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Rhodium Mediated C–H Bond Functionalisation Leading to Carboxylate Derivatives

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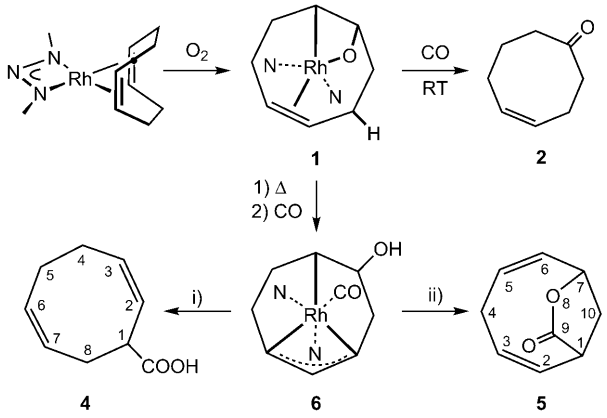
Carboxylic acids, their esters and lactones are among the most common functional groups and a large number of fine chemicals are accessible from these functionalities.[1] Typical organic synthetic procedures[2] towards carboxylic acid synthesis include the oxidation of alcohols and aldehydes and the hydrolysis of nitriles, although the carboxylation of organic substrates containing C–X bonds is, perhaps, the best established approach to carboxylic acids that is mediated by transition metal complexes.[3] From an atom economy perspective, the direct functionalisation of C–H bonds to C–CO_2R groups is a highly desirable alternative, since it avoids classical functional group manipulations. Although scarce, such palladium-catalysed reactions have recently been reported.[4] From a formal point of view, a COO moiety could be inserted into a C–H bond by combining oxygenation and carbonylation, involving simply O_2 and CO as attractive and cheap substrates. In this field, 2-metallaoxetanes[5] emerge as valuable candidates to test this possibility, since they can be obtained by oxygenation of olefins with dioxygen.[6] Although the reactivity of 2-metallaoxetanes is currently in its infancy,[7] two of them have been reported as suitable for C–X (X = N, O) bond formation, as shown by the reactions of 2-rhoda- and 2-platinaoxetanes with acetonitrile[8] and carbon monoxide,[9] respectively. Herein, we describe new reactions leading to carboxylic acids and lactones, involving the stoichiometric functionalisation of an allylic C–H bond in 1,5-cyclooctadiene (COD) with carbon monoxide and dioxygen, which proceeds through a discrete 2-rhodaoxetane intermediate.

We have previously reported the selective reaction of $[Rh(C_8H_{12})(PhN_3Ph)]$ (C_8H_{12} = 1,5-cyclooctadiene, PhN_3Ph = 1,3-diphenyltriazenide) with molecular oxygen to give dinuclear 2-rhoda(III)oxetane complex **1**, $[\{Rh(PhN_3Ph)(OC_8H_{12})\}_2]$ (Scheme 1).[6a] Diffusion of carbon monoxide through a solution of **1** in dichloromethane at room temperature gave carbonyl complex **3**, $[\{Rh(CO)_2(\mu\text{-}PhN_3Ph)\}_2]$, quantitatively, along with 4-cyclooctenone (**2**, 65%). Although complex **1** contains three different types of metal–X σ bond (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 that in previously reported reactions of complex **1** with phosphanes.[10] The second organic compound produced by the reaction (35% yield) was identified as cycloocta-2,6-diene carboxylic acid **4** (see the Experimental Section). As the most relevant resonance, the proton from the –COOH moiety, unobserved at room temperature, was located as a sharp singlet (δ = 13.67 ppm) at −70 °C in



Scheme 1. Elimination reactions from 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 in **1** and **6** represent the anionic PhN_3Ph ligand. The numbering scheme shown is used for NMR characterisation.

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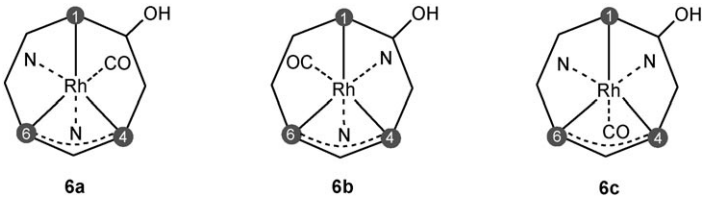
[D_8]toluene, whereas the carboxylic carbon appeared at the usual chemical shift ($\delta = 180.7$ ppm) in the $^{13}C\{^1H\}$ attached proton test (APT) spectrum.

