PMe_3)^+$), 238 (20, $Cp*Rh^+$), 154 (100, Ph_2^+). ^{1}H-NMR (CDCl$_3$, 500 MHz): 7.76 (d, $J(HH) = 7.9$ Hz, 4H, H(2)/H(6)), 7.15 (t, $J(HH) = 6.9$ Hz, 2H, H(4)), 6.97 (dd, $J(H) = 7.9$ and 6.9 Hz, 4H, H(3)/H(5)), 1.89 (d, $J(PH) = 2.9$ Hz, 15H, C_5Me_5), 1.70 (d, $J(PH) = 9.8$ Hz, PMe$_3$). ^{13}C-NMR (CDCl$_3$, 75.0 MHz): 141.2 (C(2)/C(6)), 127.5 (C(3)/C(5)), 125.8 (C(4)), 107.9 (dd, $J(TeC) = 353$ Hz, $J(RhC) = 0.5$ Hz, $J(PC) = 3.5$ Hz, C(1)), 99.6 (dd, $J(RhC) = 4.4$ Hz, $J(PC) = 3.3$ Hz, C_5Me_5), 20.9 (dd, $J(TeC) = 8$ Hz, $J(RhC) = 0.5$ Hz, $J(PC) = 35.4$ Hz, PMe$_3$), 10.8 (d, $J(PC) = 0.9$ Hz, C_5Me_5).

3.8. CpRh(PMe$_3$)(S$_2$C$_6$H$_4$) (6a)

A solution of **5** (115 mg, 0.23 mmol) in 30 ml of THF was treated with 1,2-benzenedithiol (41 μl, 0.23 mmol) and triethylamine (65 μl, 0.47 mmol), and the mixture was stirred for 18 h at r.t. The solvent from the resulting dark red solution was removed under vacuum and the residue chromatographed on Al$_2$O$_3$V. Eluation with toluene gave an orange–brown band that was taken to dryness under vacuum to give a red–brown solid (47 mg (53%), m.p. (dec.) 207°C). EI MS: m/e (relative intensity %): 384 (25, $CpRh(PMe_3)(S_2C_6H_4)^+$), 308 (100, $CpRh(S_2C_6H_4)^+$), 168 (14, $CpRh^+$). ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.12 (m, 2H, H(3)/H(6)), 6.61 (m, 2H, H(4)/H(5)), 5.39 (d, $J(PH) = 2.2$ Hz, 5H, C_5H_5), 1.53 (d, $J(PH) = 11.2$ Hz, 9H, PMe$_3$). ^{13}C-NMR (CDCl$_3$, 62.9 MHz): 143.9 (C(1)/C(2)), 127.2 (C(3)/C(6)), 121.8 (C(4)/C(5)), 91.3 (dd, $J(RhC) = 4.2$ Hz, $J(PC) = 4.2$ Hz, C_5H_5), 17.4 (d, $J(PC) = 37.9$ Hz, PMe$_3$).

3.9. Cp*Rh(PMe₃)(S₂C₆H₄) (7a)

A suspension of **3** (307 mg, 0.80 mmol) in 10 ml of THF was treated with 1,2-benzenedithiol (100 μl, 0.87 mmol) and triethylamine (250 μl, 1.81 mmol) and the mixture was stirred for 2 h at r.t. The solvent was removed from the resulting dark red solution under vacuum and the residue chromatographed on a column filled with Al_2O_3V. Eluation with toluene gave an orange–red band that was taken to dryness under vacuum to give an orange–brown solid (337 mg (93%), m.p. (dec.) 134°C). EI MS: m/e (relative intensity %): 454 (3, Cp*Rh(PMe₃)(S₂C₆H₄)⁺), 378 (100, Cp*Rh(S₂C₆H₄)⁺). ¹H-NMR (CDCl₃, 250 MHz): 7.14 (m, 2H, H(3)/H(6)), 6.59 (m, 2H, H(4)/H(5)), 1.71 (d, $J(PH)$ = 3.2 Hz, 15H, C_5Me_5), 1.37 (d, $J(PH)$ = 10.7 Hz, 9H, PMe₃). ¹³C-NMR (CDCl₃, 62.9 MHz): 144.9 (C(1)/C(2)), 127.4 (C(3)/C(6)), 121.2 (C(4)/(5)), 100.2 (dd, $J(RhC)$ = 4.3 Hz, $J(PC)$ = 4.3 Hz, C_5Me_5), 14.5 (d, $J(PC)$ = 35.9 Hz, PMe₃), 9.4 (d, $J(PC)$ = 1.4 Hz, C_5Me_5).

