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Stoichiometric C–H Bond Cleavage Reaction in a Bis(carboxylato)ruthenium(II) Complex and Its Application to the Catalytic H–D Exchange Reaction of Carboxylic Acids

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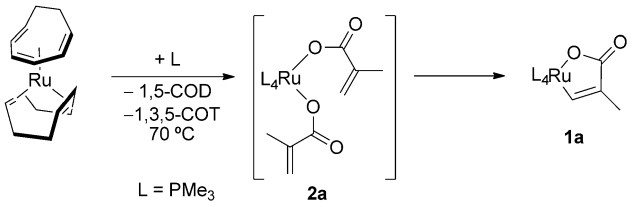
A cationic complex [Ru{OC(O)CMe=CH_2-κ^2*O*,*O*′}$(PMe_3)_4$]$^+$$CH_2$=$CMeCO_2^-$ (**5a**) and its related carboxylato complexes are newly prepared by the reaction of [*cis*-$RuH_2(PMe_3)_4$] (**4**) with carboxylic acids in methanol in 76–100% yield. Complex **5a** reversibly transforms to the neutral form [*cis*-Ru{OC(O)CMe=CH_2-κ^1*O*}$_2(PMe_3)_4$] (**2a**) in nonpolar solvents. Complex **2a** reversibly liberates a PMe_3 group to give [Ru{OC(O)CMe=CH_2-κ^1*O*}{OC(O)CMe=CH_2-κ^2*O*,*O*′}$(PMe_3)_3$] (**12a**) from which a stereoselective C–H bond cleavage reaction occurs to give a ruthenalactone [Ru{OC(O)CMe=CH-κ^2*O*,*C*}$(PMe_3)_4$] (**1a**) from the release of methacrylic acid. Complexes **2a** and **5a** also give **1a** but the prior dissociation of a PMe_3 is indispensable for the C–H bond cleavage reaction. Complex **1a** establishes an equilibrium with **2a** (or **5a**) in solution. In this reaction, one coordinated carboxylato ligand is engaged in the C–H bond cleavage reaction as a proton acceptor, but neither the added carboxylato anion nor typical proton acceptors such as proton sponge assist the reaction. In [D_4]MeOH, a catalytic stereospecific deuteration of carboxylic acids has been achieved by **4**, in which the equilibrium between **5a** and **1a** plays a key role.

Introduction

The activation of an inactive C–H bond by transition metal complexes is a new frontier in synthetic organic chemistry.[1] Together, these stoichiometric and catalytic reactions provide new methodologies in this field. We have previously reported internal C–H bond cleavage reactions in Ru^{II}[2] and Pt^{II}[3] complexes that have a metal–chalcogen bond. Interestingly, a late-transition-metal complex that has two metal–chalcogen bonds, such as bis(arenethiolato) or bis(aryloxo) complexes, showed quite high activity toward the internal C–H (and C–O) bond activation reaction.[2b,e,3] We have also documented a stoichiometric reaction of [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)]/PMe_3 (COD = cyclooctadiene, COT = cyclooctatriene) with methacrylic acid to produce a ruthenalactone [Ru{OC(O)CMe=CH-κ^2*O*,*C*}$(PMe_3)_4$] (**1a**) by the C–H bond cleavage reaction (Scheme 1).[4]

During the formation of **1a**, an elusive intermediate assigned to a new bis(methacrylato) complex, [*cis*-Ru{OC(O)CMe=CH_2-κ^1*O*}$_2(PMe_3)_4$] (**2a**), was observed as a key compound for the internal C–H bond cleavage reaction. We have retained a strong interest in **2a** because one of its carboxylato ligands is considered to act as a hydrogen acceptor for the C–H bond cleavage reaction. The carboxylato anion is currently employed as a good hydrogen acceptor, or more precisely, as a proton acceptor[5] in some catalytic processes, and this concept is a breakthrough in catalysis that involves a C–H bond cleavage step in inactive compounds.[6] Moreover, the addition of carboxylic acids as cocatalysts is known to enhance some catalytic C–H bond activation processes promoted by bis(carboxylato) complexes of Pd^{II} and Ru^{II}.[7] Despite such an outstanding potential for the carboxylato complexes, detailed studies that focus on their reactivities, particularly on C–H bond activation, are largely unknown at the molecular level.



Scheme 1. Bis(methacrylato)ruthenium(II) intermediate **2a**.

In pioneering work that focused on carboxylato complexes and C–H bond activation, Sakaki and co-workers shed light on Fujiwara's early finding of catalytic C–H bond activation promoted by a (carboxylato)palladium(II) complex that used [$PdCl_2$](styrene)/acetic acid or [$Pd(OAc)_2$]/styrene/acetic acid[8] and theoretically revealed the role and importance of the carboxylato ligand in [$Pd(O_2CH$-κ^2*O*,*O*′$)_2$] in C–H bond cleavage reactions.[9] Afterwards, Davies, Macgregor and a co-worker documented the role of the acetato ligand in the Pd^{II} complex

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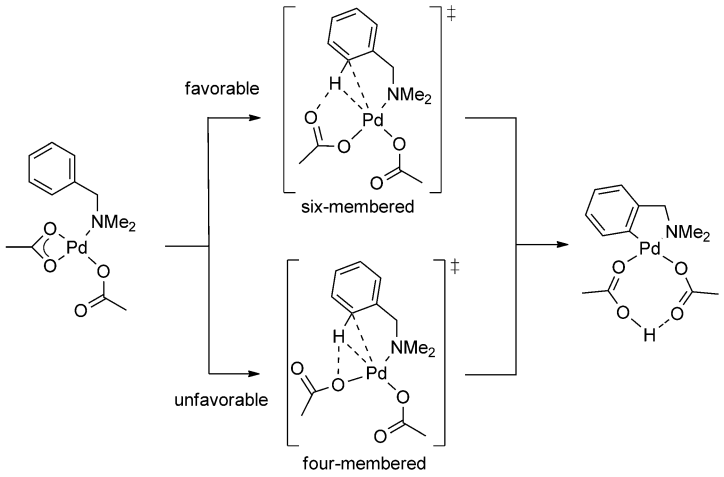


Scheme 2. Six- and four-membered transition states for C–H bond activation.

is to abstract the agostic H atom via a six-membered transition state rather than the alternative four-membered state (Scheme 2).[10]

However, detailed experimental studies on stoichiometric reactions of carboxylato complexes on C–H bond activation still remain largely unexplored, although several C–H bond activation processes by isolable mono(carboxylato)palladium(II) complexes have been elucidated.[11] Such studies would provide an intrinsic understanding of the nature of carboxylato complexes of late transition metals, and the bis(carboxylato) complex **2** would be one of the best examples to achieve this.

In this article, we report the isolation of a series of Ru^{II} complexes with mono- and bis(carboxylato) groups, a mechanism for the C–H bond cleavage reaction, and an application toward the catalytic H–D exchange reaction of carboxylic acids by the C–H bond cleavage reaction.

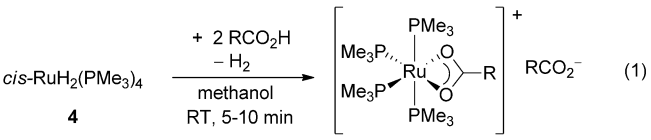
Results and Discussion

Preparation of (carboxylato)ruthenium(II) complexes

Cationic carboxylato complexes

As briefly described in the introduction, we have previously unsuccessfully tried to prepare $[Ru\{OC(O)R\}_2(PMe_3)_4]$ (**2**) from $[Ru(\eta^4\text{-}1,5\text{-}COD)(\eta^6\text{-}1,3,5\text{-}COT)]$. Instead, an aqua complex [*cis*,*fac*-$Ru\{OC(O)CMe{=}CH_2\text{-}\kappa^1O\}_2(PMe_3)_3(H_2O)$] (**3a**)[4] was formed by the reaction with a trace amount of contaminated water. Our next strategy was the metathesis reaction of $[RuCl_2(PMe_3)_4]$ with a carboxylate salt, but this method also gave a complex mixture. Protonolysis of [*cis*-$RuH_2(PMe_3)_4$] (**4**) with carboxylic acid in benzene produced a certain amount of **2**, but it decomposed during the work-up. However, we finally succeeded to prepare cationic mono(carboxylato)ruthenium(II) **5**, an ionized isomer of **2**, by employing methanol as a solvent, and **5** was obtained in 76–100% yield [Eq. (1)]. The quantitative formation of **5a–f** was observed by NMR studies in $[D_4]$MeOH.

As a typical example, the characterization of cationic methacrylato complex **5a** is described. The $^{31}P\{^1H\}$ NMR spectrum of **5a** in $[D_4]$MeOH showed a typical A_2X_2 pattern at $\delta = -1.08$ and 22.29 ppm, which suggests a *cis* configuration in an octahedral geometry. In the ^1H NMR spectrum, a virtual triplet and a multiplet at $\delta = 1.43$ (18H) and 1.45 ppm (18H) are assigned to the mutually *trans* and *cis* PMe_3 ligands, respectively. A set of singlets at $\delta = 1.89$ (s, 3H), 5.49 (s, 1H), and 5.98 ppm (s, 1H) are assigned as the coordinating methacrylato resonances. As the intensity of the resonances at $\delta = 1.87$ (3H), 5.18 (1H), and 5.70 ppm (1H) increased upon the stepwise addition of sodium methacrylate without change to the chemical shift or half-widths, these resonances are assigned to the liberated methacrylato anion. The IR spectrum of **5a** in KBr involves intense bands at



(1)

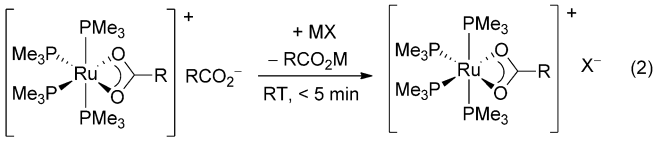
R = $CMe{=}CH_2$ (**5a**): 100%
$CH{=}CH_2$ (**5b**): 98%
CMe=CMeH (*E*-form) (**5c**): 98%
Et (**5d**): 87%
$CHMe_2$ (**5e**): 86%
Ph (**5f**): 98%

1597(vs) and 1429(s) cm^{-1}, probably assignable to the asymmetric and symmetric stretching vibration of the C=O bond in the methacrylato anion. Nakamoto documented the relationship between the coordination mode of a carboxylato ligand and the differential frequency between the asymmetric and symmetric νCO bands (Δ) for which bidentate, ionic, and monodentate carboxylato ligands have $\Delta = 42$–190, 164–201, and 228–470 cm^{-1}, respectively.[12] According to this criterion, the value observed ($\Delta = 168$ cm^{-1}) is an intermediate between the bidentate and ionic carboxylato ligands.

An independent experiment of the reaction of **4** with methacrylic acid under reduced pressure showed the formation of H_2 in 160% yield by using Töpler pump and GLC analyses. These spectroscopic and physical data are consistent with the formation of **5a**.

The recrystallization of **5a–f** failed, but the addition of $KBPh_4$ to a methanol solution of **5a** immediately resulted in a pale-yellow precipitate. Recrystallization of this precipitate from cold acetone gave the analytically pure corresponding borate salt **6a** as pale-yellow columns in 54% yield [Eq. (2)].

The $^{31}P\{^1H\}$ NMR spectrum of **6a** in $[D_6]$acetone shows an A_2X_2 pattern at $\delta = -0.47$ and 22.73 ppm. The ^1H NMR spectrum is quite similar to that of **5a**, but the resonances from the noncoordinating methacrylato anion were replaced by those for BPh_4^-. The IR spectrum in KBr showed a weak band at 1579 cm^{-1} and an intense band at 1427 cm^{-1}, which suggests asymmetric and symmetric νCO bands for the coordinat-



(2)

5a-f

R = CMe=CH$_2$, MX = NaBPh$_4$ (**6a**): 54%
CMe=CMeH (*E*-form), MX = NaBPh$_4$ (**6c**): 83%
Ph (**6f**), MX = KPF$_6$: 82%

ing carboxylato ligand, respectively. This differential ($\Delta =$ 152 cm^{-1}) is consistent with κ^2 coordination of the carboxylato group.

The molecular structure of **6a** is depicted in Figure 1. The cationic ruthenium fragment has a κ^2-methacrylato group in a slightly distorted octahedral geometry. No significant difference was observed in the Ru(1)–O(1) and Ru(1) –O(2) [2.2193(12) and 2.2130(13) Å] and C(1)–O(1) and C(1)–O(2) [1.275(2) and 1.269(2) Å] bond lengths. However, the Ru(1)–P(1) and Ru(1)–P(4) distances [2.3871(4) and 2.3810(4) Å] are significantly longer than those of Ru(1)–P(2) and Ru(1)–P(3) [2.2489(5) and 2.2619(5) Å], probably because of the strong *trans* influence of PMe$_3$.[13] Notably, the torsion angles of O(1)–C(1)–C(2)–C(3) and O(2)–C(1)–C(2)–C(3) are 2.0(2) and −177.99(16)°, respectively, which suggests conjugation of the *p* orbitals among these atoms.

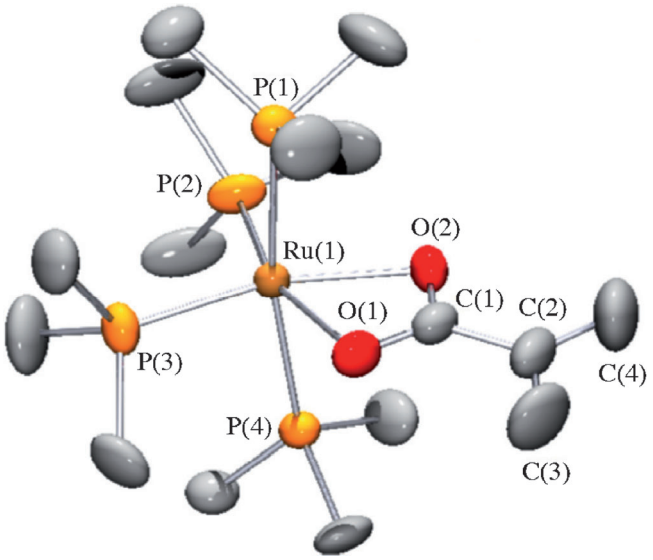
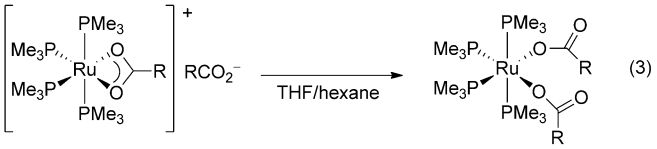


Figure 1. Molecular structure of **6a**. All H atoms and the borate anion are omitted for clarity. Ellipsoids represent 50% probability.

