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Synthesis and molecular structure of four-coordinate neutral and cationic diphenylcarbenerhodium(I) complexes

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Abstract

Neutral diphenylcarbenerhodium(I) complexes of the general composition *trans*-[RhX(=CPh_2)(P^iPr_3)$_2$] (X = F (**3**), OCN (**4**), CF_3CO_2 (**5**), $PhCO_2$ (**6**), CF_3SO_3 (**7**)) were prepared from the chloro or bromo precursors *trans*-[RhCl(=CPh_2)(P^iPr_3)$_2$] (**1**) and *trans*-[RhBr(=CPh_2)(P^iPr_3)$_2$] (**2**) by salt metathesis in acetone and isolated in excellent yields. While treatment of **1** with Tl(acac[F_6]) afforded the substitution product *trans*-[Rh(κ^1-acac[F_6])(=CPh_2)(P^iPr_3)$_2$] (**8**), the corresponding reaction of **1** with Tl(acac) gave the chelate compound [Rh(κ^2-acac)(=CPh_2)(P^iPr_3)] (**9**) with only one phosphine ligand attached to the metal center. In acetone solution, the triflato complex **7** is in equilibrium with the cation *trans*-[Rh{O=$C(CH_3)_2$}(=CPh_2)(P^iPr_3)$_2$]$^+$ which after addition of $NaBAr^F_4$ precipitates as the BAr^F_4 salt **11**. The starting material **1** as well as the bis(triphenylphosphine) and bis(triisopropylstibine) analogues **14** and **15** react with pyridine or acetonitrile in the presence of KPF_6 to yield the cationic complexes *trans*-[Rh(py)(=CPh_2)(PPh_3)$_2$]PF_6 (**16**) and *trans*-[Rh(CH_3CN)(=CPh_2)(L)$_2$]PF_6 (L = P^iPr_3 (**17**), Sb^iPr_3 (**18**)). The BAr^F_4 salt of the cation *trans*-[Rh(CH_3CN)(=CPh_2)(Sb^iPr_3)$_2$]$^+$ (**19**) was characterized by X-ray crystallography. Compounds **11**, **16**–**19** and the bis(pyridine) derivative *cis*-[Rh(=CPh_2)(NC_5H_5)$_2$(P^iPr_3)]PF_6 (**12**) are the first representatives of four-coordinate cationic diphenylcarbenerhodium(I) complexes.

Keywords: Rhodium; Carbene complexes; Acetylacetonate complexes; Phosphine complexes; Stibine complexes

1. Introduction

Following the discovery that square-planar vinylidene and allenylidene rhodium(I) complexes *trans*-[RhCl(=C=CRR′)(P^iPr_3)$_2$] and *trans*-[RhCl(=C=C=CRR′)(P^iPr_3)$_2$] are quite stable and offer a rich chemistry, including the chance to perform novel metal-assisted C–C coupling reactions [1,2], we succeeded recently to prepare also the corresponding carbene rhodium(I) counterparts *trans*-[RhCl(=CRR′)(P^iPr_3)$_2$] [3]. The key to success was to use instead of a bis(triisopropylphosphine) rhodium(I) compound, the bis(triisopropylstibine) rhodium(I) derivative *trans*-[RhCl(C_2H_4)(Sb^iPr_3)$_2$] as the starting material which affords, upon treatment with diazoalkanes R′RCN_2 via displacement of ethene and elimination of N_2, the carbene complexes *trans*-[RhCl(=CRR′)(Sb^iPr_3)$_2$] in excellent yields. Subsequent substitution of the two stibine by two phosphine ligands resulted in the formation of the wanted products [3,4]. With regard to the reactivity of the carbene complexes *trans*-[RhCl(=CRR′)(P^iPr_3)$_2$], we found that the carbene ligand is displaced easily by CO and ethene [3] and, moreover, that half sandwich-type compounds [(η^5-C_5H_5)Rh(=CRR′)(P^iPr_3)] [5] and [(η^5-C_9H_7)Rh(=CRR′)(P^iPr_3)] [6] are accessible from *trans*-[RhCl(=CRR′)(P^iPr_3)$_2$] and NaC_5H_5 or C_9H_7K, respectively.

In the continuation of our work, we report in this paper the preparation of a series of new four-coordinate carbenerhodium(I) complexes including those with only one triisopropylphosphine ligand, and the synthesis of the first representatives of square-planar carbenerhodium(I) cations of which one was characterized by X-ray crystal structure analysis.

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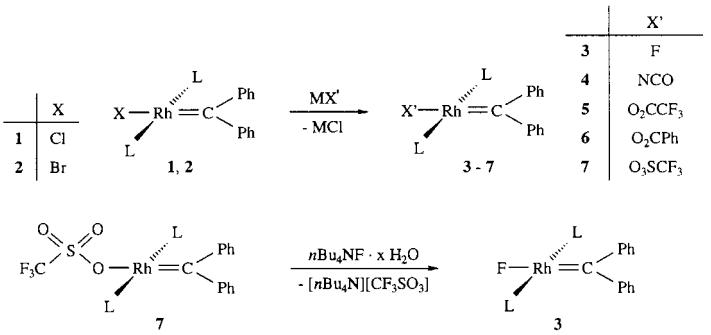


Scheme 1.

2. Results and discussion

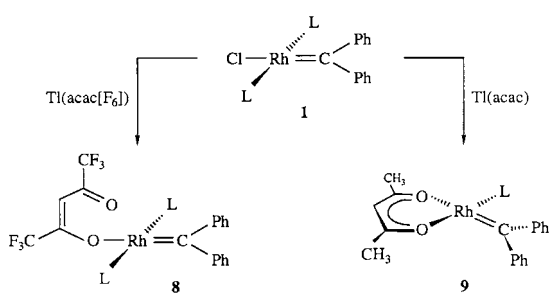
Under rather mild conditions, the chloro compound **1** (Scheme 1) does not only react with metal bromides to give the bromo derivative **2** but also with excess CsF in acetone to afford the fluoro complex **3** in excellent yield. While in our initial attempts to prepare compound **2**, the use of KBr in pentane seemed to be the method of choice [3b], we found in the course of the present investigations that replacing KBr by NaBr and using acetone as the solvent is even more convenient. The fluoro complex **3** like the other compounds of the general composition *trans*-$[RhX(=CPh_2)(P^iPr_3)_2]$ is a green, moderately air-sensitive solid which is soluble in ether, acetone and benzene but insoluble in methanol. Typical features of **3** are the doublet of doublet resonance at δ 27.9 in the ^{31}P-NMR and the doublet of triplet resonance at δ −230.8 in the ^{19}F-NMR spectrum. The signal for the carbene carbon atom in the ^{13}C-NMR spectrum of **3** appears at δ 307.1 and is shifted by ca. 10 ppm upfield compared to the chloro and bromo derivatives **1** and **2**.

