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A series of di-nuclear rhodium(I) complexes with trialkylstibines as bridging ligands †

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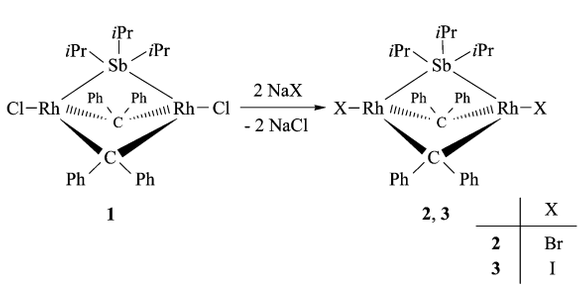
Metathetical reactions of $[Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ **1** with NaBr and NaI afforded the corresponding di-nuclear complexes $[Rh_2X_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (X = Br **2**, I **3**) in practically quantitative yields. Analogous displacement reactions of **1** with equimolar amounts of the sodium salts of acetylacetone (acacH), trifluoracetylacetone (acac-f_3-H) and dipivaloylmethane (dpmH) led to the formation of the unsymmetrical rhodium(I) compounds $[Rh_2(X)Cl(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (X = acac **4**, acac-f_3 **5**, dpm **6**). From **1** and excess of Na(acac) and Na(dpm), the symmetrical complexes $[Rh_2X_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (X = acac **7**, dpm **8**) were formed. Treatment of **7** with acetic acid and trifluoracetic acid in the molar ratio of 1 : 1 gave the unsymmetrical compounds $[Rh_2X(acac)(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (X = CF_3CO_2 **9**, CH_3CO_2 **10**), while with an excess of CR_3CO_2H the symmetrical complexes $[Rh_2(\kappa^2\text{-}O_2CR_3)_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (R = F **11**, H **12**) were obtained. The X-ray crystal structure analysis of **12** revealed that analogously to **1** the stibine ligand occupies a symmetrical bridging position. The reactions of **1**, **4** and **7** with $SbEt_3$ and $Sb(CH_2Ph)_3$ led to bridge-ligand exchange and gave the di-nuclear compounds $[Rh_2(acac)Cl(\mu\text{-}CPh_2)_2(\mu\text{-}SbEt_3)]$ **13** and $[Rh_2X(X')(\mu\text{-}CPh_2)_2\{\mu\text{-}Sb(CH_2Ph)_3\}]$ (X = X′ = Cl **14**, X = Cl, X′ = acac **15**, X = X′ = acac **16**) without cleavage of the $[Rh_2(\mu\text{-}CPh_2)_2]$ core fragment.

In the context of investigations about the reactivity of carbene-rhodium(I) complexes *trans*-$[RhCl(=CR_2)(Sb\textit{i}Pr_3)_2]$, we recently observed that these compounds are thermally quite labile and react upon heating by partial elimination of $Sb\textit{i}Pr_3$ to afford dinuclear complexes such as **1** (see Scheme 1) in excellent yields.[1] Taking into consideration that the bridging coordination mode of trialkylstibines was not only new but also unexpected,[2] we were really surprised that these dinuclear molecules with rhodium(I) in a distorted tetrahedral geometry are remarkably stable and decompose at temperatures around 190 °C or even above. Moreover, in some explorative studies we found that the bridging stibine ligand can be replaced by CO or CN*t*Bu without breaking the $[Rh(\mu\text{-}CPh_2)_2Rh]$ core unit.[1] The terminal chlorides in **1** could be replaced by acetylacetonate to give $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$, being the starting material for the synthesis of a whole family of unsymmetrical mixed-valence dirhodium compounds for which there was no precedence.[3]



Scheme 1

The present paper describes a significant extension of our initial work on ligand displacement reactions of the dichloro complex **1** as well as of the chloro(acac) and bis(acac) counterparts and illustrates that these dinuclear stibine-bridged rhodium(I) compounds have a rich chemistry indeed.

† Dedicated to Professor Wolfgang Malisch, a respected colleague and creative scientist, on the occasion of his 60th birthday.

Results and discussion

Substitution reactions of the chloro ligands

In attempting to prepare the analogues of **1** with bromide and iodide as terminal ligands, we heated the corresponding mononuclear precursors *trans*-$[RhX(=CR_2)(Sb\textit{i}Pr_3)_2]$ in benzene to 60–80 °C but instead of obtaining $[Rh_2X_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (X = Br, I), we isolated a mixture of products.[4] Although the required molecules are probably formed (though in lower yield), attempts to separate the components failed.

In contrast, the reactions of **1** with excess of NaBr or NaI in acetone affords the dibromo and diiodo complexes **2** and **3** in virtually quantitative yield (Scheme 1). Both **2** and **3** are deeply coloured, moderately air-stable solids which decompose at 174 (**2**) and 136 °C (**3**), respectively. The ^1H and ^{13}C NMR data are quite similar to those of **1** and thus there is no doubt that the proposed structure is correct. We note that all attempts to replace the chloro ligands in **1** by fluoride, using either NaF or CsF as fluoride source, remained unsuccessful.

The reactions of **1** with equimolar amounts of the sodium salts of acetylacetone (acacH), trifluoracetylacetone (acac-f_3-H) and dipivaloylmethane (dpmH) lead to the formation of the unsymmetrical dinuclear rhodium(I) compounds **4**–**6** in 92–95% isolated yield (Scheme 2). For the preparation of **4**, Na(acac) is the preferred substrate while in our initial studies Tl(acac) was used as the acac source.[3] With regard to the spectroscopic data of **4**–**6**, the remarkable feature is that the resonance for the ^{13}C nuclei of the bridging carbene carbon atoms appear in the ^{13}C NMR spectra of **4** and **5** as a multiplet but in the spectrum of **6** as a doublet of doublets due to coupling to two different rhodium atoms. In the case of the symmetrical complexes **1**–**3**, the corresponding signal is a triplet.

