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A Polymeric Chain in Which $\mu_2,\eta^2:\eta^2$-Ethene Symmetrically Bridges Tetra(trifluoroacetato) Dirhodium Molecules

F. Albert Cotton,* Evgeny V. Dikarev,
Marina A. Petrukhina, and Robert E. Taylor

Laboratory for Molecular Structure and Bonding
Department of Chemistry, Texas A&M University
P.O. Box 30012, College Station, Texas 77842-3012

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It was only in 1986 that the first recognized examples of symmetric $\mu_2,\eta^2:\eta^2$-ethene bridging were reported,[1,2] and only a few others have been prepared since.[3] It is interesting to note that the majority of the previous examples have involved zirconium; none has involved rhodium. We report here a new example, obtained in an unconventional way. The new compound, $[Rh_2(O_2CCF_3)_4 \cdot C_2H_4]_\infty$, is built of infinite chains of alternating $Rh_2(O_2CCF_3)_4$ molecules and C_2H_4 molecules, in which the Rh−Rh axes are aligned and CH_2CH_2 molecules are placed symmetrically between the adjacent rhodium atoms.

The preparation of this compound is a continuation of a program of "solventless synthesis" that has been ongoing in this laboratory for several years.[4] $Rh_2(O_2CCF_3)_4$ is a very strong bifunctional Lewis acid and to form complexes with relatively weak Lewis bases, it is expedient to exclude solvent molecules which might be competitive. Thus, by a process of sublimation−deposition of $Rh_2(O_2CCF_3)_4$ in the presence of various volatile ligands, a variety of novel products has been isolated in crystalline form. In one previous case,[4c] the intended Lewis base reacted to generate a product that was more than a simple combination of itself with the $Rh_2(O_2CCF_3)_4$. In the present work we have another example of such a reactive interaction.

The cosublimation of $Rh_2(O_2CCF_3)_4$ with 1,2-diiodoethane, ICH_2CH_2I, performed at 105 °C affords[5] the compound $[Rh_2(O_2CCF_3)_4 \cdot C_2H_4]$ (**1**), in the form of dark green crystals. This product can be obtained reproducibly in 15−20% yield. It is thermally quite stable at ambient temperature, but it is sensitive to moisture. It is soluble in benzene at room temperature, but this process is accompanied by disintegration of the chain structure of **1** and the evolution of ethylene. The latter is partly soluble in benzene and can be detected by NMR spectroscopy. The ^{1}H NMR spectrum of **1** in C_6D_6 showed a single peak at 5.321 ppm, which is coincident with signals of protons of uncoordinated ethylene.[6] This unambiguously confirmed the presence of $CH_2{=}CH_2$ in the crystalline adduct **1**. The IR spectrum of **1** is not greatly different from the spectrum of the starting dirhodium tetra(trifluoroacetate). Evidently, the interaction of the ethene molecules with the $Rh_2(O_2CCF_3)_4$ molecules does not perturb the latter detectably, at least in the range of the IR scanned (400−4000 cm^{-1}). The C=C stretching should not be IR-active.

Structural data obtained for **1** by single-crystal X-ray diffraction[7] revealed that **1** is a copolymer of ethylene and the dirhodium complex. In the structure of **1** the $CH_2{=}CH_2$ molecules bridge two dirhodium units to form infinite poly(dirhodium)ethylene chains, as shown in Figure 1.

The coordination mode of ethylene is $\mu_2,\eta^2:\eta^2$, and all Rh−C distances are equal at 2.484(3) Å. All characteristics of the dirhodium tetra(trifluoroacetate) unit in **1** are typical for $Rh_2(O_2CCF_3)_4$, having axially coordinated neutral donors. That implies there is no charge transfer in the case of **1**, and the coordinated $CH_2{=}CH_2$ is to be regarded as a practically neutral molecule. The Rh−C contacts in **1** can be compared with those in the only other known example of axial coordination of a double carbon−carbon bond to a dirhodium(II) complex, $[Rh_2(O_2CCF_3)_4 \cdot ((-)\text{-trans-caryophyllene})_2]$.[8] The shorter rhodium−carbon distance for the terminally coordinated η^2-olefin ligand in the caryophyllene bis-adduct is 2.46(1) Å, while the longer one to the more hindered carbon atom is 2.63(1) Å.