The preparation of the isocyanato derivative **4** from **1** and excess NaOCN proceeds analogously to that of **3**. The coordination of the isocyanate ligand in **4** via the nitrogen instead of the oxygen atom is indicated in the IR spectrum by the symmetrical NCO stretch at 1441 cm^{-1} which is characteristic for this bonding mode [7]. We note that some relatives of **4** with an allenylidene instead of a carbene ligand have been prepared recently in our laboratory by salt metathesis from *trans*-$[RhCl(=C=C=CRR')(P^iPr_3)_2]$ and KOCN [8]. With regard to the synthesis of **3** and **4** it should be mentioned also that attempts to prepare the analogous compounds with azide or isothiocyanate as anionic ligands failed.

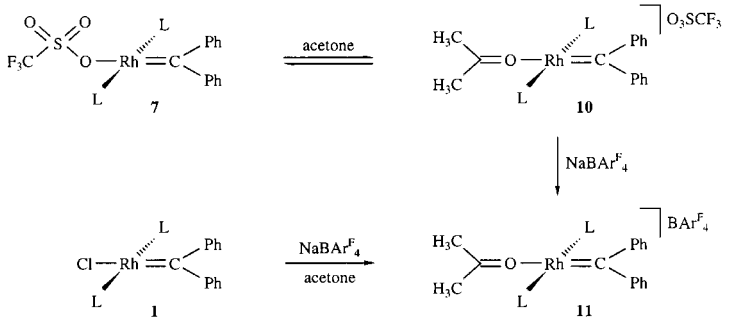
Apart from halides and isocyanate, also O-donors such as trifluoracetate, benzoate and triflate can be linked to the $[Rh(=CPh_2)(P^iPr_3)_2]^+$ fragment. Whereas the starting material **1** is rather inert toward CH_3CO_2Tl, it reacts with thallium trifluoracetate in the molar ratio of 1:1.2 to give the substitution product **5** (Scheme 1) in 90% isolated yield. Below the decomposition temperature of 76°C, compound **5** does not eliminate the carbene moiety to generate the well-known chelate complex $[Rh(\kappa^2\text{-}O_2CCF_3)(P^iPr_3)_2]$ [9]. For the preparation of the benzoato compound **6**, the bromo derivative **2** has to be used as the precursor since upon treatment of **1**, even with an excess of $PhCO_2Tl$, only a mixture of **1** and **6** was obtained. Both **5** and **6** are relatively air-stable solids, which have been characterized by elemental analysis and mass spectrometry. Owing to the IR data of **5** and **6** there is no doubt that the carboxylato ligand is coordinated in a κ^1 bonding mode [10]. This is probably also true in the case of the triflato complex **7,** which has been prepared from **1** and equimolar amounts of CF_3SO_3Tl. The IR spectrum of **7** (in benzene) displays two bands for the symmetrical and unsymmetrical S=O stretching vibrations at 1230 and 1311 cm^{-1}, the positions of which appear typical for the monodentate coordination of the CF_3SO_3 unit [11].

Upon treatment of **7** with hydrated $[^nBu_4N]F$, the triflate ligand is easily displaced by fluoride to give the fluoro complex **3** in 92% yield. This methodology has also been used for the synthesis of some other fluororhodium(I) compounds including the highly reactive dimer $[Rh(\mu\text{-}F)(P^iPr_3)_2]_2$ [12].

The reactions of the starting material **1** with the thallium salts of acetylacetone and its hexafluoro derivative led to two different types of products (see Scheme 2). While treatment of **1** with $Tl(acac[F_6])$ gives the bis(phosphine) compound **8** containing a monodentate hexafluoroacetylacetonato unit, the corresponding



Scheme 2.



Scheme 3.

reaction of **1** with Tl(acac) affords the chelate complex **9**. This result is surprising insofar as the related rhodium(I) carbonyl *trans*-[Rh(κ^1-acac)(CO)(P^iPr_3)$_2$], which was prepared from [Rh(κ^2-acac)(CO)$_2$] and two equivalents of P^iPr_3, contains two phosphine ligands [13]. The ^{13}C-NMR spectrum of **8** shows only one quartet for the carbon atoms of the CO and one for the carbon atoms of the CF_3 groups indicating that in solution the molecule exhibits a fluxional behavior with respect to the NMR timescale. A similar observation has been made with the structurally related palladium(II) complex *trans*-Pd(κ^1-acac[F$_6$])(py′)(PEt$_3$)$_2$] and explained by a head-to-tail exchange of the hexafluoroacetylacetonato ligand [14]. The ^{19}F spectrum of **8** in C_6D_6 displays at room temperature only a single resonance at δ −74.1 and thus supports the assumption of a fluxional structure for the compound in solution.

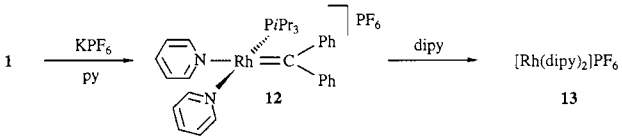
The acac complex **9** is considerably more stable than the hexafluoro-acac derivative. In contrast to **8**, the ^{1}H-NMR spectrum of **9** shows for the PCHCH_3 methyl protons, instead of a virtual triplet a doublet of doublets at δ 1.14 which is typical for a mono(triisopropylphosphine)rhodium(I) moiety. Accordingly, the ^{13}C-NMR spectrum of **9** exhibits for the carbene carbon atom also a doublet of doublets at δ 294.8 due to ^{103}Rh–^{13}C and ^{31}P–^{13}C coupling. With regard to the composition of **9** we note that an analogous ethene complex [Rh(κ^2-acac)(C_2H_4)(P^iPr_3)] is known and has been obtained from [Rh(κ^2-acac)(C_2H_4)$_2$] and triisopropylphosphine [15].

Cationic diphenylcarbenerhodium(I) compounds with [Rh(=CPh$_2$)(P^iPr_3)$_2$] as the building block have been prepared either from **1** or the corresponding triflate **7** as the precursor. We observed that if **7** is dissolved in acetone, a gradual change of color from bright green to olive-green occurs which is accompanied by slight changes in the ^{1}H and ^{31}P spectra. The formation of an ionic species is confirmed by conductivity measurements, the data of which are in agreement with the presence of a 1:1 electrolyte. However, attempts to isolate **10** by evaporation of the solvent regenerated the starting material **7** (Scheme 3).