From **1** and a twofold excess of Na(acac) the bis(acetylacetonato) compound **7** [previously prepared from **1** and Tl(acac) in the molar ratio of 1 : 2.4][3] has been obtained. If under similar conditions (acetone, room temperature) the reaction of **1** with Na(dpm) was carried out, a mixture of products was isolated with **8**, the analogue of **7**, as the dominating species. While it was possible to separate **8** from **6** and other by-products by

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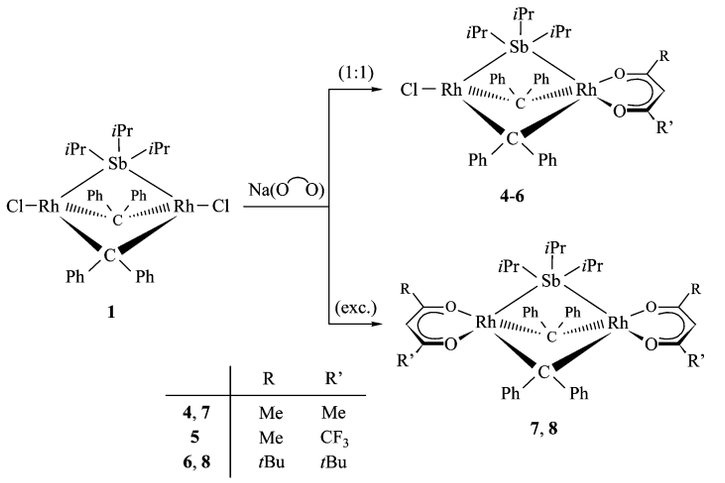
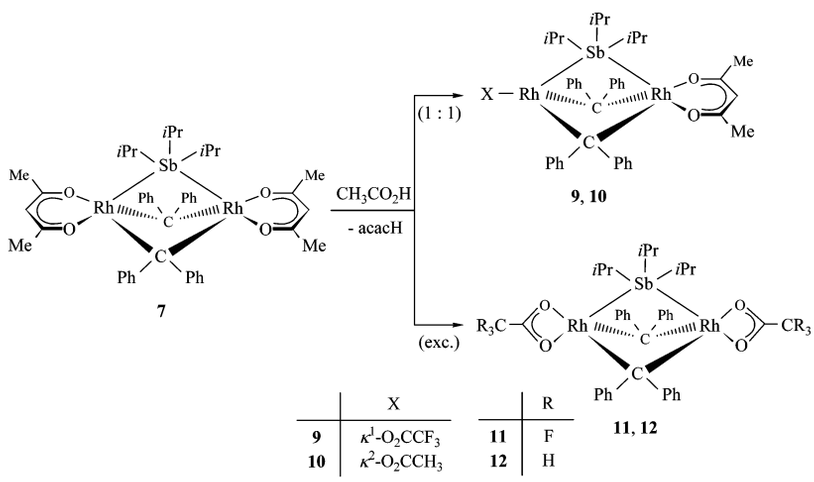


Scheme 2



Scheme 3

column chromatography, we could not remove small amounts of Na(dpm), used in excess, either by fractional crystallization or chromatographic techniques. Therefore, compound **8** was characterized spectroscopically.

Substitution reactions of the acetylacetonato ligands

Besides **1**, also the bis(acac) complex **7** has been used as starting material for the preparation of new dinuclear rhodium(I) derivatives with a bridging Sb*i*Pr$_3$ ligand. Treatment of **7** with CF_3CO_2H in the molar ratio of 1 : 1.1 gives the mixed Rh_2(acac)-(O_2CCF_3) compound **9** in 91% yield (Scheme 3). Attempts to prepare **9** on an alternative route from **4** and CF_3CO_2Tl led (even by using an excess of CF_3CO_2Tl) to a 1 : 2 mixture of **4** and **9** which we failed to separate by fractional crystallization or column chromatography. From the IR spectrum of **9**, which displays an absorption at 1704 cm^{-1}, the trifluoracetate is bonded as a monodentate ligand, similarly as in the mononuclear complex *trans*-[Rh(κ^1-O_2CCF_3)(=CPh$_2$)(P*i*Pr$_3$)$_2$].[5]

The reaction of **7** with an equimolar amount of acetic acid in toluene at −78 °C led to a mixture of **10** (*ca*. 80%), **12** (*ca*. 10%) and **7** (*ca*. 10%) which we could not separate. However, when we used an excess of CH_3CO_2H the starting material **7** reacted clearly to give the bis(acetato) compound **12** as a brown, slightly air-sensitive solid in 85% yield. The $Rh_2(O_2CCF_3)_2$ counterpart **11** (initially prepared from **1** and CF_3CO_2Tl) was obtained in a similar way. In contrast to **9**, the IR data of **11** and **12** leave no doubt that the acetato as well as the trifluoracetato ligands are coordinated in a chelating fashion.[6]

