

JOM 23736PC

Preliminary Communication

Reversible electrophilic Rh–C bond cleavage in metallated dirhodium(II) compounds by carboxylic acids.
Crystal structure of a new variety of rhodium(II) complex

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(Received February 5, 1993)

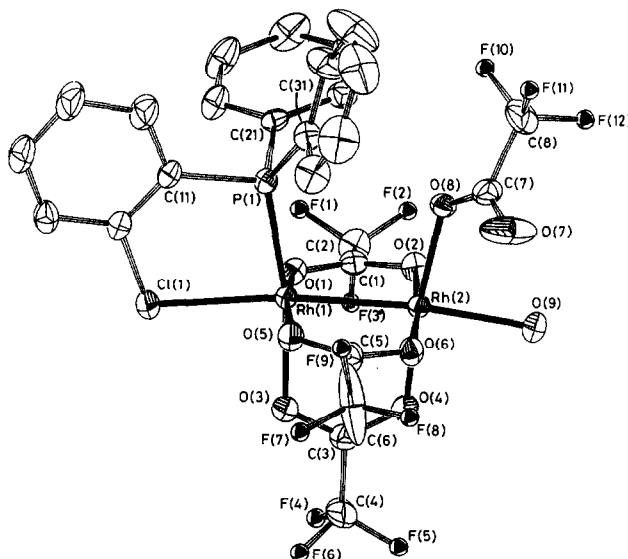


Fig. 1. Molecular structure of compound 1 showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Rh(1)–Rh(2) 2.469(1), Rh(1)–P(1) 2.240(1), Rh(1)–Cl(1) 2.577(2), Rh(1)–O(1) 2.038(4), Rh(1)–O(3) 2.132(3), Rh(1)–O(5) 2.057(4), Rh(2)–O(2) 2.029(4), Rh(2)–O(4) 2.024(3), Rh(2)–O(6) 2.029(4), Rh(2)–O(8) 2.017(3), Rh(2)–O(9) 2.196(4); O(3)–Rh(1)–O(5) 86.1(2), O(1)–Rh(1)–O(5) 170.5(1), O(1)–Rh(1)–O(3) 87.1(1), P(1)–Rh(1)–O(5) 96.3(1), P(1)–Rh(1)–O(3) 170.1, P(1)–Rh(1)–O(1) 91.5(1), P(1)–Rh(1)–Cl(1) 84.75(6), O(8)–Rh(2)–O(9) 88.3(1), O(6)–Rh(2)–O(9) 95.9(1), O(6)–Rh(2)–O(8) 97.1(1), O(4)–Rh(2)–O(9) 85.2(1), Rh(2)–O(8) 172.5(2), O(4)–Rh(2)–O(6) 87.3(2), O(2)–Rh(2)–O(9) 88.8(2), O(2)–Rh(2)–O(8) 87.1(1), O(2)–Rh(2)–O(6) 173.7(1), O(2)–Rh(2)–O(4) 89.0(2), Rh(2)–Rh(1)–O(5) 87.2(1), Rh(2)–Rh(1)–O(3) 86.2(1), Rh(2)–Rh(1)–O(1) 85.8(1), Rh(2)–Rh(1)–Cl(1) 170.89(6), Rh(2)–Rh(1)–P(1) 103.51(5), Rh(1)–Rh(2)–O(9) 171.8(1), Rh(1)–Rh(2)–O(8) 99(1), Rh(1)–Rh(2)–O(6) 86.7(1), Rh(1)–Rh(2)–O(4) 87.1(1), Rh(1)–Rh(2)–O(2) 88.0(1).

Abstract

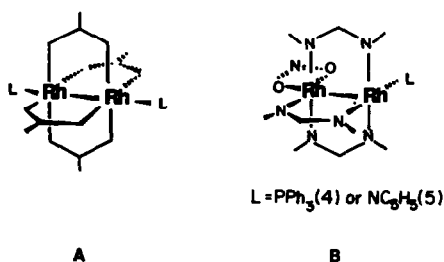
Treatment of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{C}_6\text{H}_4)\text{P}(\text{2-ClC}_6\text{H}_4)\text{Ph}](\text{HO}_2\text{CCH}_3)_2$, **2**, with trifluoroacetic acid at room temperature affords $[\text{Rh}_2(\mu\text{-O}_2\text{CCF}_3)_3(\eta^1\text{-O}_2\text{CCF}_3)(\eta^2\text{-P}(\text{2-ClC}_6\text{H}_4)\text{Ph}_2)(\text{H}_2\text{O})]$, **1**. An X-ray study of **1** shows a Rh_2^{4+} unit bridged by three trifluoroacetates; one monodentate trifluoroacetate, one $\text{P}(\text{2-ClC}_6\text{H}_4)_2$, acting as a (P, Cl) donor and one molecule of H_2O complete the coordination sphere. Compound **1** in chloroform solution undergoes reversible metallation at room temperature.