Neutral bis(carboxylato) complexes

The NMR spectra of **5a** measured in [D$_6$]benzene revealed two methacrylato groups in the ^{1}H NMR spectrum that were equivalent to an A_2X_2 pattern in the ^{31}P{^{1}H} NMR spectrum along with the presence of a small amount of the aqua adduct **3a**. This means that the two methacrylato ligands are completely equivalent, which suggests the conversion of **5a** to the neutral bis(methacrylato)ruthenium(II) complex **2a** in a nonpolar solvent. Thus, we recrystallized **5a** from carefully distilled water- and oxygen-free THF and hexane to give pale-yellow single crystals of **2a** in 70% yield [Eq. (3)].



(3)

5a-f

R = CMe=CH$_2$ (**2a**): 70%
CH=CH$_2$ (**2b**): 52%
CMe=CMeH (*E*-form) (**2c**): 65%
Et (**2d**): 53%
CHMe$_2$ (**2e**): 70%
Ph (**2f**): 54%

The ^{31}P{^{1}H} NMR spectrum of **2a** in [D$_6$]benzene shows an A_2X_2 pattern at $\delta = -2.62$ and 14.57 ppm. In the ^{1}H NMR spectrum, a multiplet at $\delta = 1.07$ ppm (18H) and a virtual triplet at $\delta = 1.33$ ppm (18H) are assigned to the mutually *cis* and *trans* PMe$_3$ ligands. A set of resonances at $\delta = 2.28$ (s, 6H), 5.34 (dd, 2H), and 6.29 ppm (d, 2H) are assigned to the methyl and alkenyl protons, which suggests that two methacrylato ligands are equivalent. The IR spectrum of **2a** in KBr showed an intense band at 1562 cm^{-1} assigned to the asymmetric νCO band, but the corresponding symmetric νCO band is obscure. More unambiguous structural information was obtained from the XRD structure analysis (Figure 2).

The Ru(1)–O(1) and Ru(1)–O(3) [2.153(2) and 2.182(2) Å] bond lengths are typical of Ru–O covalent bonds. However, those of Ru(1)–O(2) and Ru(1)–O(4) are beyond covalent bonds [more than 3.3 Å]. These two methacrylato groups are thus regarded as κ^1-carboxylato ligands. The C(2)–C(3) and C(6)–C(7) [1.331(4) and 1.341(5) Å] bond lengths indicate their C=C character. Therefore, these methacrylato groups have

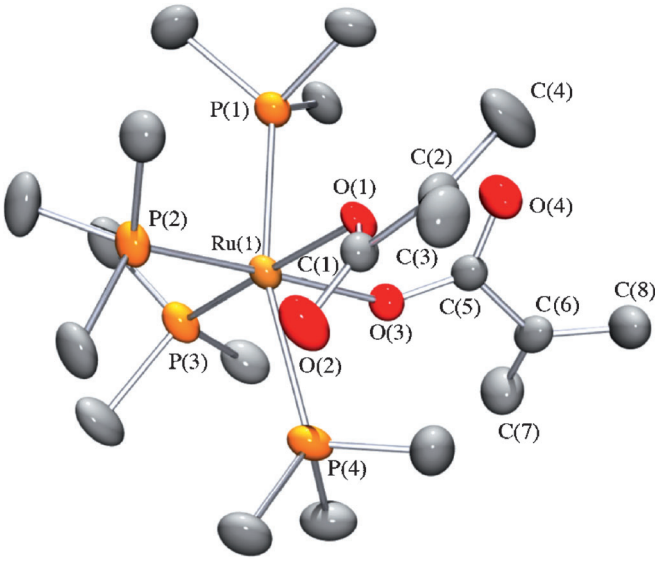
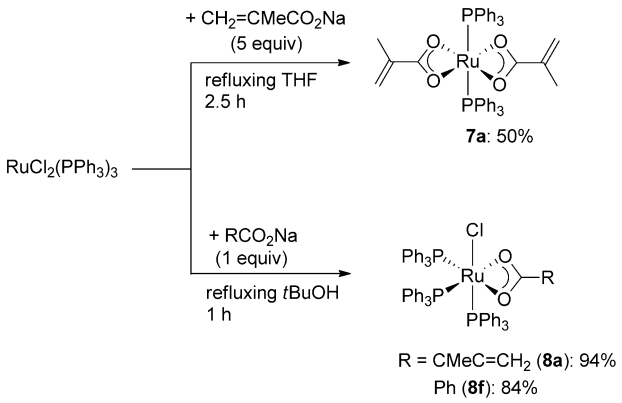


Figure 2. Molecular structure of **2a**. All H atoms are omitted for clarity. Ellipsoids represent 50% probability.

cisoid and transoid conformations in the solid state. However, the cisoid and transoid conformers would change quickly in solution because these methacrylato groups are observed to be equivalent in the ^{1}H NMR spectrum.

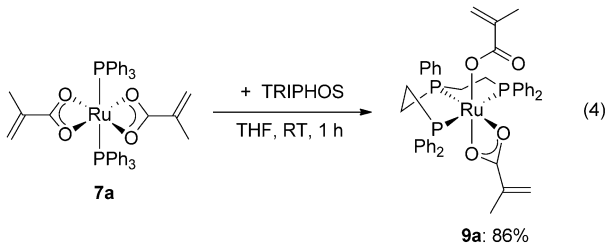
Other carboxylato complexes

Andersen and Mainz reported the formation of [*cis*-Ru(OAc-$\kappa^1O)_2(PMe_3)_4$] from the phosphine exchange reaction of [Ru(OAc-$\kappa^2O,O')_2(PPh_3)_2$] with PMe_3.[14] This method is also a potential route to **2** and related compounds with PMe_3 ligands. By a modification of this method, we prepared the bis(carboxylato) complex of PPh_3 as the first step to **2**. The metathesis reaction of [$RuCl_2(PPh_3)_3$] with five equivalents of sodium methacrylate produced a bis(triphenylphosphine) complex, [*trans*-Ru{OC(O)CMe=CH_2-κ^2O,O'}$_2(PPh_3)_2$] (**7a**), and the related tris(triphenylphosphine) complexes **8a** and **8f** were obtained with one equivalent of sodium carboxylate (Scheme 3).



Scheme 3. Metathesis reactions that use carboxylato anions.

However, attempts to prepare **2a** by the addition of PMe_3 to **7a** gave a complex mixture that involved **5a**. However, the treatment of **7a** with TRIPHOS ($Ph_2PC_2H_4PPhC_2H_4PPh_2$) produced analytically pure pale-yellow crystals of **9a** in 86% yield [Eq. (4)].



(4)

The NMR spectrum of **9a** showed dynamic behavior in solution, which was probably a result of the flexibility of the TRIPHOS ligand and not because of the fluxionality of the methacrylato fragments as these magnetically inequivalent methacrylato resonances remained sharp throughout the variable-temperature NMR experiments. XRD analysis provided compelling

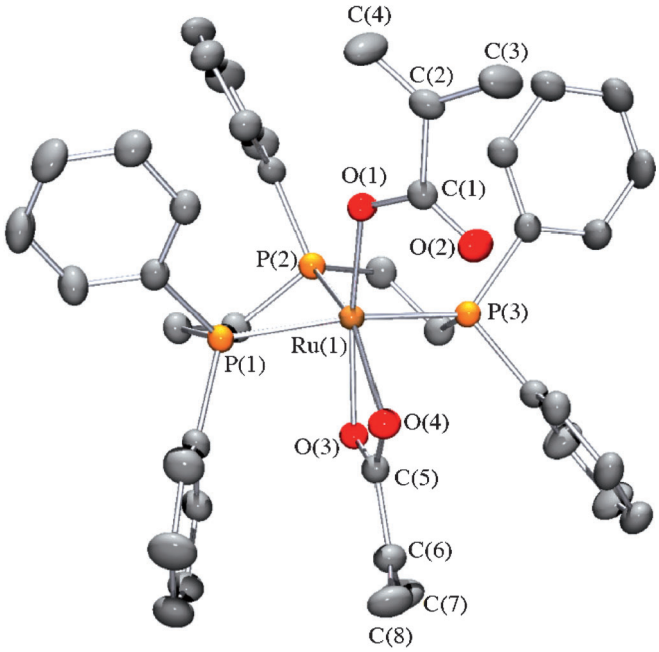
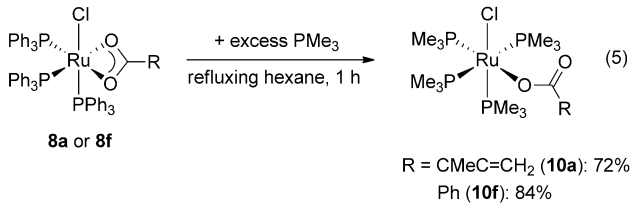


Figure 3. Molecular structure of **9a**. All H atoms are omitted for clarity. Ellipsoids represent 50% probability.

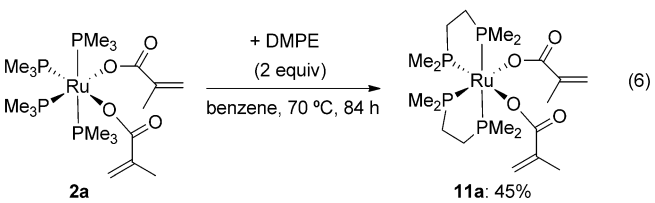
structural information that **9a** has κ^1- and κ^2-methacrylato groups with a meridional TRIPHOS ligand (Figure 3).

The addition of excess PMe_3 to the carboxylato(chlorido) complexes **8a** or **8f** in boiling hexane produced [*cis*-Ru{OC(O)R-κ^1O}Cl$(PMe_3)_4$] [R = CMe=CH_2 (**10a**), Ph (**10f**)] in 72–84% yield [Eq. (5)].



(5)

The treatment of **2a** with DMPE ($Me_2PC_2H_4PMe_2$) in benzene at 70 °C resulted in a phosphine-exchange reaction that gave [*cis*-Ru{OC(O)CMe=CH_2-κ^1O}$_2$(DMPE)$_2$] (**11a**) in 45% yield [Eq. (6)].



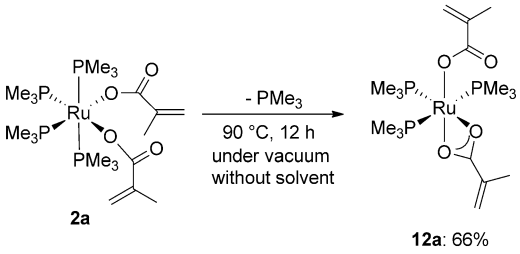
(6)

Notably, Field and co-workers have recently documented the direct formation of a similar compound [*cis*-Ru{OC(O)Me-κ^1O}$_2$(DMPE)$_2$] by the reaction of [*cis*-$RuMe_2$(DMPE)$_2$] with CO_2,[15] and Bergman and co-workers have reported the formation of [*cis*-Ru{OC(O)Ph-κ^1O}$_2$(DMPE)$_2$] by the acidolysis of [*cis*-$RuMe_2$(DMPE)$_2$] with benzoic acid.[16]

Reactions of (carboxylato)ruthenium(II) complexes

Reversible dissociation of PMe_3 and the formation of aqua adducts

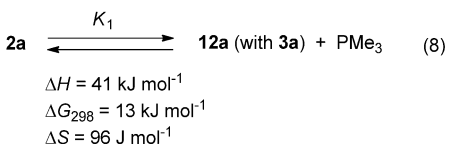
Complex **2a**, which has four PMe_3 ligands, is prone to the liberation of a PMe_3 ligand by heat or even at room temperature (RT). Heating solid **2a** without solvent at 90 °C under vacuum produced a κ^1- and κ^2-methacrylato complex with three PMe_3 ligands **12a** [Eq. (7)].



(7)

The $^{31}P\{^1H\}$ NMR spectrum of **12a** in [D_8]toluene showed a slightly broad singlet at $\delta = 28.3$ ppm at 20 °C, which broadened on cooling. Although we could not stop the fluxionality even at the lowest accessible temperature (−90 °C), we observed two broad signals at around $\delta = 34$ and 24 ppm in a 2:1 ratio. In the ^1H NMR spectra, the three PMe_3 and two methacrylato resonances were equivalent and appeared at 20 °C at $\delta = 1.13$ (27H), 2.16 (6H), 5.23 (2H), and 6.30 ppm (2H) but they broadened significantly at −90 °C. This dynamic behavior of **12a** probably arises from rapid exchange between the κ^1- and κ^2-methacrylato ligands through a five-coordinate intermediate on the NMR time-scale. Although we could not determine the meridional/facial geometry of **12a** because of the fluxionality, we drew the meridional geometry in Equation (7) in keeping with its analogue **9a**.

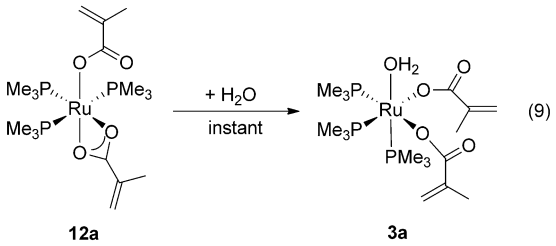
If a [D_6]benzene solution of **2a** was heated, the reversible formation of **12a** and its aqua adduct **3a** with the liberation of a PMe_3 ligand was observed. Compound **3a** is formed by the unavoidable contamination of water, and at low temperatures (below 20 °C), the resonances of **3a** and **12a** could be separately assigned in the NMR spectrum, however, they overlap at temperatures near RT. Thus, we treated the total amount of **12a** and **3a** as a single RuP_3 species for descriptive purposes and evaluated the equilibrium that concerns the reversible liberation of PMe_3 by the van 't Hoff plot [Eq. (8)].