This coordination mode was confirmed by the X-ray crystal structure analysis of **12**, the result of which is shown in Fig. 1. The coordination geometry around each of the rhodium centres can be best described as distorted square-pyramidal with the antimony atom in the apical position. The respective metal atom lies above the plane formed by the oxygen atoms and the carbene carbon atoms of the bridging CPh$_2$ ligands. Whereas the Rh(1)–Rh(2) distance [2.5429(3) Å, Table 1] is almost identical to that of the dichloro analogue **1** [2.5349(5) Å], the Rh–Sb bond lengths in **12** [2.6902(2) and 2.7126(2) Å] are slightly longer than in **1** [2.6695(5) and 2.6868(5) Å]. The fact that most of the structural data for the core units, Rh_2(μ-CPh$_2$)$_2$(μ-Sb*i*Pr$_3$), of **1** and **12** are quite similar, is noteworthy insofar as the coordination numbers of the rhodium atoms in the two molecules are different. It should also be mentioned that while in the bis(acac) complexes [Rh_2(κ^2-acac)$_2$(μ-CPh$_2$)$_2$-(μ-CO)][3] and [Rh_2(κ^2-acac)$_2$(μ-CPh$_2$)$_2$(μ-PMe$_3$)][7] the two planes containing the chelating systems are twisted (like a propeller), the two rhodium atoms and the four oxygen atoms of **12** lie in the same plane, the angles Rh(1)–Rh(2)–C(5) and Rh(2)–Rh(1)–C(3) being nearly 180° (Table 1).

With regard to the relatively short Rh–Rh distance, the question arises whether a metal–metal bond should be drawn. However, if we accept that the bridging carbene ligands are neutral species, the oxidation state of both rhodium centres is +1 and the electron configuration d^8. Under these circumstances, the proposal of a metal–metal bond appears unrealistic. We assume that due to the steric requirements (size of the bridging carbon, presence of three bridging ligands building a trigonal bipyramid with the two rhodium atoms) the metal centres are pushed together without forming a direct bond.

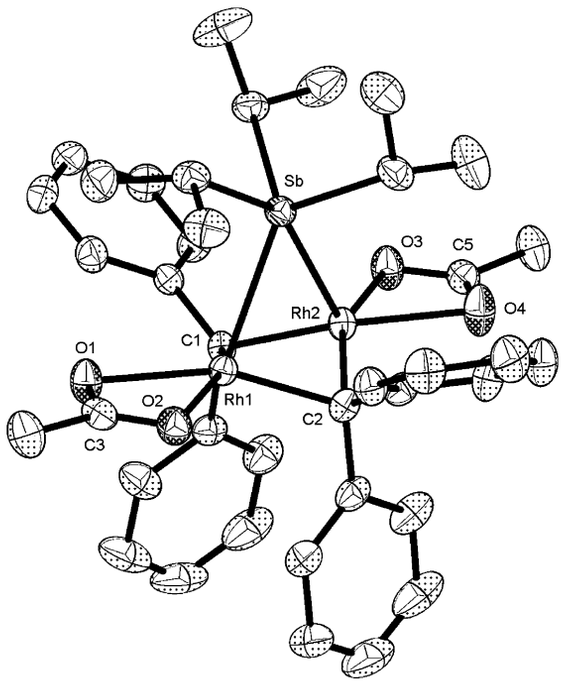


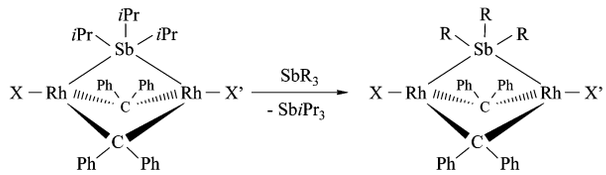
Fig. 1

Table 1 Selected bond lengths (Å) and angles (°) for compound **12**

Rh(1)–Rh(2)	2.5429(3)	Rh(2)–C(2)	1.992(2)
Rh(1)–Sb	2.6902(2)	Rh(1)–O(1)	2.2192(16)
Rh(2)–Sb	2.7126(2)	Rh(1)–O(2)	2.2455(16)
Rh(1)–C(1)	2.005(2)	Rh(2)–O(3)	2.1994(17)
Rh(1)–C(2)	2.008(2)	Rh(2)–O(4)	2.2305(17)
Rh(2)–C(1)	1.997(2)		
Rh(1)–Sb–Rh(2)	56.154(6)	O(3)–Rh(2)–O(4)	58.57(6)
Rh(1)–Rh(2)–Sb	61.478(7)	O(1)–C(3)–O(2)	119.6(2)
Rh(2)–Rh(1)–Sb	62.368(6)	O(3)–C(5)–O(4)	118.6(2)
Rh(1)–C(1)–Rh(2)	78.89(8)	Rh(1)–Rh(2)–C(5)	179.66(6)
Rh(1)–C(2)–Rh(2)	78.94(8)	Rh(2)–Rh(1)–C(3)	178.45(6)
O(1)–Rh(1)–O(2)	58.48(6)		

