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Reactions of rhodium trifluoroacetate with triphenylphosphine and pyridine. Molecular structure of $Rh_2(O_2CCF_3)_4(py)_4$

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Abstract

$Rh_2(O_2CCF_3)_4$ reacts with two mol of triphenylphosphine forming the adduct $Rh_2(O_2CCF_3)_4(PPh_3)_2$. This compound in solution, even at room temperature, undergoes slow stepwise orthometalation of the phosphine ligands forming the doubly metalated compound $Rh_2(O_2CCF_3)_2[(C_6H_4)P(C_6H_5)_2]_2$. This reaction has been monitored by ^{31}P NMR spectroscopy detecting in solution three reaction intermediates. $Rh_2(O_2CCF_3)_4$ reacts with excess of pyridine to form the compound $Rh_2(O_2CCF_3)_4(py)_4$ that can be structurally classified as a class III adduct. It contains two bridging and two monodentate equatorial carboxylates and two equatorial and two axial pyridine ligands. The structure of this compound has been determined by X-ray diffraction. $M_r = 974.3$, monoclinic, space group $P2_1/n$, $a = 10.504(1)$, $b = 18.108(1)$, $c = 35.377(1)$ Å, $\beta = 96.416(8)°$, $V = 6686.6(8)$ Å^3, $Z = 8$, $D_x = 1.94$ Mg/m^3. Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å), μ(Mo Kα) = 10.89 cm^{-1}, $F(000) = 3824$, $T = 293$ K. Final conventional R factor = 0.12 for 2258 'observed' reflections and 312 variables. The structure was solved by Patterson interpretation using the program SHELXS86 and the Fourier synthesis.

Introduction

It is known [1] that $Rh_2(O_2CCH_3)_4$ reacts with triphenylphosphine in refluxing acetic acid giving a compound of formulation $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$, where two orthometalated phosphines are bridging the rhodium atoms. More recently the monometalated compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2](HO_2CCH_3)_2$ has also been isolated [2a,b] from the same reaction and characterized by X-ray methods. An additional intermediate with one metalated phosphine and one equatorial phosphine has been photochemically prepared [2c]. It has been structurally identified based on the observation of a characteristic high field resonance in the ^{31}P NMR spectrum [2c–e].

We were interested in extending our studies to $Rh_2(O_2CCF_3)_4$ and comparing the behavior of these two dimers in metalation reactions with triphenylphosphine. It is known [3] that, due to the strongly electron-withdrawing nature of the CF_3 group, bridging $CF_3CO_2^-$ groups are easily displaced by Lewis bases leading to monodentate coordination. According to that, the displacement of one carboxylate group by one phosphine giving doubly metalated compounds should be more favored, and consequently the metalation should be easier, in $Rh_2(O_2CCF_3)_4$ than in $Rh_2(O_2CCH_3)_4$. In order to confirm this point, we have studied the reaction of $Rh_2(O_2CCF_3)_4$ with triphenylphosphine.

We present here spectroscopic evidence that the class I adduct [3a] $Rh_2(O_2CCF_3)_4(PPh_3)_2$, in solution, even at room temperature, undergoes stepwise orthometalation of the phosphine ligands forming the doubly metalated compound $Rh_2(O_2CCF_3)_2[(C_6H_4)P(C_6H_5)_2]_2$. We also report in this paper the crystal structure of the class III compound $Rh_2(O_2CCF_3)_4(py)_4$ that had been previously described but not fully characterized [3d].

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Results and discussion

Reaction of $Rh_2(O_2CCF_3)_4$ with PPh_3

We have studied the behavior of $Rh_2(O_2CCF_3)_4(PPh_3)_2$ in $CHCl_3$ or toluene solution. This compound, in the temperature range 25–45 °C, undergoes chemical evolution that was monitored by ^{31}P NMR spectroscopy. The spectra show changes in the nature and relative intensity of the NMR signals. In the first hours of reaction at 45 °C in toluene, the spectra are quite complicated, but after 120 h of reaction the mixture is very simple showing only a doublet at 17.8 ppm (^1J(Rh–P) = 175 Hz). Based on spectroscopic and elemental analysis this reaction compound was identified as $Rh_2(O_2CCF_3)_2[(C_6H_4)P(C_6H_5)_2]_2$ (**V**). The ^{13}C NMR spectrum of **V** shows a multiplet signal centered at 161.8 ppm corresponding to the metalated carbon atom. The quartet signal at 114.9 ppm and ^1J(C–F) = 289 Hz is assigned to the carbon atoms of CF_3 groups. The same compound can be obtained by dissolving $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2$ in trifluoroacetic acid for 24 h.