On raising the temperature of the reaction, the amount of carboxylic acid **4** produced increases until it becomes the major product at 60 °C in C_6D_6, provided that carbon monoxide is allowed to diffuse slowly through a solution of **1** (Scheme 1). Noticeably, the slow diffusion and dilution of carbon monoxide is crucial for the regioselective synthesis of **4**. If a solution of **1** is heated at 60 °C and then mixed with CO at 0 °C under vigorous shaking a different product is formed, that is, the new 8-oxabicycle[5.2.1]deca-2,5-dien-9-one (**5**, Scheme 1). Again [{$Rh(CO)_2(\mu\text{-}PhN_3Ph)$}$_2$] (**3**) is the only rhodium containing product. Prolonged heating [100 °C, CO (3 bar)] gave a mixture, probably the thermodynamic one, containing **5** and two isomeric oxabicycles containing the olefinic bonds in positions 2 and 4 (**5b**), and 3 and 5 (**5c**). Compound **5** was identified on the basis of its spectroscopic data (see the Experimental Section and Supporting Information). From the six CH signals observed in the $^{13}C\{^1H\}$ APT NMR spectrum four of them correspond to the olefinic carbons, while those at $\delta = 40.3$ and 76.9 ppm correspond to C1 and C7, which are 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 spectroscopy allowed the observation of the common active species leading to **4** and **5**. This species was found to be eighteen-electron rhodium(III) complex [$Rh(PhN_3Ph)(HO{-}C_8H_{11})(CO)$] (**6**, Scheme 1), which was isolated in a separate experiment by working quickly at 0 °C to prevent the elimination reaction. The phenyl groups in **6** are non-equivalent and the allyl moiety was clearly identified by 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(C,Rh) = 18.5 Hz] in the $^{13}C\{^1H\}$ APT spectrum whereas 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 ν(CO) stretching band at 2083 cm^{-1} in the IR spectrum.

Complex **6** is the result of the isomerisation of rhodaoxetane(III) complex **1** into 16-valence-electron hydroxy–alkyl–allyl species [$Rh(PhN_3Ph)(HO{-}C_8H_{11})$] followed by coordination of carbon monoxide. We have previously reported (as a coordination polymer) the hydroxy–alkyl–allyl species [$Rh(PhN_3Ph)(HO{-}C_8H_{11})$], without the CO ligand, which was formed in the reaction of [$Rh(C_8H_{12})(PhN_3Ph)$] with oxygen through isomerisation of the 2-rhodaoxetane intermediate.[6a] Related isomerisation reactions have previously been reported for similar 2-metallaoxetane complexes,[6,5 g] but follow-up reactivity for these species have not been described. In principle, complex **6** could exist in three different isomeric forms, as shown in Scheme 2, but the reaction selectively produces isomer **6a**, in which the carbonyl group is in close proximity to the hydroxyl group (as evidenced by NOESY spectroscopy; see the Supporting Information).



Scheme 2. The possible stereoisomers of [$Rh(PhN_3Ph)(HO{-}C_8H_{11})(CO)$]. Isomers **6b** and **6c** were not observed. The two nitrogen atoms on rhodium represent the triazenide ligand.

Figure 1 shows the DFT optimised 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 around rhodium. The strong *trans* influence of the alkyl carbon (C1) is clearly demonstrated by the considerable elongation of the Rh–N1 bond *trans* to it (2.244 Å) in comparison with the other Rh–N bond (2.188 Å), which is *trans* to the allylic C4 atom. Within the allyl group, the Rh–C4 bond is found to be shorter (2.200 Å) than the Rh–C6 bond (2.337 Å). The optimised geometries of isomers **6b** (+4.0 kcal mol^{-1}) and **6c** (+4.3 kcal mol^{-1}) are clearly higher in energy (see the Supporting Information).