Although some mononuclear rhodium(II) compounds have been recently characterized [1], most rhodium(II) compounds are formulated $[\text{Rh}_2(\text{ABC})_4\text{L}_2]$ and have the lantern-type structure characteristic of dimetal tetracarboxylate compounds (Scheme 1, A) [2]. Only a limited number of dirhodium(II) compounds with three bridging ligands have been structurally characterized [3–5]. In this communication we report the synthesis and the crystal structure of $[\text{Rh}_2(\mu\text{-O}_2\text{CCF}_3)_3(\eta^1\text{-O}_2\text{CCF}_3)(\eta^2\text{-P}(\text{2-ClC}_6\text{H}_4)\text{Ph}_2)(\text{H}_2\text{O})]$, **1**. This compound, which undergoes an orthometallation reaction in CH_2Cl_2 at room temperature, has a molecular structure of a type that is very seldom observed for dirhodium(II) compounds.

The reaction of the recently reported $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{C}_6\text{H}_4)\text{P}(\text{2-ClC}_6\text{H}_4)\text{Ph}](\text{HO}_2\text{CCH}_3)_2$, **2** [6], with trifluoroacetic acid at room temperature has been monitored by ^1H and ^{31}P NMR spectroscopy. * We first observed that the proton signals due to the methyl groups of the carboxylate ligands undergo a complex sequence of changes and finally collapse into a single resonance at 2.17 ppm assigned to uncoordinated acetic acid. In a second and slightly slower process, the final

* ^1H and ^{31}P NMR spectra were recorded on a VARIAN-300 spectrometer. Chemical shifts are referenced to internal Me_4Si (^1H) or external 85% H_3PO_4 in H_2O (^{31}P).

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Scheme 1.

³¹P NMR spectrum shows only a new resonance at 41.34 ppm, characteristic of equatorial nonmetallated phosphines [3,4]. These data clearly indicate that CF₃CO₂H reacts with **2** in two ways simultaneously: i) substitution of acetate by trifluoroacetate and ii) cleavage of the Rh–C bond producing the demetallation of the phosphine (Scheme 2). As a result of these two processes, [Rh₂(μ-O₂CCF₃)₃(η¹-O₂CCF₃)(η²-P(2-ClC₆H₄)Ph₂)(H₂O)], **1** is quantitatively formed. *

The structure of compound **1** has been confirmed by X-ray crystallography. ** An ORTEP view of the molecule of **1** is shown in Fig. 1. It contains a Rh₂⁴⁺ unit with a metal–metal bond distance of 2.469(1) Å,

bridged by three trifluoroacetates. What makes the structure of this compound uncommon is the presence of one monodentate trifluoroacetate group in one equatorial position, and one chelating P(2-ClC₆H₄)Ph₂ occupying an equatorial (P) and one axial (Cl) coordination site of the other rhodium. One molecule of water in the second axial position completes the coordination sphere around the Rh₂⁴⁺ unit. The two molecules in the unit cell are associated in centrosymmetric dimers through an H-bond involving the hydrogen atoms of the axial water molecule and the acceptors O(7) (strong, H···O = 1.619 Å) and F(8), (weaker, H···F = 2.203 Å).

The three bridging trifluoroacetate groups in **1** display Rh–O bonds with only slight deviation from the perfect octahedral coordination (average Rh–Rh–O angles 86.8(1)°). Higher distortion is observed for the other two equatorial bonds, Rh(1)–Rh(2)–O(8) 99.1(1)° and Rh(2)–Rh(1)–P 103.5(1)°.

Two dirhodium(II) compounds structurally related to compound **1** have been described by Piraino *et al.* [3]. The structure of these compounds is schematically represented in Scheme 1, **B** with three *N,N'*-di-4-tolylformamidate groups as bridges. The NO₃⁻ is a chelating ligand and triphenylphosphine (**4**) and pyridine (**5**) are equatorial ligands. In these compounds one of the axial coordination sites is empty whereas in **1** there is a molecule of water. The observation in **1** of almost the same Rh–Rh–P_{eq} angle value as in **4**, where the phosphine is monodentate, indicates that the intramolecular Rh–Cl bond formation does not produce any significant distortion in **1**.

Compound **1** in chloroform solution and in the absence of trifluoroacetic acid, metallates in 24 h at room temperature giving [Rh₂(μ-O₂CCF₃)₃((C₆H₄)P(2-ClC₆H₄)(C₆H₅))(H₂O)₂], **3**, which has been isolated and spectroscopically characterized. †