3.10. X-ray structure analysis of Cp*Rh(PMe₃)(SePh)₂ (4b)

Single crystals were grown from CH₂Cl₂:pentane at −78°C. Crystal: C₂₅H₃₄PRhSe₂, dark red prism, with the dimensions $0.30 \times 0.20 \times 0.15$ mm. Space group $P2_1/c$ (monoclinic) with the lattice parameters a = 9.991(2), b = 15.608(2), c = 16.661(2) Å and β = 96.86(2)°, V = 2579.5(7) Å³, Z = 4. D_{calc} 1.613 g cm³, μ (Mo–K$_\alpha$) 35.56 cm⁻¹, min./max. transmission 0.4038/0.4869. Data collection: Siemens P4, Mo–K$_\alpha$ radiation (λ = 0.71073 Å), graphite monochromator, T = 296 K. 2θ Scan range 3.0–55.0°. Collected reflections 7581, of which 5853 were independent and 4584 independent observed [$F_o >$ $2\sigma(F_o)$]. Control by three standard per 100 reflections, variation in standards ± 1%. Refinement: R 5.64, Rw 3.82% ($w^{-1} = \sigma^2(F_o)$) with 263 refined parameters, max./min. residual electron density $0.62/ -1.23$ e Å⁻³. Goodness-of-fit 1.22.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114027. Copies of these 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).

References

[1] (a) P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121. (b) I.G. Dance, Polyhedron 5 (1986) 1037. (c) B. Krebs, G. Henkel, Angew. Chem. 103 (1991) 785; Angew. Chem. Int. Ed. Engl. 30 (1991) 769. (d) J.R. Dilworth, J. Hu, Adv. Inorg. Chem. 40 (1993) 411.

[2] J. Arnold, Progr. Inorg. Chem. 43 (1995) 353.

[3] D.P. Klein, G.M. Kloster, R.G. Bergman, J. Am. Chem. Soc. 112 (1990) 2022.

[4] M. Herberhold, G.-X. Jin, A.L. Rheingold, J. Organomet. Chem. 570 (1998) 241.

[5] (a) M.J.H. Russel, C. White, A. Yates, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1978) 849. (b) Z. Hou, Y. Ozawa, K. Isobe, Chem. Lett. (1990) 1863. (c) J.J. Garcia, H. Torrens, H. Adams, N.A. Bailey, P.M. Maitlis, J. Chem. Soc. Chem. Commun. (1991) 74. (d) J.J. Garcia, H. Torrens, H. Adams, N.A. Bailey, A. Shacklady, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1993) 1529. (e) Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe, M. Hidai, Inorg. Chim. Acta 267 (1998) 73.

[6] (a) N.G. Connelly, G.A. Johnson, J. Chem. Soc. Dalton Trans. (1978) 1375. (b) N.G. Connelly, G.A. Johnson, B.A. Kelly, P. Woodward, J. Chem. Soc. Chem. Commun. (1977) 436.

[7] J. Andrade, J.J. Garcia, H. Torrens, F. del Rio, C. Claver, N. Ruiz, Inorg. Chim. Acta 255 (1997) 389.

[8] V. Tedesco, W. von Philipsborn, Magn. Reson. Chem. 34 (1996) 373.

[9] R. Xi, M. Abe, T. Suzuki, T. Nishioka, K. Isobe, J. Organomet. Chem. 549 (1997) 117.

[10] M. Herberhold, G.-X. Jin, A.L. Rheingold, G.F. Sheats, Z. Naturforsch. 47b (1992) 1091.

[11] M. Herberhold, M. Keller, W. Kremnitz, T. Daniel, W. Milius, B. Wrackmeyer, H. Nöth, Z. Anorg. Allg. Chem. 624 (1998) 1324.

[12] J. Mason, Adv. Inorg. Chem. Radiochem. 22 (1979) 199.

[13] H.C.E. McFarlane, W. McFarlane, in: J. Mason (Ed.), Multinuclear NMR, Plenum Press, New York, 1987, Ch. 15.

[14] L.B. Krivdin, G.A. Kalabin, Zh. Org. Khim 25 (1989) 690.

[15] (a) W. McFarlane, Annu. Rep. NMR Spectrosc. 1 (1968) 135. (b) W. McFarlane, Annu. Rep. NMR Spectrosc. 5A (1972) 353.

[16] (a) P.L. Goggin, R.J. Goodfellow, R.J. Knight, M.G. Norton, B.F. Taylor, J. Chem. Soc. Dalton Trans. (1973) 2220. (b) C. Crocker, R.J. Goodfellow, J. Chem. Res. (S) (1981) 38; J. Chem. Res. (M) (1981) 742. (c) E.M. Hyde, J.D. Kennedy, B.L. Shaw, W. McFarlane, J. Chem. Soc. Dalton Trans. (1977) 1571.

[17] D.P. Drolet, A.J. Lees, J. Am. Chem. Soc. 114 (1992) 4186.

[18] K. Isobe, P.M. Bailey, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1981) 2003.

[19] R.A. Periana, R.G. Bergman, J. Am. Chem. Soc. 108 (1986) 7332.

[20] R. Freeman, W.A. Anderson, J. Chem. Phys. 37 (1962) 2053.