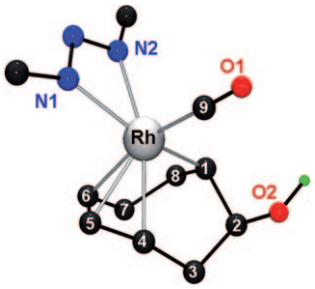
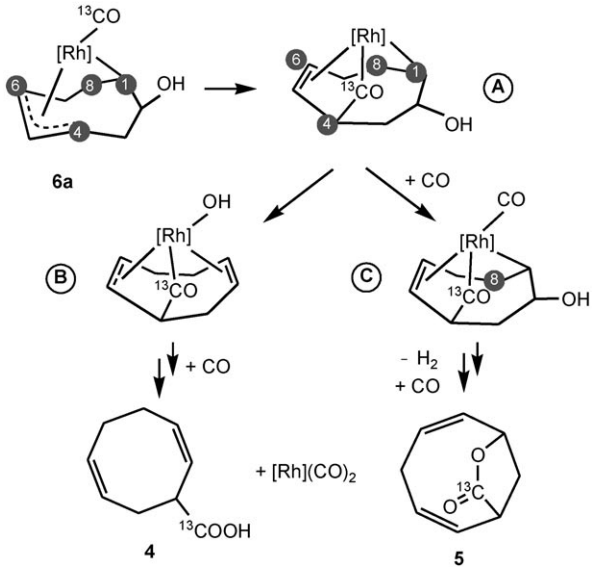


Figure 1. The DFT calculated structure of **6a**. Selected distances [Å]: Rh–C1 2.094, Rh–C4 2.200, Rh–C5 2.181, Rh–C6 2.337, Rh–N1 2.244, Rh–N3 2.188, Rh–C9 1.906. Only the *ipso* carbons of the phenyl groups are shown for clarity.

Starting from an isolated sample of **6a**, carboxylic acid **4** and oxabicycle **5** were synthesised and the new organic compounds were isolated (see the Experimental Section). Moreover, we have verified that carbon monoxide is not needed for the formation of carboxylic acid **4** from **6a**, except for liberation from rhodium's coordination sphere, whereas the formation of lactone **5** requires carbon monoxide as a reagent. Furthermore, when the reaction of **6a** with ^{13}CO was carried out under the two different experimental conditions ^{13}CO was found to only be fully incorporated into the product [{$Rh(^{13}CO)_2(\mu\text{-}PhN_3Ph)$}$_2$] (**3-^{13}CO**) in both cases, indicating that the carbonyl group in both **4** and **5** is that already coordinated to rhodium in complex **6a**. In reverse order, the reaction of labelled complex **6a-^{13}CO** with unlabelled carbon monoxide gave either **4-^{13}CO** or **5-^{13}CO** as the only labelled compounds. The selectivity observed in the labelling experiments indicates that **4** and **5** come from an intra-

molecular reaction undergone by **6a** and suggests that both reactions proceed through a common intermediate which would result from the coupling of the carbonyl group (^{13}CO) with C4 (**A**, Scheme 3). This step is possible through a



Scheme 3. The formation of **4** and **5** from **6a**. [Rh] represents the rhodium(triazenide) fragment. The numbering follows convention and corresponds to that in Figure 1.

change in the coordination mode of the η^3-allyl group to a σ-allyl group, perhaps assisted by the hydroxyl moiety, to allow the carbonyl insertion into the Rh–C4 bond. Precedents for reactions of this type, assisted by hemilabile ligands, are known in palladium chemistry.[11]

The route to **4** from **A** requires cleavage of the C–OH bond in the organic moiety. A viable possibility involves a β-hydroxy elimination reaction from coordinatively unsaturated acyl intermediate **A**, to give rhodiumhydroxo(η^2,η^2-cycloocta-2,5-dien-1-carbonylate)-complex **B** (Scheme 3). Precedents for β-hydroxy elimination within the coordination sphere of platinum are known.[5a,7a] Reductive elimination of the hydroxyl and carbonyl groups, to produce the COOH group, gives diene ligand **4**, which, according to the experimental data, is eventually replaced by carbon monoxide in the rhodium complex. This mechanism, proceeding via a β-hydroxy elimination from coordinatively unsaturated intermediate **A**, should be stopped by CO coordination, which drives the reaction to form intermediate **C** (Scheme 3) and, thus, readily explains why this reaction path is suppressed by the presence of CO.

