Rhodium Mediated C–H Bond Functionalization Leading to Carboxylate Derivatives

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Carboxylic acids and their esters or lactones are among the most common functionalities, and a large number of fine chemicals are accessible from this functionality.^[1] Typical organic synthetic procedures^[2] towards carboxylic acids include oxidation of alcohols and aldehydes and hydrolysis of nitriles, while carboxylation of organic substrates containing C–X bonds is perhaps the best established approach to carboxylic acids mediated by transition metal complexes.^[3] From an atom economy perspective, direct functionalization of C–H bonds to C–CO₂R bonds is a highly desirable alternative, since it avoids classical functional group manipulations. Although scarce, such palladium catalysed reactions were recently reported.^[4] From a formal point of view, a COO moiety could be inserted into a C–H bond by the combination of oxygenation and carbonylation involving simply O₂ and CO as attractive and cheap substrates. In this line, 2-metallaioxetanes^[5] emerge as valuable candidates to test this possibility, since they could be obtained by oxygenation of olefins with dioxygen.^[6] Although the reactivity of 2-metallaioxetanes is currently in its infancy,^[7] two of them have been reported to be suitable for C–X (X = N, O) bond formation, as shown for the reactions of 2-rhoda- and 2-platina-oxetanes with acetonitrile^[8] and carbon monoxide,^[9] respectively. In this communication we describe new reactions leading to carboxylic acids and lactones, involving the stoichiometric functionalization of an allylic C–H bond of cod with carbon monoxide and dioxygen which proceeds via a discrete 2-rhodaioxetane intermediate.

We previously reported the selective reaction of [Rh(C₈H₁₂)(PhN₃Ph)] (C₈H₁₂ = 1,5-cyclooctadiene, PhN₃Ph = 1,3-diphenyltriazene) with molecular oxygen to give the dinuclear 2-rhoda(III)oxetane complex [{Rh(PhN₃Ph)(OC₈H₁₂)}₂] (**1**, Scheme 1).^[6a] Diffusion of carbon monoxide through a dichloromethane solution of **1** at room temperature gave the carbonyl complex [{Rh(CO)₂(μ-PhN₃Ph)}₂] (**3**) quantitatively, along with 4-cyclooctenone (**2**, 65 %). Although complex **1** contains three different types of metal–X σ-bonds (X = O, N, C), each in principle suitable for carbon monoxide insertion, the

reaction predominantly leads to elimination of the oxygenated fragment as 4-cyclooctenone (**2**). The way in which **2** is eliminated upon exposure of **1** to CO should be similar to the reactions previously reported for the reactions of complex **1** with phosphanes.^[10] The second organic compound in the reaction (in 35 % yield) was further identified as the cycloocta-2,6-diene carboxylic acid (**4**) (see Experimental Section). As most relevant resonances, the proton from the –COOH moiety, unobserved at room temperature, was located as a sharp singlet (at δ = 13.67 ppm) at –70 °C in [D₈]-toluene while the carboxylic carbon appeared at the usual chemical shift (δ = 180.7 ppm) in the ¹³C{¹H}–apt spectrum.

On raising the temperature of the reaction, the amount of carboxylic acid **4** increases and becomes the major product at 60 °C in C₆D₆, provided that carbon monoxide is allowed to diffuse slowly through a solution of **1** (Scheme 1).

Scheme 1. Elimination reactions from the 2-rhoda(III)oxetane complex **1** on reaction with carbon monoxide under different conditions. i) slow diffusion and ii) vigorous stirring. The two nitrogen atoms on **1** and **6** represent the anionic PhN₃Ph ligand. The numbering scheme is used for NMR characterization.

