Journal of Organometallic Chemistry, 272 (1984) C62—C66
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

DIMERIC RUTHENIUM(II) COMPLEXES CONTAINING BRIDGING CARBOXYLATO AND AQUO LIGANDS. THE CRYSTAL STRUCTURE OF μ-AQUOBIS(μ-TRIFLUOROACETATO)BIS[(η^4-CYCLOOCTA-1,5-DIENE)-(TRIFLUOROACETATO)RUTHENIUM(II)]

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(Received April 30th, 1984)

Summary

Protonation of $[Ru(\eta^3\text{-}C_3H_4R)_2(C_8H_{12})]$ (R = H, Me; C_8H_{12} = cycloocta-1,5-diene) with haloacetic acids gives the dimers $[Ru_2(C_8H_{12})_2(O_2CR')_2(\mu\text{-}O_2CR')_2(\mu\text{-}OH_2)]$ (R' = CF_3, CCl_3 and CH_2Cl), which are precursors for a range of monomeric and dimeric ruthenium carboxylate complexes. The complex $[Ru_2(C_8H_{12})_2(O_2CCF_3)_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}OH_2)]$ has been characterized by X-ray analysis.

The carboxylato ligand has found wide application in transition metal chemistry and numerous routes have been devised for introducing this ligand into metal complexes [1]. One example [2] exists of the formation of a metal carboxylate complex by protonation of an η^3-allylrhodium complex with trifluoroacetic acid. Considering the large number of η^3-allylic complexes known, especially homoleptic η^3-allyl complexes, protonation of this group by carboxylic acids could provide a versatile and simple route to a wide range of metal carboxylate complexes. As the first part of our studies into the viability of this route, we now report on the synthesis of novel, highly reactive, dinuclear ruthenium(II) complexes from the protonation of the complexes $[Ru(\eta^3\text{-}C_3H_4R)_2(C_8H_{12})]$ (R = H, Me; C_8H_{12} = cycloocta-1,5-diene) with carboxylic acids.

The reaction of the haloacetic acids R'COOH (R' = CF_3, CCl_3 and CH_2Cl) with $[Ru(\eta^3\text{-}C_3H_4R)_2(C_8H_{12})]$ [3] in diethyl ether at 25°C gave, on addition of pentane, yellow-orange crystals analyzing for $\{[Ru(C_8H_{12})(O_2CR')_2]_x(H_2O)\}$ (I; R' = CF_3, CCl_3 and CH_2Cl). The IR spectra of these compounds contained characteristic ν(COO) vibrations in the range 1610—1680 cm^{-1} from which it was not possible to determine the mode of bonding of the carboxylato ligands.

0022-328X/84/$03.00

Molecular weight determinations done osmometrically in benzene indicated $x = 2$, and resonances in the range 13.0—13.8 ppm in the ^1H NMR spectrum, which disappeared on D_2O exchange, indicated water molecules held in the complex by strong hydrogen bonding. Consequently, complete characterization by X-ray analysis was sought. Crystals of I ($R' = CF_3$) were suitable for such a study.

Crystal Data

$C_{24}H_{26}F_{12}O_9Ru_2$, $M = 888.58$, triclinic, space group $P\bar{1}$, a 13.731(5), b 11.001(5), c 10.593(5) Å, α 101.04(2), β 100.21(2), γ 97.77(2)°, U 1521.8 Å^3, D_c 1.93 Mg m^{-3} for $Z = 2$, $R = 0.055$ for 3694 reflections with $F_o \geqslant 6\sigma(F_o)$. Intensity data were collected on a Philips PW1100 four-circle diffractometer (National Physical Research Laboratory, CSIR) by the $\omega—2\theta$ scan technique using graphite-crystal monochromatized Mo-K_α radiation. The structure was solved by Patterson and difference electron density synthesis methods, and was refined by 2-block-matrix least squares using the SHELX [4] program system. All hydrogen atom positions were located from subsequent difference electron density synthesis and were refined. Anisotropic temperature factors were used for all non-hydrogen atoms and separate common isotropic temperature factors