Starting from **C** (Scheme 3), independent of the exact order of steps, the formation of **5** would require nucleophilic attack of the hydroxyl group on the acyl group to form a protonated γ-lactone ring. β-Hydride elimination of the C8–H bond, along with the acidic proton, would give dihydrogen and compound **5**, probably coordinated to rhodium. Finally, replacement of **5** by carbon monoxide renders the organic compound and the rhodium complex, [{$Rh(CO)_2$(μ-PhN_3Ph)}$_2$]. A similar sequence of reactions involving C1 would give a four-membered β-lactone ring, which is disfavoured due to ring-strain.

In summary, rhodium complexes containing 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. The oxygenation of 1,5-cyclooctadiene to [Rh(PhN_3Ph)(HO–C_8H_{11})] by O_2, together with the carbon monoxide reactions described here, disclose a new sequence of stoichiometric reactions for the regioselective functionalisation of allylic C–H bond, which is currently a major challenge in chemistry.[12] Further studies into the reaction mechanisms and to uncover synthetic applications of this new reaction are underway.

Experimental Section

[{$Rh(CO)_2$(μ-PhN_3Ph)}$_2$] (3): A suspension of [Rh(PhN_3Ph)(C_8H_{12})] (100.0 mg, 0.25 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 was washed with cold hexane (2 mL). Yield: 73.7 mg (85 %); ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.66 (dd, ^3J(H,H) = 8.6, 1.1 Hz, 8H; H^o), 7.04 (tt, ^3J(H,H) = 7.8 Hz, 8H; H^m), 6.88 ppm (tt, ^3J(H,H) = 7.4, 1.1 Hz, 4H; H^p); $^{13}C\{^1H\}$ NMR (500 MHz, C_6D_6, 25 °C): δ = 185.9 (d, J(C,Rh) = 66.5 Hz, CO), 152.1 (C^{ipso}), 128.9 (C^m), 125.8 (C^p), 122.9 ppm (C^o).

[Rh(PhN_3Ph)(HO–C_8H_{11})(CO)] (6): A suspension of [{Rh(PhN_3Ph)(OC_8H_{12})}$_2$] (**1**; 100.0 mg, 0.118 mmol) in toluene (10 mL) was warmed at 100 °C for 1.5 h to ensure the full transformation of **1** into [Rh(PhN_3Ph)(HO–C_8H_{11})]. The suspension was cooled to 0 °C and the argon atmosphere 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 × 2 mL) and dried under vacuum. Yield: 70.3 mg (76 %); ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.52 (d, ^3J(H,H) = 6.8 Hz, 2H; H^o), 7.27 (t, ^3J(H,H) = 7.9 Hz, 2H; H^m), 7.17 (t, ^3J(H,H) = 7.9 Hz, 2H; $H^{m'}$), 7.12 (d, ^3J(H,H) = 7.9 Hz, 2H; $H^{o'}$), 7.01 (t, ^3J(H,H) = 7.6 Hz, 1H; H^p), 6.92 (tt, ^3J(H,H) = 7.1, ^4J(H,H) = 1.2 Hz, 1H; $H^{p'}$), 5.48–5.42 (m, 1H; H^6), 4.71 (t, ^3J(H,H) = 8.0 Hz, 1H; H^5), 4.56–4.50 (m, 1H; H^4), 2.99 (d, ^3J(H,H) = 3.0 Hz, 1H; H^2), 2.84 (d, ^3J(H,H) = 6.3 Hz, 1H; H^1), 2.06–2.00 (m, 1H; H^{8a}), 1.50–1.46 (m, 1H; H^{3a}), 1.36–1.30 (m, 1H; H^{7a}), 1.14 (dt, ^3J(H,H) = 14.7, 4.6 Hz, 1H; H^{3b}), 0.91 (br s, 1H; OH), 0.86–0.82 (m, 1H; H^{7b}), 0.80–0.76 ppm (m, 1H; H^{8b}); $^{13}C\{^1H\}$ NMR (500 MHz, C_6D_6, 25 °C): δ = 190.9 (d, J(C,Rh) = 76 Hz, Rh–CO), 151.4 (C^{ipso}), 149.1 (C^{ipso}), 129.4 ($C^{m'}$), 129.2 (C^m), 123.8 (C^p), 123.6 ($C^{p'}$), 118.4 (C^o), 117.0 ($C^{o'}$), 106.9 (d, J(C,Rh) = 4.2 Hz, C5), 96.4 (d, J(C,Rh) = 5.2 Hz, C6), 87.3 (C2), 69.4 (d, J(C,Rh) = 9.4 Hz, C4), 54.8 (d, J(C,Rh) = 18.5 Hz, C1), 41.1 (C8), 34.6 (C3), 21.8 ppm (C7); elemental analysis calcd (%) for $C_{21}H_{22}N_3O_2Rh$: 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 [{Rh(PhN_3Ph)(OC_8H_{12})}$_2$] (**1**) (20.0 mg, 0.024 mmol) in CD_2Cl_2 (0.5 mL) was connected to a balloon filled with CO and left undisturbed at room temperature. After 48 h, complete disappearance of **1** was observed while the reaction mixture contained 4-cyclooctanone (**2**, 65 %), cycloocta-2,6-diene carboxylic acid (**4**, 35 %) and [{$Rh(CO)_2$(μ-PhN_3Ph)}$_2$] (**3**) by NMR spectroscopy.