Noticeably, the slow diffusion and dilution of carbon monoxide is crucial for the regioselective synthesis of **4**. If the solution of **1** is heated at 60 °C and then mixed with CO at 0 °C under vigorous shaking a different product is formed, i.e. the new 8-oxabicyclo[5.2.1]deca-2,5-dien-9-one (**5**, Scheme 1). Again [{Rh(CO)₂(μ-PhN₃Ph)}₂] (**3**) is the single rhodium product. Prolongated heating (100 °C, 3 bar of CO) gave a mixture, probably the thermodynamic one, containing **5** and the isomeric oxabicycles with the olefinic bonds in positions 2,4 (**5b**) and 3,5 (**5c**). Compound **5** was identified on the basis of its spectroscopic data (see Experimental Section and Supporting Information). From the six CH signals observed in the apt-¹³C{¹H} NMR

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spectrum four of them correspond to the olefinic carbons, while those at $\delta = 40.3$ and 76.9 ppm correspond to C1 and C7 bound to the C=O and O, respectively. As expected, the carboxylic carbon (C9) was observed at a typical chemical shift ($\delta = 176.3$ ppm).

Monitoring the reactions by ^1H NMR allowed the observation of the common active species leading to cycloocta-2,6-diene carboxylic acid (**4**) and 8-oxabicyclo[5.2.1]deca-2,5-dien-9-one (**5**). This species was found to be the eighteen-electron rhodium(III) complex $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})(\text{CO})]$ (**6**) (Scheme 1), which was isolated in a separate experiment working quickly at 0°C to prevent the elimination reaction. The phenyl groups of **6** are non-equivalent, and the allyl moiety was clearly identified by the sharp resonances at $\delta = 5.45$, 4.71 and 4.53 ppm in the ^1H NMR spectrum. The alkyl carbon bound to rhodium produces a sharp doublet at $\delta = 54.8$ ppm ($J(\text{C},\text{Rh}) = 18.5$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ -APT spectrum while the carbon bearing the hydroxyl group gives a sharp singlet at $\delta = 87.3$ ppm. The terminal carbonyl group bound to rhodium was identified by a strong $\nu(\text{C}-\text{O})$ stretch band at 2083 cm^{-1} with IR spectroscopy.

Complex **6** is the result of the isomerization of the rhodaoxetane(III) complex **1** into the 16 v.e. hydroxy-alkyl-allyl species $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})]$ followed by the coordination of carbon monoxide. We previously reported the hydroxy-alkyl-allyl species $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})]$ without CO ligands (coordination polymer) formed in the reaction of $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{PhN}_3\text{Ph})]$ with oxygen through isomerisation of the 2-rhodaoxetane intermediate.^[6a] Related isomerisation reactions have been previously reported for similar 2-metallaioxetane complexes,^[6,5g] but follow-up reactivity for these species have not been described. In principle, complex **6** could exist in three possible isomeric forms as shown in Figure 1, but the reaction selectively produces only isomer **6a** with the carbonyl group in close proximity to the hydroxo group (as evidenced by NOESY spectroscopy, see Supporting Information).

Figure 1. Possible stereoisomers of $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})(\text{CO})]$. Isomers **6b** and **6c** were not observed. The two nitrogen atoms on the rhodium represent the triazenide ligand.

Figure 2 shows the DFT optimized geometry of **6a**. The hydroxy-alkyl-allyl moiety behaves as a *fac*-tridentate ligand; a chelating triazenide ligand and one carbonyl group complete an almost octahedral environment for the rhodium. The strong *trans*-influence of the alkyl carbon (C1) is clearly evidenced by the considerable elongation of the Rh–N1 bond in *trans* ($2.244\text{ \AA}$) when compared to the other Rh–N3 bond ($2.188\text{ \AA}$) *trans* to the C4 atom in the allyl group. Within the allyl group, the Rh–C4 bond is found to be shorter ($2.200\text{ \AA}$) than the Rh–C6 bond ($2.337\text{ \AA}$). The optimized geometries of isomers **6b** ($+4.0\text{ kcal mol}^{-1}$) and **6c** ($+4.3\text{ kcal mol}^{-1}$) are clearly higher in energy (see Supporting Information).

Figure 2. DFT calculated structure of **6a**. Selected distances ($\text{\AA}$): Rh–C1 2.094 , Rh–C4 2.200 , Rh–C5 2.181 , Rh–C6 2.337 , Rh–N1 2.244 , Rh–N3 2.188 , Rh–C9 1.906 . Only the *ipso* carbons of the phenyl groups are shown for clarity.