(8)

This reaction is slightly exothermic, and the positive entropy value is consistent with the liberation of a PMe_3 ligand.

The aqua adduct **3a** was also produced by the reaction of **12a** with water. The treatment of **12a** with one equivalent of water in [D_6]benzene gave **3a** instantly and quantitatively [Eq. (9)].



(9)

Alternatively, **3a** can be prepared by the reaction of **2a** with water. However, this reaction did not reach completion and gave a mixture of **2a** and **3a** in 26 and 74%, respectively. The liberated PMe_3 probably suppresses the formation of **3a**. In the case of the benzoato complex **2f**, the aqua complex **3f** was obtained by the treatment of **2f** with water in 48% yield (95% by NMR). The molecular structure of **3f** is depicted in Figure 4.

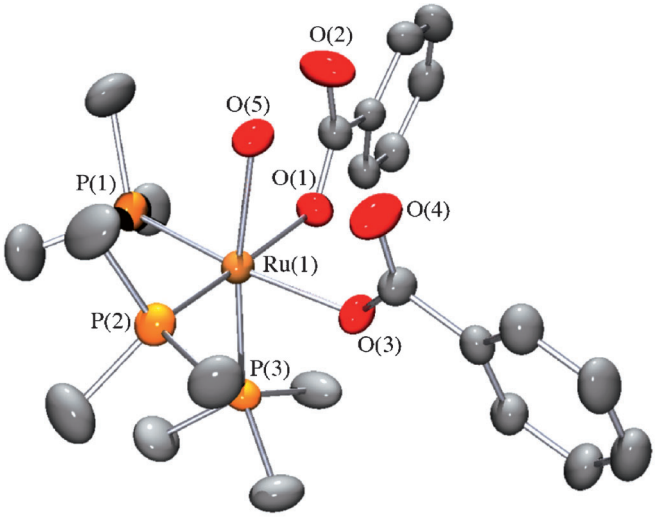
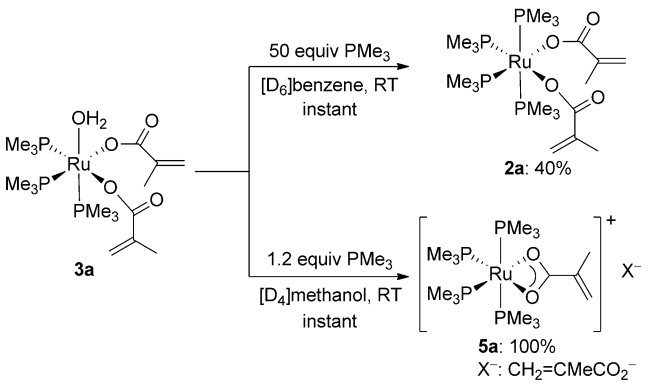


Figure 4. Molecular structure of **3f**. All H atoms are omitted for clarity. Ellipsoids represent 50% probability.

Although O(2) and O(4) are orientated toward O(5), the O(5)–O(2) and O(5)–O(4) [2.600(4) and 2.631(4) Å] distances are significantly shorter than the sum of the van der Waals radius of O [2.80 Å].[17] Thus, these O atoms must interact weakly through H bonding. The H atoms in the aqua ligand were found from the differential Fourier map and they pointed at the carbonyl O atoms in the benzoate ligands (not shown in Figure 4).

Comparatively, the bis(methacrylato)ruthenium(II) complex with a bidentate ligand **11a** did not react with water even at 70 °C. Thus, the liberation of a phosphine ligand promotes the formation of the aqua complex.

Complex **3a** reproduced **2a** by the addition of PMe_3 in [D_6]benzene, and the same reaction in [D_4]MeOH gave **5a** (Scheme 4).



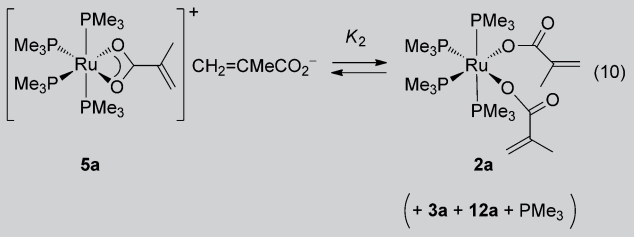
Scheme 4. Reaction of **3a** with PMe_3.

Interconversion between cationic and neutral bis(carboxylato) complexes

The results described above indicate the formation of cationic mono(carboxylato)ruthenium(II) complex **5** and neutral bis(carboxylato)ruthenium(II) complex **2** depending on the solvent. To clarify this solvent-dependent reaction, the isomerization between **5a** and **2a** was observed by NMR spectroscopy (Table 1).[18]

As shown in Table 1, the forward and backward reactions gave the same results within experimental errors, and the equilibrium shifts to the **5a** and **2a** sides in polar and nonpolar solvents, respectively. In acetone, a mixture of cationic and neutral carboxylato complexes was observed. The formation of **3a** and **12a** was suppressed at low temperature in [D_6]acetone.

Table 1. Reversible isomerization between **5a** and **2a**.[a]



	Solvent	Starting compound	NMR yield [%] 5a	2a	3a + 12a	PMe_3
1	[D_6]benzene	**5a**	0	73	24	20
2	[D_6]benzene	**2a**	0	66	34	23
3	[D_6]acetone	**5a**	32	37	31	25
4	[D_6]acetone	**2a**	29	42	24	17
5	[D_4]MeOH	**5a**	100	0	0	0
6	[D_4]MeOH	**2a**	100	0	0	0
7	[D_6]DMSO	**5a**	93	0	7	0
8	[D_6]DMSO	**2a**	100	0	0	0

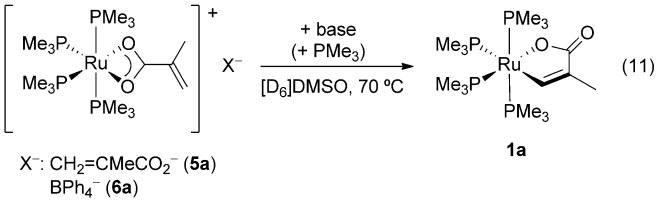
[a] $T = 20\,^{\circ}C$, starting complex = 0.020–0.025 mmol, solvent = 550–600 μL.

The van 't Hoff plot for K_2 (K_2 = [**2a**]/[cation of **5a**][methacrylato anion]) in the range of −30 to 10 °C gave the following thermodynamic parameters: $\Delta H = -9.0\ kJ\,mol^{-1}$, $\Delta G_{298} = -12\ kJ\,mol^{-1}$, $\Delta S = 11\ J\,mol^{-1}\,K^{-1}$. This shows that the thermodynamic energy difference between **5a** and **2a** is small and a slightly positive entropy may suggest the slight association of the solvent molecule for cationic **5a**.

Formation of ruthenalactone by C–H bond activation

Cationic carboxylato complexes

Heating **5a** at 70 °C in the presence of 30 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in [D_6]DMSO produced a ruthenalactone **1a** in 93% yield within 10 h. If this reaction took place in the presence of 30 equivalents of DBU and 10 equivalents of PMe_3, the formation of **1a** was significantly suppressed (8% in 20 h and 63% in 457 h) [Eq. (10)].



Similar treatment of the cationic complex **6a** with 30 equivalents of DBU at 70 °C gave **1a** in 94% in 20 h. In the presence of 10 equivalents of PMe_3 under the same conditions, **6a** gave **1a** only in 23% after 291 h. The treatment of **6a** with potassium phenoxide also gave **1a** in 79% yield. However, the treatment of **6a** with sodium methacrylate produced **1a** only in 11% yield, and **1a** was not formed by treatment with proton sponge (1,8-bis(dimethylamino)naphthalene), NEt_3, TMEDA ($Me_2NC_2H_4NMe_2$), pyridine, or DMAP (4-*N*,*N*-dimethylaminopyridine). These results suggest that i) the C–H bond cleavage reaction requires prior dissociation of PMe_3, ii) some bases assist the C–H bond cleavage reaction but those abilities cannot be explained by their basicity,[19] iii) the added carboxylato anion does not promote the C–H bond cleavage reaction at all, and iv) this C–H bond cleavage reaction is not a spontaneous deprotonation from the carboxylato ligand.

Single crystals of **1a** were obtained from cold toluene/hexane, and the molecular structure is depicted in Figure 5.

The overall structure of **1a** is a ruthenalactone with an octahedral geometry. The Ru(1)–C(3) and Ru(1)–O(1) bond lengths are 2.0869(17) and 2.1428(15) Å, respectively. One of the authors previously reported the formation and molecular structure of [*fac*-RuH(CH=CMeCO$_2$Bu-κ^2*C*,*O*)(PPh_3)$_3$] by the C–H bond activation of butyl methacrylate with [*cis*-$RuH_2(PPh_3)_4$], in which Ru–O is a coordinate bond.[20] According to this report, the Ru–C and Ru–O distances are 2.061(10) and 2.246(7) Å, respectively. The similar length of the Ru–C bond and significantly shorter Ru–O bond in **1a** reflect covalent bonding characters for both. The O(2)–C(1) [1.234(3) Å] and C(2)–C(3)

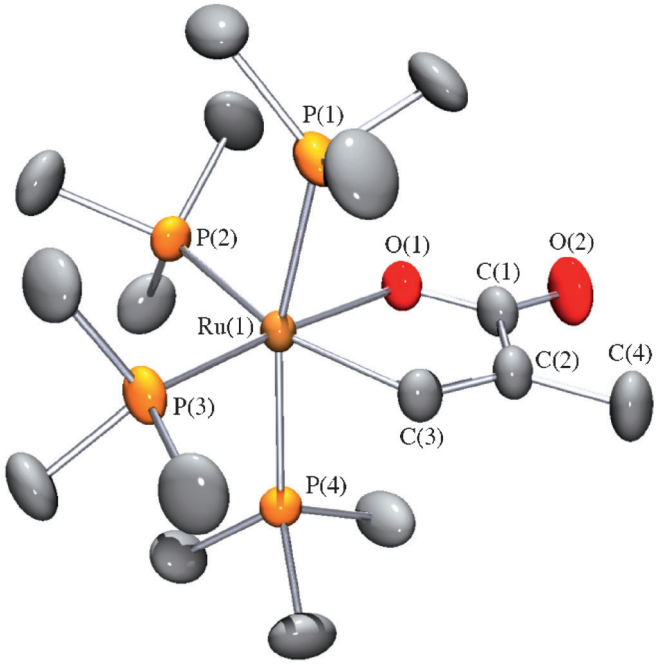


Figure 5. Molecular structure of **1a**. All H atoms are omitted for clarity. Ellipsoids represent 50% probability.

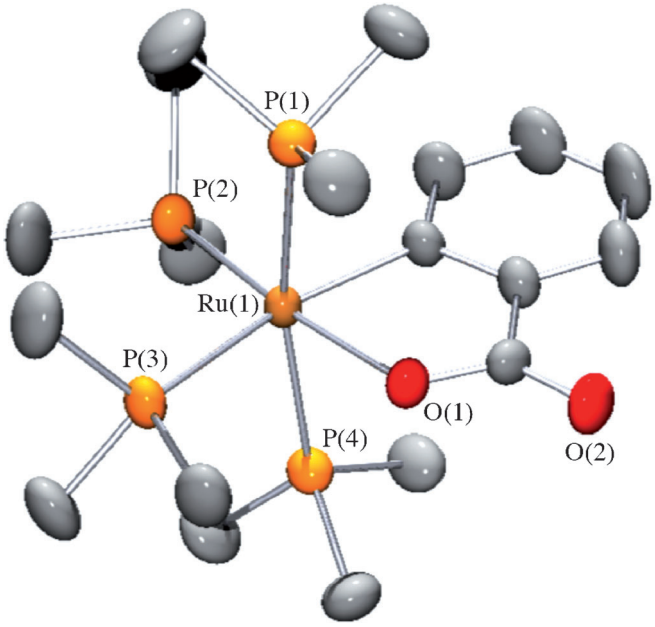


Figure 6. Molecular structure of **1f**. All H atoms are omitted for clarity. Ellipsoids represent 50% probability.

[1.340(3) Å] bond lengths suggest double bond characters, whereas O(1)–C(1) [1.295(2) Å], C(1)–C(2) [1.494(3) Å], and C(2)–C(4) [1.512(3) Å] are regarded as single bonds. This result shows that an sp^2 C–H bond in the methacrylato ligand in **5a** or **6a** is cleaved to give **1a**.

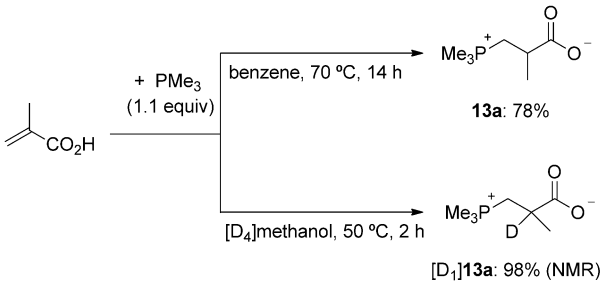
Complex **1a** shows an AM_2X pattern at $\delta = 11.6$, 0.22, and −11.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum in [D_6]benzene, and two doublets at $\delta = 0.88$ (9H) and 1.09 ppm (9H) and a virtual triplet at $\delta = 0.96$ ppm (18H) are observed in the ^1H NMR spectrum. This pattern is consistent with the *cis* structure of **1a** in an octahedral geometry. The ^1H NMR spectrum shows a singlet at $\delta = 2.43$ ppm (3H) and broad peak in the alkenyl region at $\delta = 7.86$ ppm (1H), which are assigned to the methyl and methine protons, respectively.