The structural characteristics of the bridging $CH_2{=}CH_2$ in **1** are of principal interest, but the situation is complicated by a disorder of the ethylene molecules over two equally populated orientations bisecting the $[RhO_4]$ plane (Figure 2). Due to the disorder of the C_2H_4 moieties, as well as their position between two relatively heavy metal atoms, the C=C distance, which was refined to a value of 1.27(3) Å, is undoubtedly even less precise than the esd would imply. The C=C distance in free ethene[9] is 1.337(2) Å. It seems very unlikely that the distance in **1** could really be shorter than it is in the uncoordinated molecule. It may also be noted that even though the neighboring $Rh_2(O_2CCF_3)_4$ molecules are eclipsed, they are sufficiently far from one another to avoid repulsive contacts of either the O···O or F···F types. The hydrogen atoms of the ethene molecule have been found from the difference Fourier map to be positioned in a plane perpendicular to the Rh−Rh axis (or parallel to the $[RhO_4]$ plane). This location seems chemically reasonable as it maximizes the distances to the acidic metal centers while it also minimizes interactions with carboxylic oxygen atoms (2.58−2.63 Å).

This is not the first time that a $\mu_2,\eta^2:\eta^2$-ethene compound has been prepared not from ethene itself but by halogen expulsion from an XCH_2CH_2X precursor. The zirconium and hafnium compounds first reported in 1986 were prepared by reactions of $ClCH_2CH_2Cl$ with the appropriate $M_2X_4(\mu\text{-}X)_2(PR_3)_4$ molecule in a 1:2 molar ratio, whereby the products $M_2X_6(\mu\text{-}C_2H_4)(PR_3)_4$ and $MX_3Cl(PR_3)_2$ were formed in a 1:2 mole ratio. In the present

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* Corresponding author. E-mail: cotton@tamu.edu.

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(2) In 1976 the compound $[Cp_2Zr(ClAlEt_3)]_2C_2H_4$ was reported, in which there is an unsymmetrical ethylene bridge which the authors considered to be a distorted $-CH_2CH_2-$ bridge, rather than an unsymmetrical $\mu_2,\eta^2:\eta^2$-bridged. Kaminsky, W.; Korp, J.; Sinn, H.; Vallmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629.

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(5) Preparation of $[Rh_2(O_2CCF_3)_4 \cdot C_2H_4]$ (**1**): A mixture of $Rh_2(O_2CCF_3)_4$ (0.066 g, 0.1 mmol) and 1,2-diiodoethane (0.028 g, 0.1 mmol) was sealed under vacuum in a Pyrex tube. The ampule was then placed in an electric furnace at 105 °C. Crystals of product were deposited on the walls of the tube from the hot zone to the cold zone, where the temperature set up 5° lower. The reaction was stopped after 4 days, affording 15−20% of a dark green crystalline product (**1**). It was mixed with some unidentified black residue in the hot zone, which proved to be insoluble in acetone and ethanol. ^{1}H NMR (C_6D_6, 22°C, 300 MHz, δ): 5.321 ppm (s, $CH_2{=}CH_2$). IR (KBr, cm^{-1}): 2958.9 (vw), 2863.5 (vw), 1653.5(m, s), 1189.9(m, s), 1027.1(w), 861.2(m), 832.4(w), 803.9(w), 785.9(m), 739.4(s), 541.9(m), 527.6(m). Anal. Calcd: C, 17.51; Found: C, 17.97.

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(7) Crystal Data for **1** at 173 K: $Rh_2O_8F_{12}C_{10}H_4$, FW = 685.95, tetragonal, $I4/m$, a = 11.5136(5) Å, c = 7.2291(8) Å, V = 958.3(1) Å^3, Z = 2. The final R factor was 0.0312 for 457 reflections with $I > 2\sigma(I)$, ($wR2$ = 0.0794 for all 458 data), GOF = 1.117. The CF_3 disorder was modeled over four rotational orientations.