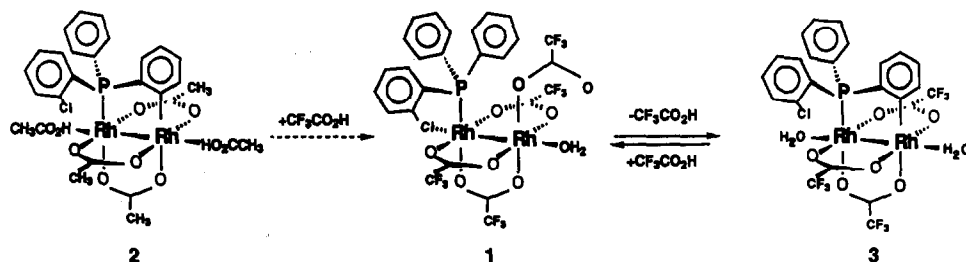
In trifluoroacetic acid solution **3** undergoes electrophilic Rh–C bond cleavage giving **1**. An equilibrium **3** ⇌ **1** is observed when the reaction is performed in chloroform–trifluoroacetic acid mixtures (Scheme 2). Such chemical behavior involving clean and reversible

* 100 mg (0.125 mmol) of [Rh₂(O₂CCH₃)₃((C₆H₄)P(2-ClC₆H₄)Ph)(HO₂CCH₃)₂] [6] were dissolved in 5 ml of CF₃CO₂H and stirred at room temperature during 18 h. The CF₃CO₂H was removed under reduced pressure and the crude green solid was precipitated with 5 ml of CH₂Cl₂/hexane (1:1) yielding a crystalline powder containing [Rh₂(μ-O₂CCF₃)₂(η¹-O₂CCF₃)(η²-P(2-ClC₆H₄)Ph₂)(H₂O)], **1** (yield 80%). Spectroscopic data of **1**: ³¹P NMR (in ppm): 41.34 (¹J_{Rh–P} = 146.0 Hz); ¹H NMR (in ppm): 7.2–7.6 (broad signal, aromatic protons, 14H).

** Crystal data. Rh₂C₂₆H₁₆ClF₁₂O₉P, M_r = 972.63, triclinic, space group P $\bar{1}$, a = 9.631(2), b = 10.744(2), c = 17.390(3) Å, α = 94.44(2), β = 102.32(2), γ = 106.49(2)°, V = 1667.3(6) Å³, Z = 2, D_x = 1.94 Mg m⁻³, Mo-Kα radiation (graphite crystal monochromator, λ = 0.71073 Å), μ = 12.15 cm⁻¹, F(000) = 948, T = 293 K. Intensity data collected on an Enraf-Nonius CAD-4 single-crystal diffractometer using a green crystal of dimensions 0.16 × 0.12 × 0.12 mm. The unit-cell dimensions were determined from the angular settings of 25 reflections. Symmetry equivalent reflections were averaged, R_{int} = Σ(I – ⟨I⟩)/ΣI = 0.013, resulting in 5876 'unique' reflections of which only 4605 were 'observed' with I > 3σ(I). The intensities were corrected for Lorentz and polarization effects. The structure was solved by Patterson and Fourier methods using the program SHELXS86 [7]. Empirical absorption correction was applied using DIFABS [8]. Hydrogen atoms were isotropically refined. R = 0.038 and R_w = 0.043 for 488 variables refined [weighting scheme applied: w = 1/(σ²(F_o) + 0.0001F_o²) with σ(F_o) from counting statistics]. Geometrical calculations were made with PARST [9]. All calculations were made on a MicroVAX-3400 at the Scientific Computer Center of the University of Oviedo.

Atomic coordinates, thermal parameters and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre.

† 100 mg of **1** (0.9 mmol) were dissolved in 5 ml of CH₂Cl₂ and the resulting green solution was stirred during 24 h at room temperature. The solvent was removed under reduced pressure and the crude solid was precipitated by 5 ml of CH₂Cl₂/hexane (1:1) yielding the compound [Rh₂(μ-O₂CCF₃)₃((C₆H₄)P(2-ClC₆H₄)Ph)(H₂O)₂], **3** (yield 88%). Spectroscopic data for **3**: ³¹P NMR (in ppm): 14.64 (¹J_{Rh–P} = 144.5 Hz, ²J_{Rh–P} = 5.7 Hz); ¹H NMR (in ppm): 3.95 (broad, H₂O), 6.95 (t, aromatic, 1H), 7.2–7.3 (m, aromatic, 10H), 7.7 (t, aromatic, 1H), 7.95 (q, aromatic, 1H). ¹³C NMR (in ppm): 124–139 (m, aromatic). Anal. Found: C = 32.92%; H = 1.63%. Calcd. for Rh₂C₂₄H₁₇ClF₉O₈P: C = 32.88%; H = 1.95%.



Scheme 2.

metallation–demetallation is not common and, to our knowledge, has never been described for metallated dinuclear compounds. Similar behaviour has been observed for $[\text{Cp}'_2\text{Th}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_2]$ [10] ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$) which undergoes a reversible reaction with $[\text{Cp}'_2\text{ThCH}_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)]$ and $\text{Si}(\text{CH}_3)_4$.

The mechanism of the cleavage reactions of M–C bonds in mononuclear transition metal compounds has attracted considerable attention in recent years [11]. Mechanistic studies of the reversible metallation–demetallation reaction described above are in progress.

Acknowledgements

We thank the DGICYT for financial support.

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