These results indicate that the adduct $Rh_2(O_2CCF_3)_4(PPh_3)_2$ undergoes chemical evolution resulting in the substitution of two trifluoroacetate groups by two orthometalated triphenylphosphine anions. A similar metalation reaction has been reported for the adduct $Rh_2(O_2CCH_3)_4(PPh_3)_2$ [1] in refluxing acetic acid.

Some representative ^{31}P NMR spectra, corresponding to different reaction times at 45 °C in toluene, are represented in Fig. 1. There is already enough work done to allow the spectroscopic parameters to have diagnostic value. Signals in the chemical shift range of 0 to −40 ppm are assigned to phosphines in axial coordination; metalated phosphines give resonances in the range 7–25 ppm while higher chemical shift values, 30–40 ppm, are characteristic for non-metalated phosphines in equatorial coordination.

At least three intermediate compounds **II**–**IV** (Scheme 1 can be identified in solution. Two signals at 21.1 ppm (metalated phosphine, ^1J(Rh–P) = 154 Hz; ^3J(P–P) = 8 Hz) and −7.7 ppm (axial phosphine, ^1J(Rh–P) = 114 Hz; ^2J(Rh–P) = 22 Hz; ^3J(P–P) = 8 Hz) correspond to the monometalated compound in the form of its adduct with triphenylphosphine $Rh_2(O_2CCF_3)_3[(C_6H_4)P(C_6H_5)_2](PPh_3)$ (**III**). This assignement has been confirmed by preparing the same compound via carboxylate exchange reaction with trifluoroacetic acid in $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)_2]$ [2b] followed by further addition of triphenylphosphine. However a close inspection of the ^{31}P NMR in the first twelve hours of evolution shows an additional doublet at 23.4 ppm which is apparently in equilibrium with the signal at 21.1 ppm assigned to the monometalated species **III**. Considering the ability of $CF_3CO_2^-$ groups to act as monodentate ligands in this type of compounds [3], the above mentioned spectroscopic observation might be due to an equilibrium involving bridging and monodentate $CF_3CO_2^-$ groups in species **III**. The other two compounds detected in solution contain one triphenylphosphine in equatorial coordination and show the characteristic low field signal. We have proposed this type of compound as intermediate in the metalation reaction [2b, d]. There are two examples of dirhodium(II) compounds with equatorial phosphines that have been structurally characterized by X-ray methods [2e, 4], one of them [2e] contains a very similar structure to that proposed for species **IV**.

It is interesting to remark that although a similar reaction scheme had been previously proposed to describe the reactivity of $Rh_2(O_2CCH_3)_4$ and triarylphosphines [2b], the first two steps of the reaction scheme have never been spectroscopically observed. In the present reaction with $Rh_2(O_2CCF_3)_4(PPh_3)_2$ all the reaction steps can be studied. However the intermediate **IV** is detected in solution only in a very small amount.

In order to simplify the spectra and to get further information about this metalation reaction we have also studied the reaction of $Rh_2(O_2CCF_3)_4$ and PPh_3 in a 1:1 molar ratio. In these conditions mainly compound **III**, now without triphenylphosphine in the axial position, is spectroscopically detected in solution with some amounts (*c.* 20%) of the doubly metalated compound **V**. The intermediate compound **II** with one equatorial phosphine is clearly observed in solution showing a ^{31}P NMR resonance at *c.* 34 ppm.

The spectroscopic study of the reaction of $Rh_2(O_2CCF_3)_3[(C_6H_4)P(C_6H_5)_2]$ with one mol of phosphine supports the proposed reaction. The intermediate compound **IV** is observed in solution showing resonances at 40.3 ppm (equatorial phosphine, ^1J(Rh–P) = 193 Hz) and 8.5 ppm (metalated phosphine, ^1J(Rh–P) = 134 Hz, ^3J(P–P) = 10 Hz).

These results clearly indicate that the bis adduct $Rh_2(O_2CCF_3)_4(PPh_3)_2$ undergoes in solution rearrangement of one phosphine from axial to equatorial coordination, structure **II**, which reacts giving the monometalated compound **III**. The same sequence of reactions is repeated, **III**–**IV**–**V**, yielding the doubly metalated compound **V** (Scheme 1). These results also confirm that the metalation of triphenylphosphine is, as expected, considerably faster in $Rh_2(O_2CCF_3)_4$ than in $Rh_2(O_2CCH_3)_4$.

