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Carbenerhodium(I) complexes of the half-sandwich-type: reactions with electrophiles

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The reaction of the carbenerhodium(I) complexes $[(\eta^5\text{-}C_5H_5)Rh(=CR_2)(L)]$ (R = aryl) with HX (X = Cl, CF_3CO_2) led, depending on the size and donor properties of the ligand L, to two different types of products. While compounds **1**, **2** with R = Ph and L = CO or PMe_3 react with HX to give rhodium(III) alkyls $[(\eta^5\text{-}C_5H_5)RhX(CHPh_2)(L)]$ **3**, **4a**,**b**, the analogues **5a** and **5b** with R = Ph, *p*-Tol and L = PPr^i_3 afford upon treatment with HX (X = Cl, Br, I, CF_3CO_2) the ring-substituted products $[\{\eta^5\text{-}C_5H_4(CHR_2)\}RhHX(PPr^i_3)]$ **6a**–**e**. In the presence of excess HX, the latter are converted into the dihalo or bis(trifluoroacetato) derivatives $[\{\eta^5\text{-}C_5H_4(CHR_2)\}RhX_2(PPr^i_3)]$ **7a**–**e**. A labelling experiment using $[(\eta^5\text{-}C_5D_5)Rh(=CPh_2)(PPr^i_3)]$ **5a**-d_5 as a precursor indicates that the migratory insertion of the carbene into a C–H bond of the cyclopentadienyl ring probably occurs *via* an η^4-cyclopentadienerhodium(I) species as an intermediate. The triphenylphosphine complex $[\{\eta^5\text{-}C_5H_4(CHPh_2)\}RhCl_2(PPh_3)]$ **7f** was prepared analogously from **5c** and two equiv. of HCl. The reactions of **5a** and **5d** (R = Ph, L = $SbPr^i_3$) with either HBF_4, $[Me_3O]BF_4$ or methyl triflate give *via* attack of the electrophile on the carbene carbon atom and subsequent σ/π rearrangement cationic η^3-benzylrhodium(III) complexes **9** and **10a**–**c** in good to excellent yields. Treatment of **5a** and **5d** with iodine results in the cleavage of the metal–carbene bond and affords the diiodo compounds $[(\eta^5\text{-}C_5H_5)RhI_2(L)]$ **12a**,**b**.

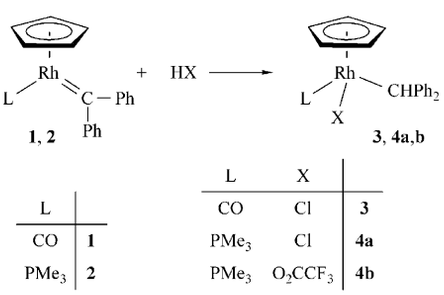
In the context of our investigations on the reactivity of square-planar carbenerhodium(I) complexes *trans*-$[RhCl(=CRR')(L)_2]$, where L is a tertiary phosphine, arsine or stibine,[1] we recently found that the chloro ligand of these compounds can easily be displaced not only by other halides but also by C-, N- or O-nucleophiles.[2] Among the products obtained by the substitution reactions, the cyclopentadienyl derivatives $[(\eta^5\text{-}C_5H_5)Rh(=CRR')(L)]$ deserve particular attention insofar as they belong to the type of half-sandwich compounds which in general behave as *metal bases*.[3] Extensive work from our laboratory in the period of 1975–1985 has shown that complexes such as $[(\eta^5\text{-}C_5H_5)M(PR_3)_2]$, $[(\eta^5\text{-}C_5H_5)M(CO)(PR_3)]$ or $[(\eta^5\text{-}C_5H_5)M(C_2H_4)(PR_3)]$ with M = Co, Rh, or Ir react, in some cases under extremely mild conditions, with electrophiles EX by oxidative addition to form products with a new M–E bond.[4] Since the related carbene compounds $[(\eta^5\text{-}C_5H_5)Rh(=CRR')(L)]$, like the vinylidene counterparts,[5] contain a highly reactive Rh–C double bond the question arose whether electrophiles such as HX or RX would preferentially attack the metal centre or the more electronegative carbene carbon atom.

The results reported in this paper show that, independent of the direction of the attack of the electrophile, the compounds formed in the initial step of the reaction of the half-sandwich-type carbenerhodium(I) complexes with HX or RX are mostly quite labile and rearrange either by migratory insertion or by generating an η^3-benzyl system. The interesting aspect is that more than the donor/acceptor capabilities the size of the ligand L plays a dominating role in determining the structure of the final product. Some preliminary observations of these studies have already been communicated.[6]

Results and discussion

Addition of HX to the Rh=C double bond

Like the four-coordinate carbenerhodium(I) complex *trans*-$[RhCl(=CPh_2)(PPr^i_3)_2]$, which upon treatment with HCl affords the five-coordinate alkylrhodium(III) compound $[RhCl_2(CHPh_2)(PPr^i_3)_2]$,[1] the cyclopentadienyl derivatives $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(L)]$ with L = CO (**1**) and PMe_3 (**2**) also react with Brønsted acids by oxidative addition to give the complexes **3** and **4a**,**b** in good to excellent yields (Scheme 1). The phosphine



Scheme 1

compound **2** is considerably more reactive than the carbonyl analogue which probably reflects the greater metal basicity of **2** compared with **1**. The rhodium(III) alkyls **3** and **4a**,**b** are red to orange-red solids which can be stored under argon for days but more or less rapidly decompose in benzene solution. Not unexpectedly, the carbonyl compound **3** is more labile than the phosphine counterparts **4a**,**b**. The most typical spectroscopic features are the ^{1}H NMR resonance of the C*H*Ph_2 proton at around δ 4.8–5.6 (which appears as a doublet for **3** and as a doublet of doublets for **4a** and **4b**) and the ^{13}C NMR signal of the corresponding alkyl carbon atom *C*HPh_2 at δ 42.4 (**4a**) and 47.0 (**4b**), respectively. The assignment of the latter has been confirmed by DEPT measurements. It should be mentioned that the formation of **4a** was observed for the first time when we attempted to purify the starting material **2** by column chromatography using acidic Al_2O_3 as the support. This result can be understood by taking into consideration that all the

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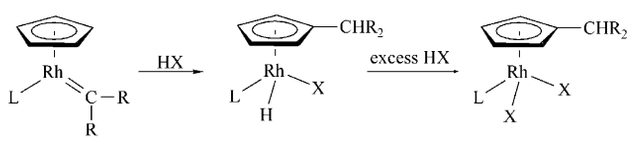
commercial samples of acidic alumina contain traces of chloride ions thus making the conversion of **2** to **4a** possible.

With regard to the mechanism of the reaction of **1** and **2** with HX to yield **3** and **4a**,**b**, two routes are conceivable. First, the electrophile could attack the *C*Ph_2 carbon atom which in the simplified terminology is part of a Schrock-type carbene ligand. Second, the attack of the electrophile could be directed at the electron-rich metal centre generating a cationic species $[(\eta^5\text{-}C_5H_5)RhH(=CPh_2)(L)]^+$ as an intermediate which, assisted by the anion X^-, rearranges to give the final product. We feel that the course of the reactions of $[(\eta^5\text{-}C_5H_5)Rh(CO)(PMe_3)]$[7] and $[(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(PMe_3)]$[8] with HX to afford the cations $[(\eta^5\text{-}C_5H_5)RhH(L)(PMe_3)]^+$ (L = CO, C_2H_4) supports the second possibility.

HX-induced migratory insertion reactions

In contrast to **1** and **2**, the structurally related carbene complexes **5a** and **5b** containing the more bulky phosphine PPr^i_3 as ancillary ligand react with an equimolar amount of HX (X = Cl, Br, I, CF_3CO_2) to form the ring-substituted products **6a**–**e** in 84–93% isolated yield (Scheme 2). For the preparation



5a–c **6a–e** **7a–f**

L	R	
PPr^i_3	Ph	**5a**
PPr^i_3	*p*-Tol	**5b**
PPh_3	Ph	**5c**

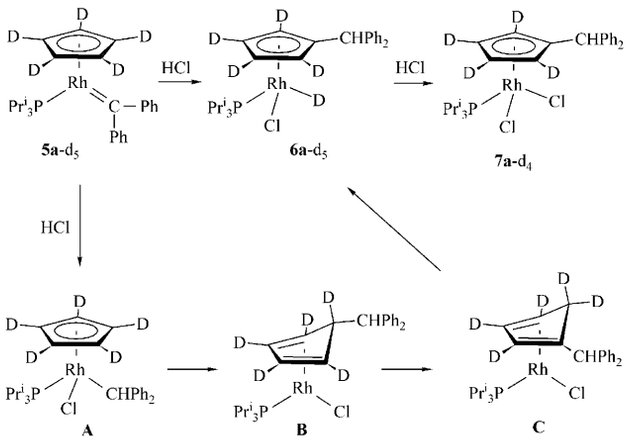
L	R	X	
PPr^i_3	Ph	Cl	**6a**, **7a**
PPr^i_3	Ph	Br	**6b**, **7b**
PPr^i_3	Ph	I	**6c**, **7c**
PPr^i_3	Ph	CF_3CO_2	**6d**, **7d**
PPr^i_3	*p*-Tol	Cl	**6e**,**7e**
PPh_3	Ph	Cl	**7f**

Scheme 2

of **6a**, **6b** and **6e**, instead of HCl or HBr also Me_3SiCl or Me_3SiBr can be used as the substrate which in the presence of traces of water generate *in situ* the corresponding Brønsted acid HX. In agreement with the proposed structure, the ^{1}H NMR spectra of **6a**–**e** display a hydride resonance at δ −11 to −13, which due to Rh–H and P–H couplings is split into a doublet of doublets. The C_5H_4 ring protons give rise to four separated signals between δ 5.4–4.2, thus confirming the non-equivalence of these protons in the chiral compounds.

