stituted $(SiMe_3)(C_6H_5)Cr(CO_3$ complexes.

In the binuclear cis complex IV the orientation of the $Cr(CO)_3$ fragment is close to the eclipsed conformation (the mean value of the α angle is 14.7° and 3.5° for the Cr(I) and Cr(2) atoms). Probably such mutual orientation of the $Cr(CO)_3$ groups is determined by a tendency to minimize steric repulsions between CO groups at adjacent Cr atoms. Indeed, there are some short nonbonding contacts in molecule IV (C(18)···C(22) = 3.49, C(18)···O(6) = 3.26, C(19)···O(6) = 3.13, and C(20)···O(2) = 3.24 Å with the sums of van der Waals radii being C···C = 3.60 and C···0 = 3.20 Å).

Registry No. II, 84179-62-4; III, 84179-63-5; IV, 84236-68-0.

Supplementary Material Available: Anisotropic temperature factors, hydrogen atom coordinates, bond lengths and angles, planes and deviations therefrom, and structure factor (121 pages). Ordering information is given on any current masthead page.

Communications

New Bridged Ruthenium Carboxylate Complexes. Structure and Catalytic Activity

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Received May 31, 1984

Summary: The reaction of $Ru_3(CO)_{12}$ with benzoic acid and 2-methylbutyric acid gives two structurally different and unexpected complexes. X-ray crystallographic analyses gave the structure of $[Ru(\mu\text{-}PhCO_2)(\eta^1\text{-}PhCO_2H)(CO)_2]_2$ and $[(Ru_2(\mu\text{-}sec\text{-}C_4H_9CO_2)_2(\eta^1\text{-}sec\text{-}C_4H_9CO_2H)(CO)_4]_2$ for the complexes obtained with the above two acids. The latter complex is a logical structural model for the previously reported ruthenium carboxylate polymers. Both complexes are catalytically active in the addition reactions of carboxylic acids to acetylenes.

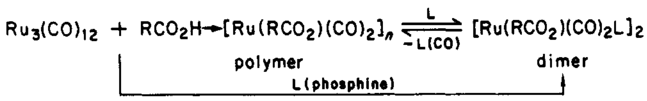
In a recent communication[1] we reported on a new catalytic reaction of $Ru_3(CO)_{12}$, described in a general form, by eq 1. Three isomeric vinyl esters are produced in good yields and selectivity.

$$R'CO_2H + RC{\equiv}CR \xrightarrow{Ru_3(CO)_{12}} \underset{E+Z}{R'CO_2(R)C{=}CHR} + R'CO_2(H)C{=}CR_2 \quad (1)$$

R = H, alkyl, aryl; R′ = alkyl, aryl

In conjunction with the above reaction we are studying the chemistry of $Ru_3(CO)_{12}$ and carboxylic acids. This subject was previously investigated by the groups of Lewis[2] and Schumann.[3,4] Their findings are summarized in Scheme I. The molecular structure of the insoluble polymer is not known. An X-ray crystallographic analysis[3] of a complex obtained from $Ru_3(CO)_{12}$, butyric acid, and tri-*tert*-butylphosphine revealed a structure of bis(μ-*n*-butyrato)bis[dicarbonyl(tri-*tert*-butylphosphine)ruthenium(I)]. Consequently, all the reported dimers[2,4] most probably possess similar bridging dicarboxylato core structure, $Ru\text{–}[O\text{–}C(R)\text{–}O]_2\text{–}Ru$.

Scheme I



$R = H, CH_3, C_2H_5, C_3H_7, C_9H_{19}, C_{17}H_{35}$; L = CO, phosphines, amines, arsines

In the present work we have studied the reactions of benzoic and 2-methylbutyric acids with $Ru_3(CO)_{12}$, which were carried out in toluene in a glass-lined reactor at 145 °C under nitrogen[5] (in eq 2 and 3 the number in parentheses represents moles of reactants).

$$PhCO_2H\ (15) + Ru_3(CO)_{12}\ (1) \rightarrow \underset{1\ (48\%)}{[Ru(PhCO_2)(CO)_2(PhCO_2H)]_2} \quad (2)$$

$$sec\text{-}C_4H_9CO_2H\ (6) + Ru_3(CO)_{12}\ (1) \rightarrow \underset{2\ (67\%)}{[Ru_2(sec\text{-}C_4H_9CO_2)_2(CO)_4(sec\text{-}C_4H_9CO_2H)]_2} \quad (3)$$