Substitution reactions of the triisopropylstibine ligand

It has already been mentioned that not only in the dichloro complex **1** but also in the bis(acac) counterpart **7** the stibine ligand is easily replaced by CO and CN*t*Bu to afford products with a triply bridged $[Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$ and $[Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CN\textit{t}Bu)]$ fragment.[1,3] Moreover, compounds **1** and **7** react with $SbEt_3$ to give the corresponding $[Rh_2X_2(\mu\text{-}CPh_2)_2(\mu\text{-}SbEt_3)]$ dervatives.[3] We have now found that the unsymmetrical chloro(acac) species **4** behaves similarly and upon treatment with a slight excess of $SbEt_3$ yields the dinuclear complex **13** (Scheme 4). Under analogous conditions (benzene, room temperature), reactions of **1**, **4** and **7** with $Sb(CH_2Ph)_3$ also take place and afford the related dirhodium compounds **14**–**16** in excellent yields. In neither case, a cleavage of the $Rh(\mu\text{-}CPh_2)_2Rh$ bridges has been observed. Regarding the properties of the two series of compounds, **1**, **4**, **7** and **14**–**16**, the surprising fact is that the symmetrical bis(acac) derivatives are thermally significantly less stable than the unsymmetrical counterparts. The ^{13}C NMR spectra of **13** and **15** exhibit the resonance for the two carbene carbon atoms as a doublet of doublets with a difference of the two ^{13}C–^{103}Rh coupling constants of 5.7–5.8 Hz. The corresponding signal of $\mu\text{-}CPh_2$ for **16** appears as a triplet. We finally note that while it is easy to substitute the bridging $SbiPr_3$ ligand in **1**, **4** and **7** for $SbEt_3$ and $Sb(CH_2Ph)_3$, all attempts to prepare a dinuclear rhodium complex with $SbPh_3$ in the bridging position failed.



1, 4, 7 **13-16**

	X	X'	R
13	Cl	κ^2-acac	Et
14	Cl	Cl	CH_2Ph
15	Cl	κ^2-acac	CH_2Ph
16	κ^2-acac	κ^2-acac	CH_2Ph

Scheme 4

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting material **1** was prepared as described in the literature.[1] NMR spectra were recorded at room temperature on Bruker AC 200, Bruker DRX 300 and Bruker AMX 400 instruments, IR spectra on an IFS 25 FT-IR spectrometer, and mass spectra on a Finnigan 90 MAT instrument. Melting points were measured by differential thermal analysis (DTA) with a Thermoanalyzer Du Pont 9000. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broadened signal; coupling constants *J* in Hz.

Preparations

$[Rh_2Br_2(\mu\text{-}CPh_2)_2(\mu\text{-}SbiPr_3)]$ 2. A solution of **1** (67 mg, 0.08 mmol) in acetone (30 cm^3) was treated with finely divided NaBr (80 mg, 0.78 mmol) and stirred for 15 h at room temperature. The solvent was evaporated *in vacuo* and the residue extracted with benzene (20 cm^3). After the extract was brought to dryness *in vacuo*, the red solid was washed with pentane–ether (1 : 1, 5 cm^3) and dried: yield 71 mg (96%); mp 174 °C (decomp.) (Found: C, 44.51; H, 4.48. $C_{35}H_{41}Br_2Rh_2Sb$ requires C, 44.29; H, 4.35%). MS (FAB): *m*/*z* 948 (M^+), 869 ($M^+ - Br$). NMR (C_6D_6): δ_H (400 MHz) 7.86, 7.62 (8 H, both m, *ortho*-H of C_6H_5), 6.64 (12 H, m, *meta*- and *para*-H of C_6H_5), 1.13 [18 H, d, *J*(H,H) = 7.3, $SbCHCH_3$], 0.77 [3 H, sept, *J*(H,H) = 7.3, $SbCHCH_3$]; δ_C (100.6 MHz) 185.2 [t, *J*(Rh,C) = 26.4, CPh_2], 154.9, 151.5 (both s, *ipso*-C of C_6H_5), 128.5, 127.9, 127.6, 127.4, 127.1, 123.6 (all s, C_6H_5), 22.6 (s, $SbCHCH_3$), 22.1 (s, $SbCHCH_3$).

$[Rh_2I_2(\mu\text{-}CPh_2)_2(\mu\text{-}SbiPr_3)]$ 3. A solution of **1** (85 mg, 0.10 mmol) in acetone (30 cm^3) was treated with NaI (148 mg, 0.99 mmol) and stirred for 3 h at room temperature. The solvent was evaporated *in vacuo* and the residue extracted three times with pentane–dichloromethane (2 : 1, 20 cm^3 each). After the combined extracts were brought to dryness *in vacuo*, the black solid was washed twice with pentane (10 cm^3 each) and dried: yield 100 mg (97%); mp 136 °C (decomp.) (Found: C, 39.98; H, 3.91. $C_{35}H_{41}I_2Rh_2Sb$ requires C, 40.30; H, 3.96%). MS (FAB): *m*/*z* 1042 (M^+), 915 ($M^+ - I$), 792 ($M^+ - SbiPr_3$). NMR (C_6D_6): δ_H (400 MHz) 8.03, 7.74 (8 H, both m, *ortho*-H of C_6H_5), 6.68 (12 H, m, *meta*- and *para*-H of C_6H_5), 1.14 [18 H, d, *J*(H,H) = 7.4, $SbCHCH_3$], 0.82 [3 H, sept, *J*(H,H) = 7.4, $SbCHCH_3$]; δ_C (100.6 MHz) 180.8 [t, *J*(Rh,C) = 26.5, CPh_2], 154.7, 150.6 (both s, *ipso*-C of C_6H_5), 128.9, 128.4, 127.5, 127.4, 127.1, 123.7 (all s, C_6H_5), 22.4 (s, $SbCHCH_3$), 22.1 (s, $SbCHCH_3$).

$[Rh_2(\kappa^2\text{-acac})Cl(\mu\text{-}CPh_2)_2(\mu\text{-}SbiPr_3)]$ 4. A solution of **1** (4.34 g, 5.05 mmol) in acetone (1.1 dm^3) was treated at −78 °C with Na(acac) (616 mg, 5.05 mmol) and, after warming to room temperature, stirred for 30 min at room temperature. The solvent was evaporated *in vacuo* and the residue extracted five

times with hexane–dichloromethane (1 : 1, 200 cm^3 each). After the combined extracts were concentrated to *ca.* 50 cm^3 and stored at −78 °C for 15 h, pale-brown crystals precipitated, which were separated from the mother liquor, washed twice with hexane (15 cm^3 each) and dried. The isolated product was characterized spectroscopically by comparison of the data with those of an authentic sample:[3] yield 4.43 g (95%).