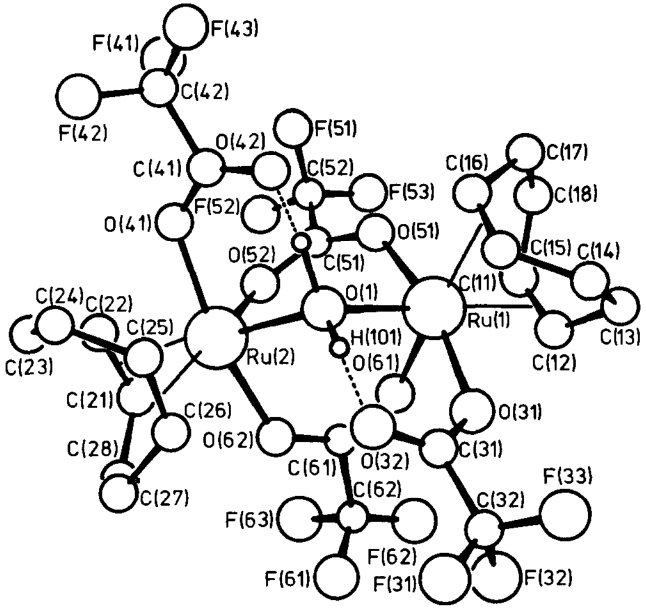
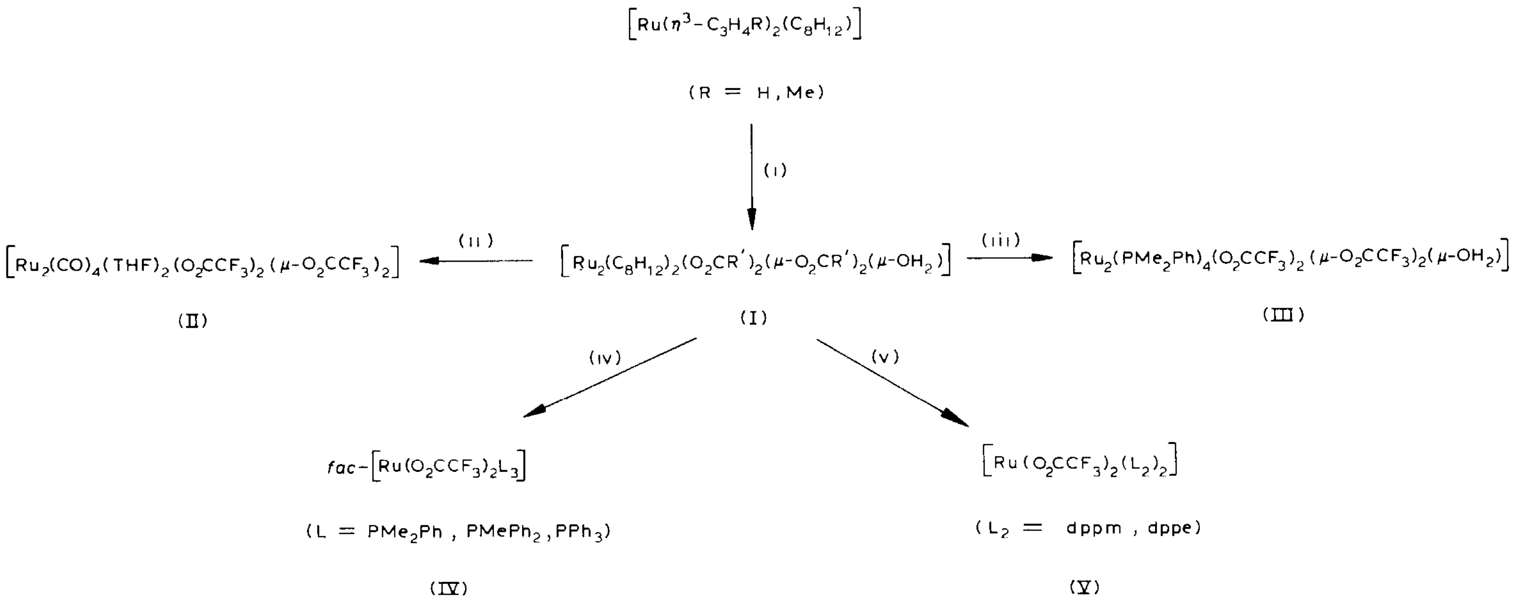