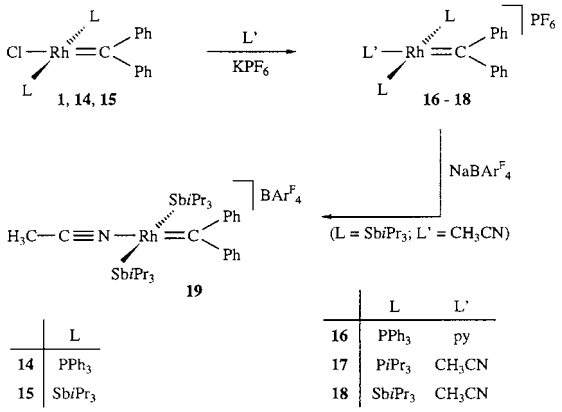
A stable salt of the acetone-containing cation of **10** is obtained upon addition of Na[B{3.5-C$_6$H$_3$(CF$_3$)$_2$}$_4$] (NaBAr$^F_4$) to the acetone solution of **7**. Alternatively, compound **11** can also be prepared from **1** and NaBAr$^F_4$ in acetone. In contrast to **1** or **7**, the ionic product **11** is a violet, highly air-sensitive solid which at room temperature in solution (acetone, dichloromethane, nitromethane) decomposes in less than 1 h.

The reaction of **11** with an equimolar amount of pyridine in dichloromethane at −40°C leads to complete decomposition of the starting material. This observation is surprising insofar as the related vinylidene and allenylidene complexes *trans*-[Rh{O=C(CH$_3$)$_2$}-{=(C=)$_n$CRR′}(P^iPr_3)$_2$]PF$_6$ (n = 1, 2) react with pyridine by ligand exchange to yield the stable salts *trans*-[Rh(py)(=C=CRR′)(P^iPr_3)$_2$]PF$_6$ and *trans*-[Rh(py)(=C=C=CRR′}(P^iPr_3)$_2$]PF$_6$, respectively [16]. However, we succeeded with the preparation of a rhodium(I) cation with diphenylcarbene and pyridine as ligands by treatment of the chloro compound **1** with an excess of pyridine in the presence of KPF$_6$. Complex **12**, which is a bright green, thermally less stable solid showing the conductivity of a 1:1 electrolyte, was isolated in 93% yield (Scheme 4). The ^{31}P-NMR spectrum of **12** exhibits a doublet at δ 42.0 with a ^{103}Rh–^{31}P coupling constant of 198.8 Hz which is typical for a mono(phosphine)carbene complex of rhodium(I) [5,6].

Similar to **11**, compound **12** decomposes also in solution at room temperature within 5–10 min. We assume that the decomposition is initiated by the dissociation of one pyridine ligand generating a 14-electron intermediate, which can not be stabilized by dimerisation. In the presence of excess pyridine, solutions of **12** are considerably more stable. The reaction of **12** with 2.2′-dipyridyl (undertaken to stabilize the *cis*-



Scheme 4.



Scheme 5.

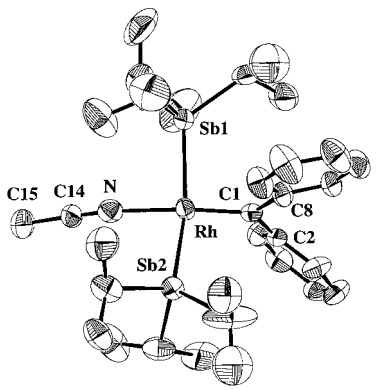


Fig. 1. Molecular structure of the cation of compound **19**; anisotropic displacement parameters are depicted at the 50% probability level.

Table 1
Selected bond distances (Å) and bond angles (°) with estimated S.D. for compound **19**

Bond distances			
Rh–C(1)	1.850(6)	Rh–Sb(2)	2.5905(8)
Rh–N	2.120(6)	N–C(14)	1.138(8)
Rh–Sb(1)	2.5847(8)	C(14)–C(15)	1.453(10)
Bond angles			
C(1)–Rh–Sb(1)	94.89(19)	C(14)–N–Rh	170.1(6)
C(1)–Rh–Sb(2)	93.64(19)	N–C(14)–C(15)	177.9(9)
Sb(1)–Rh–Sb(2)	161.19(3)	N–Rh–Sb(1)	88.16(16)
C(1)–Rh–N	171.8(3)	N–Rh–Sb(2)	85.71(15)

$[Rh(=CPh_2)(P^iPr_3)]$ moiety) led to the formation of the chelate complex $[Rh(dipy)_2]PF_6$ (**13**). Salts of the $[Rh(dipy)_2]^+$ cation with Cl^-, NO_3^- and ClO_4^- as anions have already been described in the literature [17].

Using instead of the triisopropylphosphine compound **1** the PPh_3 analogue **14** as the starting material, the reaction with pyridine and KPF_6 yields the carbenerhodium(I) complex **16** with only one pyridine ligand (Scheme 5). The *trans* disposition of the two phosphines in **16** is indicated by the doublet of triplet resonance at δ 352.1 in the ^{13}C-NMR and by the doublet resonance at δ 22.5 in the ^{31}P-NMR spectrum. The acetonitrile complexes **17** and **18** have been prepared on an analogous route using the chlororhodium(I) derivatives **1** and **15** as the precursors. The remarkably stable BAr^F_4 salt **19** of the cation *trans*-$[Rh(CH_3CN)(=CPh_2)(Sb^iPr_3)_2]^+$ was obtained on salt metathesis from **18** and $NaBAr^F_4$ in nearly quantitative yield. We note that the IR spectra of **18** and **19** exhibit the C–N stretching mode at ca. 2330 cm^{-1} which is at higher wavenumbers (ca. 65 cm^{-1}) compared to free CH_3CN. Similar observations have been reported by Shriver et al. in the case of other cationic acetonitrile transition-metal compounds [18].

The result of the X-ray crystal structure analysis of **19** (Fig. 1) confirms the structural proposal outlined in Scheme 5. The geometry around the metal center is distorted square-planar [bond angles Sb(1)–Rh–Sb(2) 161.19(3)° and C(1)–Rh–N 171.8(3)°] with the two stibines as well as the acetonitrile ligand and the carbene fragment in *trans* disposition. The bond lengths Rh–Sb and Rh–C(1) (Table 1) are quite similar to those in **15** indicating that the lower electron density at the rhodium center of **19**, due to the positive charge of the molecule, is compensated by the donor strength of the acetonitrile ligand. The Rh–N bond distance of **19** [2.120(6) Å] is somewhat shorter than in the structurally related cation *trans*-$[Rh(py)(=C=CH_2)(P^iPr_3)_2]^+$ [2.151(3) Å] [16a].