[Rh_2(κ²-acac-f_3)Cl(μ-CPh_2)$_2$(μ-Sb*i*Pr_3)] 5. A solution of **1** (246 mg, 0.29 mmol) in acetone (50 cm^3) was treated at −78 °C with Na(acac-f_3) (50 mg, 0.29 mmol) and, after warming to room temperature, stirred for 30 min at room temperature. The solvent was evaporated *in vacuo* and the residue extracted five times with hexane–dichloromethane (2 : 1, 30 cm^3 each). After the combined extracts were concentrated to *ca.* 10 cm^3 and stored at −60 °C for 15 h, brown crystals precipitated, which were separated from the mother liquor, washed with hexane (3 cm^3, 0 °C) and dried: yield 256 mg (92%); mp 137 °C (decomp.) (Found: C, 48.68; H, 4.38. $C_{40}H_{45}ClF_3O_2Rh_2Sb$ requires C, 49.13; H, 4.64%). IR (KBr): ν(CO) = 1611 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 8.21, 7.37 (8 H, both m, *ortho*-H of C_6H_5), 6.95 (4 H, m, *meta*-H of C_6H_5), 6.80 (2 H, *para*-H of C_6H_5), 6.60 (6 H, m, *meta*- and *para*-H of C_6H_5), 6.02 (1 H, s, CH of acac-f_3), 1.82 (3 H, s, CH_3 of acac-f_3), 1.64 [3 H, sept, J(H,H) = 7.4, SbC*H*CH_3], 0.95 [18 H, d, J(H,H) = 7.4, SbCHC*H*$_3$]; δ_C (100.6 MHz) 196.4 (s, CO of acac-f_3), 179.2 (m, *C*Ph_2), 169.9 [q, J(F,C) = 32.5, CO of acac-f_3], 155.9, 154.6 (both s, *ipso*-C of C_6H_5), 127.7, 127.4, 126.9, 126.4, 125.0 (all s, C_6H_5), 119.9 [q, J(F,C) = 284.8, CF_3], 96.8 (s, CH of acac-f_3), 29.2 (s, CH_3 of acac-f_3), 25.4 (s, Sb*C*HCH_3), 21.4 (s, SbCH*C*H_3); δ_F (188.3 MHz) −74.7 (s).

[Rh_2(κ²-dpm)Cl(μ-CPh_2)$_2$(μ-Sb*i*Pr_3)] 6. A solution of **1** (115 mg, 0.13 mmol) in acetone (20 cm^3) was treated at −78 °C with Na(dpm) (28 mg, 0.13 mmol) and, after warming to room temperature, stirred for 1 h at room temperature. The solvent was evaporated *in vacuo* and the residue extracted twice with pentane (50 cm^3 each). After the combined extracts were brought to dryness *in vacuo*, the remaining pale-brown solid was washed twice with pentane (2 cm^3 each, 0 °C) and dried: yield 124 mg (92%); mp 84 °C (decomp.) (Found: C, 54.72; H, 5.71. $C_{46}H_{60}ClO_2Rh_2Sb$ requires C, 54.81; H, 6.00%). IR (KBr): ν(CO) = 1551, 1501 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 8.44, 7.43 (8 H, both m, *ortho*-H of C_6H_5), 6.95 (4 H, m, *meta*-H of C_6H_5), 6.81 (2 H, m, *para*-H of C_6H_5), 6.65 (4 H, m, *meta*-H of C_6H_5), 6.58 (2 H, m, *para*-H of C_6H_5), 6.29 (1 H, s, CH of dpm), 1.56 [3 H, sept, J(H,H) = 7.3, SbC*H*CH_3], 1.35 (18 H, s, $C(CH_3)_3$), 0.98 [18 H, d, J(H,H) = 7.3, SbCHC*H*$_3$]; δ_C (100.6 MHz) 198.7 (s, CO), 176.1 [dd, J(Rh,C) = 25.4, J(Rh′,C) = 21.3, *C*Ph_2], 155.7, 155.1 (both s, *ipso*-C of C_6H_5), 128.3, 127.7, 127.1, 126.8, 126.5, 126.0 (all s, C_6H_5), 92.0 (s, CH of dpm), 42.0 [s, *C*$(CH_3)_3$], 29.2 [s, C(*C*$H_3)_3$], 24.2 (s, Sb*C*HCH_3), 21.6 (s, SbCH*C*H_3).

[Rh_2(κ²-acac)$_2$(μ-CPh_2)$_2$(μ-Sb*i*Pr_3)] 7. A solution of **1** (6.50 g, 7.56 mmol) in acetone (1.0 dm^3) was treated with Na(acac) (9.23 g, 75.6 mmol) and stirred for 24 h at room temperature. The solvent was evaporated *in vacuo* and the residue extracted five times with hexane–dichloromethane (2 : 1, 150 cm^3 each). After the combined extracts were brought to dryness *in vacuo*, the residue was suspended in hexane–diethyl ether (2 : 1, 75 cm^3) and stored at −78 °C for 15 h. The mother liquor was withdrawn, the remaining solid washed twice with hexane (15 cm^3) and dried. The isolated product was characterized spectroscopically by comparison of the data with those of an authentic sample:[3] yield 6.43 g (86%).

