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Preliminary Communication

Simultaneous substitution of bridging acetate groups and reversible Rh–C bond cleavage in $[Rh_2(O_2CCH_3)_3\{(C_6H_4)PPh_2\}(HO_2CCH_3)_2]$ in the presence of CF_3CO_2H. Crystal structure of $[Rh_2(O_2CCF_3)_3\{(C_6H_4)PPh_2\}(HO_2CCF_3)_2]$

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Abstract

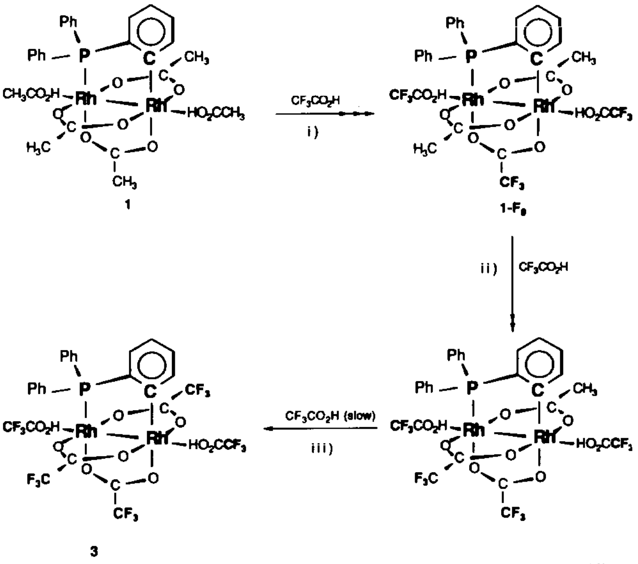
The reaction of the monometallated compound $[Rh_2(O_2CCH_3)_3\{(C_6H_4)PPh_2\}(HO_2CCH_3)_2]$ (1) with CF_3CO_2H at room temperature yields $[Rh_2(O_2CCF_3)_3\{(C_6H_4)PPh_2\}(HO_2CCF_3)_2]$ (3) as the only isolable product. Compound 3 has been characterized by X-ray methods. 3 crystallizes in the space group $P2_1/n$. It contains three trifluoroacetate groups bridging a Rh_2^{4+} unit with a Rh–Rh bond distance of 2.438(1) Å; the fourth bridging ligand is a triphenylphosphine metallated at one of the *ortho* positions. Two molecules of trifluoroacetic acid occupy the axial coordination positions. In addition to the substitution of acetate groups, reversible electrophilic Rh–C bond activation is observed.

It is known that $[Rh_2(O_2CCH_3)_4]$ and PPh_3 react to give mono- and di-metallated compounds $[Rh_2(O_2CCH_3)_3\{(C_6H_4)PPh_2\}(HO_2CCH_3)_2]$ (1) and $[Rh_2(O_2CCH_3)_2\{(C_6H_4)PPh_2\}_2(HO_2CCH_3)_2]$ (2) [1]. Although it has been recently reported that 2 reacts with thiocarboxylic acids under reflux causing electrophilic cleavage of the Rh–C bond [2], we wanted to explore the utility of these complexes for the preparation of other metallated compounds by reaction with carboxylic acids under milder conditions.

We report in this paper the reaction of **1** with CF_3CO_2H at room temperature. This reaction yields $[Rh_2(O_2CCF_3)_3\{(C_6H_4)PPh_2\}(HO_2CCF_3)_2]$ as a final product, and involves not only stepwise substitution of acetate groups but also reversible Rh–C bond activation.

When compound **1** is dissolved in a mixture of $CDCl_3/CF_3CO_2H$ ($[CF_3CO_2H]/[Rh_2] = 8$) three consecutive processes of progressively decreasing rate are detected by ^1H NMR spectroscopy. (i) The signal due to the *trans* acetate disappears ($t < 1$ min); (ii) the signal due to the two *cis* acetates decreases to half its intensity ($t < 5$ min); (iii) this signal completely disappears ($t < 3$ h). These data are consistent with the stepwise substitution shown in Scheme 1. The spectrum of a freshly prepared solution ($t < 1$ min) of **1** in a mixture of $CDCl_3/CF_3CO_2H$ ($[CF_3CO_2H]/[Rh_2] = 8$) is consistent with the existence of the partially substituted compound $[Rh_2(O_2CCH_3)_{2cis}(O_2CCF_3)_{trans}\{(C_6H_4)P(C_6H_5)_2\}(HO_2CCF_3)_2]$ (**1-F$_9$**)*, as the main product (step i). This compound has been isolated and characterized by elemental analysis and ^1H and ^{31}P NMR spectroscopy.