We have confirmed the previous observations made by Telser and Drago [3d, 5] that an excess of triphenylphosphine cleaves the metal–metal bond producing a mixture of rhodium(I) and rhodium(III) compounds. However with a stoichiometric amount of

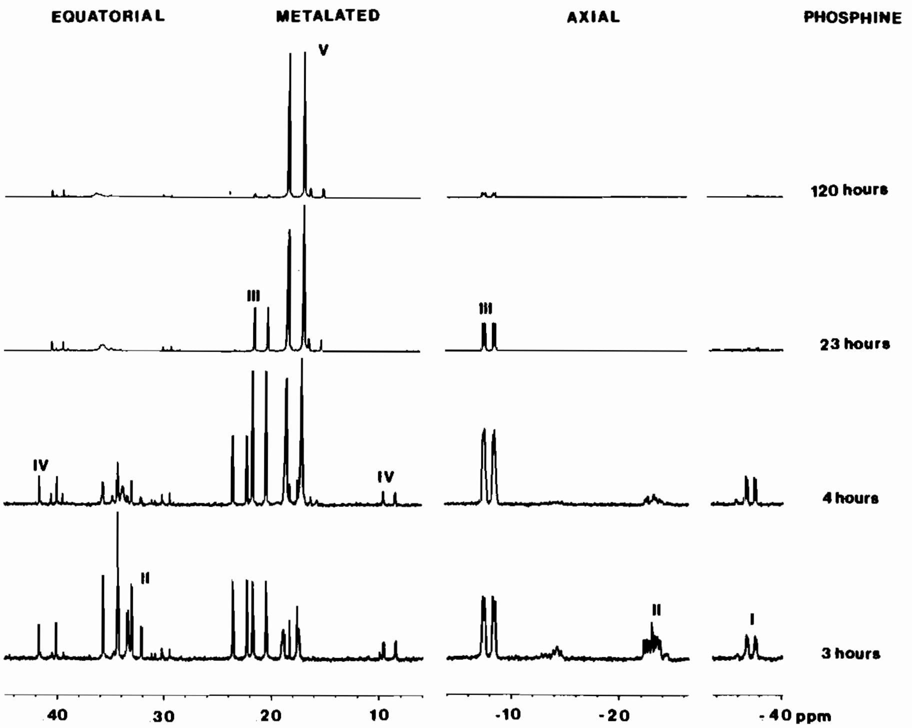
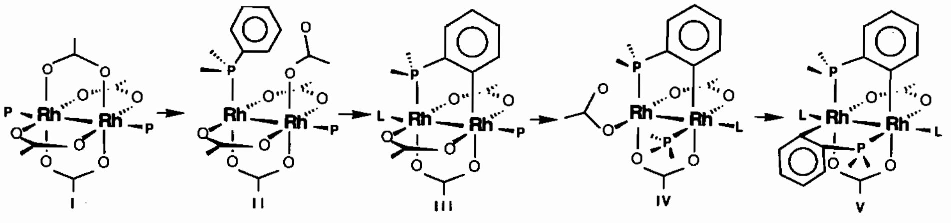


Fig. 1. ^{31}P NMR spectra of the reaction of $Rh_2(O_2CCF_3)_4$ and PPh_3 1:2 molar ratio in toluene at 45 °C.



L = CF_3CO_2H

Scheme 1.

phosphine no decomposition is observed and only metalated compounds are formed.

Reaction of $Rh_2(O_2CCF_3)_4$ with pyridine

Only phosphine metalated dirhodium(II) compounds have been described until now. As orthometalation of pyridine rings has been observed in diirdium(II) compounds [6] we decided to explore this type of reaction in dirhodium(II) compounds.

When a solution of $Rh_2(O_2CCF_3)_4$ in a mixture of toluene:pyridine (4:1) is boiled for 45 min, a red solution is formed, from which a red compound (VI) can be isolated. The same compound is obtained by stirring $Rh_2(O_2CCF_3)_4$ in a $CHCl_3$:pyridine mixture at room temperature. The IR of this compound ($CHCl_3$ solution) shows two absorption bands at 1707 and 1643 cm^{-1} and the ^{13}C NMR spectrum also shows two quartet signals centered at 112.8 and 111.6 ppm ($^1J(C–F) = 285$ Hz and $^1J(C–F) = 285$ Hz, respectively) corresponding to two different types of carbon atom in the CF_3 groups. These data are consistent with the presence of bridging and monodentated $CF_3CO_2^-$ groups. The ^1H and ^{13}C NMR spectra indicate the presence of two different sets of pyridine ligands in the molecule (^1H NMR: 8.53 (doublet), 7.75 (triplet) and 7.35 (triplet) ppm for NC_5H_5 in axial position and 8.42 (doublet), 7.69 (triplet) and 7.17 (triplet) ppm for NC_5H_5 in equatorial position; ^{13}C NMR: 149.4, 137.1 and 124.4 ppm corresponding to NC_5H_5 in axial position and 151.9, 136.4 and 123.6 ppm for NC_5H_5 in equatorial position). This assignment is based on the observation that the ^1H and ^{13}C NMR spectra of samples of compound **VI** show important changes in the relative intensity of the signal in the aromatic region after being passed through a chromatography column. In particular one of the two sets of pyridine resonances decreases considerably after this treatment. Due to that we assign this set of signals to the axial pyridine ligands.