Starting from isolated samples of **6a**, the carboxylic acid **4** and the oxabicyclo **5** were synthesized and the new organic compounds were isolated (see Experimental Section). Moreover, we have verified that carbon monoxide is not needed for the formation of the carboxylic acid **4** from **6a** except for being liberated from the rhodium coordination sphere, while the formation of the lactone **5** requires carbon monoxide as reactant. Furthermore, when the reactions of **6a** with ^{13}CO were carried out under the two different experimental conditions all ^{13}CO was found to be fully incorporated only into the complex $[\{\text{Rh}(^{13}\text{CO})_2(\mu\text{-PhN}_3\text{Ph})\}_2]$ (**3- ^{13}CO**) in both cases, indicating that the carbonyl group in **4** and **5** comes from that previously coordinated to rhodium in complex **6a**. In a reverse order, the reactions of the labeled complex **6a- ^{13}CO** with carbon monoxide gave either **4- ^{13}CO** or **5- ^{13}CO** as the sole labeled compounds. The selectivity observed in the labeling experiments indicates that **4** and **5** come from an intramolecular reaction undergone by **6a**, and suggests both reactions to proceed through a common intermediate, which would result from the coupling of the carbonyl group (^{13}CO) with the C4 atom (A, Scheme 2). This step is available through a change in the coordination mode of the η^3 -allyl group into a σ -allyl one, perhaps assisted by the hydroxyl moiety, to produce the carbonyl insertion into the Rh–C4 bond. Precedents for facile reactions of this type assisted by hemilabile ligands are known in palladium chemistry.^[11]

The way to **4** from **A** requires a cleavage of the C–OH bond in the organic moiety. A viable possibility is a β -hydroxy elimination reaction from the coordinatively unsaturated acyl intermediate **A** to give the rhodiumhydroxo(η^2, η^2 -cycloocta-2,5-dien-1-carboxylate) complex (**B**, Scheme 2). Precedents for β -hydroxy elimination in the coordination sphere of platinum^[5a, 7a] are known. Reductive elimination of the hydroxy and carbonyl groups (producing the COOH group) renders the diene ligand, which is eventually replaced by carbon monoxide in the rhodium complex, according to the experimental data. This mechanism, proceeding via β -hydroxy elimination from the coordinatively unsaturated intermediate **A** should be blocked by CO coordination driving the reaction to **C** (Scheme 2), and thus it readily explains why this reaction channel is suppressed in the presence of CO.

Scheme 2. Formation of **4** and **5** from **6a**. [Rh] represents the rhodium(triarylide) fragment. The numbering is conventional and it corresponds to Figure 2.

Starting from **C** (Scheme 2), and with independence of the exact order of steps, formation of **5** would require a nucleophilic attack of the hydroxo to the acyl group to form a protonated γ -lactone ring. β -hydrogen elimination from the C8–H bond along with the acidic proton would give dihydrogen and **5**, probably coordinated to rhodium. Finally, replacement of **5** by carbon monoxide renders the organic compound and the rhodium complex $[\text{Rh}(\text{CO})_2(\mu\text{-PhN}_3\text{Ph})_2]$. A similar sequence of reactions involving C1 would give a four-membered β -lactone ring, which is disfavoured by ring-strain.

In summary, rhodium complexes bearing a hydroxy-alkyl-allyl moiety are suitable intermediates for the regioselective synthesis of either carboxylic acids or γ -lactones. In these reactions, carbon monoxide is incorporated into the organic fragment along with the formation of new C–C and C–O bonds. Taking together with the oxygenation of 1,5-cyclooctadiene to $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})]$ by O_2 , the carbon monoxide reactions described here disclose a new sequence of stoichiometric reactions for the regioselective functionalization of an allylic C–H bond, which is a main challenge in current chemistry.^[12] Further studies to understand the reaction mechanisms and to uncover synthetic applications of this new reaction are underway.