Fig. 1. The structure of I ($R' = CF_3$). Selected bond lengths (Å) and angles (°), Ru(1)—O(1) 2.160(5), Ru(2)—O(1) 2.168(5), Ru(1)—O(31) 2.094(5), Ru(2)—O(41) 2.104(6), Ru(1)—O(51) 2.097(5), Ru(1)—O(61) 2.131(5), Ru(2)—O(52) 2.124(5), Ru(2)—O(62) 2.078(5), Ru(1)···Ru(2) 3.733(1), O(1)···O(32) 2.530(10), O(1)···O(42) 2.495(10), Ru(1)—O(1)—Ru(2) 119.2(2), O(1)—Ru(1)—O(31) 88.0(2), O(1)—Ru(1)—O(51) 85.3(2), O(1)—Ru(1)—O(61) 93.5(2), O(31)—Ru(1)—O(51) 164.6(2), O(31)—Ru(1)—O(61) 81.1(2), O(51)—Ru(1)—O(61) 85.5(2), O(1)—Ru(2)—O(41) 88.2(2), O(1)—Ru(2)—O(52) 91.7(2), O(1)—Ru(2)—O(62) 85.8(2), O(41)—Ru(2)—O(52) 81.0(2), O(41)—Ru(2)—O(62) 166.9(2), O(52)—Ru(2)—O(62) 87.6(2).



SCHEME 1. Synthesis and selected reactions of I. (i) R′COOH (R′ = CF_3, CCl_3 and $CHCl_2$) in Et_2O at 25°C, 18 h, yield 70—79%. (ii) 1 atmosphere CO, THF at 50°C, 1 h, yield 85%. (iii) 4 equivalents of PMe_2Ph in THF at 25°C, 1 h, yield 50%. (iv) 6 equivalents L in Et_2O at 25°C, 18 h, yield 50—70%. (v) 4 equivalents L_2 in Et_2O at 25°C, 18 h, yield 70—90%.

were refined for the hydrogen atoms of each cyclooctadiene ligand and the bridging aquo ligand.

The structure is shown in Figure 1 together with selected dimensions*.

The crystal data show complex I (R′ = CF_3) to be dinuclear with the two ruthenium atoms bridged by two trifluoroacetato groups and a water molecule. A cycloocta-1,5-diene ligand and a monodentate trifluoroacetato ligand complete the coordination sphere of each ruthenium atom. The ruthenium—ruthenium interatomic distance is 3.733(1) Å. A notable feature of the structure is the strong intramolecular hydrogen bonding between the non-coordinated oxygen atoms of the monodentate trifluoroacetato ligands and the bridging aquo ligand, with O(trifluoroacetato)····H(aquo) distances of 1.55(8) and 1.31(8) Å, and O(trifluoroacetato)····O(aquo) distances of 2.53(1) and 2.50(1) Å. This explains the large chemical shift at 13.0 ppm observed for the protons of the aquo ligand in the ^1H NMR spectrum of this complex (cf. CF_3COOH resonates at 9.83 ppm).

A selection of reactions carried out using complex I (R′ = CF_3) is shown in Scheme 1. Two types of substitution reactions are observed, the one involving retention of the metal carboxylate framework, and the other, breakdown to monomeric ruthenium(II) carboxylates. Thus, reactions of CO with I in tetrahydrofuran (THF) gave II (ν(CO) 1960, 2000, 2030, 2100 cm^{-1}; ν(COO) 1680 cm^{-1}), and stoichiometric additions of PMe_2Ph in THF produced III (ν(COO) 1700 cm^{-1}; ^1H NMR multiplet 1.5 ppm (methyl); *M* (osmometrically) 1020, calcd. 1224). With excess ligands L (L = PMe_2Ph, $PMePh_2$ and PPh_3) in diethyl ether, the complexes IV were obtained and assigned a facial configuration from ^1H NMR data for IV (L = PMe_2Ph) [5]. Diphosphine ligands and I gave the complexes V. For L_2 = bis(diphenylphosphino)methane a *trans*-configuration of monodentate trifluoroacetato ligands was assigned (^{31}P NMR singlet at −8.9 ppm relative to H_3PO_4) and for L_2 = 1,2-bis(diphenylphosphino)ethane a *cis*-configuration (complex ^{31}P multiplet centred at 59.3 ppm relative to H_3PO_4 consistent with an A_2B_2 spin system). Other substitution reactions of I (R′ = CF_3) with $Co_4(CO)_{12}$ and CH_2N_2 have given carboxylate-carbonyl clusters and complexes containing the methylene fragment, but full characterization by X-ray crystallographic analysis is awaited. I (R′ = CF_3) is converted to salts with readily accessible coordination sites on protonation with acids with non-coordinating anions. The salt $[Ru(C_8H_{12})(NCMe)_4](PF_6)_2$ [6] has been characterised in acetonitrile as donor solvent. This route has also been used in THF to give highly active catalysts which isomerize and hydrogenate olefins, including *trans,trans,cis*-1,5,9-cyclododecatriene.

Acknowledgments. We wish to thank Dr M. Laing for helpful discussions.

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

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