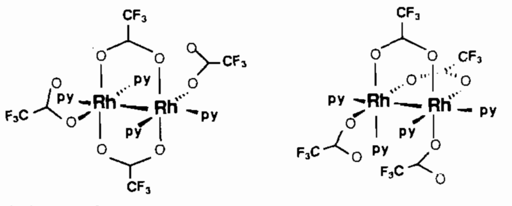
In addition to the above described compound two more products, not well characterized, were isolated from the reaction mixture after the thermal treatment. The ^{1}H and ^{31}C NMR spectra suggest that replacement of the axial pyridines had occurred.

Telser and Drago [3d] isolated a compound from the reaction of $Rh_2(O_2CCF_3)_4$ and pyridine at room temperature that had similar IR values to those observed for compound **VI**. They assigned to that compound a transoid configuration (Scheme 2). We have solved the crystal structure of compound **VI** confirming that this compound has a cisoid configuration (Scheme 2) and not a transoid configuration proposed before.

Crystal structure

The structure consists of two crystallographically independent molecules 1 and 2, each having the same chemical composition. No significant structural differences were found between the two molecules and so for simplicity only one molecule is shown in Fig. 2, where the atomic numbering scheme is given. The positional and thermal parameters for both molecules are given in Table 1. A selection of bond distances and angles are collected in Table 2.

Each molecule consists of a binuclear dirhodium unit with Rh–Rh bond distances of 2.56(1) and 2.54(1) Å for molecules 1 and 2, respectively. The coordination around each rhodium atom is completed by two bridging



Scheme 2.

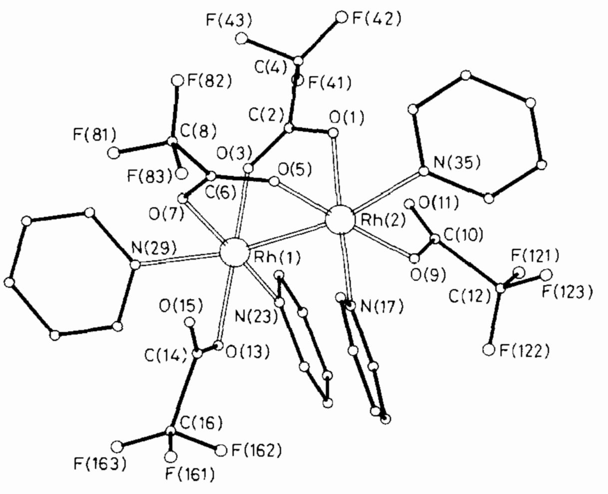


Fig. 2. PLUTO drawing of one of the two independent molecules of $Rh_2(O_2CCF_3)_4(py)_4$.

TABLE 1. Fractional positional and thermal parameters (with e.s.d.s) for $Rh_2(O_2CCF_3)_4(py)_4$