[Rh_2(dpm)$_2$(μ-CPh_2)$_2$(μ-Sb*i*Pr_3)] 8. A solution of **1** (762 mg, 0.89 mmol) in acetone (150 cm^3) was treated with Na(dpm) (914 mg, 4.43 mmol) and stirred for 1 d at room temperature. After the solution was evaporated *in vacuo*, the remaining residue was suspended in hexane (5 cm^3) and the suspension chromatographed on Al_2O_3 (neutral, activity grade V, length of column 15 cm). With hexane, a first off-white fraction was eluted which was withdrawn. Continuing elution with hexane gave a second brown fraction, which was brought to dryness *in vacuo*. The ^{1}H NMR spectrum of the light brown solid revealed that a mixture of **8** and Na(dpm) was obtained which could not be separated by fractional crystallization or column chromatography. ^{1}H NMR (C_6D_6) of **8**: δ_H (200 MHz) 8.16 (4 H, m, *ortho*-H of C_6H_5), 7.10, 7.00, 6.65 (16 H, all m, C_6H_5), 6.18 (2 H, s, CH of dpm), 2.15 [3 H, sept, J(H,H) = 7.3, SbC*H*CH_3], 1.24 [36 H, s, $C(CH_3)_3$], 1.65 [18 H, d, J(H,H) = 7.3, SbCHC*H*$_3$].

[Rh_2(κ²-acac)(κ¹-O_2CCF_3)(μ-CPh_2)$_2$(μ-Sb*i*Pr_3)] 9. A solution of **7** (67 mg, 0.07 mmol) in benzene (15 cm^3) was treated at 5 °C with CF_3CO_2H (0.6 cm^3, 0.07 mmol) and after warming stirred for 1 h at room temperature. The solvent was evaporated *in vacuo*, the remaining light brown solid was washed three times with pentane (3 cm^3 each) and dried: yield 62 mg (91%); mp 100 °C (decomp.) (Found: C, 50.27; H, 4.82. $C_{42}H_{48}F_3O_4Rh_2Sb$ requires C, 50.38; H, 4.83%). IR (KBr): ν(OCO) = 1704, $\nu(CO_{acac})$ = 1581, 1518 cm^{-1}; NMR (C_6D_6): δ_H (400 MHz) 8.24, 7.29 (8 H, both m, *ortho*-H of C_6H_5), 7.00 (4 H, m, *meta*-H of C_6H_5), 6.84 (2 H, m, *para*-H of C_6H_5), 6.59 (6 H, m, *meta*-H and *para*-H of C_6H_5), 5.55 (1 H, s, CH of acac), 1.96 (6 H, s, CH_3 of acac), 1.67 [3 H, sept, J(H,H) = 7.4, SbC*H*CH_3], 0.93 [18 H, d, J(H,H) = 7.4, SbCHC*H*$_3$]; δ_C (100.6 MHz) 188.8 (s, CO of acac), 180.9 [dd, J(Rh,C) = 20.3, J(Rh′,C) = 25.4, *C*Ph_2], 164.5 [q, J(F,C) = 37.6, O_2CCF_3], 156.7, 155.7 (both s, *ipso*-C of C_6H_5), 127.5, 127.3, 126.9, 126.4, 125.6, 124.8 (all s, C_6H_5), 117.9 [q, J(F,C) = 284.8, CF_3], 101.3 (s, CH of acac), 28.3 (s, CH_3 of acac), 25.8 (s, Sb*C*HCH_3), 21.5 (s, SbCH*C*H_3); δ_F (188.3 MHz) −74.1 (s).

[Rh_2(κ²-acac)(κ²-O_2CCH_3)(μ-CPh_2)$_2$(μ-Sb*i*Pr_3)] 10. A solution of **7** (207 mg, 0.21 mmol) in toluene (20 cm^3) was treated dropwise at −78 °C with a solution of acetic acid (0.12 cm^3, 0.21 mmol) in toluene (10 cm^3). After the reaction mixture was warmed to room temperature, it was stirred for 1 h and then brought to dryness *in vacuo*. The ^{1}H NMR spectrum of the residue revealed that a mixture of **7** (*ca.* 10%), **10** (*ca.* 80%) and **12** (*ca.* 10%) was isolated. Attempts to separate the mixture of compounds by fractional crystallization or column chromatography failed. Data for **10**: IR (KBr): $\nu(CO_{acac})$ = 1581, 1519; $\nu(OCO)_{sym}$ = 1452 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 8.38, 7.38 (8 H, both m, *ortho*-H of C_6H_5), 7.10 (4 H, m, *meta*-H of C_6H_5), 6.95 (2 H, m, *para*-H of C_6H_5), 6.68 (4 H, m, *meta*-H of C_6H_5), 6.59 (2 H, m, *para*-H of C_6H_5), 5.56 (1 H, s, CH of acac), 2.24 (3 H, s, O_2CCH_3), 1.99 (6 H, s, CH_3 of acac), 1.73 [3 H, sept, J(H,H) = 7.3, SbC*H*CH_3], 1.02 [18 H, d, J(H,H) = 7.3, SbCHC*H*$_3$]; δ_C (100.6 MHz) 188.5 (s, CO of acac), 186.9 (s, O_2CCH_3), 178.5 [dd, J(Rh,C) = 22.9, J(Rh′,C) = 21.0, *C*Ph_2], 157.3 (s, *ipso*-C of C_6H_5), 156.3 (m, *ipso*-C of C_6H_5), 127.4, 127.1, 126.8, 126.3, 126.0, 125.6 (all s, C_6H_5), 101.0 [d, J(Rh,C) = 1.9, CH of acac], 65.9 (s, O_2CCH_3), 28.3 (s, CH_3 of acac), 25.3 (s, Sb*C*HCH_3), 21.6 (s, SbCH*C*H_3).