Experimental Section

$[\text{Rh}(\text{CO})_2(\mu\text{-PhN}_3\text{Ph})_2]$ (3**).** A suspension of $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{OC}_8\text{H}_{12})_2]$ (100.0 mg, 0.12 mmol) in toluene (5 mL) was warmed for 2 h at 80 °C under a CO atmosphere. The resulting red solution was evaporated to dryness, left under vacuum for one day, and the red residue washed with 2 mL of cold hexane. ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 7.66 (dd, $^3J(\text{H},\text{H})$ = 8.6, 1.1 Hz, 8H; H^a), 7.04 (tt, $^3J(\text{H},\text{H})$ = 7.8 Hz, 8H; H^m), 6.88 (tt, $^3J(\text{H},\text{H})$ = 7.4, 1.1 Hz, 4H; H^b); $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6 , 25 °C): δ = 185.9 (d, $J(\text{C},\text{Rh})$ = 66.5 Hz, CO), 152.1 (C^1), 128.9 (C^m), 125.8 (C^b), 122.9 (C^a).

$[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})(\text{CO})]$ (6**).** A suspension of $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{OC}_8\text{H}_{12})_2]$ (**1**) (100.0 mg, 0.118 mmol) in toluene (10 mL) was warmed at 100 °C for 1 h 30 min to ensure the full transformation of **1** into $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})]$. The suspension was cooled at 0 °C and the argon atmosphere was replaced by carbon monoxide. After stirring for 15 min, the resulting brown solution was concentrated to 3 mL and hexane (10 mL) was added under a CO atmosphere to precipitate a brown solid. The mother liquor was decanted and the solid was washed with cold hexane (3 x 2 mL) and dried under vacuum. Yield: 70.3 mg (76 %); ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 7.52 (d, $^3J(\text{H},\text{H})$ = 6.8 Hz, 2H; H^a), 7.27 (t, $^3J(\text{H},\text{H})$ = 7.9 Hz, 2H; H^m), 7.17 (t,

$^3J(\text{H},\text{H})$ = 7.9 Hz, 2H; H^b), 7.12 (d, $^3J(\text{H},\text{H})$ = 7.9 Hz, 2H; H^a), 7.01 (t, $^3J(\text{H},\text{H})$ = 7.6 Hz, 1H; H^b), 6.92 (tt, $^3J(\text{H},\text{H})$ = 7.1, $^4J(\text{H},\text{H})$ = 1.2 Hz, 1H; H^b), 5.45 (m, 1H; H^b), 4.71 (t, $^3J(\text{H},\text{H})$ = 8.0 Hz, 1H; H^b), 4.53 (m, 1H; H^b), 2.99 (d, $^3J(\text{H},\text{H})$ = 3.0 Hz, 1H; H^b), 2.84 (d, $^3J(\text{H},\text{H})$ = 6.3 Hz, 1H; H^b), 2.03 (m, 1H; H^b), 1.48 (m, 1H; H^b), 1.33 (m, 1H; H^b), 1.14 (dt, $^3J(\text{H},\text{H})$ = 14.7, 4.6 Hz, 1H; H^b), 0.91 (br s, 1H, OH), 0.84 (m, 1H; H^b), 0.78 (m, 1H; H^b); $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6 , 25 °C): δ = 190.9 (d, $J(\text{C},\text{Rh})$ = 76 Hz, Rh–CO), 151.4 and 149.1 (C^{iso}), 129.4 (C^m), 129.2 (C^m), 123.8 (C^b), 123.6 (C^b), 118.4 (C^a), 117.0 (C^a), 106.9 (d, $J(\text{C},\text{Rh})$ = 4.2 Hz; C^5), 96.4 (d, $J(\text{C},\text{Rh})$ = 5.2 Hz; C^6), 87.3 (C^2), 69.4 (d, $J(\text{C},\text{Rh})$ = 9.4 Hz; C^4), 54.8 (d, $J(\text{C},\text{Rh})$ = 18.5 Hz; C^1), 41.1 (C^8), 34.6 (C^3), 21.8 (C^7); elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{22}\text{N}_3\text{O}_2\text{Rh}$: C 55.89, H 4.91; N 9.31; found: C 55.97, H 5.05; N 9.18.

