

Degradation and Oxidation of 1,1,1-Trichloroethane-Mediated Rhodium Compounds. A New Entry in the Synthesis of Bridging Vinylidene and η^1 -Chlorovinyl Complexes

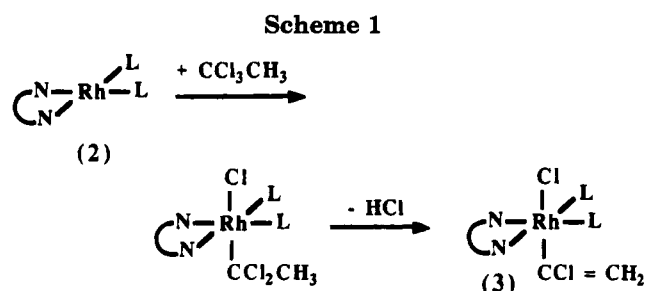
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Summary: 1,1,1-Trichloroethane reacts with $[\text{Rh}(\text{HBiIm})(\text{CNBu}^t)_2]$ and $[\text{Rh}(\mu\text{-pz})(\text{CNBu}^t)_2]_2$ ($\text{H}_2\text{BiIm} = 2,2'$ -biimidazole, $\text{pz} = \text{pyrazolate}$) to give $[\text{RhCl}(\eta^1\text{-CCl}=\text{CH}_2)(\text{HBiIm})(\text{CNBu}^t)_2]$ and $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2\}_2(\mu\text{-C}=\text{CH}_2)]$ respectively with spontaneous elimination of HCl. Further reaction of the vinylidene-bridged compound with HBF_4 and oxygen gives the acyl complex $[\{\text{Rh}(\mu\text{-pz})(\text{CNBu}^t)_2\}_2(\mu\text{-Cl})\text{Cl}(\eta^1\text{-COCH}_3)]\text{BF}_4$, which constitutes, on the whole, a model for the degradation and oxidation of organic chlorocarbons.

The presence of organochloro pollutants in the environment has stimulated the search for their degradation by either catalytic¹ or stoichiometric reactions² or biological systems.³ On the other hand, the conversion of C_1 chloro derivatives into useful organic compounds has directed attention to the reactivity of di- and trichloromethane with transition-metal complexes.⁴ However, the corresponding reactivity of *gem*-trichloroalkanes has been practically unexplored except for the elegant studies of Seyferth⁵ and Mansuy.⁶ We have reported that the complex $[\text{Rh}(\mu\text{-pz})(\text{CNBu}^t)_2]_2$ (**1**; $\text{pz} = \text{pyrazolate}$, $\text{CNBu}^t = \text{tert-butyl isocyanide}$) is able to activate dichloromethane and chloroform, yielding^{4b} the methylene- and chloromethylene-bridged complexes $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2\}_2(\mu\text{-CHX})]$ ($\text{X} = \text{H}, \text{Cl}$). Looking for differences in reactivity between isolated and interacting metal centers, we have prepared the related



mononuclear complex $[\text{Rh}(\text{HBiIm})(\text{CNBu}^t)_2]$ (**2**; $\text{H}_2\text{BiIm} = 2,2'$ -biimidazole), having a chemical environment on the metal likely similar to those of **1**. Herein, we report our results on the reactions of 1,1,1-trichloroethane with the above-mentioned mono- and dinuclear rhodium complexes with azolate ligands, which involve the breakdown of the organic molecule to give an unprecedented entry into η^1 -chlorovinyl complexes as well as into bridging-vinylidene complexes via spontaneous β -dehydrohalogenation and oxidation of the vinylidene to an acyl group, which is on the whole a model for the catalytic destruction and oxidation of chlorocarbons.

