Ethane and Ethylidene Dicarboxylates from the Ruthenium(II)-Catalyzed “Disproportionative Addition” of Carboxylic Acids to Ethene**

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Ethene is of paramount importance in chemistry and the addition reactions to the simplest olefin are paradigmatic. It is known that the acid-catalyzed addition of carboxylic acids yields esters.[1] Herein we report a Ru^{II}-catalyzed “disproportionative addition” (that is, addition to give both oxidized and reduced products simultaneously) of carboxylic acids to give ethane and ethylidene dicarboxylate [Eq. (1)].

$$\begin{gathered}2\,C_2H_4 + 2\,RCOOH \xrightarrow{[RuL_n(CO)_2]^{(2-n)+}} C_2H_6 + CH_3CH(OOCR)_2 \\ L = RCOO^-,\ CF_3SO_3^-;\ R = C_2H_5,\ CH_3\end{gathered} \tag{1}$$

This novel reaction is carried out in anhydrous carboxylic acids. A number of ruthenium complexes can be employed as precursors, provided they generate $[RuL_n(CO)_2]^{(2-n)+}$ ($L = RC(O)O^-$, $CF_3SO_3^-$) intermediates. For instance, the triflate salt of the Ru^{II}–ethyl complex $[Ru_2(C_2H_5)_2(CO)_4(H_2O)_4]^{2+}$ (**1**)[2] is a suitable precursor for the reaction described in Equation (1), performed in propionic acid containing 10% of propionic anhydride. In that reaction medium, ethane and ethylidene dipropionate are formed in equimolar amounts with a turnover frequency (TOF) of $3\,h^{-1}$ at 130° ($P_{ethene} =$ 25 atm; $[Ru] = 0.05\,M$), with the TOF remaining almost unchanged after 10 h. With regard to the activation of precursor **1,** it had already been shown that, in solution, the dinuclear complex is converted into the mononuclear $[RuL(C_2H_5)(CO)_2(H_2O)_2]$ (**2**, L = propionato or triflato)[2]. At 90 °C under an inert atmosphere, complex **2** (0.1 M in propionic acid/anhydride) is dehydrated by the anhydride while, on acidolysis, quantitative ethane formation occurs. The IR absorptions of **1** in propionic acid/anhydride at 2049(s) and 1970(vs) cm^{-1} are shifted to 2090(s) and 2024(vs) cm^{-1}, which are attributable to *cis*-$[RuL_n(CO)_2]^{(2-n)+}$ ($L = RC(O)O^-$ or $CF_3SO_3^-$) species. When ethene ($P_{ethene} =$ 25 atm, $T = 90$ °C) is added, a reaction occurs that leaves the *cis*-$(CO)_2Ru$ group intact and gives rise to new absorptions at 2059(s), 1984(vs), and 1600(s) cm^{-1}. To elucidate this reaction, the propionic acid/anhydride solvent was removed under vacuum and the residue extracted with toluene. Upon addition of hexane, crystalline $[\{Ru(CF_3SO_3)(CHCH_3\{OC(O)C_2H_5\})(CO)_2\}_2]$ (**3**) was isolated in 37% yield. The molecular structure of **3** is shown in Figure 1; two bridging triflato ligands bind two *cis*-dicarbonyl–Ru^{II} units. The coordination sphere of each ruthenium is approximately octahedral being completed by the $CHCH_3(OC(O)C_2H_5)$ group, which acts as a bidentate ligand through the ester oxygen atom. The IR spectrum of **3** in the solid state displays stretching frequencies of the terminal *cis*-CO groups at 2064(vs) and 1994(vs) cm^{-1}, and that of the coordinated ester carbonyl at 1633(s) cm^{-1}. In propionic acid/anhydride solution, **3** shows absorptions at 2059(s), 1984(vs), and 1600(s) cm^{-1}, identical to the frequencies reported above. This suggests that **3**, which is dinuclear in the solid state, exists as a mononuclear Ru^{II} complex in solution. This is particularly noteworthy as complexes contatining bridging triflates are rare[3] and only documented in the solid state.