4-Cyclooctanone (2**).** A solution of $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{OC}_8\text{H}_{12})_2]$ (**1**) (20.0 mg, 0.024 mmol) in CD_2Cl_2 was connected to a balloon filled with CO and left undisturbed at room temperature. After 48 h the complete disappearance of **1** was observed while the reaction mixture contained 4-cyclooctanone (**2**, 65 %), cycloocta-2,6-diene carboxylic acid (**4**, 35 %) and $[\text{Rh}(\text{CO})_2(\mu\text{-PhN}_3\text{Ph})_2]$ (**3**) (by NMR).

Cycloocta-2,6-diene carboxylic acid (4**).** A suspension of $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{OC}_8\text{H}_{12})_2]$ (20.0 mg, 0.024 mmol) was warmed at 60 °C in C_6D_6 under argon and the evolution monitored by ^1H NMR to ensure the complete transformation of **1** into $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})]$. Then, it was connected to a balloon filled with CO and argon in approximately equimolar amounts and left undisturbed for 1 h at 60 °C (slow and diluted diffusion). The resulting dark red solution contained equimolar amounts of **3** and **4** by NMR as the sole products. **4**: ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 5.77 (m, $^3J(\text{H},\text{H})$ = 11.5 and 6.6 Hz, 1H; H^b), 5.52 (m, 1H; H^b), 5.44 (m, 2H; $\text{H}^{a,7}$), 3.57 (m, 1H, H^1), 2.64 (m, 1H, H^{8a}), 2.45 (dt, $^3J(\text{H},\text{H})$ = 16.1 and 3.7 Hz, 1H, H^{8b}), 2.17 (m, 1H, H^{4a}), 2.14 (m, 1H, H^{5a}), 1.99 (m, 1H, H^{4b}), 1.84 (m, 1H, H^{5b}); $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6 , 25 °C): δ = 180.7 (COOH), 130.5 (C^2), 129.6 (C^7), 126.5 (C^7), 126.4 (C^2), 45.3 (C^1), 30.9 (C^8), 27.9 (C^5), 27.6 (C^4). In a independent experiment, the acid **4** was isolated as follows: A solution of **6** (100 mg) in toluene (5 mL) was left under argon for two days at room temperature or for 3 h at 60 °C. The ^1H NMR spectrum of the resulting brown-red solution showed unresolved signals in the δ : 6–2 ppm region. Shaking this solution with CO for 5 min resulted in a dark-red one showing well-resolved multiplets in the ^1H NMR spectrum, which corresponds to the quantitative formation of the organic **4** and $[\text{Rh}(\text{CO})_2(\mu\text{-PhN}_3\text{Ph})_2]$ (**3**). The solution was shaken with a solution of aq. NaHCO_3 (1.0 g in 25 mL). The aqueous phase was separated, acidified with aq. HCl 1M, and extracted with diethyl ether (15 mL). After drying with MgSO_4 , evaporation of the organic extract under vacuum gave the acid **4** as a pale-yellow oil (15 mg), which was characterized by high resolution mass spectra and NMR spectroscopy (see Supporting Information).