Atom	x	y	z	U_{eq}/U_{iso} ($\times 100$)^{a}
Molecule 1				
Rh1	−0.1440(5)	0.2078(3)	0.1928(2)	3.8(2)*
Rh2	−0.0611(4)	0.3314(3)	0.2209(2)	4.2(2)*
O1	−0.168(4)	0.308(2)	0.264(1)	7(2)*
C2	−0.242(6)	0.251(4)	0.260(2)	5(2)
O3	−0.260(3)	0.207(2)	0.234(1)	4(1)
C4	−0.320(5)	0.250(3)	0.294(2)	10(3)
F41	−0.428(5)	0.239(3)	0.276(2)	29(1)
F42	−0.329(5)	0.294(3)	0.321(2)	29(1)
F43	−0.277(5)	0.190(3)	0.308(2)	29(1)
O5	0.079(3)	0.270(2)	0.249(1)	4(2)*
C6	0.078(6)	0.200(4)	0.250(2)	5(2)
O7	−0.004(4)	0.161(2)	0.230(1)	4(1)
C8	0.186(4)	0.166(3)	0.275(2)	9(3)
F81	0.166(4)	0.100(3)	0.265(2)	29(1)
F82	0.196(4)	0.169(3)	0.311(2)	29(1)
F83	0.286(4)	0.188(3)	0.263(2)	29(1)
O9	−0.192(4)	0.402(2)	0.193(1)	7(2)*
C10	−0.319(6)	0.411(3)	0.197(2)	5(2)
O11	−0.391(4)	0.373(3)	0.212(1)	7(1)
C12	−0.357(5)	0.483(3)	0.169(2)	19(5)
F121	−0.474(5)	0.490(3)	0.171(2)	29(1)
F122	−0.339(5)	0.475(3)	0.135(2)	29(1)
F123	−0.298(5)	0.538(3)	0.182(2)	29(1)
O13	−0.037(4)	0.206(2)	0.146(1)	4(1)
C14	0.081(5)	0.195(3)	0.148(1)	2(1)
O15	0.170(4)	0.194(2)	0.171(1)	6(1)
C16	0.104(5)	0.173(3)	0.103(1)	14(4)
F161	0.214(5)	0.186(3)	0.095(1)	29(1)
F162	0.029(5)	0.222(3)	0.089(1)	29(1)
F163	0.068(5)	0.111(3)	0.090(1)	29(1)
N17	0.052(3)	0.359(2)	0.1791(9)	2(1)
C18	0.183(3)	0.360(2)	0.1915(9)	4(2)
C19	0.269(3)	0.386(2)	0.1673(9)	4(2)
C20	0.225(3)	0.410(2)	0.1307(9)	4(2)
C21	0.095(3)	0.408(2)	0.1183(9)	6(2)
C22	0.008(3)	0.383(2)	0.1425(9)	5(2)
N23	−0.293(3)	0.245(2)	0.156(1)	3(1)
C24	−0.271(3)	0.279(2)	0.122(1)	6(2)
C25	−0.374(3)	0.297(2)	0.095(1)	8(2)
C26	−0.499(3)	0.282(2)	0.103(1)	9(3)
C27	−0.521(3)	0.249(2)	0.137(1)	9(3)
C28	−0.418(3)	0.231(2)	0.164(1)	8(2)
N29	−0.210(3)	0.092(1)	0.177(1)	3(1)
C30	−0.214(3)	0.039(1)	0.206(1)	2(1)
C31	−0.251(3)	−0.033(1)	0.196(1)	7(2)
C32	−0.284(3)	−0.052(1)	0.158(1)	7(2)
C33	−0.281(3)	0.001(1)	0.130(1)	6(2)
C34	−0.244(3)	0.073(1)	0.139(1)	4(2)
N35	0.014(3)	0.428(2)	0.257(1)	3(1)
C36	0.000(3)	0.500(2)	0.243(1)	5(2)
C37	0.032(3)	0.560(2)	0.267(1)	2(1)
C38	0.079(3)	0.549(2)	0.305(1)	3(2)
C39	0.093(3)	0.477(2)	0.319(1)	3(2)
C40	0.061(3)	0.417(2)	0.295(1)	6(2)
Molecule 2				
Rh1′	−0.1476(4)	0.1917(2)	−0.1054(2)	3.8(2)*
Rh2′	−0.1885(5)	0.2894(3)	−0.0568(2)	5.6(2)*

(*continued*)

TABLE 1. (*continued*)