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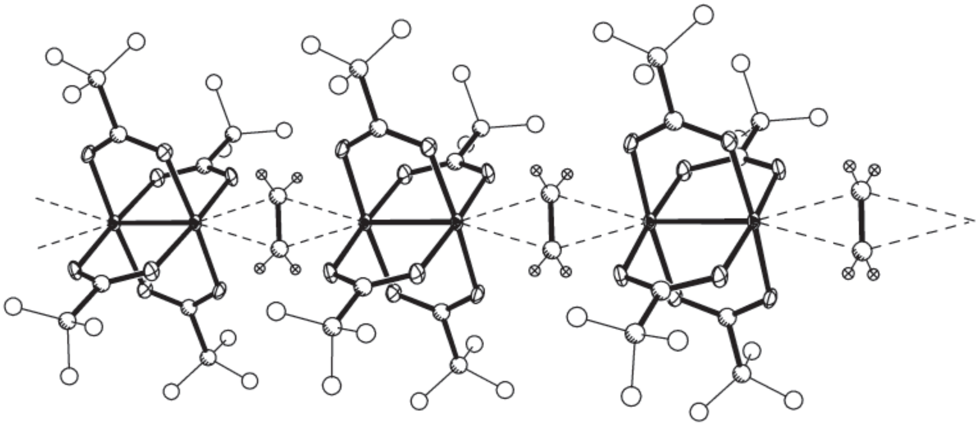

Figure 1. A fragment showing the alternating arrangement of $Rh_2(O_2CCF_3)_4$ and coordinated ethylene molecules in the polymeric chain of **1**. Only one orientation of each disordred C_2H_4 and CF_3 groups is depicted. The Rh−C contacts are drawn as dashed lines.

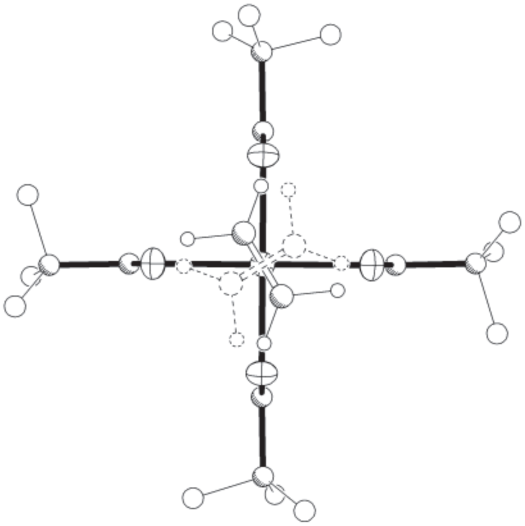

Figure 2. The view down the Rh−Rh axis of the $[Rh_2(O_2CCF_3)_4{\cdot}C_2H_4]$ unit showing two orientations of coordinated ethylene molecules.

case, the fate of the lost iodine atoms is unknown. It may be noted that the $M_2X_6(\mu\text{-}C_2H_4)(PR_3)_4$ compounds may also be made by direct reaction of C_2H_4 with $M_2X_4(\mu\text{-}X)_2(PR_3)_4$.[1,10]

It is also possible for an olefin to react oxidatively to form a product containing an $M{-}CR_2CR_2{-}M$ moiety, and it is clear from its ^{31}P NMR spectrum that this is the case[10] for $Zr_2Cl_6(CH_3CHCH_2)(PR_3)_4$. However, oxidation of $Rh_2(O_2CCF_3)_4$ is not to be expected, and it will be interesting to see if substituted ethenes can also form polymeric chains with the dirhodium complex. For the $M_2Cl_6(\text{olefin})(PR_3)_4$ molecules this appears to be impossible for steric reasons (as in $CH_3CH{=}CH_2$ versus $CH_2{=}CH_2$), but that need not be the case for $Rh_2(O_2CCF_3)_4$. Another interesting implication of the present work is that it may be possible in other cases to use the strong Lewis acid (which is otherwise relatively unreactive) as a trap for catching and stabilizing novel reactive species and reactive intermediates that are fragments of known but thermally unstable molecules.

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Supporting Information Available: X-ray crystallographic file for **1**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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