[Rh_2(κ²-O_2CCF_3)$_2$(μ-CPh_2)$_2$(μ-Sb*i*Pr_3)] 11. A solution of **7** (107 mg, 0.11 mmol) in benzene (5 cm^3) was treated with excess of CF_3CO_2H (83 μl, 1.08 mmol) and stirred for 5 min at room temperature. The solvent was evaporated *in vacuo* and the remaining residue recrystallized from pentane (5 cm^3) at −78 °C to give dark red crystals which were identified by comparison of the ^{1}H and ^{19}F NMR data with those from the literature as **11**:[3] yield 103 mg (94%).

[Rh_2(κ²-O_2CCH_3)$_2$(μ-CPh_2)$_2$(μ-Sb*i*Pr_3)] 12. A solution of **7** (478 mg, 0.48 mmol) in benzene (50 cm^3) was treated with CH_3CO_2H (900 μl, 15.7 mmol) and stirred for 1 h at room

temperature. The solvent was evaporated *in vacuo* and the remaining brown solid washed twice with diethyl ether (5 cm^3 each) and dried: yield 374 mg (85%); mp 147 °C (decomp.) (Found: C, 51.93; H, 5.40. $C_{39}H_{47}O_4Rh_2Sb$ requires C, 51.63; H, 5.22%). IR (KBr): $\nu(OCO)_{asym}$ = 1525, $\nu(OCO)_{sym}$ = 1453 cm^{-1}; NMR (C_6D_6): δ_H (300 MHz) 8.41, 7.60 (8 H, both m, *ortho*-H of C_6H_5), 7.03 (4 H, m, *meta*-H of C_6H_5), 6.82 (2 H, m, *para*-H of C_6H_5), 6.69 (4 H, m, *meta*-H of C_6H_5), 6.59 (2 H, m, *para*-H of C_6H_5), 2.22 (6 H, s, O_2CCH_3), 1.19 [3 H, br sept, J(H,H) = 5.4, $SbCHCH_3$], 1.13 [18 H, br d, J(H,H) = 5.4, $SbCHCH_3$]; δ_C (75.5 MHz) 187.4 (s, O_2CCH_3), 179.3 [t, J(Rh,C) = 22.9, CPh_2], 157.5 (s, *ipso*-C of C_6H_5), 154.8 [t, J(Rh,C) = 2.2, *ipso*-C of C_6H_5], 127.7, 127.4, 126.8, 126.6, 124.9, 124.4 (all s, C_6H_5), 23.9 (s, O_2CCH_3), 23.8 (s, $SbCHCH_3$), 21.8 (s, $SbCHCH_3$).

[$Rh_2(\kappa^2$-acac)Cl(μ-$CPh_2)_2$(μ-$SbEt_3$)] 13. A solution of **4** (100 mg, 0.11 mmol) in benzene (10 cm^3) was treated with $SbEt_3$ (26 μl, 0.16 mmol) and stirred for 1 h at room temperature. The solvent was removed *in vacuo*, and the remaining pale-brown solid was washed twice with pentane (5 cm^3 each) and dried: yield 90 mg (94%); mp 176 °C (decomp.) (Found: C, 50.15; H, 4.89. $C_{37}H_{42}ClO_2Rh_2Sb$ requires C, 50.40; H, 4.80%). IR (KBr): ν(CO) = 1578, 1517 cm^{-1}; NMR (C_6D_6): δ_H (400 MHz) 8.23, 7.46 (8 H, both m, *ortho*-H of C_6H_5), 7.01 (4 H, m, *meta*-H of C_6H_5), 6.88 (2 H, m, *para*-H of C_6H_5), 6.63 (6 H, m, *meta*-H and *para*-H of C_6H_5), 5.44 (1 H, s, CH of acac), 1.92 (6 H, s, CH_3 of acac), 1.09 [6 H, q, J(H,H) = 7.9, $SbCH_2CH_3$], 0.74 [9 H, t, J(H,H) = 7.9, $SbCH_2CH_3$]; δ_H (100.6 MHz) 188.8 (s, CO of acac), 178.4 [dd, J(Rh,C) = 25.4, J(Rh′,C) = 19.6, CPh_2], 156.5, 153.9 (both s, *ipso*-C of C_6H_5), 127.6, 127.2, 126.6, 126.5, 126.2, 124.8 (all s, C_6H_5), 101.0 [d, J(Rh,C) = 1.5, CH of acac], 28.1 (s, CH_3 of acac), 10.8 (s, $SbCH_2CH_3$), 10.2 (s, $SbCH_2CH_3$).

[Rh_2Cl_2(μ-$CPh_2)_2${μ-$Sb(CH_2Ph)_3$}] 14. A solution of **1** (65 mg, 0.08 mmol) in benzene (5 cm^3) was treated with $Sb(CH_2Ph)_3$ (90 mg, 0.23 mmol) and stirred for 12 h at room temperature. Brown crystals precipitated, which were separated from the solution, washed twice with benzene (2 cm^3) and dried: yield 65 mg (86%); mp 155 °C (decomp.) (Found: C, 56.32; H, 4.44. $C_{47}H_{41}Cl_2Rh_2Sb$ requires C, 56.21; H, 4.12%). NMR (CD_2Cl_2): δ_H (400 MHz) 8.13 (4 H, m, *ortho*-H of C_6H_5), 7.33, 6.84 (25 H, both m, C_6H_5), 6.09 (6 H, m, *ortho*-H of $SbCH_2C_6H_5$), 3.13 (6 H, s, $SbCH_2$); δ_C (100.6 MHz) 185.0 (m, CPh_2), 155.5, 153.3 (both s, *ipso*-C of C_6H_5), 135.5 (s, *ipso*-C of $SbCH_2C_6H_5$), 129.7, 128.7, 128.5, 127.7, 127.5, 126.7, 126.4, 126.0, 125.1 (all s, C_6H_5), 30.7 (s, $SbCH_2$).