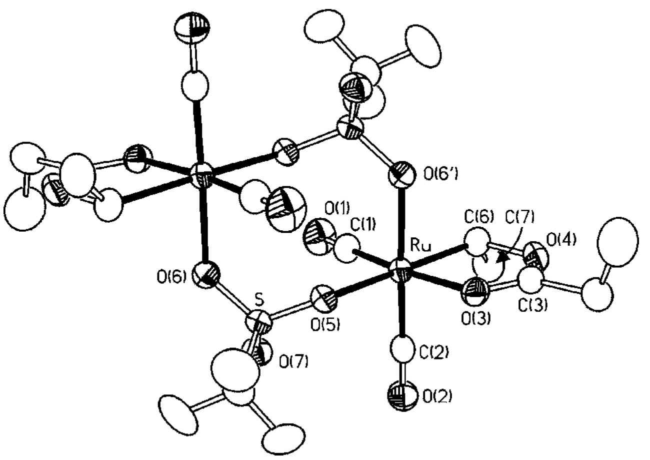

Figure 1. The molecular structure of $[\{Ru(OSO_2CF_3)(CH(OCOC_2H_5)CH_3)(CO)_2\}_2]$ (**3**); ellipsoids are at 30% probability. Selected bond lengths [Å] and angles [°]: Ru-C(1) 1.870(5), Ru-C(2) 1.842(5), Ru-C(6) 2.050(5), Ru-O(3) 2.091(3), Ru-O(6′) 2.171(3), Ru-O(5) 2.293(3); C(2)-Ru-C(1) 87.6(2), C(2)-Ru-C(6) 93.1(2), C(1)-Ru-C(6) 93.2(2), C(2)-Ru-O(3) 93.4(2), C(1)-Ru-O(3) 173.0(2), C(6)-Ru-O(3) 79.8(2), C(2)-Ru-O(6′) 176.6(2), C(1)-Ru-O(6′) 95.7(2), C(6)-Ru-O(6′) 86.6(2), O(3)-Ru-O(6′) 83.3(1), C(2)-Ru-O(5) 93.7(2), C(1)-Ru-O(5) 99.0(2), C(6)-Ru-O(5) 166.2(2), O(3)-Ru-O(5) 87.8(1), O(6′)-Ru-O(5) 85.8(1), C(3)-O(3)-Ru 112.4(3), O(3)-C(3)-O(4) 122.5(4), C(3)-O(4)-C(6) 117.8(4), O(4)-C(6)-Ru 107.2(3). Symmetry operation for primed atoms: $-x$, $-y+1$, $-z$.

The ^1H NMR spectrum of **3** in $[D_4]$acetic acid shows three main quartet resonances between $\delta = 6.1$ and 6.5 ppm, attributed to the methine hydrogen atom of the alkyl ligand. These resonances, however, are affected by the addition of either the triflate or propionate salts of cesium, which are able to shift coordination equilibria in solution. For example, the addition of C_2H_5COOCs to a solution of **3** (0.2 M, molar ratio $C_2H_5COOCs{:}Ru = 2$) in $[D_4]$acetic acid yields a ^1H NMR spectrum that shows only a single quartet at $\delta = 6.16$ ppm, which originates from the propionato complex. Based on the structure of **3** in the solid state, and from its spectroscopic properties, we conclude that precursor **1** at 90 °C under ethene (25 atm) in propionic acid/anhydride is converted into the mononuclear ethylidene carboxylate dicarbonyl Ru^{II} complex **4** (Scheme 1), which is involved in coordination equilibria with triflato or propionato ligands.

As specified before, such a conversion is a consequence of the dehydration and subsequent acidiolysis of **2**, which leads to the formation of a $[RuL_n(CO)_2]^{(2-n)+}$ ($L = RC(O)O^-$ or