Cycloocta-2,6-diene carboxylic acid (4): A suspension of [{Rh(PhN_3Ph)(OC_8H_{12})}$_2$] (20.0 mg, 0.024 mmol) was warmed at 60 °C in C_6D_6 (0.5 mL) under argon and the evolution of the reaction monitored by ^{1}H NMR to ensure the complete transformation of **1** into [Rh(PhN_3Ph)(HO–C_8H_{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, dilute diffusion). The resulting dark red solution contained equimolar amounts of **3** and **4**, by NMR, as the only products. **4**: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 5.77$ (dd, $^3J(H,H) = 11.5$, 6.6 Hz, 1H, H^2), 5.55–5.49 (m, 1H; H^3), 5.46–5.42 (m, 2H; $H^{6,7}$), 3.60–3.54 (m, 1H; H^1), 2.68–2.60 (m, 1H; H^{8a}), 2.45 (dt, $^3J(H,H) = 16.1$, 3.7 Hz, 1H; H^{8b}), 2.20–2.14 (m, 1H; H^{4a}), 2.15–2.13 (m, 1H; H^{5a}), 2.03–1.95 (m, 1H; H^{4b}), 1.87–1.81 ppm (m, 1H; H^{5b}); ^{13}C{^{1}H} NMR (500 MHz, C_6D_6, 25 °C): $\delta = 180.7$ (COOH), 130.5 (C2), 129.6 (C7), 126.5 (C7), 126.4 (C2), 45.3 (C1), 30.9 (C8), 27.9 (C5), 27.6 ppm (C4). In an independent experiment, 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 ^{1}H NMR spectrum of the resulting brown-red solution showed unresolved signals in the $\delta = 6$–2 ppm region. Shaking this solution with CO for 5 min resulted in a dark-red solution showing well-resolved multiplets in the ^{1}H NMR spectrum, which corresponds to the quantitative formation of organic compound **4** and $[\{Rh(CO)_2(\mu\text{-}PhN_3Ph)\}_2]$ (**3**). The solution was added to and shaken with a solution of aqueous $NaHCO_3$ (1.0 g in 25 mL). The aqueous phase was separated, acidified with aqueous HCl (1 M) and extracted with diethyl ether (15 mL). After drying with $MgSO_4$, evaporation of the organic extract under vacuum gave acid **4** as a pale yellow oil (15 mg), which was characterized by high-resolution mass spectrometry and NMR spectroscopy (see the Supporting Information).