In summary, the present investigations have shown that the chloro or bromo ligand of the starting materials *trans*-$[RhX(=CPh_2)(P^iPr_3)_2]$ (X = Cl, Br) can be displaced by various anions including not only fluoride and isocyanate but also O-donors such as carboxylates, triflate and acetylacetonates. An interesting aspect is that while Tl(acac[F_6]) reacts with *trans*-$[RhCl(=CPh_2)(P^iPr_3)_2]$ by substitution of the chloride for hexafluoroacetylacetonate, the analogous reaction with Tl(acac) yields the chelate complex $[Rh(\kappa^2\text{-acac})(=CPh_2)(P^iPr_3)]$ via elimination of one phosphine ligand. In the presence of KPF_6 or $NaBAr^F_4$, the Rh–Cl bond of the precursors *trans*-$[RhCl(=CPh_2)(L)_2]$ (L = P^iPr_3, PPh_3, Sb^iPr_3) is easily cleaved by acetone, acetonitrile or pyridine to generate stable salts of the cations *trans*-$[Rh(=CPh_2)(L')(L)_2]^+$. To the best of our knowledge, these are the first representatives of four-coordinate cationic carbenerhodium(I) complexes containing non-Fischer-type carbene ligands.

3. Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**, **2**, **14** and **15** [3b] were prepared as described in the literature. NMR spectra were recorded at room temperature (r.t.) on Bruker AC 200 and Bruker

AMX 400 instruments, IR spectra on a Perkin–Elmer 1420 or an IFS 25 FT-IR infrared spectrometer, and molar conductivities were measured with a Schott Konduktometer CG 851. Melting points were determined by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; sept, septet; m, multiplet; br, broadened signal; $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$.

3.1. Preparation of trans-[RhF(=CPh$_2$)(P^{i}Pr$_3$)$_2$] (3)

A solution of 88 mg (0.14 mmol) of **1** in 5 ml of acetone was treated with 214 mg (1.40 mmol) of finely divided CsF and stirred for 5 h at r.t. The solvent was removed in vacuo and the residue was extracted with 30 ml of pentane. After the solution was concentrated to ca. 2 ml, it was stored for 48 h at −60°C. Deep green crystals were formed, which were separated from the mother liquor and dried; yield 68 mg (79%), m.p. (dec.) 68°C. Anal. Found: C, 61.09; H, 8.59; Rh, 16.72. Calc. for $C_{31}H_{52}FP_2Rh$: C, 61.18; H, 8.61; Rh, 16.91%. MS (FAB): m/z 608 (79, M^+), 589 (82, $M^+ - F$), 448 (100, $M^+ - P^iPr_3$), 429 (91.0, $M^+ - F - P^iPr_3$). ^{1}H-NMR (C_6D_6, 200 MHz): δ 7.89 (m, 4H, *ortho*-H of C_6H_5), 7.31–6.93 (m, 6H, *meta*- and *para*-H of C_6H_5), 2.05 (m, 6H, PC*H*CH$_3$), 1.18 [dvt, $N = 13.2$, $J(H,H) = 6.8$ Hz, 36H, PCHC*H*$_3$]. ^{13}C-NMR (C_6D_6, 50.3 MHz): δ 307.1 (m, Rh=C), 161.9 (s, *ipso*-C of C_6H_5), 128.3, 127.8, 127.5, 127.3 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 23.5 (vt, $N = 15.9$ Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$). ^{19}F-NMR (C_6D_6, 376.5 MHz): δ −230.8 [dt, $J(P,F) = 30.5$, $J(Rh,F) = 9.6$ Hz]. ^{31}P-NMR (C_6D_6, 81.0 MHz): δ 27.9 [dd, $J(Rh,P) = 176.8$, $J(F,P) = 30.5$ Hz].

3.2. Preparation of trans-[Rh(NCO)(=CPh$_2$)(P^{i}Pr$_3$)$_2$] (4)

This compound was prepared analogously as described for **3** from 78 mg (0.12 mmol) of **1** and 41 mg (0.62 mmol) of finely divided NaOCN in 8 ml of acetone. After the solvent was evaporated in vacuo, a green solid was obtained, which was washed twice with 1 ml portions of pentane (−20°C) and dried; yield 75 mg (95%), m.p. (dec.) 82°C. Anal. Found: C, 60.64; H, 8.48; N, 2.16. Calc. for $C_{32}H_{52}NOP_2Rh$: C, 60.85; H, 8.30; N, 2.22%. IR (C_6H_6): $\nu(NCO_{asym.})$ 2215, $\nu(NCO_{sym.})$ 1441 cm^{-1}. ^{1}H-NMR (C_6D_6, 200 MHz): δ 7.88 (m, 4H, *ortho*-H of C_6H_5), 7.28–6.90 (m, 6H, *meta*- and *para*-H of C_6H_5), 1.98 (m, 6H, PC*H*CH$_3$), 1.09 [dvt, $N = 13.3$, $J(H,H) = 6.8$ Hz, 36H, PCHC*H*$_3$]. ^{13}C-NMR ([D$_8$]-Toluol, 100.6 MHz): δ 321.9 (m, Rh=C), 160.4 (s, *ipso*-C of C_6H_5), 140.2 (m, NCO), 129.1, 128.2, 128.1 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 24.5 (vt, $N = 17.2$ Hz, P*C*HCH$_3$), 19.6 (s, PCH*C*H$_3$). ^{31}P-NMR (C_6D_6, 81.0 MHz): δ 26.6 [d, $J(Rh,P) = 166.2$ Hz].