The compound **2** reacts with 1,1,1-trichloroethane rapidly in benzene (*Caution!* benzene is suspected to be a carcinogen agent) to give a yellow crystalline solid identified as the η^1 -chlorovinyl derivative $[\text{RhCl}(\text{CCl}=\text{CH}_2)(\text{HBiIm})(\text{CNBu}^t)_2]$ (**3**) in 60% isolated yield. Monitoring this reaction by ¹H NMR reveals that the oxidative-addition product $[\text{RhCl}(\text{CCl}_2\text{CH}_3)(\text{HBiIm})(\text{CNBu}^t)_2]$ (Scheme 1) appears at the first stage of the reaction. Then, this species spontaneously extrudes HCl from the dichloroethyl ligand to render the final product **3**, so that both steps are consecutive and completed in about 15 min. Formation of **3** represents one of the few examples for the electrophilic introduction of a vinyl moiety in a metal complex, a reaction for which the usual vinylating agents are nucleophiles.⁷

In view of this unexpected result, we decided to test the reaction of 1,1,1-trichloroethane with the dinuclear complex **1** with the aim of finding how the second metal center can affect the course of the reaction and the nature of the products (see Scheme 2). Under conditions identical with those above, this reaction occurs rapidly to give a green solution from which $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2\}_2(\mu\text{-C}=\text{CH}_2)]$ (**4**) crystallizes out as a pale

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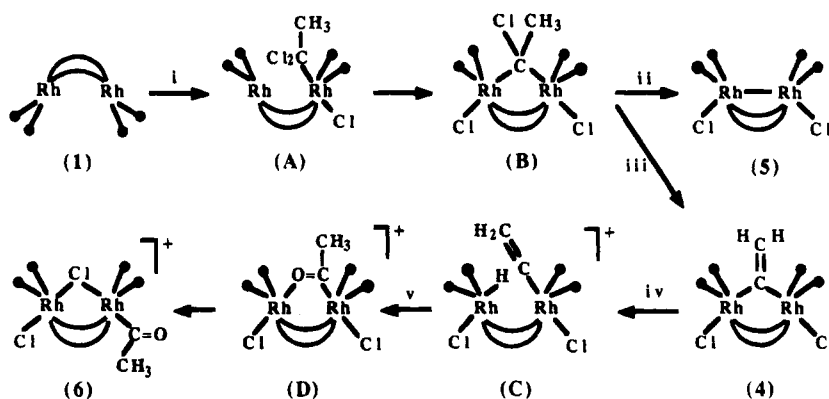
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Scheme 2^a

^a Legend: ● = CNBu^t ; (i) $+\text{CCl}_3\text{-CH}_3$; (ii) $-\text{CH}_2=\text{CHCl}$; (iii) $-\text{HCl}$; (iv) $+\text{HBF}_4$; (v) $+\text{O}_2$.

yellow solid. A byproduct is the previously reported^{4b} dirhodium(II) complex $[\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2]_2$ (5), which is separated from the principal product by recrystallization in ethyl acetate. The released HCl can be trapped as HNET_3Cl by addition of NEt_3 to the reaction mixture; in this way, the isolated yield of 4 is improved up to 60%.⁸ Characterization of 4 relies on characteristic spectroscopic data and on a X-ray structure of its monohydrate ($\text{C}_{28}\text{H}_{44}\text{Cl}_2\text{N}_8\text{Rh}_2\cdot\text{H}_2\text{O}$).⁹ The structure of complex 4, represented in Figure 1, shows the vinylidene group bridging the two Rh atoms in a nearly symmetrical mode. Electron counting of 4 gives 36 valence electrons, whereas most of the homodinuclear bridging-vinylidene complexes previously reported have 30, 32, or 34 valence electrons.¹⁰ A second indication of the electron counting, confirmed by the long Rh–Rh separation (3.275(2) Å), is the lack of a metal–metal bond, which is present in most of the bridging-vinylidene complexes so far described.¹¹

The formation of 4 constitutes a complete dechlorination of a *gem*-trichloroalkane by a dinuclear complex. In a formal sense, two of the abstracted Cl atoms end up as chloro ligands, while the third is lost as HCl and the hydrocarbyl moiety remains bonded to the metal atoms. The terminal or even bridging vinylidene ligand is a known functionality in transition-metal chemistry, including that of rhodium. However, to the best of our knowledge, in no case have compounds of this type been obtained from *gem*-trichloroalkanes. Basically, 1-alkynes are employed as the common source of the C_2 moiety.^{10–12}