Similarly, treatment of the benzoato complex **6f** with DBU in [D_6]DMSO at 100 °C produced the corresponding ruthenalactone **1f** in 43% yield (Figure 6).

Neutral carboxylato complexes

The reaction of **2a** with a base showed a more complicated result. For example, the treatment of **2a** with five equivalents of DBU in [D_6]benzene at 70 °C for 3 h produced **1a** in 49% yield with the concomitant formation of a mixture of tris(phosphine) species **3a** and **12a** (41%) and liberated PMe_3 (35%). This reaction reached a steady state, which suggests the presence of an equilibrium between **1a** and **2a**. The yield of **1a** increased to 64% with an increase of DBU (10 equivalents), and decreased to 31% with a decrease of DBU (one equivalent) under similar conditions. The yield of **1a** decreased to 6–9% if proton sponge, pyridine, or 2,6-lutidine was employed in the reaction. This suggests that the trapping of the evolved methacrylic acid by base was key in this reaction. However, in spite of almost the same basicity of DBU ($pK_a = 12$) and proton sponge ($pK_a = 12.34$), the significant difference in their reactivities suggests that they do not perform just as Brønsted bases. We believe that they participate in the C–H bond cleavage step (vide infra).

If we employed PMe_3 as a base in this reaction, **1a** was obtained quantitatively in the presence of 30 equivalents of PMe_3 in [D_6]benzene at 70 °C, although the reaction was slow (175 h at 70 °C). In this reaction, the formation of phosphabetaine **13a** was observed, which was independently characterized by the reaction of methacrylic acid with PMe_3 (Scheme 5).[21]



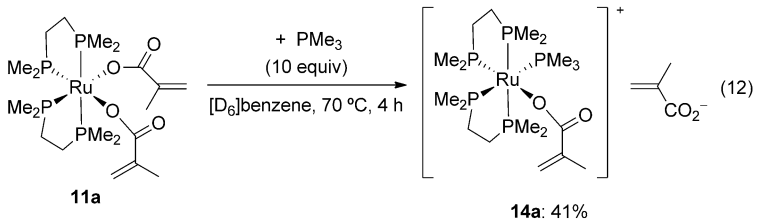
Scheme 5. Reaction of methacrylic acid with PMe_3.

As the incorporation of a deuterium atom was observed in the 2-position of the phosphabetaine if the reaction took place in [D_4]MeOH, the most probable formation mechanism of the phosphabetaine would be the protonation of PMe_3 by methacrylic acid to give $[HPMe_3]^+[CH_2{=}CMeCO_2]^-$ followed by hydrophosphination to the unsaturated counteranion.

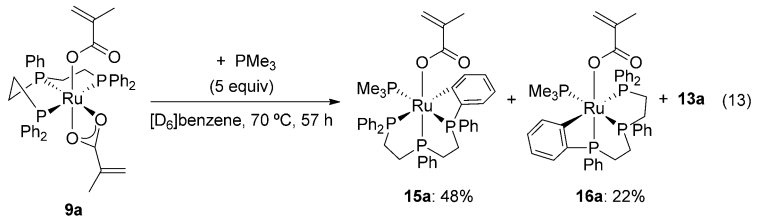
Contrary to the PMe_3 complex **2a**, the reaction of the DMPE analogue **11a** with PMe_3 did not give the ruthenalactone but

gave a cationic complex [Ru{OC(O)CMe=CH_2-κ^1O}-$(DMPE)_2(PMe_3)$]$^+$[CH_2=$CMeCO_2$]$^-$ (**14a**) in 41% yield [Eq. (11)].

This result suggests the importance of the prior dissociation of PMe_3 for the C–H bond cleavage reaction. Similar treatment of the TRIPHOS complex **9a** with PMe_3 produced a mixture of orthometalated complexes of the TRIPHOS ligand **15a** and **16a** [Eq. (12)].



(12)



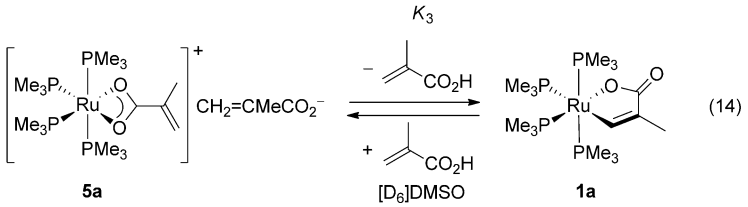
(13)

Although **9a** has almost the same structure as the PMe_3 complex **12a**, the orthometalation of the phenyl group proceeds for **9a** prior to the internal C–H bond cleavage reaction of the carboxylato ligand. Thus, we concluded that monodentate alkylphosphines such as PMe_3 encourage the C–H bond activation of the carboxylato group.

Reversibility of the reaction between the bis(methacrylato) complex and ruthenalactone

In the absence of base, heating a [D_6]DMSO solution of the cationic methacrylato complex **5a** at 70 °C reached a steady state of a mixture of **5a** (74%) and **1a** (22%) along with small amount of **3a** (4%) n 1 h [Eq. (13)].

For the backward reaction, the treatment of **1a** with one equivalent of methacrylic acid gave a mixture of **5a** (75%), **1a** (22%), and **3a** (4%) under the same conditions. Therefore, this system constitutes the equilibrium between **5a** and **1a** in [D_6]DMSO. As the [**5a**]:[**1a**] ratio was almost independent ([**5a**]:[**1a**] = 3.9–3.0) of the initial concentration of **5a** (0.014–0.0533 M), the ionic pairwise interaction is weak in [D_6]DMSO solution. Thus, the equilibrium



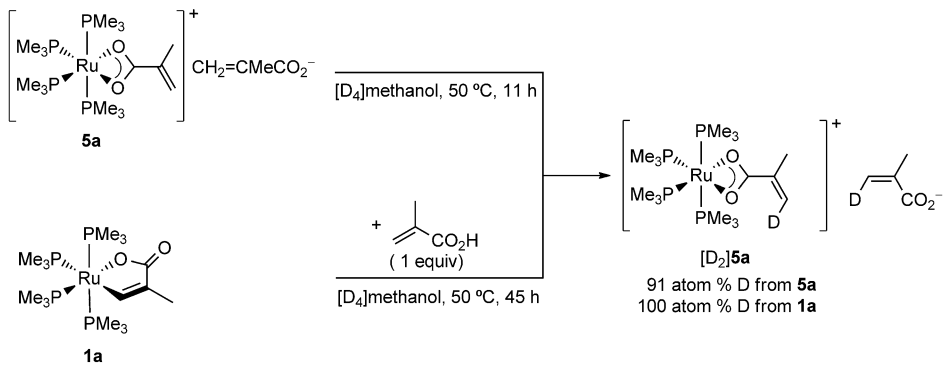
(14)

constant is described as K_3 = [cation of **5a**][methacrylato anion]/[**1a**][methacrylic acid]. The K_3 value was almost independent (K_3 = 0.055–0.070) of the temperature (50–80 °C), which suggests that there is little thermodynamic difference between the compounds.

Heating the neutral bis(benzoato) complex **2f** to 70 °C yielded the orthometalated product **1f** in 21% in 10 h in the presence of DBU. However, the similar treatment of **2f** with PMe_3 did not afford **1f** at all, and **2f** was recovered in 79%. As the liberated benzoic acid cannot form a phosphabetaine such as **13a**, PMe_3 may not be an effective base in this reaction. A similar orthometalation from [*cis*-Pt{O-C(O)Ph}$_2$($PiPr_2C_2H_4PiPr_2$)] at 160 °C for 8 d has recently been documented by Jones and co-workers.[22]

The reaction in [D_4]MeOH is notable. In [D_4]MeOH, ruthenalactone **1a** was not observed at all on the treatment of **5a** at 50 °C for 11 h. Instead, regio- and stereoselective deuteration occurred to give [D_2]**5a** (Scheme 6).

The H–D exchange reaction exclusively occurred at the *cis* position to the carbonyl group in both coordinated and liberated methacrylato anions and no incorporation of D was observed in other positions. The similar treatment of **1a** in the presence of one equivalent of methacrylic acid in [D_4]MeOH at 50 °C for 45 h gave [D_2]**5a** in quantitative yield with 100 at% D. These results strongly suggest that this reaction proceeds by the C–H bond cleavage reaction via ruthenalactone. However, no incorporation of D was observed by the similar treatment of **11a** in [D_4]MeOH. This suggests the importance of the prior dissociation of a P atom from the Ru^{II} center. Consistently, the aqua complex **3a**, which has three PMe_3 ligands, underwent a *cis*-selective H–D exchange reaction of the methacryla-

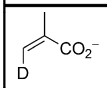
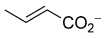
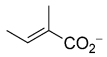
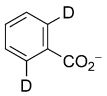
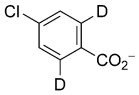
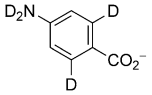
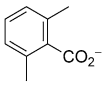


Scheme 6. Stoichiometric regio- and stereoselective deuteration.

to ligands to give [D_2]**3a** in 96 at% D in 6.8 h at 50 °C in [D_4]MeOH.

To understand the general feature of this stoichiometric deuteration of carboxylato anions, we screened several carboxylato complexes (Table 2). No H–D exchange reaction took place for the crotonato, tiglato, or 2-methylpropanoato anions. The *ortho* deuteration in benzoato and related compounds proceeded, but these reactions were sluggish.

Table 2. Stoichiometric deuteration of the β-position in the carboxylato anion in [D_4]MeOH.[a]

Carboxylato anion	*t* [h]	D content [atom%]
	11	91
	n.a.	–[b]
	77	0
	46	0
	145	0
	315	28
	315	74
	313	34
	104	0

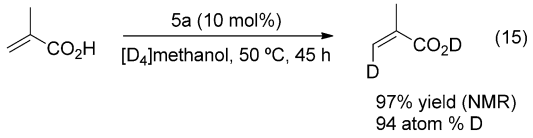
[a] Conditions: starting complex = 0.022–0.024 mmol, [D_4]MeOH = 600 μL, *T* = 50 °C. [b] Complex mixture.

Catalytic H–D exchange reaction

Catalytic regio- and stereoselective H–D exchange reaction

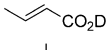
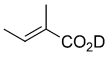
The C–H bond cleavage reaction of carboxylic acid itself is largely unexplored and only pioneering catalytic *ortho* halogenation, alkylation, alkenylation, arylation, and carboxylation processes have been documented by Yu, Satoh, and Miura's groups.[23] The stoichiometric reaction described above promises regio- and stereoselective catalytic H–D exchange reactions of carboxylic acids. Complex **4a** (10 mol%) catalyzed the H–D exchange reaction of methacrylic acid in [D_4]MeOH at 50 °C to give [D_2]methacrylic acid in 97% yield with 94 at% D [Eq. (14)].

The reaction proceeded regio- and stereoselectively and the H atom *cis* to the carbonyl group was exclusively deuterated along with the acidic proton. Similarly, the catalytic deuteration of aliphatic carboxylic acids was performed by **4** as a catalyst precursor (Table 3).



(15)

Table 3. Catalytic deuteration of the β-hydrogen atom in carboxylic acids.[a]

Carboxylic acid	*t* [h]	Yield [%]	D content [atom%]
	36	82	94
	24	63	85
	48	86	93
	56	–	0
	46	–	0

[a] Conditions: Catalyst = **4** (0.02 mmol), carboxylic acid (0.2 mmol), [D_4]MeOH, *T* = 60 °C.

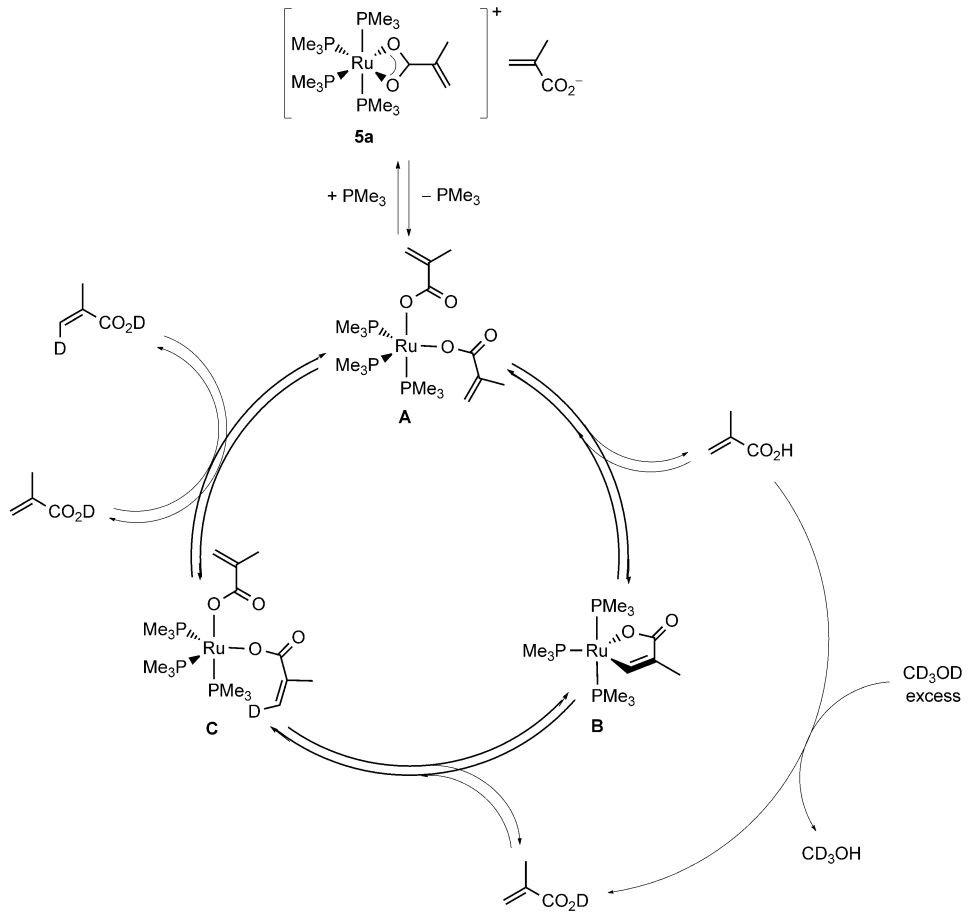
The catalytic H–D exchange reaction of benzoic acid by **4** as a catalyst precursor failed, although the stoichiometric reaction proceeded. If the trisphosphine complex **3f** was employed, the catalysis slowly proceeded to give the *ortho* deuterated benzoic acid with 28 at% D in 315 h in [D_4]MeOH at 50 °C.