3.3. Preparation of trans-[Rh(κ^1-O$_2$CCF$_3$)(=CPh$_2$)(P^{i}Pr$_3$)$_2$] (5)

A solution of 63 mg (0.10 mmol) of **1** in 10 ml of acetone was treated with 38 mg (0.12 mmol) of TlO_2CCF_3 and stirred for 30 min at r.t. The solvent was removed in vacuo, the residue suspended in 20 ml of pentane and the suspension was filtered. After the filtrate was concentrated to ca. 2 ml, it was stored for 12 h at −78°C. A green microcrystalline solid precipitated, which was separated from the mother liquor and dried; yield 64 mg (90%), m.p. (dec.) 76°C. Anal. Found: C, 55.94; H, 7.35; Rh, 15.20. Calc. for $C_{33}H_{52}F_3O_2P_2Rh$: C, 56.41; H, 7.46; Rh, 14.65%. MS (FAB): m/z 702 (16, M^+), 589 (36, $M^+ - CF_3CO_2$), 542 (100, $M^+ - P^iPr_3$). IR (KBr): $\nu(OCO_{asym.})$ 1684, $\nu(OCO_{sym.})$ 1404 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 8.02 (m, 4H, *ortho*-H of C_6H_5), 7.26–6.93 (m, 6H, *meta*- and *para*-H of C_6H_5), 1.87 (m, 6H, PC*H*CH$_3$), 1.08 [dvt, $N = 13.2$, $J(H,H) = 6.8$ Hz, 36H, PCHC*H*$_3$]. ^{13}C-NMR (C_6D_6, 100.6 MHz): δ 319.4 [dt, $J(Rh,C) = 35.2$, $J(P,C) = 8.0$ Hz, Rh=C], 161.1 [q, $J(F,C) = 34.2$ Hz, *C*O$_2$CF$_3$], 158.3 (s, *ipso*-C of C_6H_5), 129.0, 128.3, 128.1 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 117.5 [q, $J(F,C) = 294.8$ Hz, CO$_2$*C*F$_3$], 24.4 (vt, $N = 16.4$ Hz, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$). ^{19}F-NMR (C_6D_6, 376.5 MHz): δ −74.2 (s). ^{31}P-NMR (C_6D_6, 162.0 MHz): δ 26.4 [d, $J(Rh,P) = 179.0$ Hz].

3.4. Preparation of trans-[Rh(κ^1-O$_2$CPh)(=CPh$_2$)(P^{i}Pr$_3$)$_2$] (6)

A solution of 64 mg (0.10 mmol) of **2** in 5 ml of acetone was treated with 31 mg (0.10 mmol) of TlO_2CPh, and the reaction mixture was stirred for 30 min at r.t. A change of color from yellow–green to green occurred. The solvent was removed in vacuo and the residue was extracted with 10 ml of benzene. The extract was brought to dryness in vacuo and the resulting solid was dissolved in 2 ml of pentane. After storing the solution for 12 h at −60°C, green crystals were formed, which were separated from the mother liquor and dried; yield 64 mg (94%), m.p. (dec.) 56°C. Anal. Found: C, 64.09; H, 8.01. Calc. for $C_{38}H_{57}O_2P_2Rh$: C, 64.22; H, 8.08%. IR (C_6H_6): $\nu(OCO_{asym.})$ 1615, $\nu(OCO_{sym.})$ 1345 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 8.56 (m, 2H, *ortho*-H of $C_6H_5CO_2$), 8.16 (m, 4H, *ortho*-H of C_6H_5), 7.70 (m, 3H, *meta*- and *para*-H of $C_6H_5CO_2$), 7.30–7.01 (m, 6H, *meta*- and *para*-H of C_6H_5), 1.91 (m, 6H, PC*H*CH$_3$), 1.12 [dvt, $N = 13.1$, $J(H,H) = 6.5$ Hz, 36H, PCHC*H*$_3$]. ^{13}C-NMR (C_6D_6, 100.6 MHz,): δ 171.1 (s, $C_6H_5CO_2$), 159.4 (s, *ipso*-C of C_6H_5), 138.3 (s, *ipso*-C of *C*$_6$H$_5$CO$_2$), 132.0, 130.2, 129.4, 128.3, 128.1, 127.9 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5 and of *C*$_6$H$_5$CO$_2$), 24.5 (vt, $N = 12.7$ Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$), the signal for Rh=C

could not be exactly located. ^{31}P-NMR (C_6D_6, 81.0 MHz): δ 25.6 [d, J(Rh,P) = 180.7 Hz].

3.5. Preparation of *trans*-[Rh(κ^1-O_3SCF_3)(=CPh_2)(P^iPr_3)$_2$] (7)

A solution of 78 mg (0.12 mmol) of **1** in 10 ml of acetone was treated with 44 mg (0.12 mmol) of TlO_3SCF_3, and the reaction mixture was stirred for 30 min at r.t. A change of color from bright green to olive-green occurred and a white precipitate was formed. The solvent was removed in vacuo, the residue was suspended in 20 ml of benzene and the suspension was filtered. The filtrate was concentrated to ca. 1 ml in vacuo and upon addition of pentane (20ml) a green solid precipitated (10°C). This was separated from the solution and dried; yield 78 mg (85%), m.p. (dec.) 60°C. Anal. Found: C, 51.54; H, 7.26; S, 4.14. Calc. for $C_{32}H_{52}F_3O_3P_2RhS$: C, 52.03; H, 7.10; S, 4.34%. IR (C_6H_6): ν(S=$O_{asym.}$) 1311, ν(S=$O_{sym.}$) 1230, ν(S–O–Rh) 1214 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 7.90 (m, 4H, *ortho*-H of C_6H_5), 7.23–6.91 (m, 6H, *meta*- and *para*-H of C_6H_5), 2.07 (m, 6H, PC*H*CH_3), 1.09 [dvt, N = 13.6, J(H,H) = 6.9 Hz, 36H, PCHC*H*$_3$]. ^{13}C-NMR (C_6D_6, 100.6 MHz): δ 156.9 (s, *ipso*-C of C_6H_5), 129.9, 128.3, 128.1 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 121.7 [q, J(F,C) = 321.0 Hz, CF_3], 24.6 (vt, N = 16.9 Hz, P*C*HCH_3), 20.3 (s, PCH*C*H$_3$), the signal for Rh=C could not be exactly located. ^{19}F-NMR (C_6D_6, 188.3 MHz): δ −77.0 (s). ^{31}P-NMR (C_6D_6, 162.0 MHz,): δ 28.7 [d, J(Rh,P) = 175.1 Hz].

3.6. Preparation of *trans*-[Rh(κ^1-acac[F_6])(=CPh_2)(P^iPr_3)$_2$] (8)

This compound was prepared analogously as described for **5**, from 82 mg (0.13 mmol) of **1** and 54 mg (0.13 mmol) of Tl(acac[F_6]) in 10 ml of acetone. After storing the solution for 6 h at −78°C a green solid was obtained, which was separated from the mother liquor and dried; yield 81 mg (78%), m.p. (dec.) 56°C. Anal. Found: C, 54.37; H, 6.91. Calc. for $C_{36}H_{53}F_6O_2P_2Rh$: C, 54.28; H, 6.71%. IR (C_6H_6): ν(CO) 1700, 1690 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 8.02 (m, 4H, *ortho*-H of C_6H_5), 7.23 (m, 2H, *para*-H of C_6H_5), 6.97 (m, 4H, *meta*-H of C_6H_5), 1.88 (m, 6H, PC*H*CH_3), 1.08 [dvt, N = 13.2, J(H,H) = 7.2 Hz, 36H, PCHC*H*$_3$], the signal for CH of acac[F_6] could not be exactly located. ^{13}C-NMR (C_6D_6, 100.6 MHz,): δ 319.5 [dt, J(Rh,C) = 34.3, J(P,C) = 7.6 Hz, Rh=C], 161.1 [q, J(F,C) = 34.0 Hz, O*C*CF_3], 158.3 [d, J(Rh,C) = 2.4 Hz, *ipso*-C of C_6H_5], 129.0, 128.3, 128.1 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 117.5 [q, J(F,C) = 293.4 Hz, OC*C*F_3], 24.4 (vt, N = 16.4 Hz, P*C*HCH_3), 20.1 (s, PCH*C*H$_3$), the signal for CH of acac[F_6] could not be exactly located. ^{19}F-NMR (C_6D_6, 376.5 MHz): δ −74.1 (s). ^{31}P-NMR (C_6D_6, 162.0 MHz,): δ 26.4 [d, J(Rh,P) = 179.7 Hz].