Atom	x	y	z	U_{eq}/U_{iso} ($\times 100$)^a
O1′	−0.136(4)	0.359(2)	−0.097(1)	4(1)
C2′	−0.070(6)	0.329(4)	−0.119(2)	6(2)
O3′	−0.058(4)	0.269(2)	−0.133(1)	6(1)
C4′	−0.007(6)	0.392(3)	−0.137(2)	29(1)
F41′	−0.041(6)	0.450(3)	−0.122(2)	29(1)
F42′	−0.058(6)	0.389(3)	−0.170(2)	29(1)
F43′	0.112(6)	0.392(3)	−0.136(2)	29(1)
O5′	−0.360(4)	0.297(3)	−0.084(1)	7(1)
C6′	−0.386(6)	0.274(4)	−0.112(2)	5(2)
O7′	−0.310(4)	0.229(2)	−0.134(1)	6(1)
C8′	−0.507(4)	0.285(3)	−0.137(2)	11(3)
F81′	−0.587(4)	0.284(3)	−0.114(2)	29(1)
F82′	−0.531(4)	0.235(3)	−0.161(2)	29(1)
F83′	−0.512(4)	0.346(3)	−0.154(2)	29(1)
O9′	−0.012(3)	0.284(2)	−0.025(1)	6(2)*
C10′	0.097(6)	0.311(3)	−0.029(2)	4(2)
O11′	0.128(5)	0.339(3)	−0.059(2)	9(2)
C12′	0.191(5)	0.301(4)	0.006(2)	26(6)
F121′	0.293(5)	0.305(4)	−0.009(2)	29(1)
F122′	0.171(5)	0.236(4)	0.015(2)	29(1)
F123′	0.201(5)	0.340(4)	0.036(2)	29(1)
O13′	−0.238(4)	0.104(2)	−0.084(1)	6(2)*
C14′	−0.354(6)	0.089(4)	−0.080(2)	5(2)
O15′	−0.452(4)	0.128(2)	−0.091(1)	5(1)
C16′	−0.381(5)	0.009(2)	−0.064(2)	8(3)
F161′	−0.273(5)	−0.025(2)	−0.039(2)	29(1)
F162′	−0.445(5)	0.036(2)	−0.041(2)	29(1)
F163′	−0.427(5)	−0.034(2)	−0.088(2)	29(1)
N17′	−0.254(3)	0.222(2)	−0.0173(9)	4(1)
C18′	−0.170(3)	0.182(2)	0.0085(9)	5(2)
C19′	−0.218(3)	0.140(2)	0.0368(9)	6(2)
C20′	−0.350(3)	0.138(2)	0.0393(9)	5(2)
C21′	−0.433(3)	0.178(2)	0.0134(9)	4(2)
C22′	−0.386(3)	0.220(2)	−0.0149(9)	7(2)
N23′	0.017(3)	0.155(2)	−0.078(1)	5(1)
C24′	0.135(3)	0.178(2)	−0.088(1)	4(2)
C25′	0.248(3)	0.147(2)	−0.071(1)	4(2)
C26′	0.244(3)	0.092(2)	−0.043(1)	6(2)
C27′	0.126(3)	0.069(2)	−0.033(1)	5(2)
C28′	0.013(3)	0.100(2)	−0.050(1)	5(2)
N29′	−0.119(3)	0.119(2)	−0.1542(9)	6(2)
C30′	−0.118(3)	0.152(2)	−0.1899(9)	3(2)
C31′	−0.098(3)	0.109(2)	−0.2214(9)	5(2)
C32′	−0.079(3)	0.033(2)	−0.2173(9)	5(2)
C33′	−0.079(3)	0.000(2)	−0.1816(9)	7(2)
C34′	−0.099(3)	0.043(2)	−0.1501(9)	3(2)
N35′	−0.228(6)	0.390(3)	−0.020(2)	9(2)
C36′	−0.304(6)	0.440(3)	−0.034(2)	15(4)
C37′	−0.339(6)	0.499(3)	−0.012(2)	15(4)
C38′	−0.283(6)	0.509(3)	0.025(2)	14(4)
C39′	−0.190(6)	0.459(3)	0.041(2)	28(8)
C40′	−0.156(6)	0.400(3)	0.019(2)	24(7)

$^aU_{eq}=1/3\Sigma_i\Sigma_jU_{ij}a^*_ia^*_j\mathbf{a}\cdot\mathbf{a}_j$. Starred items are anisotropic.

TABLE 2. Selected bond lengths (Å) and bond angles (°) for $Rh_2(O_2CCF_3)_4(py)_4$

	Molecule 1	Molecule 2
Rh1–Rh2	2.56(1)	2.54(1)
Rh1–O3	2.00(4)	2.01(4)
Rh1–O7	2.05(4)	2.00(4)
Rh1–O13	2.11(4)	2.04(4)
Rh1–N23	2.03(3)	2.00(3)
Rh1–N29	2.25(3)	2.22(3)
Rh2–O1	2.04(5)	2.01(4)
Rh2–O5	2.02(4)	1.96(5)
Rh2–O9	2.04(4)	2.06(4)
Rh2–N17	2.06(3)	2.03(4)
Rh2–N35	2.26(3)	2.32(6)
Rh2–Rh1–O3	86,1(1)	88.1(1)
Rh2–Rh1–O7	85.3(1)	85.2(1)
O3–Rh1–O7	88.5(2)	86.0(2)
Rh2–Rh1–O13	97.8(1)	99.8(1)
O3–Rh1–O13	174.4(1)	171.9(2)
O7–Rh1–O13	95.7(2)	92.8(2)
Rh2–Rh1–N23	99.1(1)	96.0(1)
O3–Rh1–N23	88.8(1)	92.6(2)
O7–Rh1–N23	174.7(2)	178.1(2)
O13–Rh1–N23	86.6(1)	88.4(1)
Rh2–Rh1–N29	171.0(1)	171.7(1)
O3–Rh1–N29	88.3(1)	85.6(2)
O7–Rh1–N29	87.4(1)	89.0(2)
O13–Rh1–N29	88.2(1)	86.4(2)
N23–Rh1–N29	87.9(1)	89.7(1)
Rh1–Rh2–O1	85.0(1)	83.0(1)
Rh1–Rh2–O5	85.0(1)	85.8(2)
O1–Rh2–O5	86.9(2)	85.4(2)
Rh1–Rh2–O9	100.1(1)	97.0(1)
O1–Rh2–O9	95.5(2)	96.3(2)
O5–Rh2–O9	174.5(2)	176.9(2)
Rh1–Rh2–N17	97.6(1)	98.1(1)
O1–Rh2–N17	177.3(2)	176.2(2)
O5–Rh2–N17	92.5(1)	391.1(2)
O9–Rh2–N17	84.9(2)	87.1(2)
Rh1–Rh2–N35	168.5(1)	171.9(2)
O1–Rh2–N35	86.0(2)	89.3(2)
O5–Rh2–N35	87.5(1)	91.0(2)
O9–Rh2–N35	87.8(1)	86.4(2)
N17–Rh2–N35	91.3(1)	89.4(2)