Plausible catalytic cycle

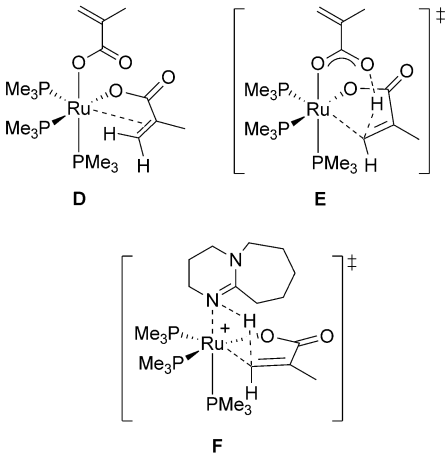
Considering all the experimental results described above, this catalysis can be explained as summarized in Scheme 7.

Both [*cis*-$RuH_2(PMe_3)_4$] and neutral bis(carboxylato) complex *cis*-$Ru(OC(O)CMe{=}CH_2)_2(PMe_3)_4$ (**2a**) are easily converted into **5a** by reaction with methacrylic acid in methanol. Complex **5a** reversibly liberates a PMe_3 ligand to give **A**. As bidentate phosphine complex **10a** is inactive for the C–H bond cleavage reaction of the carboxylato ligand, the active catalyst is considered to be a tris(phosphine) species. Then, a ruthenalactone **B** forms with the liberation of methacrylic acid. The equilibrium between a ruthenalactone and **5a** has been established [Eq. (14)]. The liberated methacrylic acid immediately exchanges the proton with D^+ in a large excess of [D_4]MeOH. The acidolysis of **B** with $CH_2{=}CMeCO_2D$ gives **C** in which the D atom is exclusively incorporated in the *cis* position to the carbonyl group. Finally, the exchange between the carboxylato and carboxylic acid releases [D_2]methacrylic acid.

In the present C–H bond cleavage process (**A** to **B** in Scheme 7), prior coordination of the C=C bond to the Ru^{II} center may be an indispensable process because a pseudo-isomorphous complex with a saturated ligand, the isobutylato group (complex **D**), did not react in either the stoichiometric or catalytic reactions.



Scheme 7. Possible mechanism for the catalytic regio- and stereoselective deuteration of methacrylic acid.



These results clearly show that the carboxylato group does not act as a simple Brønsted base. This probably suggests the high ability of the coordinating carboxylato group for proton abstraction.[5,9,10] An internal base, such as a bound carboxylato group rather than an external one, plays a key role in the C–H bond cleavage step. This mechanism is nowadays widely accepted as an internal electrophilic substitution (IES) mechanism,[24] although other names such as concerted metalation–deprotonation (CMD),[25] and ambiphilic metal–ligand activation (AMLA)[26] have been used. The six-membered transition state **E** requires a vacant site, which is consistent with the prior dissociation of PMe_3 as shown above. Probably, intermediate **D** gives the transition state **E**. However, DBU is a good base in this reaction and initiates the C–H bond cleavage reaction from **6a**. This cannot be explained by the basicity of DBU, and it must have a similar nature to the coordinating carboxylato group. Although it is not clear how DBU behaves in the C–H bond activation process, one of the hypotheses is the prior coordination of DBU to Ru^{II} though the amidine framework (depicted as **F**).[27]

Conclusions

We have documented a facile and general method to prepare bis(carboxylato)ruthenium(II) complexes **2**. Interestingly, this compound reversibly transforms to the cationic form **5** in polar solvents. The C–H bond cleavage reaction of the carboxylato ligand in **2** occurs to give a ruthenalactone **1**, which requires prior dissociation of a PMe_3 ligand from **2**. The thermodynamic stability between **2** and **1** is almost comparable and they form an equilibrium in a solution. These results show that the coordinating carboxylato ligand abstracts the proton from another carboxylato ligand at the coordinatively unsaturated Ru^{II} center. However, an added carboxylato anion has almost of no effect on the C–H bond activation. Thus, the coordinating carboxylato ligand must play a role as an internal base in this reaction. This finding sheds light on the C–H bond activation process in which a carboxylato ligand becomes engaged as a proton acceptor.

Experimental Section

All manipulations and reactions were performed under dry N_2 by using standard Schlenk and vacuum-line techniques. Benzene, toluene, hexane, pentane, THF, and Et_2O were distilled from sodium benzophenone ketyl, and acetone was distilled from Drierite. DMSO was distilled from activated molecular sieves. Methanol and ethanol were distilled from the corresponding Mg alkoxide. PMe_3 was prepared by the reaction of $P(OPh)_3$ with a methyl Grignard reagent and purified by distillation followed by repeated drying over $MgSO_4$ by using a vacuum-distillation technique. $[Ru_2(O_2CMe)_4Cl]$ was prepared according to a slightly modified literature method by using O_2 gas.[28] $[RuCl_2(PPh_3)_3]$ was prepared according to a litera-

ture method.[29] Compound **4** was prepared by the reduction of $[Ru_2(O_2CMe)_4Cl]$ with sodium amalgam in the presence of PMe_3 under a H_2 atmosphere.[30] For reactions in an NMR tube, internal $CHPh_3$ or a $[D_6]$benzene solution of PPh_3 in a flame-sealed capillary was used as the internal standard for quantitative analysis. The NMR spectra were measured by using JEOL LA300 (^1H at 300 MHz, ^{31}P at 122 MHz) and JEOL ECX400P (^1H at 399.8 MHz, ^{31}P at 162 MHz) spectrometers. The ^1H and ^{13}C chemical shifts were referenced to tetramethylsilane. The ^1H–^1H coupling constants for the complexes refer to the observed peak separations; non-first-order analysis of the spectra was not attempted. The accuracy of the coupling constants was estimated from the raw data by taking into account the experimental error based on the line shape of each resonance. IR spectra were recorded by using a JASCO FTIR4100 spectrometer. Elemental analyses were performed by using a Perkin–Elmer 2400 series II CHN analyzer. The volume of evolved H_2 gas was measured by using a Töpler pump and analyzed by GLC by using a Shimadzu GC-8A instrument with a molecular sieve column equipped with a thermal conductivity detector (TCD, 5 mm × 2 m). GC–MS analysis was performed by using a Shimadzu QP2100 instrument.

Syntheses

$[Ru\{OC(O)CMe{=}CH\text{-}\kappa^2O,C\}(PMe_3)_4]$ (**1 a**): Method A: Complex **2 a** (79.9 mg, 0.139 mmol) was treated with PMe_3 (706 μL, 6.91 mmol) in benzene at 70 °C for 120 h. After removal of all volatile materials, the resulting solid was extracted with THF. After evaporation of the solution, the solid was recrystallized from the vapor diffusion of hexane into a toluene solution to give colorless cubes of **1 a** in 16% yield (10.9 mg, 0.0223 mmol).

Method B: Complex **10 a** (816.3 mg, 1.552 mmol) was treated with KOPh (206.6 mg, 1.563 mmol) in *t*BuOH (20 mL) at 70 °C for 22 h. After the removal of volatile materials, the resulting white solid was extracted with benzene. The benzene solution was washed with aqueous NaOH repeatedly, then evaporated to dryness and dried under reduced pressure to yield almost pure **1 a** as a white powder in 49% yield (374.8 mg, 0.7658 mmol). After recrystallization of the powder from cold toluene, pure **1 a** was obtained as colorless crystals in 44% yield (337.0 mg, 0.6855 mmol).

^1H NMR (300 MHz, $[D_6]$benzene): $\delta = 0.88$ (d, $J = 7.5$ Hz, 9H, P*Me*$_3$), 0.96 (t, $J = 2.7$ Hz, 18 Hz, P*Me*$_3$), 1.09 (d, $J = 5.7$ Hz, 9H, P*Me*$_3$), 2.43 (s, 3H, CH=C*Me*CO_2), 7.86 ppm (br, 1H, C*H*=CMeCO_2); $^{31}P\{^1H\}$ NMR (122 MHz, $[D_6]$benzene): $\delta = -11.7$ (td, $J = 26$, 16 Hz, 1P, *P*Me$_3$), 0.22 (dd, $J = 35$, 26 Hz, 2P, *P*Me$_3$), 11.6 ppm (td, $J = 35$, 16 Hz, 1P, *P*Me$_3$): IR (KBr): $\tilde{\nu} = 2971$ (m), 2911 (s), 2871 (w), 1655 (w), 1586 (vs), 1549 (s), 1427 (m), 1340 (s), 1279 (s), 942 (vs), 856 (s), 711 (s), 664 cm^{-1} (s); elemental analysis calcd (%) for $C_{16}H_{40}O_2P_4Ru$ (490.45): C 39.26, H 8.24; found: C 39.43, H 7.89.

$[Ru\{OC(O)C_6H_4\text{-}\kappa^2O,C\}(PMe_3)_4]$ (**1 f**): Method A: A similar treatment of **10 f** (844.0 mg, 1.502 mmol) with KOPh (198.4 mg, 1.501 mmol) as described above for **1 a** produced **1 f** as colorless crystals in 27% yield (211.6 mg, 0.4027 mmol).

Method B: Complex **2 f** (3.2 mg, 0.0049 mmol) in an NMR tube in $[D_6]$benzene was heated at 70 °C for 10 h in the presence of DBU (22.0 μL, 0.147 mmol) to give **1 f** in 21% yield. (Method C): Complex **2 f** (10 mg, 0.015 mmol) in $[D_6]$benzene at 70 °C for 165 h in the presence of PMe_3 (18.0 μL, 0.177 mmol) produced a small amount of unknown compound with 79% recovery of **1 f**. (Method D): Complex **6 f** (3.4 mg, 0.0051 mmol) was treated with DBU (3.8 μL, 0.025 mmol) in $[D_6]$DMSO at 100 °C for 20 h to produce **1 f** in 43% yield.

^1H NMR (400 MHz, $[D_6]$acetone): $\delta = 1.02$ (t, $J = 3.0$ Hz, 18H, P*Me*$_3$), 1.49 (d, $J = 7.1$ Hz, 9H, P*Me*$_3$), 1.49 (d, $J = 7.8$ Hz, 9H, P*Me*$_3$), 6.79 (t, $J = 7.3$ Hz, 1H, C_6H_4), 6.96 (t, $J = 7.1$ Hz, 1H, C_6H_4), 7.42 (d, $J = 7.3$ Hz, 1H, C_6H_4), 7.63 ppm (t, $J = 6.2$ Hz, 1H, C_6H_4); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$acetone): $\delta = -13.7$ (td, $J = 26$, 17 Hz, 1P, *P*Me$_3$), −0.22 (dd, $J = 34$, 26 Hz, 2P, *P*Me$_3$), 9.1 ppm (td, $J = 34$, 17 Hz, 1P, *P*Me$_3$). IR (KBr): $\tilde{\nu} = 3049$ (m), 3036 (m), 2974 (m), 2905 (m), 1689 (w), 1644 (w), 1599 (vs), 1571 (s), 1432 (s), 1416 (s), 1334 (vs), 1300 (s), 1278 (s), 1142 (s), 943 (vs), 857 (s), 836 (s), 736 (s), 715 (s), 663 (s), 547 (w), 434 cm^{-1} (m); elemental analysis calcd (%) for $C_{19}H_{40}O_2P_4Ru$ (525.48): C 43.43, H 7.67; found: C 44.08, H 7.66.

$[cis\text{-}Ru\{OC(O)CMe{=}CH_2\text{-}\kappa^1O\}_2(PMe_3)_4]$ (**2 a**): Complex **5 a** (286.6 mg, 0.4980 mmol) was dissolved in dry THF (1 mL) and hexane (2 mL) was added. The solution was filtered and stored in a freezer to give pale-yellow cubes of **2 a** in 70% yield (212.5 mg, 0.3692 mmol). The other neutral bis(carboxylato) complexes were prepared in a similar way. ^1H NMR (300 MHz, $[D_6]$benzene): $\delta = 1.07$ (m, 18H, P*Me*$_3$), 1.33 (vt, $J = 3.3$ Hz, 18H, P*Me*$_3$), 2.28 (s, 6H, *Me*), 5.34 (dd, $J = 3.3$, 1.5 Hz, 2H, C*H*$_2$=CMeCO_2 *trans* to carbonyl), 6.29 ppm (d, $J = 3.6$ Hz, 2H, C*H*$_2$=CMeCO_2 *cis* to carbonyl); $^{31}P\{^1H\}$ NMR (121 MHz, $[D_6]$benzene): $\delta = -2.62$ (t, $J = 31.6$ Hz, 2P, *P*Me$_3$), 14.57 ppm (t, $J = 31.6$ Hz, 2P, *P*Me$_3$); IR (KBr): $\tilde{\nu} = 2975$ (m), 2912 (m), 1641 (w), 1562 (vs), 1454 (s), 1402 (vs), 1380 (vs), 1299 (s), 1282 (s), 1238 (s), 941 (vs), 833 (s), 721 (s), 667 (s), 619 cm^{-1} (s); elemental analysis calcd (%) for $C_{20}H_{46}O_4P_4Ru$ (575.54): C 41.74, H 8.06; found: C 41.38, H 7.83.

$[cis\text{-}Ru\{OC(O)CH{=}CH_2\text{-}\kappa^1O\}_2(PMe_3)_4]$ (**2 b**): 52%; ^1H NMR (400 MHz, $[D_6]$benzene): $\delta = 1.06$ (m, 18H, P*Me*$_3$), 1.31 (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 2.28 (s, 6H, *Me*), 5.40 (d, $J = 6.6$ Hz, 2H, CH_2=C*H*CO_2), 6.49 ppm (d, $J = 6.6$ Hz, 4H, C*H*$_2$=CHCO$_2$); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$benzene): $\delta = -2.74$ (t, $J = 31.8$ Hz, 2P, *P*Me$_3$), 14.70 ppm (t, $J = 31.8$ Hz, 2P, *P*Me$_3$).