Reaction of 4 with H^+ should proceed with attack at the β -carbon¹¹ to give the bridging-carbyne complex $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2\}_2(\mu\text{-CCH}_3)]^+$, but the addition of

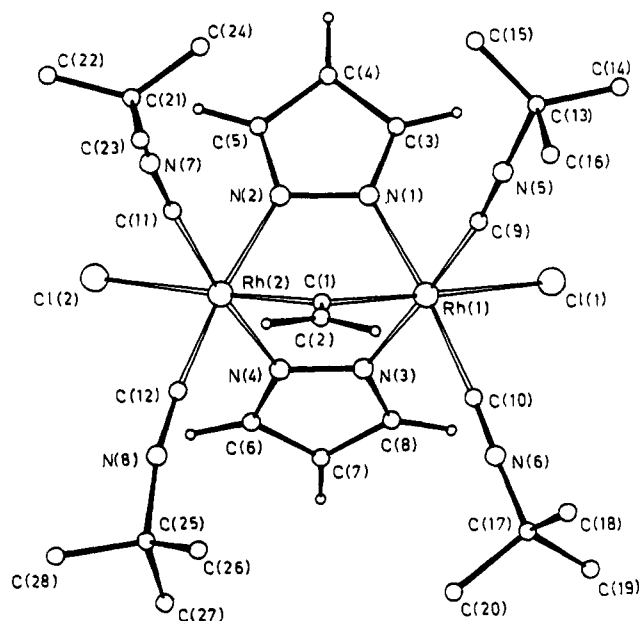


Figure 1. View of the molecular structure of the complex $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2\}_2(\mu\text{-C}=\text{CH}_2)]$ (4). Important bond distances (Å) and angles (deg): Rh(1)–Cl(1) = 2.503(5), Rh(2)–Cl(2) = 2.498(5), Rh(1)–C(1) = 1.994(14), Rh(2)–C(1) = 1.941(14), Rh(1)–N(1) = 2.00(1), Rh(1)–N(3) = 2.03(1), Rh(1)–C(9) = 1.98(2), Rh(1)–C(10) = 1.92(2), Rh(2)–N(2) = 2.01(1), Rh(2)–N(4) = 2.04(1), Rh(2)–C(11) = 1.99(2), Rh(2)–C(12) = 1.89(2), C(1)–C(2) = 1.32(2); Rh(1)–C(1)–Rh(2) = 112.6(7).

$\text{HBF}_4\cdot\text{Et}_2\text{O}$ to 4 in acetone gives an air-sensitive dark green solution where the rhodium hydride complex $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2\}_2\text{H}(\eta^1\text{-C}=\text{CH}_2)]^+$ (C) is observed instead by monitoring the reaction by ^1H NMR at -60°C in HDA and in CDCl_3 . Further reaction of C with O_2 gives the cationic dinuclear acyl derivative $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2\}_2(\mu\text{-Cl})\text{Cl}(\eta^1\text{-COCH}_3)]\text{BF}_4$ (6), which is isolated in 70% yield as yellow crystals. The reaction involves the oxidation of a vinylidene ligand by molecular oxygen, although complex 4 does not react with O_2 and vinylidene ligands are not easy to oxidize.¹³

(8) Actually, HCl protonates the starting material 1 to give green solutions and it also reacts with complexes 4 and 5. The insolubility of 4 and 5 in benzene prevents a large extension of this undesirable side reaction.