Both **1** and **2** were found to catalyze reaction 1 in the presence of their respective acids. However the structures of **1** and **2** are intriguing. The infrared spectra of **1**[6] and **2**[7] exhibit a broad O–H stretching band in the region of 2700–3200 cm^{-1} and a carbonyl band at 1670 (1675) cm^{-1}, which are indicative of carboxylic acids. Lower frequency bands (1560–1600 cm^{-1}) indicate metal-bridged carboxylato type of bonding. The presence of both carboxylato and carboxylic acid ligands in the same transition-metal complex is certainly a surprising structural feature. The ^{1}H NMR spectrum of **1**[6] gives rise to two chemically shifted Ph resonances (1:1). Two sets of *sec*-butyl resonances (1:2) were observed in the ^{1}H NMR spectrum of **2**.[7] Elemental analyses dictate a 1:2 ratio of Ru to benzoic acid in **1**[6] and a 2:3 ratio of Ru to 2-methylbutyric acid in **2**.[7]

On the basis of the spectral data and the elemental analyses we have assigned the molecular formula $Ru(PhCO_2)(CO)_2(PhCO_2H)$ to **1** and $Ru_2(sec\text{-}C_4H_9CO_2)_2$-

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(1) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689.

(2) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 2761.

(3) Schumann, H.; Opitz, J.; Pickardt, J. *J. Organomet. Chem.* **1977**, *128*, 253.

(4) Schumann, H.; Opitz, J. *Chem. Ber.* **1980**, *113*, 989.

(5) The same reaction conditions prevail during catalysis (eq 1).

(6) Anal. Calcd for $C_{16}H_{11}O_6Ru$: C, 48.00, H, 2.75. Found: C, 47.70; H, 2.69. IR (CH_2Cl_2): 3200–2700 (br), 2040, 1995, 1962, 1670, and 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.36 (t, *J* = 7.74 Hz, 2 H), 7.50 (t, *J* = 7.74 Hz, 1 H)8 7.53 (t, *J* = 7.37 Hz, 2 H), 7.68 (t, *J* = 7.37 Hz, 1 H), 7.88 (d, *J* = 7.74 Hz, 2 H), 8.20 (d, *J* = 7.37 Hz, 2 H).

(7) Anal. Calcd for $C_{19}H_{28}O_{10}Ru_1$: C, 36.89; H, 4.53; Ru, 32.7. Found: C, 36.87; H, 4.63; Ru, 32. IR (CH_2Cl_2): 3200–2700 (br), 2040, 1990, 1965, 1675, and 1560 cm^{-1}. ^{1}H NMR (acetone-d_4) δ 0.87 (t, *J* = 7 Hz, 6 H), 0.91 (t, *J* = 7 Hz, 3 H), 1.04 (d, *J* = 7 Hz, 6 H), 1.12 (d, *J* = 7 Hz, 3 H), 1.41 (m, 2 H), 1.61 (m, 4 H), 2.33 (m, 3 H).

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Organometallics 1984, *3*, 1759–1761