3.7. Preparation of [Rh(κ^2-acac)(=CPh_2)(P^iPr_3)] (9)

This compound was prepared analogously as described for **5**, from 67 mg (0.11 mmol) of **1** and 33 mg (0.11 mmol) of Tl(acac) in 10 ml of acetone. After recrystallization from pentane at −78°C a green solid was obtained; yield 47 mg (83%), m.p. (dec.) 112°C. Anal. Found: C, 60.90; H, 7.02. Calc. for $C_{27}H_{38}O_2PRh$: C, 61.36; H, 7.25%. IR (C_6H_6): ν(CO) 1582, 1519 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 7.93 (m, 4H, *ortho*-H of C_6H_5), 7.32 (m, 2H, *para*-H of C_6H_5), 6.94 (m, 4H, *meta*-H of C_6H_5), 5.25 (s, 1H, CH of acac), 1.96 [br sept, J(H,H) = 7.2 Hz, 3H, PC*H*CH_3], 1.78 (br s, 6H, OCCH_3), 1.14 [dd, J(P,H) = 13.2, J(H,H) = 7.2 Hz, 18H, PCHC*H*$_3$]. ^{13}C-NMR (C_6D_6, 100.6 MHz): δ 294.8 [dd, J(Rh,C) = 38.7, J(P,C) = 14.1 Hz, Rh=C], 185.3 (br m, O*C*CH_3), 163.3 [d, J(Rh,C) = 2.4 Hz, *ipso*-C of C_6H_5], 127.6, 127.4, 125.9 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 98.7 [d, J(Rh,C) = 2.3 Hz, CH of acac], 27.6 (br s, OC*C*H_3), 23.8 [d, J(P,C) = 20.0 Hz, P*C*HCH_3], 20.0 (s, PCH*C*H$_3$). ^{31}P-NMR (C_6D_6, 162.0 MHz): δ 50.5 [d, J(Rh,P) = 228.9 Hz].

3.8. Preparation of *trans*-[Rh{O=C(CH_3)$_2$}(=CPh_2)(P^iPr_3)$_2$]O_3SCF_3 (10)

On dissolving 54 mg (0.07 mmol) of **7** in 5 ml of acetone, a change of color from bright green to olive-green occurred. The solvent was removed in vacuo and the residue was identified as **10** by NMR techniques. If the solid was washed with pentane in order to obtain an analytically pure sample of **10**, the starting material **7** was re-isolated. Molar conductivity: Λ (acetone) 113 cm^2·Ω^{-1}·mol^{-1}. ^{1}H-NMR (acetone-d_6, 400 MHz): δ 7.97 (m, 4H, *ortho*-H of C_6H_5), 7.73 (m, 2H, *para*-H of C_6H_5), 7.47 (m, 4H, *meta*-H of C_6H_5), 2.08 [s, 6H, O=C(CH_3)$_2$], 2.04 (m, 6H, PC*H*CH_3), 1.17 [dvt, N = 13.9, J(H,H) = 7.0 Hz, 36H, PCHC*H*$_3$]. ^{19}F-NMR (acetone-d_6, 376.5 MHz,): δ −78.7 (s). ^{31}P-NMR (acetone-d_6, 162.0 MHz): δ 34.4 [d, J(Rh,P) = 181.4 Hz].

3.9. Preparation of *trans*-[Rh{O=C(CH_3)$_2$}-(=CPh_2)(P^iPr_3)$_2$][B{3.5-$C_6H_3(CF_3)_2$}$_4$] (11)

(a) A solution of 44 mg (0.06 mmol) of **7** in 5 ml of acetone was treated with 53 mg (0.06 mmol) of Na[B{3.5-$C_6H_3(CF_3)_2$}$_4$] at −30°C. After the solution was stirred for 2–3 min, the solvent was removed in vacuo and the violet residue extracted with 10 ml of

Et_2O–pentane (1:2) at −10°C. The extract was brought to dryness in vacuo to give a violet, very air-sensitive solid; yield 67 mg (74%).

(b) A solution of 97 mg (0.16 mmol) of **1** in 5 ml of acetone was treated with 138 mg (0.16 mmol) of $Na[B\{3.5\text{-}C_6H_3(CF_3)_2\}_4]$ at r.t. The solvent was removed in vacuo and the brown–violet residue was extracted with 20 ml of CH_2Cl_2 at −10°C. The red–violet solution was brought to dryness in vacuo, the residue was washed twice with 5 ml portions of pentane and dried; yield 178 mg (76%), m.p. (dec.) 74°C. Anal. Found: C, 52.01; H, 4.49. Calc. for $C_{66}H_{70}BF_{24}OP_2Rh$: C, 52.47; H, 4.67%. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.80–7.64 (m, 12H, *ortho*-H of C_6H_5 and C_6H_3), 7.60–7.52 (m, 6H, *para*-H of C_6H_5 and C_6H_3), 7.36 (m, 4H, *meta*-H of C_6H_5), 2.10 [d, J(Rh,H) = 0.7 Hz, 6H, O=C(CH_3)$_2$], 1.95 (m, 6H, PC*H*CH_3), 1.06 [dvt, N = 14.1, J(H,H) = 7.0 Hz, 36H, PCHC*H*$_3$]. ^{19}F-NMR ($CDCl_3$, 188.3 MHz): δ −62.9 (s). ^{31}P-NMR ($CDCl_3$, 81.0 MHz): δ 40.9 [d, J(Rh,P) = 182.6 Hz].