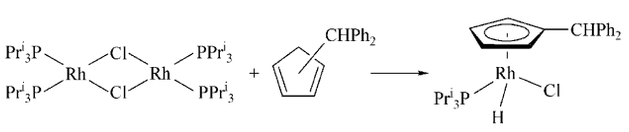
The reaction of the PPh_3-containing carbene complex **5c** with HCl probably takes a similar course to that of **5a**. Dropwise addition of Me_3SiCl to a solution of **5c** in acetone which has not been rigorously dried leads to an instant change of color from blue-violet to orange and gives, after removal of the solvent, an extremely air-sensitive residue which, from the spectroscopic data, mainly consists of the chloro(hydrido)-rhodium(III) compound $[\{\eta^5\text{-}C_5H_4(CHPh_2)\}RhHCl(PPh_3)]$. Characteristic features for this molecule are the doublet of doublets for the Rh–H proton at δ −10.47 (with J(Rh,H) 41.5 and J(P,H) 12.5 Hz) in the ^{1}H NMR and the doublet at δ 46.7 in the ^{31}P NMR spectrum; the ^{31}P–^{103}Rh coupling constant of 150.8 Hz of this signal seems to be typical for a piano-stool-type phosphinerhodium(III) species.[9] Attempts to isolate the complex $[\{\eta^5\text{-}C_5H_4(CHPh_2)\}RhHCl(PPh_3)]$ in analytically pure form failed. We note, however, that in the context of our studies on the chemistry of $(\eta^5\text{-}C_5H_4SiMe_3)Rh$ derivatives we recently prepared the related chloro(hydrido) compound $[\{\eta^5\text{-}C_5H_3(CHPh_2)SiMe_3\}RhHCl(PPh_3)]$,[10] which is considerably more stable than the $\{\eta^5\text{-}C_5H_4(CHPh_2)\}Rh$ counterpart.

In order to elucidate the mechanism of formation of the ring-substituted complexes **6a**–**e**, a labelling experiment was carried out. Treatment of **5a**-d_5, which was prepared from *trans*-$[RhCl(=CPh_2)(PPr^i_3)_2]$ and TlC_5D_5 in THF, with an equimolar amount of HCl in benzene affords exclusively the compound **6a**-d_5 (Scheme 3). Regarding the individual steps of this



Scheme 3

reaction, we assume that initially the addition of the Brønsted acid to the carbene–rhodium bond takes place, similar to the formation of **4a** from **2** and HCl (see Scheme 1). The intermediate **A** then reacts by migration of the $CHPh_2$ unit to the C_5D_5 ligand to generate the substituted cyclopentadienerhodium(I) species **B**. A subsequent 1,2-D-shift along the five-membered ring affords the intermediate **C** which, by deuterium transfer from the sp^3-carbon atom of the C_5 moiety to the metal, gives the final product **6a**-d_5. Reaction of **6a**-d_5 with HCl results in the formation of **7a**-d_4 which has been characterized spectroscopically. An isotopomer of **C** of the composition $[RhCl(\eta^4\text{-}C_5H_5CHPh_2)(PPr^i_3)]$ is probably also involved in the reaction of the dimer $[RhCl(PPr^i_3)_2]_2$ **8** with $C_5H_5CHPh_2$ to yield **6a** (Scheme 4). This alternative method to prepare **6a** is



8 **6a**

Scheme 4

reminiscent of earlier work from this laboratory which showed that treatment of **8** with cyclopentadiene results in the formation of the rhodium(III) complex $[(\eta^5\text{-}C_5H_5)RhHCl(PPr^i_3)]$ in excellent yield.[11] With regard to intermediate **B** we note that recently Hughes *et al.* reported the isolation of coordinatively saturated $(\eta^4\text{-}C_5H_5R)Rh$ compounds (R = $CF_2CF_2CF_3$, $CF(CF_3)_2$) which were formed from $[(\eta^5\text{-}C_5H_5)Rh(PMe_3)_2]$ and perfluoroalkyl iodides.[12]

The reactions of **5a** and **5b** with an excess instead of an equimolar amount of HX afford almost quantitatively the dihalo or bis(trifluoroacetato) derivatives **7a**–**e**. They are equally generated upon treatment of **6a**–**e** with HX. In contrast to **6a**–**e**, the substituted compounds **7a**–**e** are significantly more stable and for a short period of time can even be handled in air. The ^{31}P NMR spectra of **7a**–**e** display the expected doublet at δ 57–62 which is about 18–25 ppm upfield compared with **6a**–**e**. A similar upfield shift is observed for the ^{31}P resonance of the triphenylphosphine complex **7f**, prepared from **5c** and excess hydrogen chloride. In contrast to the labile chloro(hydrido) intermediate $[\{\eta^5\text{-}C_5H_4(CHPh_2)\}RhHCl(PPh_3)]$, **7f** has been characterized not only by spectroscopic data but also by elemental analysis.

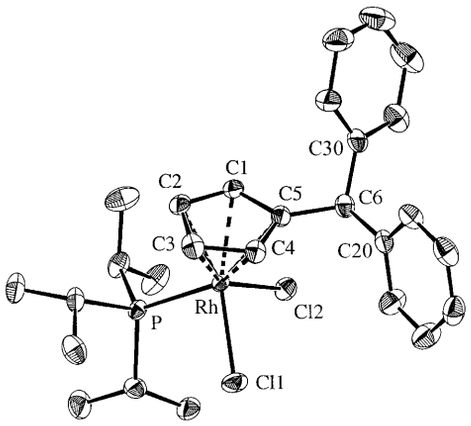


Fig. 1 ORTEP[13] plot of **7a**.

The proposed structure for the dihalorhodium(III) compounds $[\{\eta^5\text{-}C_5H_4(CHPh_2)\}RhX_2(PPr^i_3)]$ was confirmed by a single-crystal X-ray diffraction study of **7a**. The ORTEP[13] plot (Fig. 1) illustrates the three-legged piano-stool configuration of the molecule. A characteristic feature is that the $CHPh_2$ substituent is pointing away from the triisopropylphosphine therefore minimizing the steric repulsion between the two bulky moieties. While the Rh–C(ring) distances of **7a** are somewhat shorter than in the related rhodium(I) complex $[\{\eta^5\text{-}C_5H_4(CHPh_2)\}Rh(PF_3)(PPr^i_3)]$,[6] being in agreement with the higher oxidation state of the metal in **7a**, the Rh–PPr^i_3 bond length in **7a** is slightly longer than in the PF_3 derivative. The P–Rh–Cl and Cl–Rh–Cl angles in **7a** (see Table 1) are near to 90°, which reflects the pseudo-octahedral geometry of the molecule.

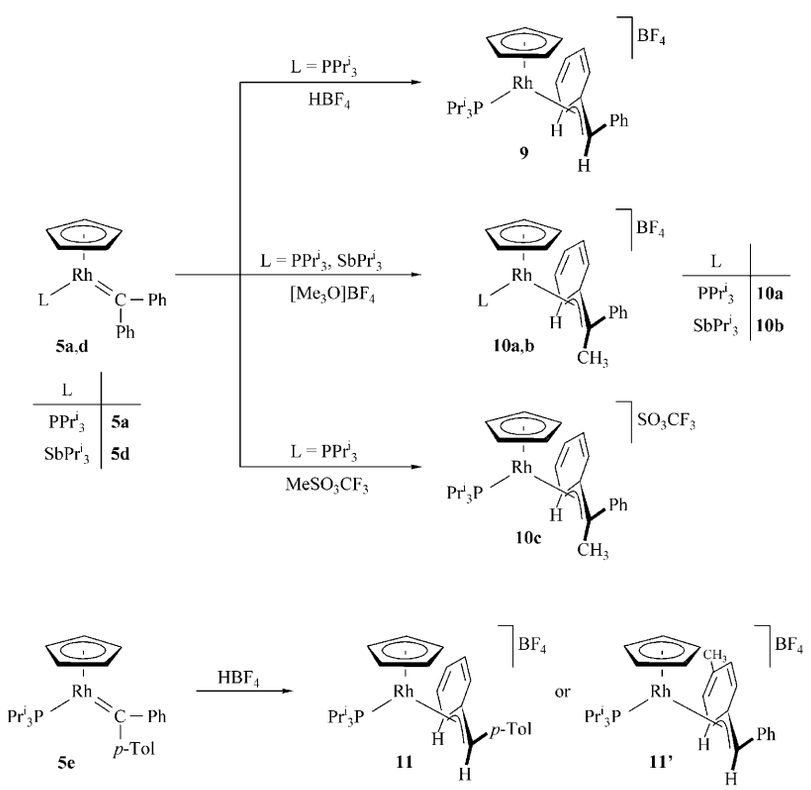
Table 1 Selected bond lengths (Å) and angles (°) for complex **7a**

Rh–P	2.328(1)	Rh–C(2)	2.167(4)
Rh–Cl(1)	2.382(1)	Rh–C(3)	2.135(4)
Rh–Cl(2)	2.400(1)	Rh–C(4)	2.237(4)
Rh–C(1)	2.155(4)	Rh–C(5)	2.226(4)
P–Rh–Cl(1)	89.79(4)	C(5)–C(6)–C(20)	111.1(4)
P–Rh–Cl(2)	95.72(4)	C(5)–C(6)–C(30)	110.2(4)
C(l)1–Rh–Cl(2)	94.30(4)	C(20)–C(6)–C(30)	115.9(4)