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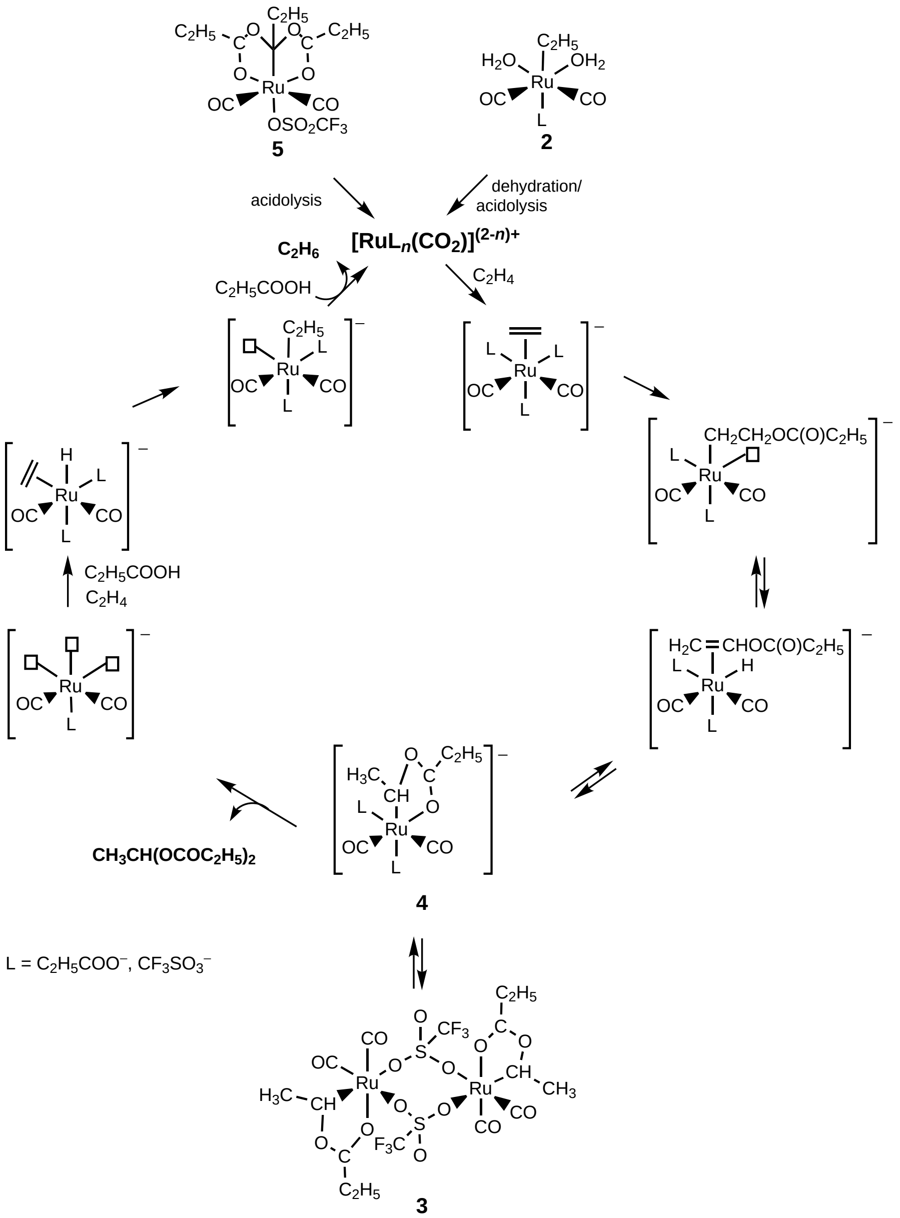

Scheme 1. Mechanism for the Ru^{II}-catalyzed disproportionative addition of carboxylic acids to ethene. The activation of precursors **2** and **5** is also displayed.

$CF_3SO_3^-$) species, followed by ethene coordination, nucleophilic attack by the propionato moiety, and rearrangement of the alkyl complex by β-activation. In complex **4**, β-activation is exemplified by the fact that deuterium atoms are incorporated at both positions of the CH–CH_3 fragment when dissolved in C_2H_5COOD at 90 °C. Such behavior can be compared to that of Pd^{II}-coordinated ethene, which also undergoes nucleophilic attack by acetate groups. In this case, β-activation results in the release of a proton from the hydridopalladium moiety, and the decomposition to vinyl acetate and palladium metal [Eq. (2)].[4]

$$C_2H_4 + CH_3COOH + PdCl_2 \rightarrow CH_2{=}CHOC(O)CH_3 + 2\,HCl + Pd \qquad (2)$$