3.10. Preparation of *cis-[Rh(=CPh$_2$)(NC$_5$H$_5$)$_2$(P^{i}Pr$_3$)]PF$_6$* (**12**)

A solution of 94 mg (0.15 mmol) of **1** in 5 ml of THF was treated with 140 mg (0.76 mmol) of KPF_6 and 2 ml (0.03 mol) of pyridine. A spontaneous change of color from green to deep green occurred. After the reaction mixture was stirred for 10 min, the volatile components were removed in vacuo and the residue was extracted with 20 ml of CH_2Cl_2 at −20°C. The extract was concentrated to ca. 1 ml in vacuo. Upon addition of pentane (20 ml) a green solid precipitated, which was separated from the solution, washed three times with 10 ml portions of pentane and dried; yield 102 mg (93%), m.p. (dec.) 39°C. Anal. Found: C, 52.26; H, 5.49; N, 3.78. Calc. for $C_{32}H_{41}F_6N_2P_2Rh$: C, 52.47; H, 5.64; N, 3.82%. Molar conductivity: Λ (CH_3NO_2) 71 cm^2 Ω^{-1} mol^{-1}. ^{1}H-NMR (acetone-d_6, 400 MHz, 223 K): δ 8.93, 8.73 (both m, 2H each, *ortho*-H of C_5H_5N), 8.57 (m, 3H, *meta*- and *para*-H of C_5H_5N), 7.89–7.06 (m, 13H, *meta*- and *para*-H of C_5H_5N and *ortho*-, *meta*- and *para*-H of C_6H_5), 1.83 [sept, J(H,H) = 7.2 Hz, 3H, PC*H*CH_3], 1.11 [dd, J(P,H) = 13.4, J(H,H) = 7.2 Hz, 18H, PCHC*H*$_3$]. ^{13}C-NMR (acetone-d_6, 100.6 MHz, 223 K): δ 325.6 [dd, J(Rh,C) = 36.2, J(P,C) = 12.1 Hz, Rh=C], 158.8 (s, *ipso*-C of C_6H_5), 150.7, 149.1 (all s, *ortho*-C of C_5H_5N), 138.1, 137.2, 135.6 (all s, *meta*- and *para*-C of C_5H_5N), 129.4, 128.0, 125.2, 124.3, 123.4 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 23.4 [d, J(P,C) = 22.1 Hz, P*C*HCH$_3$], 18.2 (s, PCH*C*H$_3$). ^{19}F-NMR (CD_2Cl_2, 188.3 MHz): δ −73.0 [d, J(P,F) = 710.8 Hz]. ^{31}P-NMR (acetone-d_6, 162.0 MHz, 223 K): δ 42.0 [d, J(Rh,P) = 198.8 Hz, P*i*Pr$_3$], −144.5 [sept, J(F,P) = 710.8 Hz, PF_6].

3.11. Preparation of *[Rh(dipy)$_2$]PF$_6$* (**13**)

A solution of 51 mg (0.07 mmol) of **12** in 10 ml of acetone was treated with 22 mg (0.14 mmol) of 2.2′-dipyridine at −40°C. After the reaction mixture was stirred for 15 min at −40°C, it was then warmed to r.t. A change of color from deep green to red occurred. The solution was concentrated to ca. 2 ml and upon addition of pentane (20 ml) a red solid precipitated. This was washed with 10 ml of pentane and recrystallized from acetone (2 ml) at −20°C (4 days). Red crystals were formed, which were separated from the mother liquor and dried; yield 37 mg (95%). The compound was identified by comparison of the IR data with those given for $[Rh(dipy)_2]X$ (X = NO_3, ClO_4) in Ref. [17b].

3.12. Preparation of *trans-[Rh(=CPh$_2$)(NC$_5$H$_5$)(PPh$_3$)$_2$]PF$_6$* (**16**)

This compound was prepared analogously as described for **12**, from 92 mg (0.11 mmol) of **14**, 102 mg (0.55 mmol) of KPF_6 and 2 ml (0.03 mol) of pyridine in 5 ml of THF. A deep green solid was obtained; yield 107 mg (95%), m.p. (dec.) 58°C. Anal. Found: C, 63.58; H, 4.32; N, 1.41. Calc. for $C_{54}H_{45}F_6NP_3Rh$: C, 63.73; H, 4.46; N, 1.38%. Molar conductivity: Λ (CH_3NO_2) 79 cm^2 Ω^{-1} mol^{-1}. ^{1}H-NMR (CD_2Cl_2, 400 MHz, 223 K): δ 7.76–6.46 (m, 45H, *ortho*-, *meta*- and *para*-H of C_6H_5, C_6H_5P and C_5H_5N). ^{13}C-NMR (CD_2Cl_2, 100.6 MHz, 223 K): δ 352.1 [dt, J(Rh,C) = 27.6, J(P,C) = 7.8 Hz, Rh=C], 154.7 (s, *ipso*-C of C_6H_5), 151.9 (s, *ortho*-C of C_5H_5N), 136.8 (s, *para*-C of C_5H_5N), 133.0 (vt, N = 12.9 Hz, *meta*-C of C_6H_5P), 131.6 (s, *meta*-C of C_5H_5N), 130.6 (vt, N = 42.3 Hz, *ipso*-C of C_6H_5P), 129.9 (s, *para*-C of C_6H_5P), 129.1 (s, *ortho*- or *meta*-C of C_6H_5), 128.1 (vt, N = 9.4 Hz, *ortho*-C of C_6H_5P), 127.7 (s, *ortho*- or *meta*-C of C_6H_5), 123.8 (s, *para*-C of C_6H_5). ^{19}F-NMR (CD_2Cl_2, 376.5 MHz, 223 K): δ −72.7 [d, J(P,F) = 709.5 Hz]. ^{31}P-NMR (CD_2Cl_2, 162.0 MHz, 223 K): δ 22.5 [d, J(Rh,P) = 178.7 Hz, PPh_3], −144.5 [sept, J(F,P) = 709.5 Hz, PF_6].