8-Oxabicyclo[5.2.1]deca-2,5-dien-9-one (5**).** A suspension of $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{OC}_8\text{H}_{12})_2]$ (20.0 mg, 0.024 mmol) was warmed at 60 °C in C_6D_6 under argon and the progress monitored by ^1H NMR to ensure the complete transformation of **1** into $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{HO}-\text{C}_8\text{H}_{11})]$. Then, it was cooled in an ice bath, saturated with CO by three vacuum/CO cycles and vigorously stirred under carbon monoxide for 6 h at 0 °C to prevent the isomerisation into the oxabicycles **5b** and **5c**. **5**: ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 5.56 (m, 2H; $\text{H}^{3,5}$), 5.43 (m, 1H; H^2), 5.21 (m, 1H; H^6), 4.33 (m, 1H; H^7), 2.95 (m, 1H; H^{4a}), 2.68 (m, 1H; H^1), 2.14 (m, 1H; H^{4b}), 1.52 (m, 2H; $\text{H}^{10a,10b}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6 , 25 °C): δ = 176.3 (CO_2), 133.8 (C^5), 132.9 (C^3), 129.8 (C^6), 128.6 (C^2), 76.9 (C^7), 40.3 (C^1), 31.6 (C^{10}), 24.2 (C^4). In a separate experiment, **5** was isolated as follows: A brown-green solution of **6** (100 mg) in toluene (5 mL) was shaken under an atmosphere of carbon monoxide at 0 °C for 6 h. The solution was concentrated under vacuum and chromatographed on a column of silica gel using a 1/10 mixture of ethyl acetate/hexane as eluent. Complex **3** came out first and then a brownish band was collected. Evaporation of the solvent gave **5** as tan oil, which was characterized by high resolution mass spectra and NMR spectroscopy (see Supporting Information).

8-Oxabicyclo[5.2.1]deca-2,4-dien-9-one (5b**) and 8-Oxabicyclo[5.2.1]deca-3,5-dien-9-one (**5c**).** A suspension of $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{OC}_8\text{H}_{12})_2]$ (40.0 mg, 0.048 mmol) in toluene was warmed at 100 °C in a low-pressure reactor under 3 bar of CO for 2 h. The solvent was evaporated to dryness and the residue dissolved in C_6D_6 showed the mixture of **5b** and **5c** (see Supporting Information). **5b**: ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 5.79 (m, 1H; H^4), 5.51 (m, 1H; H^3), 5.40 (m, 1H; H^2), 5.19 (m, 1H; H^5), 4.02 (m, 1H; H^7), 2.72 (m, 1H; H^1), 2.20 (m, 1H; H^{6a}), 1.85 (m, 1H; H^{6b}), 1.40 (m, 2H; $\text{H}^{10a,10b}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6 , 25 °C): δ = 174.9 (CO_2), 129.7 (C^4), 127.1 (C^5), 126.8 (C^3), 126.6 (C^3), 72.2 (C^7), 40.7 (C^1), 33.4 (C^6), 31.2 (C^{10}); **5c**: ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 5.84 (m, 1H; H^4), 5.38 (m, 1H; H^5), 5.32 (m, 1H; H^2), 5.28 (m, 1H; H^7), 4.26 (m, 1H; H^1), 2.11 (m, 1H; H^1), 1.97 (m, 2H; $\text{H}^{2a,2b}$), 1.36 (m, 1H; H^{10a}), 1.28 (m, 1H; H^{10b}); $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6 , 25 °C): δ = 177.7 (CO_2), 130.5 (C^4), 130.0 (C^3), 127.5 (C^6), 126.5 (C^3), 75.4 (C^7), 35.4 (C^1), 28.3 (C^2), 28.2 (C^{10}).

Computational Details. The computational method used was density functional theory (DFT) with the B3LYP exchange-correlation functional,^[13–15] using the Gaussian 03^[16] program package. The basis sets used for the full optimization of the structures and for the calculation of the single-point energies are of triple-zeta quality: LanL2TZ(t)^[17] effective core potential for the rhodium atom, and 6-311G(d,p) for the remaining atoms. Zero-point vibration energy (ZPVE) and thermal

corrections (at 298 K, 1 atm) to the energy have been estimated on the basis of the frequency calculations.