By increasing the temperature of the above-mentioned solution to 140 °C, the stepwise formation of **4** from **1** has been followed; the Ru^{II}-catalyzed formation of equimolar amounts of ethane and ethylidene dipropionate occurs, as shown in Equation (1). IR spectroscopy shows that **4** is the only detectable species during catalysis; separate experiments confirm that **4** catalyzes the reaction with no induction period and remains unchanged. We conclude that **4** is an intermediate and that the reductive elimination of ethylidene dipropionate from **4** is the slow step of the catalytic cycle. Experiments in C_2H_5COOD confirm the intermediary role of complex **4**. The ^2H NMR spectrum of the ethylidene dipropionate formed in the deuterated solvent shows deuterium incorporation in the organic product. On these grounds, the above reported H/D scrambling of **4** in C_2H_5COOD appears to be related to the H/D scrambling observed in the 1,1′-diester product of the catalytic reaction. Finally, the formation of ethane in the catalytic cycle can be rationalized on the basis of an oxidative addition of propionic acid to the Ru^0 complex, formed by reductive elimination from **4**, followed by ethene insertion into the resulting hydride (Scheme 1) and acidolysis of the ethyl complex.

It is noteworthy that the catalytic reaction described in Equation (1) can be extended to other carboxylic acids. For instance, equimolar amounts of ethane and ethylidene diacetate are formed when employing **1** as a precursor in acetic acid/anhydride, with a similar TOF to that which was recorded for the above-reported propionic acid/anhydride case. In addition, the intermediate that accumulates during the catalysis in acetic acid appears to have a similar nature to that of **4**, with C_2H_5 groups being substituted with CH_3 groups. Moreover, different precursors can be employed for the reaction described in Equation (1). For instance, the recently characterized $[Ru(CF_3SO_3)\{CC_2H_5(OC(O)C_2H_5)_2\}(CO)_2]$ (**5**)[5] has been converted into complex **4** under the conditions of the catalytic reaction. The tridentate $CC_2H_5(OC(O)C_2H_5)_2$ ligand of **5** is entirely dissociated, thus yielding the $[RuL_n(CO)_2]^{(2-n)+}$ ($L = RC(O)O^-$, $CF_3SO_3^-$) active species which initiate the cycle described in Scheme 1.

In conclusion, the carboxylic acid-induced disproportionation of ethene has been demonstrated. The reaction is industrially relevant since the dissociation of carboxylic acids from 1,1′-diester products is well known and constitutes a synthetic method for vinyl esters other than acetates.[6]

Experimental Section

Complexes **1** and **5** were prepared according to literature procedures[2,5]. Catalytic runs were performed as described in reference [2]. GC analyses of ethane/ethene mixtures were performed with a 2-m Carboxen-1004 micropacked column. Ethylidene dipropionate analyses were perfomed with a 2-m Silicone column. $C_2H_5COOD/(C_2H_5CO)_2O$ mixtures were prepared by adding D_2O to propionic anhydride and refluxing the solution for a short time. A sample of partially deuterated ethylidene dipropionate, as formed in the catalytic reaction in $C_2H_5COOD/(C_2H_5CO)_2O$, was obtained by neutralization at pH 8 with $NaHCO_3$, extraction with Et_2O, solvent evaporation, and distillation of the residue under vacuum: ^2H NMR (300 MHz, THF): $\delta = 6.7$ (br), 1.4 ppm (br).

3: Complex **5** (1.60 g, 3.25 mmol) was dissolved in $C_2H_5COOH/(C_2H_5CO)_2O$ (50 mL, 10% anhydride) and stirred under ethene (25 atm) at 130 °C. After 2 h, the gases were discharged and solvents removed by distillation (55 °C, 0.1 mmHg). The oily residue was treated first with toluene (10 mL) and then with hexane (200 mL). The first aliquot of precipitate was discarded by filtration and crystals of **3** (0.47 g, 0.6 mmol, 37% yield) were obtained by cooling the mother liquor at −20 °C. IR (nujol mull): $\tilde{\nu}_{CO} = 2064$(vs), 1994(vs), 1633(s) cm^{-1}. IR ($C_2H_5COOH/(C_2H_5CO)_2O$ solution): $\tilde{\nu}_{CO} = 2059$(s), 1984(vs), 1600(s) cm^{-1}. ^1H NMR (CD_3COOD): $\delta = 6.41$ (q), 6.35 (q), 6.16 ppm (q); $\delta = 6.16$ ppm (1 H, q) upon addition of C_2H_5COOCs (0.8 M). ^1H NMR ([D$_8$]THF): $\delta = 6.45$ (1 H, q), 2.64 (2 H, q), 1.81 (3 H,d), 1.20 ppm (3 H, t).