8-Oxabicycle[5.2.1]deca-2,5-dien-9-one (5): A suspension of $[\{Rh(PhN_3Ph)(OC_8H_{12})\}_2]$ (20.0 mg, 0.024 mmol) was warmed at 60 °C in C_6D_6 (0.5 mL) under argon and the progress of the reaction monitored by ^{1}H NMR to ensure complete transformation of **1** into $[Rh(PhN_3Ph)(HO{-}C_8H_{11})]$. 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 isomerisation into oxabicycles **5b** and **5c. 5**:^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 5.60$–5.52 (m, 2H, $H^{3,5}$), 5.46–5.40 (m, 1H; H^2), 5.25–5.18 (m, 1H; H^6), 4.35–4.32 (m, 1H, H^7), 2.98–2.92 (m, 1H; H^{4a}), 2.70–2.66 (m, 1H, H^1), 2.17–2.11 (m, 1H; H^{4b}), 1.54–1.50 ppm (m, 2H; $H^{10a,10b}$); ^{13}C{^{1}H} NMR (500 MHz, C_6D_6, 25 °C): $\delta = 176.3$ (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 ppm (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 subjected to chromatography on a column of silica gel by using a 1:10 mixture of ethyl acetate/hexane as eluent. Complex **3** emerged first and then a brownish band was collected. Evaporation of the solvent gave **5** as a tan oil, which was characterised by high-resolution mass spectrometry and NMR spectroscopy (see the Supporting Information).

8-Oxabicycle[5.2.1]deca-2,4-dien-9-one (5b) and 8-oxabicycle[5.2.1]deca-3,5-dien-9-one (5c): A suspension of $[\{Rh(PhN_3Ph)(OC_8H_{12})\}_2]$ (40.0 mg, 0.048 mmol) in toluene (2 mL) was warmed at 100 °C in a low-pressure reactor under CO (3 bar) for 2 h. The solvent was evaporated to dryness and the residue dissolved in C_6D_6 (0.5 mL), which showed a mixture of **5**, **5b** and **5c** (38:48:14) by NMR spectroscopy (see the Supporting Information). **5b**: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 5.82$–5.74 (m, 1H; H^4), 5.54–5.48 (m, 1H; H^3), 5.43–5.37 (m, 1H, H^2), 5.22–5.16 (m, 1H, H^5), 4.06–3.98 (m, 1H, H^7), 2.74–2.70 (m, 1H, H^1), 2.23–2.17 (m, 1H; H^{6a}), 1.88–1.82 (m, 1H; H^{6b}), 1.42–1.38 ppm (m, 2H; $H^{10a,10b}$); ^{13}C{^{1}H} NMR (500 MHz, C_6D_6, 25 °C): $\delta = 174.9$ (CO_2), 129.7 (C^4), 127.1 (C^2), 126.8 (C^5), 126.6 (C^3), 72.2 (C^7), 40.7 (C^1), 33.4 (C^6), 31.2 ppm (C^{10}). **5c**: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 5.87$–5.81 (m, 1H; H^4), 5.41–5.35 (m, 1H; H^5), 5.36–5.28 (m, 1H; H^3), 5.31–5.25 (m, 1H; H^6), 4.29–4.23 (m, 1H; H^7), 2.13–2.09 (m, 1H; H^1), 2.01–1.94 (m, 2H; $H^{2a,2b}$), 1.38–1.34 (m, 1H; H^{10a}), 1.30–1.26 ppm (m, 1H; H^{10b}); ^{13}C{^{1}H} NMR (500 MHz, C_6D_6, 25 °C): $\delta = 177.7$ (CO_2), 130.5 (C^4), 130.0 (C^3), 127.5 (C^6), 126.5 (C^5), 75.4 (C^7), 35.4 (C^1), 28.3 (C^2), 28.2 ppm (C^{10}).

Computational details: The computational method used was density functional theory (DFT) with the B3LYP exchange-correlation functional,[13–15] and the Gaussian 03[16] program package. The basis sets used for full optimisation of the structures and for calculation of the single-point energies are of triple-zeta quality: LanL2TZ(f)[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 (298 K, 1 atm) to the energy have been estimated on the basis of the frequency calculations.

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Keywords: carbon monoxide · carboxylic acids · lactones · metallaoxetanes · rhodium

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