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- [1] a) L. J. Gooßen, N. Rodríguez, K. Gooßen, *Angew. Chem.* **2008**, *120*, 3144–3164; *Angew. Chem. Int. Ed.* **2008**, *47*, 3100–3120; b) L. K. Gooßen, K. Gooßen, N. Rodríguez, M. Blanchot, C. Linder, B. Zimmermann, *Pure Appl. Chem.* **2008**, *80*, 1725–1733.
- [2] M. A. Ogliaruso, J. F. Wolfe, in *Synthesis of Carboxylic Acids, Esters and Their Derivatives*, (Eds: S. Patai, Z. Rappaport), Wiley, New York, **1991**.
- [3] See for example: a) A. S. Veige, *Polyhedron*, **2008**, *27*, 3177–3189; b) R. H. Munday, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2008**, *130*, 2754–2755; c) J. Muzart, *Tetrahedron*, **2005**, *61*, 9423–9463; d) A. Haynes, P. M. Maitlis, G. E. Morris, G. J. Sunley, H. Adams, P. W. Badger, C. M. Bowers, D. B. Cook, P. I. P. Elliott, T. Ghaffar, H. Green, Tim R. Griffin, M. Payne, J. M. Pearson, M. J. Taylor, P. W. Vickers, R. J. Watt, *J. Am. Chem. Soc.* **2004**, *126*, 2847–2861; e) E. Daura-Oller, J. M. Poblet, C. Bo, *Dalton Trans.* **2003**, 92–98; f) C. M. Thomas, G. Süß-Fink, *Coord. Chem. Rev.* **2003**, *243*, 125–142; g) I. Ryu, *Chem. Soc. Rev.*, **2001**, *30*, 16–25; h) *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1 (Eds: B. Cornils, W. A. Hermann) VCH: Weinheim, **1996**; i) J. Tsuji, in *Palladium Reagents and Catalysts*; Wiley & Sons, New York, **1995**.
- [4] a) R. Giri, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 14082–14083; b) Y. Zhao, L. Jin, P. Li, and A. Lei, *J. Am. Chem. Soc.* **2008**, *130*, 9429–9433; c) W.-Y. Yu, W. N. Sit, K.-M. Lai, Z. Zhou, A. S. C. Chan, *J. Am. Chem. Soc.* **2008**, *130*, 3304–3306.
- [5] For representative examples of LTM-metallaoxetanes, see for example: a) N. M. Welianje, E. Szuromi, P. R. Sharp, *J. Am. Chem. Soc.* **2009**, *131*, 8736–8737; b) J. Wu, P. R. Sharp, *Organometallics*, **2008**, *27*, 1234–1241 and references therein; c) J. R. Khusnutdinova, L. L. Newman, P. Y. Zavalij, Y.-F. Lam, A. N. Vedernikov, *J. Am. Chem. Soc.* **2008**, *130*, 2174–2175; d) C. Tejel, M. A. Ciriano, *Top. Organomet. Chem.* **2007**, *22*, 97–124; e) M. A. Cinellu, G. Minghetti, F. Cocco, S. Stoccoro, A. Zucca, M. Manassero, *Angew. Chem.* **2005**, *117*, 7052–7055; *Angew. Chem. Int. Ed.* **2005**, *44*, 6892–6895; f) B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2004**, *116*, 4236–4251; *Angew. Chem. Int. Ed.* **2004**, *43*, 4142–4157; g) E. Szuromi, H. Shan, P. R. Sharp, *J. Am. Chem. Soc.* **2003**, *125*, 10522–10523; h) C. T. Flood, M. Iimura, J. M. Perotti, A. L. Rheingold, T. E. Concolino, *Chem. Commun.* **2000**, 1681–1682; i) B. de Bruin, M. J. Boerakker, J. J. M. Donners, B. E. C. Christiaans, P. P. J. Schlebos, R. de Gelder, J. M. M. Smits, A. L. Spek, A. W. Gal, *Angew. Chem.* **1997**, *109*, 2153–2157; *Angew. Chem. Int. Ed.* **1997**, *36*, 2064–2067.
- [6] a) C. Tejel, M. A. Ciriano, E. Sola, M. P. del Río, G. Ríos-Moreno, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **2005**, *117*, 3331–3335; *Angew. Chem. Int. Ed.* **2005**, *44*, 3267–3271; b) B. de Bruin, J. A. Brands, J. J. M. Donners, M. P. J. Donners, R. De Gelder, J. M. M. Smits, A. W. Gal, A. L. Spek, *Chem. Eur. J.* **1999**, *5*, 2921–2936; c) V. W. Day, W. G. Klemperer, S. P. Lockledge, D. J. Main, *J. Am. Chem. Soc.* **1990**, *112*, 2031–2033.