$[cis\text{-}Ru\{OC(O)CMe{=}CHMe\text{-}\kappa^1O\}_2(PMe_3)_4]$ (**2 c**): 65%; ^1H NMR (400 MHz, $[D_6]$benzene): $\delta = 1.11$ (m, 18H, P*Me*$_3$), 1.36 (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 1.72 (d, $J = 6.9$ Hz, 6H, β-*Me*), 2.21 (s, 6H, α-*Me*), 7.06 ppm (qd, $J = 7.3$, 1.4 Hz, 2H, C*H*Me=CMeCO_2); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$benzene): $\delta = -3.09$ (t, $J = 30.6$ Hz, 2P, *P*Me$_3$), 14.0 ppm (t, $J = 30.6$ Hz, 2P, *P*Me$_3$).

$[cis\text{-}Ru\{OC(O)Et\}_2(PMe_3)_4]$ (**2 d**): 53%; ^1H NMR (400 MHz, $[D_6]$benzene): $\delta = 1.05$ (m, 18H, P*Me*$_3$), 1.35 (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 1.40 (t, $J = 7.6$ Hz, 6H, CH_2*Me*), 2.44 ppm (q, $J = 7.6$ Hz, 4H, C*H*$_2$Me). $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$benzene): $\delta = -3.48$ (t, $J = 31.8$ Hz, 2P, *P*Me$_3$), 14.0 ppm (t, $J = 31.8$ Hz, 2P, *P*Me$_3$); elemental analysis calcd (%) for $C_{18}H_{46}O_4P_4Ru$ (551.52): C 39.20, H 8.41; found: C 38.79, H 7.96.

$[cis\text{-}Ru\{OC(O)CH_2CHMe_2\}_2(PMe_3)_4]$ (**2 e**): 70%; ^1H NMR (400 MHz, $[D_6]$benzene): $\delta = 1.0$–1.2 (m, 4H, C*H*$_2$), 1.10 (m, 18H, P*Me*$_3$), 1.30 (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 1.43 (d, $J = 6.9$ Hz, 12H, CH*Me*$_2$), 2.68 ppm (sept, $J = 6.9$ Hz, 2H, C*H*Me$_2$); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$benzene): $\delta = -4.35$ (t, $J = 31.6$ Hz, 2P, *P*Me$_3$), 13.84 ppm (t, $J = 31.6$ Hz, 2P, *P*Me$_3$); elemental analysis calcd (%) for $C_{20}H_{50}O_4P_4Ru$ (579.57): C 41.45, H 8.70; found: C 41.43, H 8.63.

$[cis\text{-}Ru\{OC(O)Ph\}_2(PMe_3)_4]$ (**2 f**): 54%; ^1H NMR (400 MHz, $[D_6]$benzene): $\delta = 1.06$ (m, 18H, P*Me*$_3$), 1.36 (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 7.22 (t, $J = 7.3$ Hz, 2H, *para*-Ph), 7.36 (t, $J = 7.3$ Hz, 4H, *meta*-Ph), 8.72 ppm (dd, $J = 6.9$, 1.4 Hz, 4H, *ortho*-Ph); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$benzene): $\delta = -2.61$ (t, $J = 31.6$ Hz, 2P, P*Me*$_3$), 14.71 ppm (t, $J = 31.6$ Hz, 2P, P*Me*$_3$); IR (KBr): $\tilde{\nu} = 3036$ (w), 3016 (w),

2975 (m), 2913 (s), 1604 (vs), 1569 (vs), 1425 (m), 1366 (vs), 1337 (vs), 1300 (m), 1275 (m), 1167 (w), 1062 (w), 1024 (w), 975 (sh), 943 (vs), 855 (m), 832 (w), 714 (vs), 668 cm^{-1} (s).

[*fac*-Ru{OC(O)CMe=CH_2-κ^1O}$_2$(PMe_3)$_3$(H_2O)] (**3 a**): (Method A): Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (572.3 mg, 1.814 mmol) was treated with PMe_3 (740 μL, 7.28 mmol) and then methacrylic acid (306 μL, 3.62 mmol) and distilled water (33 μL, 1.8 mmol) at 50 °C for 48 h. The resulting white precipitate was washed with hexane (3× 20 mL), and the crude product was dried under reduced pressure to give **3 a** as an almost pure white powder in 84% yield (789.1 mg, 1.525 mmol). The powder was recrystallized from THF/hexane to produce pale-yellow microcrystals of **3 a** in 58% yield (544.8 mg, 1.053 mmol).

Method B: Complex **5 a** (12.2 mg, 0.0244 mmol) was treated with water (0.5 μL, 0.03 mmol) in [D_6]benzene at RT. Complex **3 a** was immediately formed in quantitative yield.

^{1}H NMR (300 MHz, [D_6]benzene): δ = 1.05 (br s, 27 H, P*Me*$_3$), 2.09 (br s, 6 H, CH_2=C*Me*CO_2), 5.25 (t, *J* = 1.8 Hz, 2 H, *C*H_2=$CMeCO_2$), 6.22 (d, *J* = 2.7 Hz, 2 H, *C*H_2=$CMeCO_2$), 10.3 ppm (br s, 2 H, *H*$_2$O); ^{31}P{^{1}H} NMR (122 MHz, [D_6]benzene): δ = 25.9 (br d, *J* = 38 Hz, 2 P, *P*Me_3), 28.0 ppm (br t, *J* = 38 Hz, 1 P, *P*Me_3); IR (KBr): $\tilde{\nu}$ = 3000–2700 (br), 1565 cm^{-1}.

[*fac*-Ru{OC(O)Ph-κ^1O}$_2$(PMe_3)$_3$(H_2O)] (**3 f**): Compound **4** (399.7 mg, 0.9812 mmol) was treated with benzoic acid (239.4 mg, 1.960 mmol) in methanol (4 mL) to give **5 f**. Afterwards, **5 f** was dissolved in benzene (15 mL) and water (78.0 μL, 4.33 mmol), and the mixture was heated at 60 °C for 42 h followed by removal of all volatile matter and then recrystallization of the residue from cold THF to produce pale-yellow microcrystals of **3 f** in 48% yield (258.8 mg, 0.4389 mmol). ^{1}H NMR (400 MHz, [D_6]benzene): δ = 1.03 (br s, 18 H, P*Me*$_3$), 1.20 (br s, 9 H, P*Me*$_3$), 7.11 (t, *J* = 7.3 Hz, 2 H, *para*-Ph), 7.17 (t, *J* = 7.1 Hz, 4 H, *meta*-Ph), 8.37 (d, *J* = 6.9 Hz, 4 H, *ortho*-Ph), 10.59 ppm (br s, 2 H, *H*$_2$O); ^{31}P{^{1}H} NMR (162 MHz, [D_6]benzene): δ = 25.8 (br d, *J* = 40.0 Hz, 2 P, *P*Me_3), 28.0 ppm (br, t, *J* = 40.0 Hz, 1 P, *P*Me_3). IR (KBr): $\tilde{\nu}$ = 3426 (br), 3200–2500 (br), 3061 (w), 2977 (w), 2911 (w), 1598 (vs), 1557 (vs), 1535 (s), 1415 (m), 1381 (vs), 1299 (m), 1280 (m), 1170 (w), 1065 (m), 1020 (w), 967 (m), 931 (vs), 851 (m), 826 (m), 724 (vs), 675 (m), 433 cm^{-1} (m).

Reactions of 4 with carboxylic acid in methanol

All reactions of **4** with carboxylic acids in methanol were carried out in a similar way. The details are described for the reaction with methacrylic acid as a typical example.

With methacrylic acid: Compound **4** (445.7 mg, 1.094 mmol) was placed in a Schlenk tube, and methanol (5 mL) was added by syringe. Methacrylic acid (185 μL, 2.19 mmol) was added by syringe, and the evolution of gas was observed. The mixture was stirred under reduced pressure for 5 min at RT, and then all volatiles were removed under reduced pressure to give of [Ru{OC(O)CMe=CH_2-κ^2O,O'}(PMe_3)$_4$]$^+$[CH_2=$CMeCO_2$]$^-$ (**5 a**) as a pale-yellow solid in 100% yield (627.9 mg, 1.091 mmol). ^{1}H NMR (300 MHz, [D_4]MeOH): δ = 1.43 (vt, *J* = 3.3 Hz, 18 H, mutually *trans*-P*Me*$_3$), 1.50 (m, 18 H, P*Me*$_3$), 1.87 (s, 3 H, *Me* in carboxylato anion), 1.89 (s, 3 H, *Me* in coordinated carboxylato), 5.18 (d, *J* = 1.8 Hz, 1 H, *C*H_2=$CMeCO_2$ *trans* to carbonyl in carboxylato anion), 5.49 (s, 1 H, *C*H_2=$CMeCO_2$ *trans* to carbonyl in coordinated carboxylato), 5.70 (s, 1 H, *C*H_2=$CMeCO_2$ *cis* to carbonyl in carboxylato anion), 5.98 (s, 1 H, *C*H_2=$CMeCO_2$ *cis* to carbonyl in coordinated carboxylato); ^{31}P{^{1}H} NMR (122 MHz, [D_4]MeOH): δ = −1.08 (t, *J* = 30.4 Hz, 2 P), 22.29 ppm (t, *J* = 30.4 Hz, 2 P); IR (KBr): $\tilde{\nu}$ = 3093 (w), 2974 (m), 2914 (m), 1695 (w), 1643 (m), 1597 (vs), 1429 (s), 1336 (vs), 1298 (s), 1279 (s), 943 (vs), 856 (s), 831 (s), 714 (vs), 665 (s), 620 (s), 600 (s), 521 cm^{-1} (w). The evolved gas was measured as follows: compound **4** (9.8 mg, 0.024 mmol) was placed in a Schlenk tube into which methanol (ca. 1.5 mL) was introduced by vacuum distillation. Onto the frozen solution was added methacrylic acid (12.0 μL, 0.142 mmol) under a N_2 atmosphere and then all materials were frozen by using liquid N_2. After evacuation of all gases at 77 K, the solid was dissolved under reduced pressure and stirred for 5 min. Afterwards, the solution was frozen again to measure the evolved gas by using a Töpler pump: H_2 (160% yield).

With acrylic acid: **5 b**: 98% yield. ^{1}H NMR (400 MHz, [D_4]MeOH): δ = 1.44 (vt, *J* = 3.4 Hz, 18 H, mutually *trans*-P*Me*$_3$), 1.50 (m, 18 H, P*Me*$_3$), 5.48 (dd, *J* = 10.1, 2.3 Hz, 1 H, *C*H_2=$CHCO_2$ *trans* to carbonyl in coordinated carboxylato), 5.80 (dd, *J* = 10.6, 1.6 Hz, 1 H, *C*H_2=$CHCO_2$ *trans* to carbonyl in carboxylato anion), 5.97 (dd, *J* = 17.4, 10.6 Hz, 1 H, CH_2=*C*HCO_2 in carboxylato anion), 6.01 (dd, *J* = 17.4, 2.3 Hz, 1 H, *C*H_2=$CHCO_2$ *cis* to carbonyl in coordinated carboxylato), 6.13 (dd, *J* = 17.4, 10.1 Hz, 1 H, CH_2=*C*HCO_2 *cis* to carbonyl in coordinated carboxylato), 6.23 ppm (dd, *J* = 17.4, 1.6 Hz, 1 H, *C*H_2=$CHCO_2$ *cis* to carbonyl in carboxylato anion); ^{31}P{^{1}H} (162 MHz, [D_4]MeOH): δ = −1.47 (t, *J* = 31.3 Hz, 2 P, *P*Me_3), 22.5 ppm (t, *J* = 31.3 Hz, 2 P, *P*Me_3).

With tiglic acid: **5 c**: 98%. ^{1}H NMR (300 MHz, [D_4]MeOH): δ = 1.41 (vt, *J* = 3.2 Hz, 18 H, P*Me*$_3$), 1.49 (m, 18 H, P*Me*$_3$), 1.69 (dq, *J* = 7.2, 1.1 Hz, 3 H, β-*Me* in carboxylato anion), 1.78 (m, 9 H, α-*Me* in coordinated carboxylato and carboxylato anion, and β-*Me* in coordinated carboxylato), 6.49 (qq, *J* = 6.9, 1.5 Hz, 1 H, *C*H*Me*=$CMeCO_2$ in carboxylato anion), 6.77 ppm (m, 1 H, *C*H*Me*=$CMeCO_2$ in coordinated anion); ^{31}P{^{1}H} NMR (121 MHz, [D_4]MeOH): δ = −0.98 (t, *J* = 30 Hz, 2 P, *P*Me_3), 21.92 ppm (t, *J* = 30 Hz, 2 P, *P*Me_3); IR (KBr): $\tilde{\nu}$ = 2976 (m), 2910 (s), 2856 (w), 1658 (s), 1577 (vs), 1562 (vs), 1429 (s), 1377 (vs), 1360 (vs), 1340 (vs), 1300 (vs), 1165 (s), 1078 (m), 1007 (w), 943 (vs), 854 (m), 810 (m), 752 (m), 721 (s), 663 (s), 561 (w), 453 cm^{-1} (m).

With propionic acid: **5 d**: 87%. ^{1}H NMR (400 MHz, [D_4]MeOH): δ = 1.08 (t, *J* = 7.6 Hz, 6 H, *Me* in carboxylato anion and coordinated carboxylato), 1.46 (vt, *J* = 3.2 Hz, 18 H, P*Me*$_3$), 1.48 (m, 18 H, P*Me*$_3$), 2.15 (q, *J* = 7.8 Hz, 2 H, *C*H_2Me in carboxylato anion), 2.26 ppm (q, *J* = 7.8 Hz, 2 H, *C*H_2Me in coordinated carboxylato). ^{31}P{^{1}H} NMR (162 MHz, [D_4]MeOH): δ = −1.85 (t, *J* = 30.4 Hz, 2 P, *P*Me_3), 22.1 ppm (t, *J* = 30.4 Hz, 2 P, *P*Me_3).