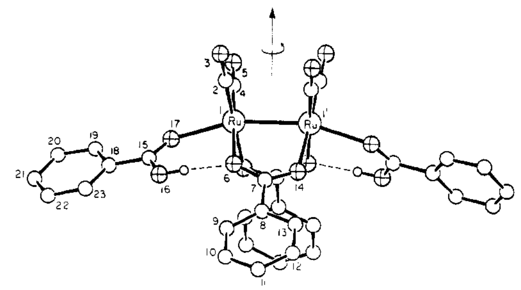

Figure 1. Molecular structure of $[Ru(PhCO_2)(CO)_2PhCO_2H]_2$ (the crossed circles represent oxygen atoms). In the crystal the molecules are located on twofold rotational axes. Selected bond lengths (Å) and angles (deg) are as follows: Ru(1)–Ru(1′) = 2.637 (2), Ru(1)–C(2) = 1.826 (7), Ru(1)–C(4) = 1.842 (6), Ru(1)–O(6) = 2.146 (3), Ru(1′)–O(14) = 2.121 (4), Ru(1)–O(17) = 2.265 (5), O(6)–C(7) = 1.265 (7), C(7)–O(14) = 1.241 (8), C(15)–O(16) = 1.316 (6), C(15)–O(17) = 1.222 (8); Ru(1′)–Ru(1)–O(17) = 162.8 (1). Geometric parameters of the OH(16)···O(6) hydrogen bond are as follows: O(16)–H(16) = 0.90 Å, O(16)···O(6) = 2.605 (7) Å, H(16)···O(6) = 1.75 Å, and O(16)–H···O(6) = 158°. The acidic hydrogen H(16) was located in a difference map.

$(CO)_4(sec\text{-}C_4H_9CO_2H)$ to **2**. However, we were unable to assign unambiguous molecular structure to **1** and **2**, which would conform with accepted structural rules or could be based on previously recorded examples. X-ray analyses of **1** and **2** were undertaken to solve their molecular structure (Figures 1 and 2).[8]

The unique feature of both structures is the side ligation of acid molecules. Such coordination represents, to the best of our knowledge, a new type of bonding of carboxylic acids in organometallic complexes. The specific hydrogen bonding in these systems (Figures 1 and 2) between the carboxyl and carboxylato oxygen atoms (O–O = 2.57 Å) must energetically support acid ligation. The severe distortion of the Ru octahedron in **1**, as reflected in the Ru–Ru–O(17) angle of 162.8°, is probably a consequence of the intramolecular hydrogen bonding. The acid carbonyl is essentially in the oxo form in view of its normal C=O distance (1.22, 1.25 Å). The average Ru–O distances involving the carboxylato and carboxylic acid oxygen atoms are 2.13 and 2.27 Å, respectively. Nevertheless, both **1** and **2** do not lose their acid ligands upon column chromatography (silica), indicating similar interactions in solution.

Complex **2** (Figure 2) is a centrosymmetric ruthenium tetramer that may be viewed as a dimer of two bis(μ-carboxylato) Ru–Ru cores, capped by two acid molecules. The dimerization involves two Ru–O bonds (2.31 Å) which, compared to the strong intracore Ru–O bonds (2.13 Å), indicate relatively tight bonding. The resulting complex is a coordinatively saturated 72-electron ruthenium tetramer. In view of the similarity of the solid and solution IR spectra of **2**, it is reasonable to assume similar structure in solution.

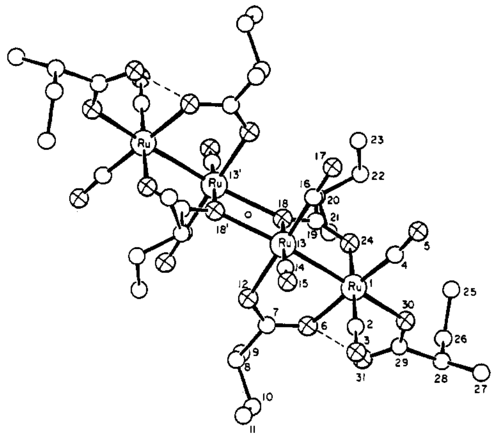

Figure 2. Molecular structure of $[Ru_2(sec\text{-}C_4H_9CO_2)_2(CO)_4(sec\text{-}C_4H_9CO_2H)]_2$ (the crossed circles represent oxygen atoms). In the crystal, the molecules are located on centers of symmetry. Selected bond lengths (Å) and angles (deg) are as follows: Ru(1)–Ru(13) = 2.630 (1), Ru(1)–O(30) = 2.26 (1), Ru(1)–O(6) = 2.13 (1), Ru(1)–O(24) = 2.10 (1), Ru(13)–O(12) = 2.10 (1), Ru(13)–O(18) = 2.16 (1), Ru(1)–C(2) = 1.83 (2), Ru(1)–C(4) = 1.81 (1), Ru(13)–C(14) = 1.82 (1), Ru(13)–C(16) = 1.80 (1), C(7)–O(6) = 1.26 (1), C(7)–O(12) = 1.25 (2), C(19)–O(18) = 1.24 (2), C(19)–O(24) = 1.26 (1), C(29)–O(30) = 1.25 (2), C(29)–O(31) = 1.25 (2), O(31)–O(6) = 2.57 (1) (hydrogen bond), Ru(13)–O(18′) = 2.314 (6) (the bridge bond; Ru(13) and O(18′) are in the two centrosymmetrically related parts of the molecule); Ru(13)–Ru(1)–O(30) = 161.7 (2), Ru(1)–Ru(13)–O(18′) = 156.5 (2). The distance between Ru(13) and Ru(13′) is 3.544 (2) Å.