- [7] 2-platinaoxetanes: a) J. Wu, P. R. Sharp, *Organometallics* **2009**, *28*, 6935–6943; E. Szuromi, J. Wu, P. R. Sharp, *J. Am. Chem. Soc.* **2006**, *128*, 12088–12089; 2-rhoda and 2-iridaoxetanes: B. de Bruin, J. A. W. Verhagen, C. H. J. Schouten, A. W. Gal, D. Feichtinger, D. A. Plattner, *Chem. Eur. J.* **2001**, *7*, 416–422; B. de Bruin, M. J. Boerakker, J. A. W. Verhagen, R. de Gelder, J. M. M. Smits, A. W. Gal, *Chem. Eur. J.* **2000**, *6*, 298–312.
- [8] B. de Bruin, M. J. Boerakker, R. De Gelder, J. M. M. Smits, A. W. Gal, *Angew. Chem.* **1999**, *111*, 118–121; *Angew. Chem. Int. Ed.* **1999**, *38*, 219–221.
- [9] a) J. Wu, P. R. Sharp, *Organometallics* **2008**, *27*, 4810–4816.
- [10] M. P. del Río, M. A. Ciriano, C. Tejel, *Angew. Chem.* **2008**, *120*, 2536–2539; *Angew. Chem. Int. Ed.* **2008**, *47*, 2502–2505.
- [11] a) P. Braunstein, J. Zhang, R. Welter, *J. Chem. Soc., Dalton Trans.* **2003**, 507–509; b) J. Zhang, P. Braunstein, R. Welter, *Inorg. Chem.* **2004**, *43*, 4172–4177.
- [12] For reviews on C–H bond functionalization see the following and leading references therein: a) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655; b) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335–344; c) P. Thansandote, M. Lautens, *Chem. Eur. J.* **2009**, *15*, 5874–5883; d) G. T. Rice, M. C. White, *J. Am. Chem. Soc.* **2009**, *131*, 11707–11711; e) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417–424; f) J. C. Lewis, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013–1025; g) R. G. Bergman, *Nature* **2007**, *446*, 391–393; h) C. I. Herréras, X. Yao, Z. Li, C.-J. Li, *Chem. Rev.* **2007**, *107*, 2546–2562; i) F. Kakiuchi, *Top. Organomet. Chem.* **2007**, *24*, 1–33; j) K. Godula, and D. Sames, *Science* **2006**, *312*, 67–72; k) H. Delcamp, M. C. White, *J. Am. Chem. Soc.* **2006**, *128*, 15076–15077; l) M. S. Chen, M. C. White, *J. Am. Chem. Soc.* **2004**, *126*, 1346–1347; m) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–514.
- [13] A. D. Becke, *Phys. Rev. A*, **1988**, *38*, 3098–3100.
- [14] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, *37*, 785–789.
- [15] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [16] Frisch, M. J.; et al. Gaussian, Inc.: Wallingford, CT, **2004** (see Supporting Information for complete citation).
- [17] L. E. Roy, P. J. Hay, R. L. Martin, *J. Chem. Theory Comput.*, **2008**, *4*, 1029–1031.

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Entry for the Table of Contents

Catch Phrase

Cristina Tejel,* M. Pilar del Río,
José A. López and Miguel A.
Ciriano Page – Page

Rhodium Mediated C–H Bond Functionalization to Carboxylate Derivatives

Selective functionalization of 1,5-cyclooctadiene either to the carboxylic acid or to the γ -lactone is achieved by a novel sequence of reactions involving quantitative oxygenation with oxygen, and

C–C coupling with carbon monoxide. The rhodium hydroxy-alkyl-allyl complex shown in the inset is the active intermediate promoting the elimination of the organic compounds.