When **1** is maintained in the $CDCl_3/CF_3CO_2H$ mixture at room temperature during several hours the



Scheme 1. Stepwise reaction for the exchange of **1** with trifluoroacetic acid.

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totally substituted compound $[Rh_2(O_2CCF_3)_3\{(C_6H_4)P(C_6H_5)_2\}(HO_2CCF_3)_2]$ (**3**)** is progressively formed (steps ii and iii). Step ii is too fast to be kinetically studied by ^1H NMR spectroscopy ($k > 10^{-3}$ s^{-1}), but step iii is slow enough and is presently under investigation. In contrast to this behaviour, the doubly-metallated compound **2** rapidly exchanges both bridging acetate groups with trifluoroacetic acid.

A view of the molecular structure of **3** is shown in Fig. 1. The two rhodium atoms are bridged by three trifluoroacetate groups and one triphenylphosphine metallated in one phenyl ring. Two oxygen atoms of two trifluoroacetic acid molecules occupying the axial positions complete the slightly distorted octahedral coordination around the metals (angles in the range 84.2(2)–97.2(2)°). The Rh–Rh bond distance is 2.438(1) Å. The Rh–Rh–O axial angles are 172.0(0)° and 168.8(2)°. The Rh–O distances involving the axial trifluoroacetic acids are long and significantly different, 2.418(7) and 2.306(6) Å. This must be attributed to the presence of the unsymmetrical metallated phosphine.

Two monometallated dirhodium(II) acetic acid adducts have been characterized [1b,3]. In one case [3] a similar difference is found for the two axial Rh–O bond distances. In all these adducts the OH groups of the axial acetic acid molecules show intramolecular hydrogen bond interactions with two oxygen atoms; in the monometallated compounds described earlier [1b,3] the interaction is with two oxygen atoms of the same bridging acetate, the one opposite to the metallated phosphine. In the present case each molecule of trifluoroacetic acid interacts with a different carboxylate group. In view of the different axial Rh–O bond lengths, only one of these interactions, O(8)–H(101) · · · O(6) is strong. The equatorial Rh–O bond distances are in the range 2.039(6)–2.240(6) Å, those *trans* to carbon or phosphorus being longer than the rest, consistent with the *trans* effect of the Rh–C and Rh–P bonds. The torsion angles about the rhodium–rhodium bond are in the range 7.91 to 12.59°, indicating a conformation closer to eclipsed than to alternate.

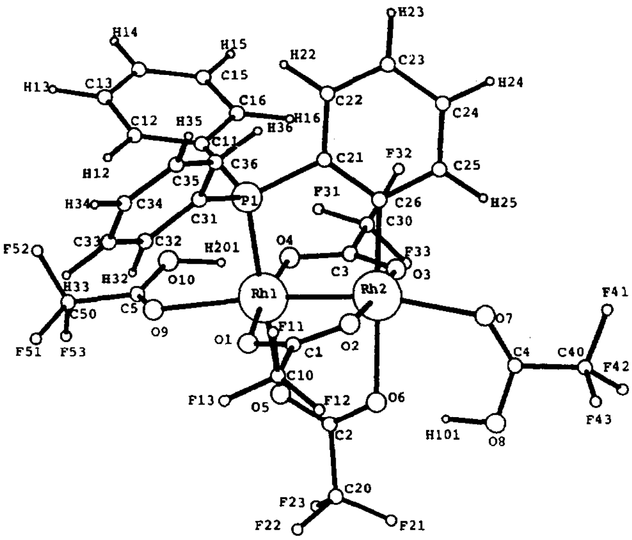

Fig. 1. A view of the complex $[Rh_2(O_2CCF_3)_3\{(C_6H_4)P(C_6H_5)_2\}(HO_2CCF_3)_2]$, **3** with the atomic numbering scheme. Selected bond distances (Å) and angles (°): Rh1–Rh2 2.438(1), Rh1–P1 2.217(2), Rh2–C26 1.971(8), Rh1–O1 2.042(6), Rh1–O4 2.052(5), Rh1–O5. 2.177(6), Rh1–O9 2.418(7), Rh2–O2 2.039(6), Rh2–O3 2.061(6), Rh2–O6 2.240(6), Rh2–O7 2.306(6), O9–Rh1–Rh2 172.0(2), O7–Rh2–Rh1 168.8(2), O3–Rh2–O2 174.6(2), O4–Rh1–O1 172.4(2), C26–Rh2–O6 179.2(3), O5–Rh1–P1 179.1(2). H101 and H201 were placed at ideal geometrical position and refined riding on their oxygen atoms.