3.13. Preparation of *trans-[Rh(=CPh$_2$)(NCCH$_3$)(P^{i}Pr$_3$)$_2$]PF$_6$* (**17**)

This compound was prepared analogously as described for **12**, from 51 mg (0.08 mmol) of **1**, 75 mg (0.41 mmol) of KPF_6 and 2 ml (0.04 mol) of acetonitrile in 5 ml of THF. A deep green solid was obtained; yield 59 mg (93%), m.p. (dec.) 90°C. Anal. Found: C, 50.95; H, 6.98; N, 1.73. Calc. for $C_{33}H_{55}F_6NP_3Rh$: C, 51.10; H, 7.15; N, 1.81%. Molar conductivity: Λ (CH_3NO_2) 107 cm^2 Ω^{-1} mol^{-1}. IR (Nujol): ν(CN) 2278 cm^{-1}. ^{1}H-NMR (CD_2Cl_2, 400 MHz, 223 K): δ 7.60 (m, 4H, *ortho*-H of C_6H_5), 7.30 (m, 6H, *meta*- and *para*-H of C_6H_5), 2.42 (s, 3H, $NCCH_3$), 1.83 (m, 6H, PC*H*CH_3),

1.05 (m, 36H, PCHCH_3). ^{13}C-NMR (CD_2Cl_2, 100.6 MHz, 223 K): δ 343.0 [dt, J(Rh,C) = 35.2, J(P,C) = 5.6 Hz, Rh=C], 155.7 (s, *ipso*-C of C_6H_5), 135.1 (s, NCCH_3), 131.2, 128.2, 127.9 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 24.1 (vt, N = 18.8 Hz, PCHCH_3), 19.3 (s, PCHCH_3), 4.0 (s, NCCH_3). ^{19}F-NMR (CD_2Cl_2, 376.5 MHz, 223 K): δ −72.9 [d, J(P,F) = 710.6 Hz]. ^{31}P-NMR (CD_2Cl_2, 162.0 MHz, 223 K): δ 27.4 [d, J(Rh,P) = 162.8 Hz, P^{i}Pr$_3$], −144.6 [sept, J(F,P) = 710.6 Hz, PF_6].

3.14. Preparation of trans-[Rh(=CPh$_2$)(NCCH$_3$)(Sb^{i}Pr$_3$)$_2$]PF$_6$ (**18**)

This compound was prepared analogously as described for **12**, from 62 mg (0.08 mmol) of **15**, 71 mg (0.38 mmol) of KPF_6 and 2 ml (0.04 mol) of acetonitrile in 5 ml of THF. A deep green solid was obtained; yield 70 mg (95%), m.p. (dec.) 118°C. Anal. Found: C, 41.05; H, 5.38; N, 1.45. Calc. for $C_{33}H_{55}F_6NPRhSb_2$: C, 41.41; H, 5.79; N, 1.46%. Molar conductivity: Λ (CH_3NO_2) 80 cm^2 Ω^{-1} mol^{-1}. IR (Nujol): ν(CN) 2331 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.80 (m, 4H, *ortho*-H of C_6H_5), 7.58 (m, 2H, *para*-H of C_6H_5), 7.31 (m, 4H, *meta*-H of C_6H_5), 2.43 (s, 3H, NCCH_3), 2.05 [sept, J(H,H) = 7.4 Hz, 6H, SbCHCH_3], 1.20 [d, J(H,H) = 7.4 Hz, 36H, SbCHCH_3]. ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ 334.4 [d, J(Rh,C) = 25.4 Hz, Rh=C], 154.5 (s, *ipso*-C of C_6H_5), 138.3 [d, J(Rh,C) = 2.5 Hz, NCCH_3], 131.5, 128.7, 128.6 (all s, *ortho*-, *meta*- and *para*-C of C_6H_5), 21.7 (s, SbCHCH_3), 19.2 [d, J(Rh,C) = 2.5 Hz, Sb$CHCH_3$], 3.6 (s, NCCH_3). ^{19}F-NMR (188.3 MHz, $CDCl_3$): δ -73.9 [d, J(P,F) = 711.2 Hz]. ^{31}P-NMR ($CDCl_3$, 162.0 MHz): δ −144.3 [sept, J(F,P) = 711.2 Hz].

3.15. Preparation of trans-[Rh(=CPh$_2$)(NCCH$_3$)(Sb^{i}Pr$_3$)$_2$][B{3.5-C$_6$H$_3$(CF$_3$)$_2$}$_4$] (**19**)

A suspension of 49 mg (0.05 mmol) of **18** in 5 ml of Et_2O was treated with 45 mg (0.05 mmol) of Na[B{3.5-$C_6H_3(CF_3)_2$}$_4$] at r.t. The resulting deep green solution was filtered and the filtrate concentrated to ca. 1 ml in vacuo. With pentane (20 ml) a green solid was precipitated, which was separated from the mother liquor and dried; yield 82 mg (96%), m.p. (dec.) 100°C. Anal. Found: C, 46.77; H, 3.91; N, 0.84. Calc. for $C_{65}H_{67}BF_{24}NRhSb_2$: C, 46.60; H, 4.03; N, 0.84%. Molar conductivity: Λ (CH_3NO_2) 61 cm^2·Ω^{-1} mol^{-1}. IR (Nujol): ν(CN) = 2333 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.82 (m, 4H, *ortho*-H of C_6H_5), 7.72 (m, 8H, *ortho*-H of C_6H_3), 7.57 (m, 2H, *para*-H of C_6H_5), 7.54 (m, 4H, *para*-H of C_6H_3), 7.32 (m, 4H, *meta*-H of C_6H_5), 2.20 (s, 3H, NCCH_3), 2.03 [sept, J(H,H) = 7.4 Hz, 6H, SbCHCH_3], 1.18 [d, J(H,H) = 7.4 Hz, 36H, SbCHCH_3]. ^{19}F-NMR ($CDCl_3$, 188.3 MHz): δ = −62.9 (s).

3.16. Crystal structure analysis of **19**

Crystals were obtained by slow diffusion of pentane into a saturated solution of **19** in ether at 0°C. Crystal structure determination of **19**: $C_{65}H_{67}BF_{24}NRhSb_2$, M_r = 1675.42; monoclinic, space group $P\bar{2}_1/c$, Z = 4, a = 19.137(2), b = 19.439(3), c = 19.382(2) Å, β = 103.86(1)°, V = 7000.3(14) Å^3, D_{calc} = 1.590 g cm^{-3}, F(000) 3328, λ = 0.71073 Å, T = 173(2) K, μ(Mo–K$_\alpha$) = 1.102 mm^{-1}. Crystal size 0.15 × 0.15 × 0.10 mm^3; $4.20 \le 2\Theta \le 50.06°$; 41 814 reflections were measured, 12 038 of these were independent (R_{int} = 0.1104) and employed in the structure refinement (927 parameters). The R values are $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0431$ [$I > 2\sigma(I)$] and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2}$ = 0.0933 (all data); min/max residual electron density: 0.819/−1.078 e Å^{-3}. Data were collected on a IPDS (STOE) diffractometer. A semi-empirical absorption correction was applied. The structure was solved by the Patterson method (SHELXS-97) [19] and refined against F^2 by least-squares (SHELXL-97) [20]. All non-hydrogen atoms were refined anisotropically except F5 and F5′. For the hydrogen atoms a riding model was employed. Three CF_3 groups of the BAr^F_4 anion were found rotationally disordered with the carbon atom as the rotation center. In each case, two independent positions were found and refined with restraints.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147786 for compound **19**. Copies of this information may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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