With isobutylic acid: **5 e**: 86%; ^{1}H NMR (400 MHz, [D_4]MeOH): δ = 1.08 (d, *J* = 6.9 Hz, 6 H, *Me* in carboxylato anion), 1.15 (d, *J* = 6.9 Hz, 6 H, *Me* in coordinated carboxylato), 1.46 (vt, *J* = 3.2 Hz, 18 H, P*Me*$_3$), 1.48 (m, 18 H, P*Me*$_3$), 2.35 (sept, *J* = 6.9 Hz, 1 H, *C*H*Me*$_2$ in carboxylato anion), 2.41 ppm (sept, *J* = 6.9 Hz, 1 H, *C*H*Me*$_2$ in coordinated carboxylato); ^{31}P{^{1}H} NMR (162 MHz, [D_4]MeOH): δ = −2.24 (t, *J* = 30.6 Hz, 2 P, *P*Me_3), 21.74 ppm (t, *J* = 30.6 Hz, 2 P, *P*Me_3).

With benzoic acid: **5 f**: 98%; ^{1}H NMR (400 MHz, [D_4]MeOH): δ = 1.43 (vt, *J* = 3.2 Hz, 18 H, P*Me*$_3$), 1.55 (m, 18 H, P*Me*$_3$), 7.47 (t, *J* = 7.1 Hz, 5 H, *meta*- and *para*-Ph in carboxylato anion and *meta*-Ph in coordinated carboxylato), 7.57 (t, *J* = 7.1 Hz, 1 H, *para*-Ph in coordinated carboxylato), 7.92 ppm (d, *J* = 7.1 Hz, 4 H, *ortho*-Ph in carboxylato anion and coordinate carboxylato); ^{31}P{^{1}H} NMR (162 MHz, [D_4]MeOH): δ = −1.15 (t, *J* = 30.3 Hz, 2 P, *P*Me_3), 22.41 ppm (t, *J* = 30.3 Hz, 2 P, *P*Me_3).

[Ru{OC(O)CMe=CH_2-κ^2O,O')(PMe_3)$_4$]$^+$$BPh_4^-$ (**6 a**): Compound **4** (469.5 mg, 1.144 mmol) was dissolved in methanol (5 mL) in a Schlenk tube. Methacrylic acid (195.0 μL, 2.308 mmol) was added by syringe, and the mixture was stirred for 5 min at RT. $KBPh_4$ (391.8 mg, 1.145 mmol) was added to the solution to give a suspen-

sion. Methanol (3 mL) was added to the suspension to give a solution, which was stirred for 10 min at RT. After removal of all volatile materials, the residual solid was extracted by acetone (total: 15 mL). The solution was concentrated to 3 mL under reduced pressure and filtered. The solution was stored in a freezer to give yellow columns of **6a** in 54% yield (617.7 mg, 0.6125 mmol). ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 1.44$ (vt, $J = 3.3$ Hz, 18H, P*Me*$_3$), 1.55 (m, 18H, P*Me*$_3$), 1.87 (s, 3H, *Me*), 5.50 (d, $J = 1.8$ Hz, 1H, C*H*$_2$=CMeCO$_2$ *trans* to carboxylato), 5.99 (s, 1H, C*H*$_2$=CMeCO$_2$ *cis* to carboxylato), 6.77 (t, $J = 7.1$ Hz, 4H, *para*-Ph), 6.92 (t, $J = 7.4$ Hz, 8H, *meta*-Ph), 7.32 ppm (m, 8H, *ortho*-Ph); ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]acetone): $\delta = -0.47$ (t, $J = 29.6$ Hz, 2P, *P*Me$_3$), 22.73 ppm (t, $J = 29.6$ Hz, 2P, *P*Me$_3$); IR (KBr): $\tilde{\nu} = 3053$ (m), 3035 (m), 2999 (m), 2981 (m), 2916 (w), 1639 (w), 1579 (m), 1504 (m), 1479 (m), 1427 (vs), 1371 (m), 1305 (s), 1286 (s), 1238 (w), 1132 (w), 1032 (m), 941 (vs), 864 (s), 730 (vs), 706 (vs), 671 (m), 611 cm^{-1} (vs); elemental analysis calcd (%) for $C_{40}H_{61}BO_2P_4Ru$ (809.69): C 59.34, H 7.59; found: C 58.89, H 8.08. The other cationic monocarboxylato complexes were prepared in a similar way.

[Ru{OC(O)Me=CHMe-κ^2*O*,*O*′}(PMe$_3$)$_4$]$^+$BPh$_4^-$ (**6c**): Yellow columns; 27%; ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 1.46$ (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 1.54 (m, 18H, P*Me*$_3$), 1.77 (br, 6H, α- and β-*Me*), 6.77 (t, $J = 6.9$ Hz, 5H, *para*-Ph and C*H*Me=CMeCO$_2$), 6.91 (t, $J = 7.4$ Hz, 8H, *meta*-Ph), 7.33 ppm (m, 8H, *ortho*-Ph); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone): $\delta = -0.34$ (t, $J = 30.4$ Hz, 2P, *P*Me$_3$), 22.38 ppm (t, $J = 30.4$ Hz, 2P, *P*Me$_3$). IR (KBr): $\tilde{\nu} = 3053$ (m), 3032 (m), 3000 (m), 2981 (m), 2913 (w), 1654 (m), 1579 (m), 1497 (m), 1429 (vs), 1380 (m), 1327 (w), 1306 (s), 1285 (s), 1174 (w), 1132 (m), 1032 (m), 943 (vs), 856 (m), 837 (m), 732 (s), 705 (s), 669 (s), 611 cm^{-1} (s); elemental analysis calcd (%) for $C_{41}H_{63}BO_2P_4Ru$ (823.71): C 59.78, H 7.71; found: C 59.34, H 7.75.

[Ru{OC(O)Ph-κ^2*O*,*O*′}(PMe$_3$)$_4$]$^+$PF$_6^-$ (**6f**): Recrystallized from THF/hexane. Pale-yellow columns; 82%; ^{1}H NMR (400 MHz, [D$_4$]MeOH): $\delta = 1.43$ (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 1.55 (m, 18H, P*Me*$_3$), 7.47 (t, $J = 7.1$ Hz, 2H, *meta*-Ph), 7.57 (t, $J = 7.1$ Hz, 1H, *para*-Ph), 7.94 ppm (t, $J = 7.1$ Hz, 2H, *ortho*-Ph); ^{31}P{^{1}H} NMR (162 MHz, [D$_4$]MeOH): $\delta = -1.15$ (t, $J = 30.3$ Hz, 2P, *P*Me$_3$), 22.41 ppm (t, $J = 30.3$ Hz, 2P, *P*Me$_3$); elemental analysis calcd (%) for $C_{19}H_{41}F_6O_2P_5Ru$ (671.46): C 33.99, H 6.15; found: C 34.40, H 6.42.

[*trans*-Ru{OC(O)CMe=CH$_2$-κ^2*O*,*O*′}$_2$(PPh$_3$)$_2$] (**7a**): RuCl$_2$(PPh$_3$)$_3$ (1.2910 g, 1.35 mmol) and sodium methacrylate (711.6 mg, 6.58 mmol) were dissolved in THF (10 mL) and heated to reflux for 2.5 h. After the reaction, the solution was filtered and all volatile materials were removed under reduced pressure. The resulting solid was washed with hexane and dried under reduced pressure to give **7a** as yellow powder in 50% yield (0.7129 g, 0.6737 mmol). ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta = 1.63$ (s, 6H, CH$_2$=C*Me*CO$_2$), 4.86 (s, 2H, C*H*$_2$=CMeCO$_2$), 5.94 (s, 2H, C*H*$_2$=CMeCO$_2$), 6.9 (m, 18H, *para*- and *meta*-Ph), 7.50 ppm (m, 12H, *ortho*-Ph); ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): $\delta = 67.42$ ppm (s); IR (KBr): $\tilde{\nu} = 1480$, 1432 cm^{-1}.

[*fac*-Ru{OC(O)CMe=CH$_2$-κ^1*O*}Cl(PPh$_3$)$_3$] (**8a**): RuCl$_2$(PPh$_3$)$_3$ (5.3954 g, 0.5631 mmol) and sodium methacrylate (608.3 mg, 5.629 mmol) were heated to reflux in *tert*-butyl alcohol (47 mL) for 1 h. The resulting brown solid was separated and washed with Et$_2$O, water, methanol, and then Et$_2$O. The brown solid was dried under reduced pressure to give **8a** in 94% yield (5.3230 g, 5.2783 mmol). ^{1}H NMR (400 MHz, [D]chloroform): $\delta = 1.31$ (s, 3H, CH$_2$=C*Me*CO$_2$), 4.75 (s, 1H, C*H*$_2$=CMeCO$_2$), 5.33 (s, 1H, C*H*$_2$=CMeCO$_2$), 6.8–7.4 ppm (m, 45H, P*Ph*$_3$); ^{31}P{^{1}H} NMR (162 MHz, [D]chloroform): $\delta = 7.33$ (d, $J = 27.7$ Hz, 2P, *P*Ph$_3$), 28.25 ppm (t, $J = 27.7$ Hz, 1P, *P*Ph$_3$).

[*fac*-Ru{OC(O)Ph-κ^1*O*}Cl(PPh$_3$)$_3$] (**8f**): This compound was prepared in a similar way to **8a**. 80%; ^{1}H NMR (400 MHz, [D]chloroform): $\delta =$ 6.8–7.4 ppm (m, OC(O)*Ph* and P*Ph*$_3$); ^{31}P{^{1}H} NMR (162 MHz, [D]chloroform): $\delta = 29.29$ (d, $J = 26.9$ Hz, 2P, *P*Ph$_3$), 50.75 ppm (d, $J = 26.9$ Hz, 1P, *P*Ph$_3$).

[*mer*-Ru{OC(O)CMe=CH$_2$-κ^1*O*}{OC(O)CMe=CH$_2$-κ^2*O*,*O*′)(TRIPHS)] (**9a**): Complex **7a** (175.8 mg, 0.2209 mmol) was treated with TRIPHOS (145.8 mg, 0.2727 mmol) in THF at RT for 3 h. Then all volatile materials were removed, and the resulting yellow powder was recrystallized from THF/hexane to give yellow microcrystals of **9a** in 22% yield (31.0 mg, 0.0478 mmol). ^{1}H NMR (400 MHz, [D$_8$]toluene, −80 °C): $\delta = 1.53$ (s, 3H, CH$_2$=C*Me*CO$_2$), 1.72 (s, 3H, CH$_2$=C*Me*CO$_2$), 1.8–2.5 (m, 8H, PC$_2$*H*$_4$P), 4.98 (s, 1H, C*H*$_2$=CMeCO$_2$), 5.0 (s, 1H, C*H*$_2$=CMeCO$_2$), 5.3 (s, C*H*$_2$=CMeCO$_2$), 6.81 (m, 6H, *Ph*), 7.3–7.5 (m, 15H, *Ph*), 7.68 (m, 2H, *Ph*), 7.86 ppm (m, 2H, *Ph*); ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]toluene, −80 °C): $\delta = 49.90$ (br, 2P, *P*Ph$_2$), 113.64 (br, 1P, *P*Ph); ^{1}H NMR (400 MHz, [D$_8$]toluene, 95 °C): $\delta = 1.27$ (s, 3H, CH$_2$=C*Me*CO$_2$), 1.53 (s, 3H, CH$_2$=C*Me*CO$_2$), 2.34 (m, 2H, PC$_2$*H*$_4$P), 2.48 (m, 2H, PC$_2$*H*$_4$P), 2.78 (m, 2H, PC$_2$*H*$_4$P), 3.20 (m, 1H, PC$_2$*H*$_4$P), 4.61 (s, 1H, C*H*$_2$=CMeCO$_2$), 4.90 (s, 1H, C*H*$_2$=CMeCO$_2$), 5.19 (s, 1H, C*H*$_2$=CMeCO$_2$), 5.84 (s, 1H, C*H*$_2$=CMeCO$_2$), 6.89 (m, 6H, *Ph*), 6.96 (m, 4H, *Ph*), 7.11 (m, 3H, *Ph*), 7.16 (m, 5H, *Ph*), 7.37 (m, 3H, *Ph*), 7.98 ppm (m, 4H, *Ph*); ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]toluene, 95 °C): $\delta = 57.11$ (br, 2P, *P*Ph$_2$), 133.56 ppm (br, 1P, *P*Ph); elemental analysis calcd (%) for $C_{42}H_{43}O_4P_3Ru$ (805.78): C 62.60, H 5.38; found: C 62.52; H 5.89.

[*cis*-Ru{OC(O)CMe=CH$_2$-κ^1*O*}Cl(PMe$_3$)$_4$] (**10a**): Complex **8a** (5.3230 g, 5.2783 mmol) was dissolved in hexane (40 mL), and PMe$_3$ (2.60 mL, 25.6 mmol) was added into the solution. After the solution was heated to reflux for 1 h, it was stored at RT to give pale-yellow crystals. The resulting crystals were separated, washed with hexane, and dried under vacuum to give **10a** in 72% yield (2.0125 g, 3.8267 mmol). ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta = 1.01$ (d, $J = 7.8$ Hz, 9H, P*Me*$_3$), 1.20 (d, $J = 8.7$ Hz, 9H, P*Me*$_3$), 1.39 (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 2.29 (s, 3H, CH$_2$=C*Me*CO$_2$), 5.35 (s, 1H, C*H*$_2$=CMeCO$_2$), 6.34 ppm (s, 1H, C*H*$_2$=CMeCO$_2$); ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): $\delta = -4.70$ (dd, $J = 33.6$, 29.5 Hz, 2P, *P*Me$_3$), 11.0 (dt, $J = 37.7$, 29.5 Hz, 1P, *P*Me$_3$), 15.6 ppm (dt, $J = 37.7$, 33.6 Hz, 1P, *P*Me$_3$); IR (KBr): $\tilde{\nu} = 3162$ (w), 3083 (w), 2975 (s), 2908 (s), 1638 (m), 1588 (vs), 1439 (sh), 1421 (s), 1392 (m), 1359 (vs), 1297 (s), 1278 (s), 1233 (s), 998 (sh), 941 (vs), 857 (s), 828 (s), 718 (s), 666 (s), 616 cm^{-1} (m).