If the isotopically labelled compound $[Rh_2(O_2CCH_3)_3\{(C_6D_4)P(C_6D_5)_2\}(HO_2CCH_3)_2]$, **1-$d_{14}$**, is dissolved in a $CDCl_3/CF_3CO_2H$ mixture, a very slow increase of two aromatic signals at $\delta_H = 6.89$ ppm, $^3J(P–H) = 10.2$ Hz, and $\delta_H = 7.49$ ppm, $^3J(P–H) = 11.1$ Hz were also observed. These signals, already present with very low intensity in the starting compound **1-d_{14}**, are due to the partial D–H exchange at the *ortho*-positions of the phenyl rings. We had previously detected a

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* Spectroscopic data. $[Rh_2(O_2CCH_3)_{2cis}(O_2CCF_3)_{trans}\{(C_6H_4)P(C_6H_5)_2\}(HO_2CCF_3)_2]$, **1-F$_9$**. $^{31}P\{^1H\}$ NMR: δ P = 16.11 ppm, $^1J(Rh–P) = 143.7$ Hz, $^2J(Rh–P) = 4.1$ Hz. ^1H NMR (in ppm): 1.25 (6H, CH_3, s), 6.3 (1H, aromatic, c), 6.5–7.9 (14H, aromatics, m). Anal. Found: C, 36.68; H, 2.69. $Rh_2PC_{28}O_{10}F_9H_{22}$ calc.: C, 36.28; H, 2.37%. Crystal data. $[Rh_2(O_2CCF_3)_3\{(C_6H_4)P(C_6H_5)_2\}(HO_2CCF_3)_2]$, **3**. $C_{28}H_{14}F_{15}O_{10}PRh_2$, M = 1032.17, monoclinic, space group $P2_1/n$, $a = 12.369(2)$, $b = 21.711(6)$, $c = 13.367(2)$ Å, $\beta = 90.11(2)°$, $V = 3590(1)$ Å^3, $Z = 4$, $D_c = 1.910$ g cm^{-3}; $F(000) = 2008$, μ(Mo Kα) = 10.747 cm^{-1}, $\lambda = 0.71073$ Å. An Enraf-Nonius CAD4 single crystal diffractometer was used. Unit cell dimensions determined from the angular settings of 25 reflections with θ in the range 15–20°. Space group $P2_1/n$ was determined from systematic absences. 6743 reflections were collected in the *hkl* range (−14, 0, 0) to (14, 25, 15) with θ limits $0° < \theta < 25°$ and 3570 independent reflections with $I > 3\sigma(I)$ were used in the analysis. $\omega–2\theta$ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. Structure was solved by Patterson interpretation, using the program SHELX86 and expanded with DIRDIF. Isotropic least-square refinement was performed using a locally modified version of SHELX76 program. The final conventional agreement factors were $R = 0.0437$ and $R_w = 0.0439$ for the 3570 observed reflections and 506 variables. Geometrical calculations made with PARST. Calculations made on a VAX 4000 at the "Departamento de Química Física" of the University of Valencia. Full lists of atomic coordinates, bond lengths and angles, and anisotropic temperature factors are available from the Cambridge Crystallographic Data Centre.

** Spectroscopic data. $[Rh_2(O_2CCF_3)_3\{(C_6H_4)P(C_6H_5)_2\}(HO_2CCF_3)_2]$, **3**. $^{31}P\{^1H\}$ NMR: δ P = 14.37 ppm, $^1J(Rh–P) = 139.2$ Hz, $^2J(Rh–P) = 3.9$ Hz. ^1H NMR (in ppm): 6.4 (1H, aromatic, c), 6.7–8.1 (14H, aromatics, m). Anal. Found: C, 32.62; H, 1.98. $C_{28}H_{14}F_{15}O_{10}PRh_2$ calc.: C, 32.49; H, 1.55%.

similar D–H exchange in the reaction of $\mathbf{1}$-d_{14} with acetic acid; in that case the exchange was slower and was only detected under refluxing conditions in pure acetic acid [4]. A reversible Rh–C bond cleavage followed by a rapid orthometallation must be invoked to explain these results. The intermediate compound resulting from the Rh–C bond cleavage must be of very short life under the experimental conditions and it is not detected by ^{31}P NMR spectroscopy.

Acknowledgements

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