Formation of η^3-benzylrhodium complexes from Rh=CRR′ precursors

The diarylcarbenerhodium(I) complexes **5a** (L = PPr^i_3) and **5d** (L = $SbPr^i_3$) are also highly reactive toward acids or methylating reagents with a non- or weakly-coordinating anion. Treatment of **5a** with an equimolar amount of HBF_4 in ether results in rapid formation of a dark red precipitate **9** the elemental analysis of which corresponds to that of a 1:1 adduct of the starting material and HBF_4. Compound **9** is thermally quite stable (it decomposes at 100 °C), only slightly air-sensitive and easily soluble in CH_2Cl_2 and nitromethane. In solutions of acetone slow decomposition occurs. The proposed structure, which is shown in Scheme 5, is supported both by the ^{1}H and the ^{13}C NMR spectra. The appearance of three resonances for the ^{13}C nuclei of the carbon atoms C^1, C^2 and C^7 (for assignment see the Experimental section) at δ 96.1, 87.3 and 64.5 is consistent with an η^3-benzylic type of coordination of the $C_6H_5CHC_6H_5$ unit, quite similarly as in the trimethylphosphine complex $[(\eta^5\text{-}C_5H_5)Rh(\eta^3\text{-}C_6H_5CHCH_3)(PMe_3)]BF_4$.[8] Since the two CH protons situated *ortho* to the CHPh fragment at the partially bonded C_6H_5 ring give rise to two separated signals in the ^{1}H NMR spectrum at δ *ca.* 7.6 and 3.5, we assume that the η^3-benzylic ligand is rigid (*i.e.*, does not rotate) on the NMR timescale. The comparison of the spectroscopic data of **9** with those of the related ruthenium complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_6H_5CHC_6H_5)(PPh_3)]$[14] suggests that the *exo* isomer with the plane of the η^3-benzylic unit pointing away from the metal centre is preferred. The chemical shift of the resonance of the $C_6H_5CHC_6H_5$ proton at δ 2.09 supports this proposal.

The reactions of **5a** and **5d** with Meerwein's reagent $[Me_3O]BF_4$ take a similar course. Addition of the oxonium salt to a solution of the respective carbene complex in ether/methanol (1:1) leads to a smooth change of color from dark blue to red and, after removal of the solvent and recrystallisation of the residue from CH_2Cl_2/ether, to the isolation of red,



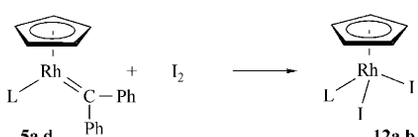
Scheme 5

moderately air-stable solids **10a**,**b** (Scheme 5) in nearly quantitative yields. Analogously to **9**, the ^{13}C NMR spectra of **10a** and **10b** exhibit three signals at, respectively, δ 100.4, 96.4, 64.5 (**10a**) and δ 100.7, 98.1, 58.1 (**10b**), supporting again the preferred *exo* configuration of the Rh{η^3-$C_6H_5C(CH_3)C_6H_5$} fragment. Moreover, the position of the resonance for the CH_3 protons of the benzylic unit at δ 1.76 with the large P–H coupling constant of 12.4 Hz in the ^1H NMR spectrum of **10a** points to an *anti* position for this methyl group.

Likewise to the reaction of **5a** with $[Me_3O]BF_4$, treatment of the same starting material with methyl triflate yields the $CF_3SO_3^-$ salt of the cation $[(\eta^5\text{-}C_5H_5)Rh\{\eta^3\text{-}C_6H_5C(CH_3)C_6H_5\}(PPr^i_3)]^+$. The spectroscopic data of the corresponding salt **10c** with $CF_3SO_3^-$ as the anion are quite similar to those of **10a** and deserve no further comment.

The protonation of carbene complex **5e** containing a carbene ligand with two different aryl groups at the carbene carbon atom proceeds analogously to that of **5a**. Owing to the ^1H and ^{13}C NMR data of the cation of **11**, it cannot be decided whether the phenyl or the *p*-tolyl unit is involved in the π-bonding. There is no doubt, however, that only *one* isomer, **11** or **11′**, is formed and that at room temperature in CD_2Cl_2 as solvent no conversion of **11** to **11′** or *vice versa* occurs.

In contrast to HI and other electrophilic substrates, iodine does not react with **5a** or **5d** by preserving the rhodium–carbon bond. Instead the carbene ligand is eliminated and the diiodorhodium(III) complexes **12a** and **12b** are formed (Scheme 6).



L	
PPr^i_3	**5a**, **12a**
$SbPr^i_3$	**5d**, **12b**

Scheme 6

The phosphine derivative **12a** was already known and had been prepared from $[(\eta^5\text{-}C_5H_5)Rh(C_2Ph_2)(PPr^i_3)]$ and iodine.[15] With regard to the formation of **12b** from **5d** and I_2, it is quite remarkable that the Rh–C and not the Rh–Sb bond is split. By taking the lability of various triisopropylstibinerhodium compounds into consideration,[1,10,16] this result has not been anticipated.

Conclusions

The work presented in this paper has shown that the reactivity of the half-sandwich-type carbenerhodium(I) complexes $[(\eta^5\text{-}C_5H_5)Rh(=CR_2)(L)]$ (R = aryl) toward Brønsted acids HX with X = Cl, Br, I and CF_3CO_2 is, as far as the initial step of the reaction is concerned, similar to that of the vinylidene counterparts $[(\eta^5\text{-}C_5H_5)Rh(=C=CHR)(L)]$ (R = alkyl, aryl).[5] The important and noteworthy difference is that, provided a bulky phosphine such as PPr^i_3 is linked as an ancillary ligand to the metal centre, the primary product formed by addition of HX to the Rh=C double bond is extremely labile and reacts to give the ring-substituted isomer $[\{\eta^5\text{-}C_5H_4(CHR_2)\}RhHX(PPr^i_3)]$. To facilitate this process, obviously the donor strength of the phosphine does not play a decisive role since the isolated PMe_3 compounds $[(\eta^5\text{-}C_5H_5)RhX(CHPh_2)(PMe_3)]$ with X = Cl and CF_3CO_2 do not rearrange to the corresponding $\{\eta^5\text{-}C_5H_4(CHPh_2)\}Rh$ derivatives.

The question whether the electrophile prefers to attack the metal centre or the carbene carbon atom remains to be answered. While on one hand the similarity between the starting materials **1**, **2**, **5a**–**e** and the related carbonyl and ethene complexes $[(\eta^5\text{-}C_5H_5)Rh(L)(PR_3)]$ (L = CO, C_2H_4) supports the proposal of a metal attack, on the other hand the structure of **3** and **4a**,**b** suggests a prefered interaction of the proton with the carbene. The composition of the products **9**, **10a**–**c** and **11**/**11′** obtained from **5a**,**d**,**e** and either HBF_4 or methylating reagents appears to favor the second possibility. With regard to the conversion of the $(\eta^5\text{-}C_5H_5)Rh$ to the $\{\eta^5\text{-}C_5H_4(CHR_2)\}Rh$ unit, we note that upon treatment of $[(\eta^5\text{-}C_5H_5)Rh(PMe_3)_2]$ with either Pr^iBr or Bu^tBr mixtures of products are formed among which the ring-substituted compounds $[(\eta^5\text{-}C_5H_4R)RhBr(PMe_3)_2]Br$ (R = Pr^i, Bu^t) are the dominating species.[17] There is some evidence (from CIDNAP measurements) that in these processes free radicals are involved.[17] The same might be true for the reaction of $[(\eta^5\text{-}C_5H_5)Rh(PPh_3)_2]$ with Pr^iI which leads to $[(\eta^5\text{-}C_5H_4Pr^i)Rh(PPh_3)I_2]$.[18] It should also be mentioned that recent investigations by Maitlis and coworkers have shown that besides the transformation of $(\eta^5\text{-}C_5H_5)Rh$ to $(\eta^5\text{-}C_5H_4R)Rh$ species the conversion of $(\eta^5\text{-}C_5Me_5)Rh$ to $(\eta^5\text{-}C_5Me_4R')Rh$ complexes (where R′ is a functionalized alkyl) is also possible, in this case an acid–base-type interaction being the important step.[19]

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**,[16] **2**[16] and **5a**–**e**[1,16] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, and IR spectra on a Perkin-Elmer 1420 or an IFS 25 FT-IR infrared spectrometer. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; sept, septet; m, multiplet; br, broadened signal; coupling constants *J* in Hz.

Preparations

$[(\eta^5\text{-}C_5H_5)RhCl(CHPh_2)(CO)]$ 3. A solution of compound **1** (68 mg, 0.19 mmol) in pentane (10 cm^3) was treated dropwise with a 0.5 M solution of HCl in benzene (375 μL, 0.19 mmol) and stirred for 30 min at room temperature. The solvent was removed *in vacuo*, and the oily residue was dissolved in ether (3 cm^3). With pentane (2 cm^3) a red solid was precipitated, which was separated from the mother liquor, washed several times with 3 cm^3 portions of pentane and dried: yield 58 mg (78%); mp 98 °C (decomp.) (Found: C, 57.61; H, 4.31. $C_{19}H_{16}ClORh$ requires: C, 57.24; H, 4.05%). IR (KBr): ν(CO) 1975 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.65 (4 H, m, *ortho*-H of C_6H_5), 7.36 (2 H, m, *para*-H of C_6H_5), 6.99 (4 H, m, *meta*-H of C_6H_5), 5.61 [1 H, d, *J*(Rh,H) 3.7, C*H*Ph_2], 4.80 [5 H, d, *J*(Rh,H) 0.7, C_5H_5]. EI MS (70 eV): *m*/*z* 399 (M^+, 0.2), 362 (M^+ − HCl, 0.5), 335 ($C_5H_5RhCHPh_2^+$, 0.6), 196 ($C_5H_5RhCO^+$, 0.9), 168 ($RhC_5H_5^+$, 16.0), 167 ($CHPh_2^+$, 100.0%).