Complex **3** (0.1 M in C_2H_5COOD) was maintained at 90 °C for 3 h. Aliquots of 1 mL, taken at 30 min intervals, were evaporated to dryness and examined by ^1H NMR spectroscopy in [D$_8$]THF. The spectra showed the gradual decrease of both the quartet ($\delta = 6.45$ ppm) and doublet ($\delta = 1.81$ ppm) signals of **3**.

Single-crystal X-ray diffraction was carried out with a Bruker P4 diffractometer using $Mo_{K\alpha}$ graphite-monochromated radiation ($\lambda = 0.71073$ Å), the sample being sealed in a glass capillary under an argon atmosphere. The crystal used for the measurement was a rather large colorless prism with approximate dimensions $0.50 \times 0.34 \times 0.21$ mm^3. Cell parameters were calculated on the setting angles of 40 strong reflections with $5.0° \leq \theta \leq 12.6°$. Crystal data: $C_{16}H_{18}F_6O_{14}Ru_2S_2$, $M_r = 814.56$, $T = 293(2)$ K, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.298(1)$, $b = 10.525(1)$, $c = 12.788(1)$ Å, $\beta = 112.26(1)°$, $V = 1407.3(2)$ Å^3, $Z = 2$, $\rho_{cald} = 1.922$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.322$ mm^{-3}, $F(000) = 800$. The intensities of 3238 reflections with $2.0° \leq \theta \leq 25°$ were collected. After merging the equivalent reflections and after corrections for Lorentz, polarization, and absorption effects with an empirical method,[7a] an internal R value of 0.0131 was obtained.

The structure was solved by standard direct and Fourier methods and refined by full-matrix least-squares procedures. The hydrogen atoms were placed in calculated positions and allowed to ride on the connected carbon atoms. In the final refinement cycle anisotropic thermal parameters were used for all heavy atoms, giving a conventional R factor (F_o) of 0.0347, calculated for 181 parameters on 2100 observed reflections [$I > 2\sigma(I)$], and a wR_2 value of 0.0436 for all 2489 data. The residual peaks in the final difference Fourier map range between 0.80 and −0.72 e Å^{-3}. The calculations were carried out using SHELX97[7b] contained in the WINGX[7c] suite.

CCDC-191095 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Selective Measurements of a Nitroxide–Nitroxide Separation of 5 nm and a Nitroxide–Copper Separation of 2.5 nm in a Terpyridine-Based Copper(II) Complex by Pulse EPR Spectroscopy**

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Coordination by transition metals is one of the main design principles of supramolecular chemistry.[1] The structures of such supramolecular assemblies are often elucidated by NMR spectroscopy and X-ray diffraction analysis. The latter method fails for the structural determination of noncrystalline assemblies. For paramagnetic transition metals, structural determination is further complicated by the failure of NMR methods from fast paramagnetic relaxation. In particular, the characterization of long-range arrangements over several nanometers has proved to be a significant barrier towards the further development of supramolecular structural design. On the other hand, it has been shown in the past few years that modern pulse EPR techniques[2] are capable of measuring separations up to at least 5 nm between organic radicals in disordered systems with high precision.[3] The application of such techniques to transition metals with considerable anisotropy of the g and/or hyperfine tensors, such as Cu^{II}, Co^{II}, V^{IV}, Mo^{V}, or Fe^{III} is more complicated, since only a small fraction of the EPR spectrum of these species can be excited by the pulses. Indeed, attempts to measure Mo⋯Fe separations in the Mo^{V}/Fe^{III} state of sulfite oxidase did not result in appreciable dipolar modulations[4] and, except for a preliminary conference report on the measurement of a Cu⋯Cu separation in azurin,[5] no applications to transition metals have been reported to date. An estimate of the separation of a transition metal and a nitroxide spin label can also be obtained from relaxation measurements. However, this approach is restricted to separations shorter than 3 nm and to systems where the

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