trifluoroacetate groups located in a cisoid configuration. One additional trifluoroacetate and two pyridine molecules, one of them occupying an axial coordination site, are also bonded to each metal atom. The two monodentate trifluoroacetate groups are also in a cisoid configuration and consequently the same happens for the equatorially coordinated pyridine molecules. This arrangement of ligands around the dirhodium unit creates a pseudo two-fold symmetry axis through the middle of the Rh–Rh bond.

Nearly the same average values are found for Rh–O bond distances corresponding to bridging (2.01(4) Å) and monodentate (2.06(4) Å) trifluoroacetate groups. The equatorial Rh–N distances are also in the same range of values (2.03(4) Å). However, the axial Rh–N bond lengths are, as expected, significantly longer than the equatorial (2.26(4) Å).

The pseudooctahedral coordination around each rhodium shows similar distortion in both molecules with values for the Rh–Rh–O angles of the bridging ligands smaller than 90° and greater than 90° for the equatorial ligands, monodentate trifluoroacetate and pyridine groups. The axial pyridine lies slightly out of the Rh–Rh bond (Rh–Rh–N axial average value 170.8(1)°).

The values for the O–Rh–O and O–Rh–N angles involving equatorial atoms are very similar and average 175.5(2)°.

Large thermal parameters are obtained for the CF_3 groups indicating existence of disorder; this fact and the large number of parameters to be refined, due to the presence of two independent molecules in the asymmetric unit, limitates the quality of the crystallographic refinement.

Experimental

Materials

$Rh_2(O_2CCF_3)_4$ [7] and $Rh_2(O_2CCF_3)_4(P(C_6H_5)_3)_2$ [3d] were prepared according to literature procedures. Commercially available $P(C_6H_5)_3$ (Aldrich) was recrystallized from hot ethanol prior to use. Pyridine and HO_2CCF_3 were used as purchased. Dichloromethane, chloroform and toluene were dried and degassed before use. All reactions were carried out under Ar atmosphere using Schlenk techniques.

Preparation of $Rh_2(O_2CCF_3)_2[(C_6H_4)P(C_6H_5)_2]_2$

A mixture of 400 mg (0.59 mmol) of $Rh_2(O_2CCF_3)_4$ and 312 mg (1.19 mmol) of PPh_3 (1:2 molar ratio) was stirred in 15 ml of $CHCl_3$ under argon atmosphere for 20 days. The solvent was removed; the dark red oil was dissolved in 6 ml of $CHCl_3$/hexane (1/1) and the solution was chromatographed in a column (30×2 cm) packed with silica gel in hexane. Elution with acetone/hexane (1/3) separated a red band that was collected. The solvent was removed until a red crystal solid of $Rh_2(O_2CCF_3)_2[(C_6H_4)P(C_6H_5)_2]_2(H_2O)_2$ was precipitated (yield 73%). *Anal.* Found: C, 48.76; H, 3.28. Calc. for $Rh_2P_2F_6O_6C_{40}H_{32}$: C, 48.46; H = 3.23%. The reaction time can be reduced by increasing the reaction temperature (*c.* 40 °C). However a careful temperature control is required to prevent the cleavage of the dinuclear unit produced under higher temperature conditions.