$[(\eta^5\text{-}C_5H_5)RhCl(CHPh_2)(PMe_3)]$ 4a. A solution of compound **2** (63 mg, 0.15 mmol) in pentane (10 cm^3) was treated dropwise with a 0.5 M solution of HCl in benzene (300 μL, 0.15 mmol). In the time of mixing, a change of color from violet to red occurred. The solvent was removed *in vacuo*, and the oily residue was dissolved in ether (3 cm^3). With pentane (2 cm^3) a red solid was precipitated, which was separated from the mother liquor, washed several times with 3 cm^3 portions of pentane and dried: yield 58 mg (87%); mp 64 °C (decomp.) (Found: C, 56.13; H, 5.69. $C_{21}H_{25}ClPRh$ requires C, 56.47; H, 5.64%). NMR (C_6D_6): δ_H (200 MHz) 8.01 (4 H, m, *ortho*-H of C_6H_5), 7.10 (2 H, m, *para*-H of C_6H_5), 6.98 (4 H, m, *meta*-H of C_6H_5), 5.34 [1 H, dd, *J*(Rh,H) = *J*(P,H) 3.5, C*H*Ph_2], 4.59 (5 H, br s, C_5H_5), 0.89 [9 H, d, *J*(P,H) 10.7, PCH_3]; δ_C (50.3 MHz) 156.1, 149.8 (both s, *ipso*-C of C_6H_5), 131.9, 129.3, 127.1, 126.7, 124.9, 123.8 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 90.3 [dd, *J*(Rh,C) = *J*(P,C) 3.6, C_5H_5], 42.4 [dd, *J*(Rh,C) 19.7, *J*(P,C) 10.1, *C*HPh_2], 16.6 [d, *J*(P,C) 32.4, PCH_3]; δ_P (81.0 MHz) 9.4

[d, J(Rh,P) 154.5]. EI MS (70 eV): *m/z* 447 (M^+, 0.3), 411 ($M^+ - Cl$, 0.2), 410 ($M^+ - HCl$, 1.8), 244 ($C_5H_5RhPMe_3^+$, 6.4), 168 ($RhC_5H_5^+$, 98.0), 167 ($CHPh_2^+$, 100.0%).

[(η⁵-C_5H_5)Rh(O_2CCF_3)($CHPh_2$)(PMe_3)] 4b. A solution of compound **2** (75 mg, 0.18 mmol) in pentane (10 cm^3) was treated at −78 °C with a solution of CF_3CO_2H (14 μL, 0.18 mmol) in pentane (3 cm^3). In the time of mixing, a change of color from violet to red and the precipitation of a solid occurred. On warming to room temperature the reaction mixture was stirred for 5 min. The solvent was removed *in vacuo*, the orange-red solid was washed several times with 3 cm^3 portions of pentane and dried: yield 86 mg (91%); mp 90 °C (decomp.) (Found: C, 52.83; H, 4.70. $C_{23}H_{25}F_3PO_2Rh$ requires: C, 52.69; H, 4.81%). IR (KBr): ν(C=O) 1679 cm^{-1}. NMR (C_6D_6) δ_H (400 MHz) 7.61 (4 H, m, *ortho*-H of C_6H_5), 7.11 (2 H, m, *para*-H of C_6H_5), 6.93 (4 H, m, *meta*-H of C_6H_5), 4.79 [1 H, dd, J(Rh,H) = J(P,H) 2.9, C*H*Ph_2], 4.66 [5 H, d, J(Rh,H) 0.9, C_5H_5], 0.69 [9 H, d, J(P,H) 11.2, PCH_3]; δ_C (100.6 MHz) 163.1 [q, J(F,C) 35.6, O_2CCF_3], 155.0, 149.1 (both s, *ipso*-C of C_6H_5), 131.3, 129.2, 128.7, 126.3, 125.1, 124.4 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 126.3 [q, J(F,C) = 261.7, O_2CCF_3], 90.1 [dd, J(Rh,C) = J(P,C) 3.7, C_5H_5], 47.0 [dd, J(Rh,C) 21.5, J(P,C) 9.1, *C*HPh_2], 15.9 [d, J(P,C) 30.5, PCH_3]; δ_F (376.5 MHz) −78.2 (s); δ_P (162.0 MHz) 10.5 [d, J(Rh,P) 159.0]. EI MS (70 eV): *m/z* 524 (M^+, 3.2), 411 ($M^+ - O_2CCF_3$, 3.0), 244 ($C_5H_5RhPMe_3^+$, 0.3), 168 ($RhC_5H_5^+$, 99.0), 167 ($CHPh_2^+$, 100.0%).

[{η⁵-C_5H_4($CHPh_2$)}RhHCl(PPr^i_3)] 6a. *Method A.* A solution of compound **5a** (119 mg, 0.24 mmol) in acetone (5 cm^3) was treated with a 0.5 M solution of HCl in benzene (481 μL, 0.24 mmol). In the time of mixing, a change of color from deep blue to orange occurred. The reaction mixture was concentrated to *ca*. 0.5 cm^3 *in vacuo* and an orange solid was precipitated with pentane. This was separated from the mother liquor, washed twice with 5 cm^3 portions of pentane and dried; yield 116 mg (91%).

Method B. As described in Method A, compound **6a** was prepared from **5a** (119 mg, 0.24 mmol) and Me_3SiCl (30 μL, 0.24 mmol) in acetone (5 cm^3), which contained traces of water; yield 114 mg (90%).

Method C. A suspension of compound **8** (72 mg, 0.10 mmol) in pentane (5 cm^3) was treated with a solution of $C_5H_5(CHPh_2)$ in pentane (2 cm^3) at room temperature. Within 10 min, a change of color from red-violet to orange occurred. The reaction mixture was concentrated to *ca*. 2 cm^3 *in vacuo*, and the solution was separated from the precipitate at 0 °C. The orange solid was washed with pentane (2 cm^3) and dried; yield 49 mg (92%); mp 56 °C (decomp.) (Found: C, 61.20; H, 7.28. $C_{27}H_{37}ClPRh$ requires: C, 61.08; H, 7.02%). IR (Nujol): ν(RhH) 2019 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.53 (4 H, m, *ortho*-H of C_6H_5), 7.20–7.03 (6 H, m, *meta*- and *para*-H of C_6H_5), 5.72 [1 H, d, J(Rh,H) 2.9, C*H*Ph_2], 5.12, 5.06, 4.43 [1 H each, all br s, $C_5H_4(CHPh_2)$], 4.38 [1 H, d, J(Rh,H) 1.3, $C_5H_4(CHPh_2)$], 2.01 (3 H, m, PC*H*CH_3), 0.98 [9 H, dd, J(P,H) 14.6, J(H,H) 7.1, PCHC*H*$_3$], 0.96 [9 H, dd, J(P,H) 14.0, J(H,H) 7.1, PCHC*H*$_3$], −12.21 [1 H, dd, J(Rh,H) 35.1, J(P,H) 13.8, RhH]; δ_C (100.6 MHz) 143.6, 143.5 (both s, *ipso*-C of C_6H_5), 130.3, 130.1, 128.6, 128.5, 126.7, 126.6 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 124.5 [dd, J(Rh,C) 5.0, J(P,C) 3.0, *ipso*-C of $C_5H_4(CHPh_2)$], 92.7 [s, $C_5H_4(CHPh_2)$], 85.9 [dd, J(Rh,C) 8.9, J(P,C) 3.6, $C_5H_4(CHPh_2)$], 81.0 [d, J(Rh,C) = 5.8, $C_5H_4(CHPh_2)$], 75.4 [d, J(Rh,C) 6.4, $C_5H_4(CHPh_2)$], 48.9 (s, *C*HPh_2), 26.7 [d, J(P,C) 24.8, P*C*HCH_3], 20.0, 19.6 (both s, PCH*C*H_3); δ_P (162.0 MHz) 81.7 [d, J(Rh,P) 145.0].

[{η⁵-C_5H_4($CHPh_2$)}RhHBr(PPr^i_3)] 6b. This compound was prepared as described for **6a** from **5a** (38 mg, 0.08 mmol) and Me_3SiBr (10 μL, 0.08 mmol) in acetone, which contained traces of water. Orange solid: yield 39 mg (88%); mp 54 °C (decomp.) (Found: C, 56.01; H, 6.27. $C_{27}H_{37}BrPRh$ requires: C, 56.36; H, 6.48%). IR (Nujol): ν(RhH) 2018 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 7.51 (4 H, m, *ortho*-H of C_6H_5), 7.21–7.02 (6 H, m, *meta*- and *para*-H of C_6H_5), 5.96 [1 H, d, J(Rh,H) 2.4, C*H*Ph_2], 5.17, 5.04, 4.55, 4.39 [1 H each, all br s, $C_5H_4(CHPh_2)$], 2.01 (3 H, m, PC*H*CH_3), 0.96 [9 H, dd, J(P,H) 15.5, J(H,H) 7.2, PCHC*H*$_3$], 0.95 [9 H, dd, J(P,H) 15.1, J(H,H) 7.0, PCHC*H*$_3$], −12.50 [1 H, dd, J(Rh,H) 35.7, J(P,H) 13.4, RhH]; δ_C (50.3 MHz) 143.9 (s, *ipso*-C of C_6H_5), 143.7 [d, J(Rh,C) 1.9, *ipso*-C of C_6H_5], 130.2, 130.0, 128.8, 128.3, 127.8, 126.6 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 122.6 [dd, J(Rh,C) 4.6, J(P,C) 1.8, *ipso*-C of $C_5H_4(CHPh_2)$], 93.4 [br s, $C_5H_4(CHPh_2)$], 86.0 [dd, J(Rh,C) 8.3, J(P,C) 3.7, $C_5H_4(CHPh_2)$], 81.1, 77.9 [both d, J(Rh,C) 5.5, $C_5H_4(CHPh_2)$], 49.2 (s, *C*HPh_2), 27.3 [d, J(P,C) 25.0, P*C*HCH_3], 20.1, 19.8 (both s, PCH*C*H_3); δ_P (81.0 MHz) 81.7 [d, J(Rh,P) 145.6].