We would like to propose that structure **2** represents a possible mode of polymerization (Scheme I) observed by Lewis et al.[2] with other acids; removal of the end acids in **2** may induce polymerization via additional Ru–O bridges. Furthermore, it is probable that the recently reported tetrameric complex[10] $Ru_4(CO)_8(CH_3CO_2)_4(PBu_3)_2$ possesses the core structure of **2**.

Acknowledgment. We wish to thank Mrs. Z. Stein for skillful assistance, The Israel Academy of Science and Humanities, Basic Research Foundations, for financial support, and the Johnson Matthey Research Centre for a loan of $RuCl_3$.

Registry No. 1, 91742-09-5; 2, 91759-07-8; $Ru_3(CO)_{12}$, 15243-33-1.

Supplementary Material Available: Tables of positional and thermal atomic parameters (6 pages). Ordering information is given on any current masthead page.

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[8] Crystal data for $[Ru(PhCO_2)(CO)_2PhCO_2H]_2$, $M_r = 800.7$: monoclinic, space group $C2/c$ with $a = 19.598$ (12) Å, $b = 16.909$ (3) Å, $c = 10.900$ (6) Å, $\beta = 118.41$ (3)°; $V = 3176.91$ (2.91) Å^3; $D_{calcd} = 1.674$ g cm^{-3} for $Z = 4$; μ(Mo Kα) = 9.93 cm^{-1}. Full-matrix anisotropic refinement of the nonhydrogen atoms converged at $R = 0.037$ and $R_w = 0.049$ for 2087 reflections with $I \geq 3\sigma(I)$ and $2\theta < 54°$. Crystal data for $[Ru_2(sec\text{-}C_4H_9CO_2)_2(CO)_4(sec\text{-}C_4H_9CO_2H)]_2$, $M_r = 1236.2$: triclinic, space group $P\bar{1}$ with $a = 9.988$ (3) Å, $b = 11.006$ (9) Å, $c = 12.916$ (4) Å. $\alpha = 107.63$ (4)°, $\beta = 90.42$ (3)°, $\gamma = 109.91$ (4)°; $V = 1262.56$ (1.28) Å^3; $D_{obsd} = 1.6$ g cm^{-3}, $D_{calcd} = 1.556$ g cm^{-3} for $Z = 1$; μ(Mo Kα) = 11.6 cm^{-1}. Anisotropic refinement of the core and carbonyl groups, and isotropic refinement of the partially disordered methylbutyric side chains and the acid ligand (the latter two with restrained geometry) let to $R = 0.055$ for 3512 reflections with $I \geq 3\sigma(I)$ and $2\theta < 54°$. Unit weights were used in this refinement. The diffraction intensities of the two compounds were measured at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å) and employing the ω–2θ scan technique. An empirical method was used to correct the intensity data for absorption effects.[9] Both structures were solved by phase refinement and weighted Fourier techniques using the MULTAN80 system of computer programs.

[9] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

[10] Bianchi, M.; Frediani, P.; Matteoli, U.; Menchi, G.; Piacenti, P.; Petrucci, G. *J. Organomet. Chem.* **1983**, *259*, 207.

Oxidatively Catalyzed CO Insertion Reactions with CpFeCO[P(OPh)$_3$](η^1-alkenyl) Complexes

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Received July 31, 1984

Summary: Treatment of CpFeCO[P(OPh)$_3$](η^1-alkenyl) complexes with oxidizing agents such as $[Cp_2Fe]BF_4$ or Ce(IV) under an atmosphere of CO leads to new alkenylacyl complexes under very mild conditions.

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