[*cis*-Ru{OC(O)Ph-κ^1*O*}Cl(PMe$_3$)$_4$] (**10f**): This compound was prepared in the same way as **10a**. 84%; ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta =$ 1.03 (d, $J = 7.8$ Hz, 9H, P*Me*$_3$), 1.23 (d, $J = 8.7$ Hz, 9H, P*Me*$_3$), 1.38 (vt, $J = 3.2$ Hz, 18H, P*Me*$_3$), 7.20 (t, $J = 7.3$ Hz, 1H, *para*-Ph), 7.30 (t, $J =$ 7.3 Hz, 2H, *meta*-Ph), 8.63 ppm (d, $J = 7.3$ Hz, 2H, *ortho*-Ph); ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): $\delta = -4.70$ (dd, $J = 33.3$, 29.5 Hz, 2P, *P*Me$_3$), 10.9 (dt, $J = 37.2$, 29.5 Hz, 1P, *P*Me$_3$), 15.4 ppm (dt, $J = 37.2$, 33.2 Hz, 1P, *P*Me$_3$); IR (KBr): $\tilde{\nu} = 3047$ (w), 3016 (sh), 2973 (s), 2910 (s), 1607 (vs), 1567 (vs), 1438 (sh), 1419 (m), 1364 (vs), 1298 (s), 1271 (m), 1170 (w), 1062 (w), 1026 (m), 951 (vs), 860 (m), 834 (m), 724 (s), 665 cm^{-1} (s).

[*cis*-Ru{OC(O)CMe=CH$_2$-κ^1*O*}$_2$(DMPE)$_2$] (**11a**): Complex **5a** (169.5 mg, 0.2966 mmol) was dissolved in benzene (3 mL), and DMPE (92.0 μL, 0.551 mmol) was added. The reaction mixture was heated at 70 °C for 12 h, and then all volatile materials were removed under reduced pressure. The residue was extracted with benzene, and the volatile materials were removed again under reduced pressure to give **11a** as a white solid in 45% yield (70.2 mg, 0.123 mmol). ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 0.66$ (d, $J = 7.2$ Hz, 6H, P*Me*$_2$),

1.03 (d, $J=9.3$ Hz, 6H, PMe_2), 1.1–1.4 (br, 8H, PC_2H_4P), 1.63 (vt, $J=2.9$ Hz, 6H, PMe_2), 1.89 (vt, $J=4.1$ Hz, 6H, PMe_2), 2.19 (m, 6H, CH_2=C$Me$$CO_2$), 5.27 (q, $J=1.6$ Hz, 2H, CH_2=$CMeCO_2$ *trans* to carbonyl), 6.21 ppm (m, 2H, CH_2=$CMeCO_2$); $^{31}P\{^1H\}$ NMR (121 MHz, [D_6]benzene): $\delta=38.10$ (t, $J=25$ Hz, 2P, PMe$_2$), 54.15 ppm (t, $J=25$ Hz, 2P, PMe$_2$); IR (KBr): $\tilde{\nu}=3083$ (w), 2964 (m), 2943 (m), 2908 (s), 1641 (sh), 1589 (vs), 1450 (sh), 1414 (s), 1392 (s), 1354 (vs), 1296 (m), 1278 (m), 1265 (m), 1228 (s), 1074 (m), 1022 (w), 931 (vs), 893 (sh), 835 (s), 796 (sh), 735 (s), 702 (s), 648 (m), 609 (m), 455 cm^{-1} (m).

Reactions with PMe_3

Phosphabetaine **13a**: PMe_3 (460.0 μL, 4.523 mmol) was treated with methacrylic acid (250.0 μL, 2.959 mmol) in methanol (5 mL) at 50 °C for 4 h. The removal of all volatile materials at 100 °C under reduced pressure produced pure $Me_3P^+CH_2CHMeCO_2^-$ (**13a**) in 94% yield (453.0 mg, 2.793 mmol). ^1H NMR (400 MHz, [D_4]MeOH): $\delta=1.27$ (dd, $J=7.0$, 1.9 Hz, 3H, CHMe), 1.84 (d, $J=14.6$ Hz, 9H, PMe_3), 2.13 (ddd, $J=15.0$, 13.5, 3.4 Hz, 1H, CH_2), 2.44 (ddd, $J=15.0$, 13.5, 11.0 Hz, 1H, CH_2), 2.58 ppm (ddq, $J=11.0$, 7.0, 3.4 Hz, 1H, CHMe); $^{31}P\{^1H\}$ NMR (162 MHz, [D_4]MeOH): $\delta=26.6$ ppm (s, PMe$_3$); IR (KBr): $\tilde{\nu}=3423$ (br), 2970 (m), 2930 (m), 2909 (m), 2871 (w), 1592 (vs), 1460 (w), 1403 (m), 1386 (m), 1358 (m), 1290 (m), 1178 (m), 1119 (m), 1077 (w), 1033 (w), 998 (s), 970 (s), 903 (m), 887 (m), 849 (m), 808 (w), 778 (m), 754 (w), 658 (w), 571 (m), 541 cm^{-1} (w).

Reaction of **9a** with PMe_3: Complex **9a** (14.1 mg, 0.0175 mmol) was reacted with PMe_3 (9.2 μL, 0.088 mmol) in benzene at 70 °C for 57 h to give a mixture of **15a** (48%) and **16a** (22%). **15a**: ^1H NMR (400 MHz, [D_6]benzene): $\delta=0.74$ (d, $J=8.7$ Hz, 9H, PMe_3), 0.8–2.8 (m, 8H, PC_2H_4P), 1.87 (s, 3H, CH_2=C$Me$$CO_2$), 5.06 (s, 1H, C$H_2$=$CMeCO_2$), 6.01 (s, 1H, C$H_2$=$CMeCO_2$), 6.64 (m, 1H, C_6H_4), 6.8–7.5 (m, 20H, aromatic), 7.75 (m, 1H, C_6H_4), 8.00 (m, 1H, C_6H_4), 8.27 ppm (m, 1H, C_6H_4); $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]benzene): $\delta=-1.26$ (dt, $J=321.3$, 31.8 Hz, 1P, PMe$_3$), 39.60 (ddd, $J=321.7$, 21.7, 14.0 Hz, 1P, PPhC$_6$H$_4$), 67.03 (ddd, $J=32.1$, 22.5, 16.3 Hz, 1P, PPh$_2$), 96.21 ppm (dt, $J=32$, 15 Hz, 1P, PPh). **16a**: ^1H NMR (400 MHz, [D_6]benzene): $\delta=1.19$ (d, $J=7.3$ Hz, 9H, PMe_3), 1.96 (s, 3H, CH_2=C$Me$$CO_2$), 5.11 (s, 1H, C$H_2$=$CMeCO_2$), 6.15 ppm (s, 1H, C$H_2$=$CMeCO_2$), other signals were overlapped with major resonances; $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]benzene): $\delta=-5.08$ (dt, $J=299.2$, 25.6 Hz, 1P, PMe$_3$), 46.10 (dd, $J=25.2$, 4.7 Hz, 1P, PPhC$_6$H$_4$), 80.95 (dd, $J=23.6$, 13.2 Hz, 1P, PPh$_2$), 95.89 ppm (ddd, $J=299.8$ Hz, 13.2, 4.7 Hz, 1P, PPh).

Reaction of **11a** with PMe_3: Complex **11a** (10.4 mg, 0.0182 mmol) and a flame-sealed capillary that contained a [D_6]benzene solution of PPh_3 were placed in an NMR tube into which [D_6]benzene (485.0 μL) and PMe_3 (19.0 μL, 0.187 mmol) were added. The solution was heated at 70 °C for 3.8 h to produce [Ru{OC(O)CMe=CH_2-κ^1O}(DMPE)$_2$(PMe_3)]$^+$[CH_2=$CMeCO_2$]$^-$ (**14a**) in 41% yield (conversion of **11a**: 41%). This compound was characterized by ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR (164 MHz, [D_6]benzene): $\delta=-8.2$ (dtd, $J=256.4$, 35.6, 29.8 Hz, 1P, PMe$_3$), 28.8 (dtd, $J=269.3$, 35.6, 13.5 Hz, 1P, P atom in DMPE *trans* to a DMPE P atom), 36–39 (m, 2P, DMPE), 45.4 ppm (tdd, $J=29.8$, 23.2, 13.5 Hz, 1P, P atom in DMPE *cis* to carboxylato).

Reaction of **3a** with PMe_3: Complex **3a** (7.1 mg, 0.014 mmol) was treated with PMe_3 (70.0 μL, 0.0688 mmol) in [D_6]benzene to give **1a** immediately in 40% yield. Further treatment at 70 °C for an hour produced **1a** quantitatively.

Equilibria

Equilibrium between **2a** and **12a**: Complex **2a** (10.8 mg, 0.0188 mmol) was placed in an NMR tube, and [D_6]benzene (600 μL) was introduced by syringe. The probe temperature of the NMR was increased from 20 to 70 °C. In these spectra, signals that arose from newly formed **12a** and **3a** overlapped and were calculated as a RuP_3 species. K_1(M) = [RuP_3][PMe_3]/[**2a**] = 0.050 (293 K), 0.0073 (303 K), 0.017 (313 K), 0.021 (323 K), 0.035 (333 K), 0.058 (343 K).

Equilibrium between **5a** and **1a** in DMSO: Complex **5a** (4.7 mg, 0.0082 mmol; 9.6 mg, 0.017 mmol; 18.4 mg, 0.0320 mmol) was dissolved in [D_6]DMSO (600 μL) and heated at 70 °C to reach equilibrium. A flame-sealed capillary that contained $P(OPh)_3$ in [D_6]benzene was employed. K_3 = [**1a**][methacrylic acid]/[cation of **5a**][methacrylato anion] = 0.066 (0.014 M), 0.088 (0.028 M), 0.108 (0.0533 M).

H–D exchange reactions

Stoichiometric H–D exchange reaction of **5a**: Complex **5a** (13.8 mg, 0.0236 mmol) was dissolved in [D_4]MeOH and heated at 50 °C for 11 h. The peak of the methylene proton *cis* to the carbonyl group decreased in the ^1H NMR spectrum in 91 at% D.

Stoichiometric H–D exchange reaction of carboxylato ligands: The stoichiometric H–D exchange reaction was carried out as follows. Compound **4** (ca. 10 mg) was placed in an NMR tube into which [D_4]MeOH was introduced. Then, a carboxylic acid was added by syringe and the reaction system was heated at 50 °C.

Stoichiometric H–D exchange reaction of **3a**: Complex **3a** (9.6 mg, 0.019 mmol) was placed in an NMR tube into which [D_4]MeOH (550 μL) was added. The mixture was heated at 50 °C for 6.8 h, which resulted in the decrease of the methylene resonance *cis* to the carbonyl group in 96 at% D.

Catalytic H–D exchange reaction of methacrylic acid: Complex **5a** (11.4 mg, 0.0198 mmol) was placed in an NMR tube into which [D_4]MeOH (600 μL) and methacrylic acid (16.7 μL, 0.198 mmol) were added. The solution was heated at 50 °C for 23 h, which resulted in the complete disappearance of the methylene resonance *cis* to the carbonyl group. $^{13}C\{^1H\}$ NMR (100 MHz, [D_4]MeOH): $\delta=$ 18.51 (s, CHD=C$Me$$CO_2$D), 125.29 (t, $J=10.1$ Hz, CHD=$CMeCO_2$D), 138.55 (s, CHD=$C$$MeCO_2$D), 171.23 ppm (s, CHD=CMe$C$$O_2$D). After the removal of [D_4]MeOH, the ^2H NMR spectrum was measured in methanol. $^2H\{^1H\}$ NMR (61.4 MHz, methanol): $\delta=6.06$ ppm (s, CHD=CO_2D).

Catalytic H–D exchange reaction of carboxylic acids: [*cis*-RuH_2(PMe_3)$_4$] (ca. 10 mg) was dissolved in [D_4]MeOH into which carboxylic acid (10 equiv) were added. The solution was heated to at 50 °C for 24–56 h.

Crystallographic analysis

A Rigaku AFC7R-Mercury II diffractometer with graphite-monochromated MoK_α radiation ($\lambda=0.71075$ Å) was used for data collection at 200.0 K. A selected crystal was mounted on a glass capillary and protected with Paraton N oil. The structures were solved by direct methods (SIR 92)[31] and refined by a full-matrix least-squares procedure by using SHELXL-97 programs[32] with CrystalStructure version 4.1.[31] The structures were depicted by ORTEP-III[33] and POV-Ray[34] for Windows. Crystallographic data [CCDC 900814 for *cis*-Ru(OC(O)CMe=CH-κ^2O,C)(PMe_3)$_4$ (**1a**), CCDC 900816 for *cis*-Ru(O-C(O)C_6H_4-κ^2O,C)(PMe_3)$_4$ (**1f**), CCDC 900815 for *cis*-Ru(OC(O)CMe=

CH_2-$\kappa^1O)_2(PMe_3)_4$ (**2a**), CCDC 900817 for *cis,fac*-Ru(OC(O)Ph-$\kappa^1O)_2$-$(PMe_3)(H_2O)$ (**3f**), CCDC 900818 for $[Ru(OC(O)CMe=CH_2$-$\kappa^2O,O')(PMe_3)_4]^+[BPh_4]^-$ (**6a**), and CCDC 900819 for *fac*-Ru(O-C(O)CMe=CH_2-$\kappa^1O)$(OC(O)CMe=CH_2—$\kappa^2O,O')$(TRIPHOS) (**9a**)] can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ul/data_request/cif.

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