[{η⁵-C_5H_4($CHPh_2$)}RhHI(PPr^i_3)] 6c. A solution of compound **5a** (56 mg, 0.11 mmol) in acetone (10 cm^3) was treated with a 7.6 M solution of HI in water (15 μL, 0.11 mmol). In the time of mixing, a change of color from deep blue to red-brown occurred. The reaction mixture was concentrated to *ca*. 5 cm^3 *in vacuo* and then stored at −78 °C for 3 d. An orange-brown solid was formed, which was separated from the mother liquor, washed twice with 5 cm^3 portions of pentane and dried: yield 59 mg (84%); mp 80 °C (decomp.) (Found: C, 51.98; H, 5.83. $C_{27}H_{37}IPRh$ requires: C, 52.11; H, 5.99%). IR (Nujol): ν(RhH) 2019 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 7.47 (4 H, m, *ortho*-H of C_6H_5), 7.19–7.02 (6 H, m, *meta*- and *para*-H of C_6H_5), 6.16 (1 H, br s, C*H*Ph_2), 5.25, 4.96, 4.81, 4.53 [1 H each, all br s, $C_5H_4(CHPh_2)$], 1.97 (3 H, m, PC*H*CH_3), 0.97 [9 H, dd, J(P,H) 13.5, J(H,H) 6.1, PCHC*H*$_3$], 0.82 [9 H, dd, J(P,H) 14.7, J(H,H) 7.1, PCHC*H*$_3$], −12.99 [1 H, dd, J(Rh,H) 33.7, J(P,H) 12.2, RhH]; δ_C (100.6 MHz) 144.6, 143.9 (both s, *ipso*-C of C_6H_5), 130.0, 129.8, 128.6, 128.5, 126.7, 126.6 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 119.4 [dd, J(Rh,C) = J(P,C) 3.6, *ipso*-C of $C_5H_4(CHPh_2)$], 94.3 [br s, $C_5H_4(CHPh_2)$], 85.6 [dd, J(Rh,C) 7.1, J(P,C) 4.1, $C_5H_4(CHPh_2)$], 82.6 [d, J(Rh,C) 5.1, $C_5H_4(CHPh_2)$], 81.8 [d, J(Rh,C) 5.1, $C_5H_4(CHPh_2)$], 50.1 (s, *C*HPh_2), 28.2 [d, J(P,C) 24.4, P*C*HCH_3], 20.3, 20.2 (both s, PCH*C*H_3); δ_P (81.0 MHz) 81.9 [d, J(Rh,P) 146.9].

[{η⁵-C_5H_4($CHPh_2$)}RhH(O_2CCF_3)(PPr^i_3)] 6d. This compound was prepared as described for **6c** from **5a** (54 mg, 0.11 mmol) and CF_3CO_2H (8 μL, 0.11 mmol) in acetone (10 cm^3). Light orange solid: yield 62 mg (93%); mp 40 °C (decomp.) (Found: C, 56.93; H, 5.89. $C_{29}H_{37}F_3O_2PRh$ requires: C, 57.24; H, 6.13%). IR (Nujol): ν(RhH) 2018 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 7.35 (4 H, m, *ortho*-H of C_6H_5), 7.20–7.00 (6 H, m, *meta*- and *para*-H of C_6H_5), 5.41 [2 H, br s, C*H*Ph_2 and $C_5H_4(CHPh_2)$], 5.02, 4.60, 4.18 [1 H each, all br s, C_5H_4-$(CHPh_2)$], 1.74 (3 H, m, PC*H*CH_3), 0.94 [9 H, dd, J(P,H) 14.8, J(H,H) 6.9, PCHC*H*$_3$], 0.81 [9 H, dd, J(P,H) 14.3, J(H,H) 6.9, PCHC*H*$_3$], −11.04 [1 H, dd, J(Rh,H) 35.5, J(P,H) 13.4, RhH]; δ_C (50.3 MHz) 163.0 [q, J(F,C) 34.2, CO_2CF_3], 143.6, 143.3 (both s, *ipso*-C of C_6H_5), 129.6, 128.7, 128.6, 128.3, 126.8, 126.7 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 123.8 [dd, J(Rh,C) = J(P,C) 3.2, *ipso*-C of $C_5H_4(CHPh_2)$], 115.8 [q, J(F,C) 292.2, CO_2CF_3], 94.2 [br s, $C_5H_4(CHPh_2)$], 81.0 [dd, J(Rh,C) 7.4, J(P,C) 4.6, $C_5H_4(CHPh_2)$], 80.1 [d, J(Rh,C) 6.5, $C_5H_4(CHPh_2)$], 76.2 [d, J(Rh,C) 5.6, $C_5H_4(CHPh_2)$], 49.9 (s, *C*HPh_2), 25.7 [d, J(P,C) 24.0, P*C*HCH_3], 19.5, 19.2 (both s, PCH*C*H_3); δ_F (188.3 MHz) −73.6 (s); δ_P (81.0 MHz) 80.5 [d, J(Rh,P) 144.1].

[{η⁵-C_5H_4CH(*p*-Tol)$_2$}RhHCl(PPr^i_3)] 6e. This compound was prepared as described for **6a** from **5b** (61 mg, 0.12 mmol) and Me_3SiCl (15 μL, 0.12 mmol) in acetone (10 cm^3), which contained traces of water. Orange solid: yield 56 mg (86%); mp 46 °C (decomp.) (Found: C, 62.01; H, 7.18. $C_{29}H_{41}ClPRh$ requires: C, 62.31; H, 7.39%). IR (Nujol): ν(RhH) 2018 cm^{-1}.

NMR (C_6D_6): δ_H (400 MHz) 7.47 (4 H, m, *ortho*-H of $C_6H_4CH_3$), 7.00 (4 H, m, *meta*-H of $C_6H_4CH_3$), 5.69 [1 H, d, *J*(Rh,H) 2.4, C*H*(*p*-Tol)$_2$], 5.20, 5.13 (1 H each, both br s, $C_5H_4CH(p\text{-Tol})_2$), 4.44 [2 H, br s, $C_5H_4CH(p\text{-Tol})_2$], 2.12, 2.09 (3 H each, both s, $C_6H_4CH_3$), 2.04 (3 H, m, PC*H*CH$_3$), 1.00, 0.98 [9 H each, both dd, *J*(P,H) 14.1, *J*(H,H) 7.0, PCHC*H*$_3$], −12.21 [1 H, dd, *J*(Rh,H) 35.2, *J*(P,H) 14.1, RhH]; δ_C (100.6 MHz) 141.0 (s, *ipso*-C of $C_6H_4CH_3$), 140.9 [d, *J*(Rh,C) 1.9, *ipso*-C of $C_6H_4CH_3$), 135.8, 135.7 (both s, *para*-C of $C_6H_4CH_3$), 130.1, 130.0, 129.3, 129.2 (all s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 124.8 [dd, *J*(Rh,C) 4.8, *J*(P,C) 2.4, *ipso*-C of $C_5H_4CH(p\text{-Tol})_2$], 92.7 [br s, $C_5H_4CH(p\text{-Tol})_2$], 85.9 [dd, *J*(Rh,C) 8.6, *J*(P,C) 3.8, $C_5H_4CH(p\text{-Tol})_2$], 81.5 [d, *J*(Rh,C) 5.7, $C_5H_4CH(p\text{-Tol})_2$], 75.0 [d, *J*(Rh,C) 6.7, $C_5H_4CH(p\text{-Tol})_2$], 48.1 [s, *C*H(*p*-Tol)$_2$], 26.7 [d, *J*(P,C) 23.8, P*C*HCH$_3$], 21.1, 21.0 (both s, $C_6H_4CH_3$), 20.1, 19.7 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 81.7 [d, *J*(Rh,P) 145.8].

[{η^5-C$_5$H$_4$(CHPh$_2$)}RhCl$_2$(PPr$^i_3$)] 7a. A solution of compound **5a** (112 mg, 0.23 mmol) in acetone (5 cm^3), which contained traces of water, was treated with Me_3SiCl (57 μL, 0.45 mmol). In the time of mixing, a change of color from deep blue to red occurred. The reaction mixture was stirred for 1 h at room temperature and concentrated to *ca*. 2 cm^3 *in vacuo*. After the solution had been stored at −78 °C for 24 h, deep red crystals were formed, which were separated from the mother liquor, washed with a small quantity of acetone (0 °C) and dried: yield 120 mg (94%); mp 224 °C (Found: C, 57.04; H, 6.34. $C_{27}H_{36}Cl_2PRh$ requires: C, 57.36; H, 6.42%). NMR (C_6D_6): δ_H (400 MHz) 7.42 (4 H, m, *ortho*-H of C_6H_5), 7.18–7.02 (6 H, m, *meta*- and *para*-H of C_6H_5), 6.03 [1 H, d, *J*(Rh,H) 6.6, C*H*Ph$_2$], 4.84, 4.65 [2 H each, both d, *J*(Rh,H) 2.0, $C_5H_4(CHPh_2)$], 2.51 (3 H, m, PC*H*CH$_3$), 1.06 [18 H, dd, *J*(P,H) 14.2, *J*(H,H) 7.0, PCHC*H*$_3$]; δ_C (100.6 MHz) 141.7 (s, *ipso*-C of C_6H_5), 130.3, 128.9, 128.3, 127.2 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 123.1 [br s, *ipso*-C of $C_5H_4(CHPh_2)$], 89.8, 79.7 [both br s, $C_5H_4(CHPh_2)$], 47.7 (br s, *C*HPh$_2$), 26.9 [d, *J*(P,C) 21.7, P*C*HCH$_3$)], 20.1 (s, PCH*C*H$_3$); δ_P (162.0 MHz) 59.4 [d, *J*(Rh,P) 135.1].