Preparation of $Rh_2(O_2CCF_3)_4(py)_4$

100 mg (0.15 mmol) of $Rh_2(O_2CCF_3)_4$ were dissolved in 10 ml of $CHCl_3$ and an excess of NC_5H_5 (2 ml) was added. The solution changed from blue to red color and was stirred for two hours at room temperature. The solvent was removed under reduced pressure and the solid was precipitated in 5 ml of CH_2Cl_2/hexane (1/1) yielding 94 mg (64.3% yield) of $Rh_2(O_2CCF_3)_4(NC_5H_5)_4$ as a red solid.

Measurements

IR spectra were recorded on a FTIR Perkin-Elmer 1750 instrument. The ^1H, ^{31}P and ^{13}C NMR data were measured on Brucker AC-200, Varian Unity 300 and Varian Unity 400 spectrometers, respectively, operating at 289 K with broad band decoupling. Chemical shifts are referred to internal Me_4Si (^1H) to external 85% H_3PO_4 in D_2O (^{31}P).

X-ray crystallographic procedures

The molecular structure of $Rh_2(O_2CCF_3)_4(py)_4$ was obtained by general procedures. A detailed description is given below. The crystal parameters and basic information dealing with data collection and structure refinement are summarized in Table 3.

Red crystal, 0.17×0.10×0.10 mm size. Mo Kα radiation, graphite crystal monochromator, Nonius CAD4 single crystal diffractometer ($\lambda = 0.71073$ Å). Unit cell dimensions determined from the angular settings of 25 reflections ($25 < \theta < 30°$). Space group $P2_1/n$ from the systematic absences. 12 911 reflections measured in *hkl* range (0, 0, −42) to (12, 21, 42), and theta limits ($0 < \theta < 30°$). ω–2θ scan technique, variable scan rate with a maximum scan time of 60 s per reflection. Intensity checked monitoring three standard reflections every 60 min. Final drift correction factors between 0.99 and 1.03. On all reflections profile analysis per-

TABLE 3. Crystallographic data for $Rh_2(O_2CCF_3)_4(py)_4$

Formula	$Rh_2N_4F_{12}O_8C_{28}H_{20}$
Formula weight	974.3
Space group	$P2_1/n$
a (Å)	10.504(1)
b (Å)	18.108(1)
c (Å)	35.377(1)
β (°)	96.416(8)
V (Å^3)	6686.6(8)
Z	8
$F(000)$	3824
D_{calc} (Mg/m^3)	1.94
Crystal size (mm)	0.17×0.10×0.10
μ(Mo Kα) (cm^{-1})	10.89
Data collection instrument	Nonius CAD4
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	293
No. unique data	11744
Total with $I > 3\sigma(I)$	2258
No. parameters	312
R^a (for some double-measurement)	0.064
R'^b	0.12
Weighting scheme	no weights applied
Largest shift/e.s.d., final cycle	3.71
Largest peak (e/Å^3)	1.99

$^aR = \Sigma(I - \langle I \rangle)/\Sigma I$. $^bR' = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

formed [8, 9]; empirical absorption correction applied, using Ψ scans [10], correction factors range 0.77 to 0.99. Some double-measured reflections averaged, $R_{\mathrm{int}} = \Sigma(I - <I>)/\Sigma I = 0.064$, resulting in 11 774 unique reflections of which only 2258 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and data reduced to $|F_o|$ values. The structure was solved by Patterson interpretation using the program SHELXS86 [11] and Fourier synthesis. Isotropic least-squares refinement, using SHELX76 [12], converged to $R = 0.127$. At this stage further absorption corrections were applied using DIFABS [13]. Maximum and minimum correction factors 1.31 and 0.69, respectively.

During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the rhodium and some oxygen atoms were refined. All fluorine and hydrogen atoms were geometrically placed and refined with a common isotropic thermal parameter. The final conventional agreement factors were $R = 12$ for the 2258 'observed' reflections and 312 variables. Function minimized $\Sigma w(F_o - F_c)^2$, $w = 1$. Maximum shift over error ratio in the last full-matrix least-squares cycle was less than 8.35 in rotations of CF_3 groups. The rest are less than 3.71. The final difference Fourier map showed no peaks higher than 1.99 e/Å^3 and deeper than -1.29 e/Å^3. All CF_3 groups are strongly disordered. This fact together with the small size of the crystal used for X-ray diffraction could justify the poor agreement factors. In fact the structure has been isotropically refined in most of its atoms. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [14]. The plot was made with the PLUTO program [15]. Geometrical calculations were made with PARST [16]. All calculations were made on a IBM 3090 Computer.

Supplementary material

Lists of structure amplitudes, anisotropic thermal parameters, distances and angles, least-squares planes' data and principal torsion angles have been deposited in the Crystallographic Cambridge Data Base.

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