[$Rh_2(\kappa^2$-acac)Cl(μ-$CPh_2)_2${μ-$Sb(CH_2Ph)_3$}] 15. A solution of **4** (47 mg, 0.05 mmol) in benzene (5 cm^3) was treated with $Sb(CH_2Ph)_3$ (60 mg, 0.15 mmol) and stirred for 12 h at room temperature. The solvent was evaporated *in vacuo* and the residue extracted twice with diethyl ether (20 cm^3 each). After the combined extracts were brought to dryness *in vacuo*, the remaining brown solid was washed twice with pentane (5 cm^3 each) and dried: yield 41 mg (75%); mp 126 °C (decomp.) (Found: C, 58.59; H, 4.90. $C_{52}H_{48}ClO_2Rh_2Sb$ requires C, 58.48; H, 4.53%). IR (KBr): ν(CO) = 1581, 1521 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 8.44, 7.45 (8 H, both m, *ortho*-H of C_6H_5), 7.15 (4 H, m, C_6H_5), 6.88 (11 H, m, C_6H_5), 6.64 (6 H, m, C_6H_5), 6.22 (6 H, m, *ortho*-H of $SbCH_2C_6H_5$), 5.67 (1 H, s, CH of acac), 3.00 (6 H, s, $SbCH_2$), 1.97 (6 H, s, CH_3 of acac); δ_C (100.6 MHz) 189.2 (s, CO of acac), 179.7 [dd, J(Rh,C) = 25.7, J(Rh′,C) = 20.0, CPh_2], 156.7, 154.1 (both s, *ipso*-C of C_6H_5), 136.9 (s, *ipso*-C of $SbCH_2C_6H_5$), 130.0, 128.8, 128.5, 128.3, 127.4, 127.0, 126.4, 125.9, 124.8 (all s, C_6H_5), 101.3 (s, CH of acac), 29.2 (s, $SbCH_2$), 28.3 (s, CH_3 of acac).

[$Rh_2(\kappa^2$-acac)$_2$(μ-$CPh_2)_2${μ-$Sb(CH_2Ph)_3$}] 16. A solution of **7** (125 mg, 0.13 mmol) in benzene (15 cm^3) was treated with $Sb(CH_2Ph)_3$ (150 mg, 0.38 mmol) and stirred for 12 h at room temperature. The solvent was evaporated *in vacuo* and the residue extracted twice with pentane (20 cm^3 each). After the combined extracts were concentrated to *ca.* 5 cm^3 *in vacuo*, the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 15 cm). With hexane, a first off-white fraction was eluted which was withdrawn. Continuing elution with hexane gave a second brown fraction, which was brought to dryness *in vacuo*. Pale-brown solid: yield 133 mg (93%); mp 80 °C (decomp.) (Found: C, 60.25; H, 5.14. $C_{57}H_{55}O_4Rh_2Sb$ requires C, 60.50; H, 4.90%). IR (KBr): ν(CO) 1581, 1518 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 8.45 (4 H, m, *ortho*-H of C_6H_5), 7.20, 6.94, 6.72, 6.64 (25 H, all m, C_6H_5), 6.39 (6 H, m, *ortho*-H of $SbCH_2C_6H_5$), 5.67 (2 H, s, CH of acac), 2.97 (6 H, s, $SbCH_2$), 2.02 (12 H, s, CH_3 of acac); δ_C (100.6 MHz) 188.8 (s, CO of acac), 176.6 [t, J(Rh,C) = 20.0, CPh_2], 156.9, 156.3 (both s, *ipso*-C of C_6H_5), 138.2 (s, *ipso*-C of $SbCH_2C_6H_5$), 130.1, 129.5, 128.7, 128.3, 127.0, 126.9, 126.1, 125.9, 125.5 (all s, C_6H_5), 100.5 (s, CH of acac), 28.7 (s, $SbCH_2$), 28.5 (s, CH_3 of acac).

Crystallography

Single crystals of **12** were grown from a saturated solution in benzene; crystal size 0.16 × 0.11 × 0.10 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 19.0176(10), b = 20.0618(11), c = 11.0473(6) Å, β = 103.3600(10)°, V = 4100.8(4) Å^3, Z = 4, D_c = 1.596 g cm^{-3}; max 2Θ = 52.74° [Mo-Kα, λ = 0.71073 Å, graphite monochromator, ω-scan, T = 173(2) K], 65655 reflections scanned, 8389 unique [R(int) = 0.0248], 8194 observed [$I > 2\sigma(I)$], Lorentz-polarization and empirical absorption corrections, direct methods (SHELXS-97),[8] atomic coordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms refined anisotropically by full-matrix least squares on F^2 (SHELXL-97),[9] one molecule of benzene in the asymmetric unit; 477 parameters, reflex/parameter ratio 17.59, $R1$ = 0.0237, $wR2$ = 0.0572, residual electron density 0.617/ −0.374 e Å^{-3}.

CCDC reference number 201827.

See http://www.rsc.org/suppdata/dt/b3/b300786n/ for crystallographic data in CIF or other electronic format.

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