[{η^5-C$_5$H$_4$(CHPh$_2$)}RhBr$_2$(PPr$^i_3$)] 7b. This compound was prepared as described for **7a** from **5a** (53 mg, 0.11 mmol) and Me_3SiBr (28 μL, 0.21 mmol) in acetone (5 cm^3), which contained traces of water. Red crystals: yield 60 mg (86%); mp 204 °C (Found: C, 49.74; H, 5.43; Rh, 16.00. $C_{27}H_{36}Br_2PRh$ requires: C, 49.57; H, 5.55; Rh, 15.73%). NMR (CD_2Cl_2): δ_H (200 MHz) 7.38–7.22 (10 H, m, *ortho*-, *meta*- and *para*-H of C_6H_5), 5.93 [1 H, d, *J*(Rh,H) 5.6, C*H*Ph$_2$], 5.40, 5.08 [2 H each, both br s, $C_5H_4(CHPh_2)$], 2.79 (3 H, m, PC*H*CH$_3$), 1.32 [18 H, dd, *J*(P,H) 14.3, *J*(H,H) 7.2, PCHC*H*$_3$]; δ_C (50.3 MHz) 141.7 (s, *ipso*-C of C_6H_5), 129.6, 128.7, 127.1 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 121.6 [dd, *J*(Rh,C) 8.4, *J*(P,C) 3.5, *ipso*-C of $C_5H_4(CHPh_2)$], 90.6 [d, *J*(Rh,C) 2.6, $C_5H_4(CHPh_2)$], 80.6 [d, *J*(Rh,C) 7.4, $C_5H_4(CHPh_2)$], 48.0 (s, *C*HPh$_2$), 28.0 [d, *J*(P,C) 22.2, P*C*HCH$_3$)], 20.4 (s, PCH*C*H$_3$); δ_P (81.0 MHz) 57.8 [d, *J*(Rh,P) 134.8]. MS (FAB): *m*/*z* 652 (M$^+$, 1.3), 573 (M$^+$ − Br, 100.0%).

[{η^5-C$_5$H$_4$(CHPh$_2$)}RhI$_2$(PPr$^i_3$)] 7c. A solution of compound **5a** (72 mg, 0.15 mmol) in acetone (10 cm^3) was treated with a 7.6 M solution of HI in water (38 μL, 0.30 mmol). In the time of mixing, a change of color from deep blue to brown occurred. The reaction mixture was stirred for 1 h at room temperature and then concentrated to *ca*. 5 cm^3 *in vacuo*. After the solution had been stored at −78 °C for 3 d, a deep brown solid was formed, which was separated from the mother liquor, washed twice with 5 cm^3 portions of pentane and dried: yield 84 mg (77%); mp 160 °C (decomp.) (Found: C, 43.19; H, 4.79. $C_{27}H_{36}I_2PRh$ requires: C, 43.33; H, 4.84%). NMR (CD_2Cl_2): δ_H (400 MHz) 7.40–7.25 (10 H, m, *ortho*-, *meta*- and *para*-H of C_6H_5), 6.34 [1 H, d, *J*(Rh,H) 6.2, C*H*Ph$_2$], 5.76 [1 H, d, *J*(Rh,H) 1.8, $C_5H_4(CHPh_2)$], 5.48 [1 H, dd, *J*(Rh,H) = *J*(H,H) 1.8, $C_5H_4(CHPh_2)$], 5.36 [1 H, ddd, *J*(Rh,H) = *J*(H,H) = *J*(P,H) 1.8, $C_5H_4(CHPh_2)$], 5.33 [1 H, br s, $C_5H_4(CHPh_2)$], 2.83 (3 H, m, PC*H*CH$_3$), 1.33 [18 H, dd, *J*(P,H) 14.4, *J*(H,H) 7.0, PCHC*H*$_3$]; δ_C (100.6 MHz) 142.5 [d, *J*(Rh,C) 2.0, *ipso*-C of C_6H_5), 129.7, 128.9, 127.3 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 118.4 [dd, *J*(Rh,C) 9.2, *J*(P,C) 3.1, *ipso*-C of $C_5H_4(CHPh_2)$], 93.1 [dd, *J*(Rh,C) 4.3, *J*(P,C) 1.8, $C_5H_4(CHPh_2)$], 89.0 [dd, *J*(Rh,C) 5.1, *J*(P,C) 2.0, $C_5H_4(CHPh_2)$], 81.3 [d, *J*(Rh,C) 7.1, $C_5H_4(CHPh_2)$], 49.6 [d, *J*(Rh,C) 2.0, *C*HPh$_2$], 30.1 [d, *J*(P,C) 22.4, P*C*HCH$_3$)], 21.2 [d, *J*(P,C) 2.0, PCH*C*H$_3$]; δ_P (162.0 MHz) 57.1 [d, *J*(Rh,P) 139.0].

[{η^5-C$_5$H$_4$(CHPh$_2$)}Rh(CF$_3$CO$_2$)$_2$(PPr$^i_3$)] 7d. This compound was prepared as decribed for **7c** from **5a** (81 mg, 0.16 mmol) and CF_3CO_2H (25 μL, 0.33 mmol) in acetone (10 cm^3). Orange solid: yield 103 mg (87%); mp 113 °C (decomp.) (Found: C, 51.71; H, 5.11. $C_{31}H_{36}F_6O_4PRh$ requires: C, 51.68; H, 5.04%). NMR (CD_2Cl_2): δ_H (400 MHz) 7.35–7.16 (10 H, m, *ortho*-, *meta*- and *para*-H of C_6H_5), 5.95 [2 H, ddd, *J*(Rh,H) = *J*(H,H) = *J*(P,H) 2.0, $C_5H_4(CHPh_2)$], 5.59 [1 H, dd, *J*(Rh,H) = *J*(H,H) 1.8, $C_5H_4(CHPh_2)$], 5.33 [1 H, s, $C_5H_4(CHPh_2)$], 5.05 [1 H, d, *J*(Rh,H) 4.7, C*H*Ph$_2$], 2.49 (3 H, m, PC*H*CH$_3$), 1.25 [18 H, dd, *J*(P,H) 14.7, *J*(H,H) 7.3, PCHC*H*$_3$]; δ_C (100.6 MHz) 163.0 [q, *J*(F,C) 35.6, *C*O$_2$CF$_3$], 140.3 (s, *ipso*-C of C_6H_5), 129.2, 129.1, 127.6 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 122.3 [dd, *J*(Rh,C) 8.1, *J*(P,C) 4.1, *ipso*-C of $C_5H_4(CHPh_2)$], 115.4 [q, *J*(F,C) 289.9, CO$_2$*C*F$_3$], 87.9 [dd, *J*(Rh,C) 6.1, *J*(P,C) 2.0, $C_5H_4(CHPh_2)$], 76.6 [d, *J*(Rh,C) 9.2, $C_5H_4(CHPh_2)$], 48.9 [d, *J*(Rh,C) 2.0, *C*HPh$_2$], 25.8 [d, *J*(P,C) 20.3, P*C*HCH$_3$)], 19.4 [d, *J*(P,C) 2.0, PCH*C*H$_3$); δ_F (376.5 MHz) −74.3 (s); δ_P (162.0 MHz) 62.4 [d, *J*(Rh,P) 130.6].

[{η^5-C$_5$H$_4$CH(*p*-Tol)$_2$}RhCl$_2$(PPr$^i_3$)] 7e. This compound was prepared as described for **7a** from **5b** (65 mg, 0.12 mmol) and Me_3SiCl (31 μL, 0.25 mmol) in acetone (5 cm^3), which contained traces of water. Red crystals: yield 61 mg (83%); mp 81 °C (Found: C, 58.84; H, 6.95. $C_{29}H_{40}Cl_2PRh$ requires: C, 58.70; H, 6.79%). NMR ($CDCl_3$): δ_H (400 MHz) 7.15 (4 H, m, *ortho*-H of $C_6H_4CH_3$), 7.03 (4 H, m, *meta*-H of $C_6H_4CH_3$), 5.48 [1 H, d, *J*(Rh,H) 5.0, C*H*(*p*-Tol)$_2$], 5.29 [2 H, dd, *J*(Rh,H) = *J*(H,H) 1.9, $C_5H_4CH(p\text{-Tol})_2$], 4.96 [2 H, ddd, *J*(Rh,H) = *J*(H,H) = *J*(P,H) 1.9, $C_5H_4CH(p\text{-Tol})_2$], 2.74 (3 H, m, PC*H*CH$_3$), 2.23 (6 H, s, $C_6H_4CH_3$), 1.26 [18 H, dd, *J*(P,H) 14.2, *J*(H,H) 7.2, PCHC*H*$_3$]; δ_C (100.6 MHz) 138.1 (s, *ipso*-C of $C_6H_4CH_3$), 136.3 (s, *para*-C of $C_6H_4CH_3$), 129.3, 129.2 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 125.2 [dd, *J*(Rh,C) 7.2, *J*(P,C) 3.3, *ipso*-C of $C_5H_4CH(p\text{-Tol})_2$], 88.1 [dd, *J*(Rh,C) 5.5, *J*(P,C) 3.1, $C_5H_4CH(p\text{-Tol})_2$], 80.3 [d, *J*(Rh,C) 7.6, $C_5H_4CH(p\text{-Tol})_2$], 46.6 [d, *J*(Rh,C) 1.9, *C*H(*p*-Tol)$_2$], 26.7 [d, *J*(P,C) 21.9, P*C*HCH$_3$], 20.9 (s, $C_6H_4CH_3$), 20.0 [d, *J*(P,C) 1.9, PCH*C*H$_3$]; δ_P (162.0 MHz) 59.1 [d, *J*(Rh,P) 132.2].