(9) Crystal data for $\text{C}_{28}\text{H}_{44}\text{Cl}_2\text{N}_8\text{Rh}_2\cdot\text{H}_2\text{O}$ (4) at 22°C : monoclinic space group $P2_1/n$, $a = 18.109(8)$ Å, $b = 17.561(7)$ Å, $c = 13.327(7)$ Å, $\beta = 92.40(2)^\circ$, $V = 4234(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.235$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 9.33$ cm⁻¹; diffractometer, Philips PW 1100; radiation, graphite-monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073$ Å). A total of 6682 reflections were collected in the range of $3 < \theta < 23^\circ$ ($\pm h, k, l$). Of these, 3166 having $I > 2\sigma(I)$ were used in the structure solution. $R = 0.0715$, $R_w = 0.0633$, and $w = 1/[\sigma^2(F_o)]$. All non-hydrogen atoms, except the carbons of the methyl groups, were refined anisotropically. Only the hydrogen atoms of the vinylidene and pyrazolate ligands were placed at their calculated positions and refined "riding" on the corresponding carbon atoms. Details of the crystallographic study will be reported in a future paper.

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Chemical studies aimed at clarifying these transformations are presently being pursued. At this stage we can state that complexes **4** and **5** originate from **1** as a result of different competitive pathways by following the progress of this reaction by ^1H NMR. In addition, the multistep reaction goes very fast, once it is started. The proposed mechanism in Scheme 2 is based on the following observations:

(i) Reaction of **1** with *gem*-trichloro derivatives without β -hydrogen, e.g. chloroform^{4b} and methyl trichloroacetate, gives complexes analogous to the intermediate **B** under similar conditions, which supports our proposal. It is reasonable to suppose that the reaction starts with the oxidative addition on one metal center to give **A** and then the coordinated dichlorocarbyl moiety ($\text{Rh}-\text{CCl}_2\text{R}$) effects the second oxidative addition to the close Rh(I) center which is in the right position and oxidation state for it to give **B**.

(ii) The diadducts of the type $[\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CCl}_2\text{R})(\text{CN}^t\text{Bu})_2]_2$ have not been detected in these reactions, even when a high excess of trichloro derivative was used. Nevertheless, complex **1** reacts with monohalogenated compounds to give the diadducts $[\text{Rh}(\mu\text{-pz})\text{XR}(\text{CN}^t\text{Bu})_2]_2$.^{4b} This means that formation of **B** is much faster than attack at the second metal center in **A** by a second molecule of the trichloro derivative.

(iii) The lack of reaction of **1** with 1,1-dichloroethene and *trans*-1,2-dichloroethene under similar conditions reveals that it is inert to $\text{Cl}-\text{Csp}^2$ activation. In addition, it suggests that η^1 -chlorovinyl derivatives are not intermediates in the mechanism giving **4** and, hence, the loss of HCl should occur after the second oxidative addition (on **B**) through a β -dehydrohalogenation. The attack of H^+ at one of the rhodium atoms in **4** instead of at the bridging vinylidene group justifies this proposal. A competitive path is a 1,2-H shift followed by extrusion of vinyl chloride to give **5**.

(iv) To learn more about the oxidation of the vinylidene ligand in **C**, we have tested that pure oxygen is the agent to give **6**. Intermediates in this reaction (Scheme 2) can be proposed in view of the ^1H NMR features of the reaction mixture. The first step probably involves an enol, which evolves to the $\mu_2\text{-}1\kappa\text{C},2\kappa\text{O}$ bridging acyl derivative $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CN}^t\text{Bu})_2\}_2(\mu\text{-COCH}_3)]\text{BF}_4$ (**D**), which cannot be isolated because it isomerizes to the final product **6**.

The search for a catalyst to oxidize halogenated volatile organic compounds is an area of current interest.¹⁴ In this context, if we combine the steps in Scheme 2, i.e., the four-electron-two-center oxidative addition of 1,1,1-trichloroethane to **1** with the associated elimination of HCl and the oxidation of **4** by molecular oxygen in the presence of H^+ to give **6**, we have an example of binuclear reactivity where a *gem*-trichloro derivative is dechlorinated and oxidized to an acetyl group. In addition, it is a model for the degradation of alkyl chloro derivatives which are exogenous environmental pollutants.

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Supplementary Material Available: Atomic coordinates, thermal parameters, and all bond distances and angles (Tables SI-IV) for complex **4** and selected spectroscopic data for the new complexes (Table SV) (8 pages). Ordering information is given on any current masthead page.

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