[{η^5-C$_5$H$_4$(CHPh$_2$)}RhCl$_2$(PPh$_3$)] 7f. This compound was prepared as described for **7a** from **5c** (54 mg, 0.09 mmol) and Me_3SiCl (23 μL, 0.18 mmol) in acetone (5 cm^3), which contained traces of water. Orange-red solid: yield 55 mg (91%); mp 88 °C (Found: C, 64.69; H, 4.49. $C_{36}H_{30}Cl_2PRh$ requires: C, 64.79; H, 4.53%). NMR (C_6D_6): δ_H (200 MHz) 7.85 (6 H, m, *ortho*-H of C_6H_5P), 7.40 (4 H, m, *ortho*-H of C_6H_5), 7.18–6.93 (15 H, m, *meta*- and *para*-H of C_6H_5P and C_6H_5), 6.17 [1 H, d, *J*(Rh,H) 5.8, C*H*Ph$_2$], 4.84 [2 H, d, *J*(Rh,H) 1.8, $C_5H_4(CHPh_2)$], 4.12 [2 H, br s, $C_5H_4(CHPh_2)$]; δ_P (81.0 MHz) 36.0 [d, *J*(Rh,P) 137.3].

[{η^5-C$_5$D$_4$(CHPh$_2$)}RhDCl(PPr$^i_3$)] 6a-d$_5$. This compound was prepared as described for **6a** (Method A) from **5a**-d$_5$ (54 mg, 0.11 mmol) and a 0.5 M solution of HCl in benzene (216 μL, 0.11 mmol). Orange solid: yield 51 mg (88%). NMR (C_6D_6):

δ_H (200 MHz) 7.52 (4 H, m, *ortho*-H of C_6H_5), 7.19–6.99 (6 H, m, *meta*- and *para*-H of C_6H_5), 5.74 [1 H, d, *J*(Rh,H) 2.9, C*H*Ph_2], 2.00 (3 H, m, PC*H*CH_3), 0.97, 0.95 [9 H each, both dd, *J*(P,H) 14.5, *J*(H,H) 7.3, PCHC*H*$_3$]; δ_P (81.0 MHz) 82.2 [dt, *J*(Rh,P) 145.3, *J*(P,^{2}H) 5.1].

[{η^5-C_5D_4(CHPh$_2$)}RhCl$_2$(PPr$^i_3$)] 7a-d$_4$. This compound was prepared as described for **7a** from **5a**-d$_5$ (57 mg, 0.11 mmol) and a 0.5 M solution of HCl in benzene (449 μL, 0.22 mmol). Red solid: yield 60 mg (92%). NMR (C_6D_6): δ_H (200 MHz) 7.42 (4 H, m, *ortho*-H of C_6H_5), 7.21–7.02 (6 H, m, *meta*- and *para*-H of C_6H_5), 6.08 [1 H, d, *J*(Rh,H) = 5.5, C*H*Ph_2], 2.47 (3 H, m, PC*H*CH_3), 1.03 [18 H, dd, *J*(P,H) 14.1, *J*(H,H) 7.0, PCHC*H*$_3$]; δ_P (81.0 MHz) 59.9 [d, *J*(Rh,P) 133.3].

[(η^5-C_5H_5)Rh(η^3-C_6H_5CHPh)(PPr$^i_3$)]BF$_4$ 9. A solution of **5a** (66 mg, 0.13 mmol) in ether (10 cm^3) was treated with a 54% solution of HBF_4 in ether (18 μL, 0.13 mmol). In the time of mixing, a change of color from deep blue to red occurred and a deep red solid precipitated. The solid was separated from the mother liquor and dissolved at −20 °C in CH_2Cl_2 (2 cm^3). Addition of ether (10 cm^3) led to the formation of a deep red microcrystalline solid, which was separated from the mother liquor, washed with small quantities of ether and dried: yield 75 mg (97%); mp 100 °C (decomp.) (Found: C, 55.63; H, 6.36. $C_{27}H_{37}BF_4PRh$ requires: C, 55.69; H, 6.40%). NMR: δ_H (CD_3NO_2, 200 MHz) 7.86–7.38 (9 H, m, C_6H_5), 5.00 [5 H, dd, *J*(Rh,H) = *J*(P,H) 0.8, C_5H_5], 3.53 [1 H, br d, *J*(P,H) 9.6, H^2],[20] 2.54 [3 H, sept, *J*(H,H) 7.1, PC*H*CH_3], 2.09 (1 H, br s, H^7), 1.47 [18 H, dd, *J*(P,H) 13.9, *J*(H,H) 7.1, PCHC*H*$_3$]; δ_C (CD_3OD, 100.6 MHz) 144.5 (s, *ipso*-C of C_6H_5), 130.2, 130.0, 129.9, 129.7, 129.6, 128.4, 128.0 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5 and C$^{3–6}$), 96.1 (s, C^1), 93.9 [dd, *J*(Rh,C) 4.8, *J*(P,C) 1.9, C_5H_5], 87.3 [dd, *J*(Rh,C) 4.8, *J*(P,C) 1.9, C^7], 64.5 [dd, *J*(Rh,C) 11.4, *J*(P,C) 4.8, C^2], 20.5 [d, *J*(P,C) 35.2, P*C*HCH_3], 19.9 [d, *J*(P,C) 4.8, PCH*C*H$_3$]; δ_F (CD_3NO_2, 188.3 MHz) −155.2 (s); δ_P (CD_3NO_2, 81.0 MHz) 54.1 [d, *J*(Rh,P) 154.5]. MS (FAB): *m*/*z* 495 (M$^+$, 100.0), 335 (M$^+$ − PPr$^i_3$, 55.1), 328 (M$^+$ − C_6H_5CHPh, 57.9), 167 (C_6H_5CHPh$^+$, 19.3%).

[(η^5-C_5H_5)Rh{η^3-C_6H_5C(CH$_3$)Ph}(PPr$^i_3$)]BF$_4$ 10a. A solution of **5a** (76 mg, 0.15 mmol) in ether/methanol (1 : 1, 10 cm^3) was treated with Meerwein's salt [Me$_3$O]BF$_4$ (23 mg, 0.15 mmol) and stirred for 10 min at room temperature. A change of color from deep blue to red occurred. The solvent was removed *in vacuo*, and the residue was dissolved at −20 °C in CH_2Cl_2 (2 cm^3). Addition of ether led to the precipitation of a deep red solid, which was separated from the mother liquor, washed with small quantities of ether and dried: yield 83 mg (91%); mp 125 °C (decomp.) (Found: C, 56.38; H, 6.51. $C_{28}H_{39}BF_4PRh$ requires: C, 56.40; H, 6.59%). NMR: δ_H (CD_3NO_2, 400 MHz) 7.85–7.37 (9 H, m, C_6H_5), 4.99 (5 H, br s, C_5H_5), 3.33 (1 H, br s, H^2),[20] 2.74 (3 H, m, PC*H*CH_3), 1.76 [3 H, d, *J*(P,H) 12.4, C_6H_5C(C*H*$_3$)Ph], 1.42 [18 H, dd, *J*(P,H) 16.4, *J*(H,H) 7.2, PCHC*H*$_3$]; δ_C (CD_3OD, 100.6 MHz) 144.5 (s, *ipso*-C of C_6H_5), 130.2, 130.0, 129.8, 129.6, 129.5, 128.4, 128.0 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5 and C$^{3–6}$), 100.4 [dd, *J*(Rh,C) 5.7, *J*(P,C) 2.9, C^1 or C^7], 96.4 [dd, *J*(Rh,C) 5.7, *J*(P,C) 2.9, C^1 or C^7], 93.9 [dd, *J*(Rh,C) 4.8, *J*(P,C) 1.9, C_5H_5], 64.5 [dd, *J*(Rh,C) 12.4, *J*(P,C) 4.8, C^2], 28.4 [d, *J*(P,C) 21.0, C_6H_5C(*C*H$_3$)Ph], 20.5 [d, *J*(P,C) 34.3, P*C*HCH_3], 19.9 [d, *J*(P,C) 4.8, PCH*C*H$_3$]; δ_F (CD_3NO_2, 376.5 MHz) −152.2 (s); δ_P (CD_3NO_2, 162.0 MHz) 52.4 [d, *J*(Rh,P) 154.9].

[(η^5-C_5H_5)Rh{η^3-C_6H_5C(CH$_3$)Ph}(SbPr$^i_3$)]BF$_4$ 10b. This compound was prepared as described for **10a** from **5d** (78 mg, 0.13 mmol) and [Me$_3$O]BF$_4$ (20 mg, 0.13 mmol) in ether/methanol (1 : 1, 10 cm^3). Red solid: yield 81 mg (88%); mp 107 °C (decomp.) (Found: C, 48.87; H, 5.69. $C_{28}H_{39}BF_4SbRh$ requires: C, 48.95; H, 5.72%). NMR (CD_3NO_2): δ_H (400 MHz) 8.00–7.39 (9 H, m, C_6H_5), 5.03 (5 H, br s, C_5H_5), 3.90 (1 H, br s, H^2),[20] 2.85 [3 H, sept, *J*(H,H) 7.6, SbC*H*CH_3], 1.43, 1.36 [9 H each, both d, *J*(H,H) 7.6, SbCHC*H*$_3$], signal for $C_6H_5C(CH_3)Ph$ presumably covered by signals of the methyl protons of the isopropyl groups; δ_C (100.6 MHz) 141.1 (s, *ipso*-C of C_6H_5), 138.3, 133.1, 131.7, 130.2, 128.7, 128.3, 127.8 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5 and C$^{3–6}$), 100.7 [d, *J*(Rh,C) 6.0, C^1 or C^7], 98.1 [d, *J*(Rh,C) 8.0, C^1 or C^7], 91.4 [d, *J*(Rh,C) 5.0, C_5H_5], 58.1 [d, *J*(Rh,C) 11.1, C^2], 22.8 [s, C_6H_5C(*C*H$_3$)Ph], 22.3 (s, SbCH*C*H$_3$), 20.6 (s, Sb*C*HCH$_3$); δ_F (188.3 MHz) −154.9 (s).

[(η^5-C_5H_5)Rh{η^3-C_6H_5C(CH$_3$)Ph}(PPr$^i_3$)]CF$_3$SO$_3$ 10c. A solution of **5a** (111 mg, 0.22 mmol) in pentane/methanol (1 : 1, 5 cm^3) was treated with CF_3SO_3Me (25 μL, 0.22 mmol) and stirred for 30 min at room temperature. A change of color from deep blue to red occurred. The solvent was removed *in vacuo*, and the oily residue was washed twice with 5 cm^3 portions of benzene and once with pentane (10 cm^3). A deep red solid was formed, which was dried *in vacuo*: yield 121 mg (82%); mp 76 °C (decomp.) (Found: C, 53.27; H, 6.09; S, 4.67. $C_{29}H_{39}F_3O_3PRhS$ requires: C, 52.89; H, 5.97; S, 4.87%). IR (Nujol): *ν*(S=O) 1275 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.80–7.38 (9 H, m, C_6H_5), 4.87 (5 H, s, C_5H_5), 3.46 [1 H, d, *J*(P,H) 10.0, H^2],[20] 2.43 (3 H, m, PC*H*CH_3), 1.43 [21 H, br m, C_6H_5C(C*H*$_3$)Ph and PCHC*H*$_3$]; δ_F (376.5 MHz) −78.6 (s); δ_P (162.0 MHz) 52.1 [d, *J*(Rh,P) 155.3].

Reaction from 5e with HBF$_4$. Compound **11** (or **11′**, see Scheme 5) was prepared as described for **9** from **5e** (69 mg, 0.14 mmol) and a 54% solution of HBF_4 in ether (19 μL, 0.14 mmol). Red solid: yield 74 mg (91%); mp 38 °C (decomp.) (Found: C, 56.19; H, 6.43. $C_{28}H_{39}BF_4PRh$ requires: C, 56.40; H, 6.59%). Molar conductivity: *Λ* (CH_3NO_2) 66 cm^2 Ω^{-1} mol^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.68–7.18 (8 H, m, C_6H_5 and C_6H_4), 4.85 (5 H, br s, C_5H_5), 3.43 [1 H, d, *J*(P,H) 9.7, H^2],[20] 2.39 [3 H, sept, *J*(H,H) 7.0, PC*H*CH_3], 2.28 (3 H, br s, $C_6H_4C*H*_3$), 1.42 [18 H, dd, *J*(P,H) 14.1, *J*(H,H) 7.0, PCHC*H*$_3$], signal for H^7 presumably covered by the signal for $C_6H_4CH_3$; δ_C (100.6 MHz) 139.1 (s, *ipso*-C of $C_6H_4CH_3$), 135.6 (s, *para*-C of $C_6H_4CH_3$), 130.7, 130.5, 130.0, 129.3, 129.2, 127.9 (all s, *ortho*- and *meta*-C of $C_6H_4CH_3$ and C$^{3–6}$), 92.8 (br s, C^1), 92.5 [dd, *J*(Rh,C) 3.8, *J*(P,C) 1.9, C_5H_5], 88.2 [dd, *J*(Rh,C) 8.6, *J*(P,C) 2.9, C^7], 63.3 [dd, *J*(Rh,C) 11.4, *J*(P,C) 5.7, C^2], 27.7 [d, *J*(P,C) 21.0, P*C*HCH_3], 20.3 (s, $C_6H_4CH_3$), 19.9 (br s, PCH*C*H$_3$); δ_F (376.5 MHz) −150.8 (s); δ_P (162.0 MHz) 51.9 [d, *J*(Rh,P) 157.7].

[(η^5-C_5H_5)RhI$_2$(PPr$^i_3$)] 12a. A solution of **5a** (40 mg, 0.08 mmol) in pentane (10 cm^3) was treated at −78 °C with a solution of iodine (21 mg, 0.08 mmol) in pentane (10 cm^3). A rapid precipitation of a red-brown solid occurred. The solvent was removed *in vacuo*, and the residue was dissolved in acetone/pentane (1 : 3, 10 cm^3). Upon storing at −60 °C for 2 d a red-brown solid was formed, which was separated from the mother liquor, washed three times with 5 cm^3 portions of pentane and dried: yield 44 mg (94%). The product was characterized by comparison of the ^{1}H and ^{31}P NMR data with those of an authentic sample.[15]

[(η^5-C_5H_5)RhI$_2$(SbPr$^i_3$)] 12b. This compound was prepared as described for **12a** from **5d** (42 mg, 0.07 mmol) and iodine (18 mg, 0.07 mmol) in pentane (20 cm^3). Red-brown solid: yield 46 mg (95%); mp 70 °C (decomp.) (Found: C, 24.74; H, 4.06. $C_{14}H_{26}I_2RhSb$ requires: C, 24.99; H, 3.89%). NMR: δ_H (C_6D_6, 200 MHz) 4.94 (5 H, br s, C_5H_5), 2.39 [3 H, sept, *J*(H,H) 7.3, SbC*H*CH_3], 1.17 [18 H, d, *J*(H,H) 7.3, SbCHC*H*$_3$]; δ_C (acetone-d$_6$, 100.6 MHz) 86.3 [d, *J*(Rh,C) 6.0, C_5H_5], 24.7 (s, Sb*C*HCH$_3$)], 22.6 (s, SbCH*C*H$_3$).

Crystallography

Single crystals of **7a** were grown from acetone (−20 °C); crystal

size 0.40 × 0.25 × 0.08 mm, monoclinic, space group *Cc* (no. 9), $a = 8.865(2)$, $b = 23.214(2)$, $c = 13.172(3)$ Å, $\beta = 106.85(1)°$, $V = 2594(1)$ Å^3, $D_c = 1.447$ g cm^{-3}; max. $2\Theta = 58°$ (Mo-Kα, $\lambda = 0.71073$ Å, graphite monochromator, ω/Θ-scan, Zr filter with factor 16.4, $T = 173(2)$ K), 3624 reflections scanned, 3624 unique [R(int) = 0.0000], 3488 observed [$I > 2\sigma(I)$], Lorentz-polarization and empirical absorption corrections (ψ-scans, min. transmission 89.48%) direct methods (SHELXS-86),[21] 290 parameters, reflex/parameter ratio 12.5, $R1 = 0.0284$, $wR2 = 0.0675$, residual electron density 0.673/−0.813 e Å^{-3}.

CCDC reference number 186/2295.

See http://www.rsc.org/suppdata/dt/b0/b008354m/ for crystallographic files in .cif format.

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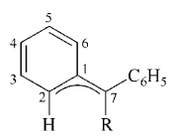
References

1 P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem.*, 1993, **105**, 1498; P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1480; H. Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert and J. Wolf, *Chem. Eur. J.*, 1997, **3**, 1375.
2 E. Bleuel, B. Weberndörfer and H. Werner, *J. Organomet. Chem.*, 2000, in press.
3 For definition see: D. F. Shriver, *Acc. Chem. Res.*, 1970, **3**, 231.
4 H. Werner, *Angew. Chem.*, 1983, **95**, 932; H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 927.
5 J. Wolf and H. Werner, *J. Organomet. Chem.*, 1987, **336**, 413; J. Wolf, R. Zolk, U. Schubert and H. Werner, *J. Organomet. Chem.*, 1988, **340**, 161; H. Werner, J. Wolf, G. Müller and C. Krüger, *J. Organomet. Chem.*, 1988, **342**, 381; A. Höhn and H. Werner, *Chem. Ber.*, 1988, **121**, 881; H. Werner, F. J. Garcia Alonso, H. Otto, K. Peters and H. G. von Schnering, *Chem. Ber.*, 1988, **121**, 1565; U. Brekau and H. Werner, *Organometallics*, 1990, **9**, 1067; H. Werner, U. Brekau and M. Dziallas, *J. Organomet. Chem.*, 1991, **406**, 237.
6 U. Herber, E. Bleuel, O. Gevert, M. Laubender and H. Werner, *Organometallics*, 1998, **17**, 10.
7 R. Feser and H. Werner, *J. Organomet. Chem.*, 1982, **233**, 193.
8 H. Werner and R. Feser, *J. Organomet. Chem.*, 1982, **232**, 351.
9 P. Schwab, Ph.D. Thesis, Universität Würzburg, 1994; H. Werner, *J. Organomet. Chem.*, 1995, **500**, 331.
10 E. Bleuel, Ph.D. Thesis, Universität Würzburg, 2000.
11 H. Werner, J. Wolf and A. Höhn, *J. Organomet. Chem.*, 1985, **287**, 395.
12 R. P. Hughes, T. L. Husebo, A. L. Rheingold, L. M. Liable-Sands and G. P. A. Yap, *Organometallics*, 1997, **16**, 5.
13 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
14 T. Braun, O. Gevert and H. Werner, *J. Am. Chem. Soc.*, 1995, **117**, 7291.
15 H. Werner, J. Wolf, U. Schubert and K. Ackermann, *J. Organomet. Chem.*, 1986, **317**, 327.
16 H. Werner, P. Schwab, E. Bleuel, N. Mahr, B. Windmüller and J. Wolf, *Chem. Eur. J.*, 2000, **6**, 4461.
17 R. Feser, Ph.D. Thesis, Universität Würzburg, 1981; H. Werner, R. Feser and J. Wolf, manuscript in preparation.
18 Y. Wakatsuki and H. Yamazaki, *J. Organomet. Chem.*, 1974, **64**, 393.
19 O. V. Gusev, A. Z. Rubezhov, J. A. Miguel-Garcia and P. M. Maitlis, *Mendeleev Commun.*, 1991, 21; J. Miguel-Garcia, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1992, 131.
20 For assignment of protons and carbon atoms see below.



21 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.