Rhodium-Catalyzed Nondecarbonylative Addition Reaction of $ClCOCOOC_2H_5$ to Alkynes

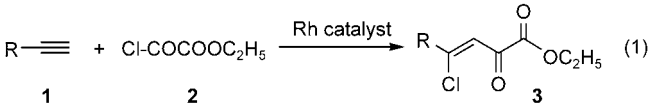
Ruimao Hua,[a] Shun-ya Onozawa,[b] and Masato Tanaka*[c]

Abstract: Addition of ethoxalyl chloride (ClCOCOOEt) to terminal alkynes at 60 °C in the presence of a rhodium(I)–phosphine complex catalyst chosen from a wide range affords 4-chloro-2-oxo-3-alkenoates regio- and stereoselectively. Functional groups such as chloro, cyano, alkoxy, siloxy, and hydroxy are tolerated. The oxidative addition of ethoxalyl chloride to $[RhCl(CO)(PR_3)_2]$ proceeds readily at 60 °C or room temperature and gives $[RhCl_2(COCOOEt)(CO)(PR_3)_2]$ (PR_3 = PPh_2Me, $PPhMe_2$, PMe_3) complexes in high yields. The structure of $[RhCl_2(COCOOEt)(CO)(PPh_2Me)_2]$ was confirmed by X-ray crystallography. Thermolysis of these ethoxalyl complexes has revealed that those ligated by more electron-donating phosphines are fairly stable against decarbonylation and reductive elimination. $[RhCl_2(COCOOEt)(CO)(PPh_2Me)_2]$ reacts with 1-octyne at 60 °C to form ethyl 4-chloro-2-oxo-3-decenoate. The catalysis is therefore proposed to proceed by oxidative addition of ethoxalyl chloride, insertion of an alkyne into the Cl–Rh bond of the resulting intermediate, and reductive elimination of alkenyl-COCOOEt.

Keywords: acid halides · addition · alkynes · homogeneous catalysis · rhodium

Introduction

Addition of inter-heteroatom σ bonds to unsaturated compounds[1] furnishes useful products that have two heteroatom–carbon bonds, which can be transformed independently in syntheses. In most synthetic applications, however, the heteroatoms introduced to the unsaturated compounds are eventually replaced by organic entities. Accordingly, heteroatom–carbon bond addition reactions are more advantageous and desirable if they are selective. In view of the synthetic versatility of carbonyl functionalities, addition reactions of E–COX bonds (E = heteroatom; COX = ester or amide functionality) are particularly useful. Such reactions that have been made possible[2] include rhodium- or nickel-catalyzed stannylamidation ($R_3Sn–CONR_2$), rhodium-catalyzed chloroesterification (Cl–COOR), and palladium-catalyzed thioesterification (RS–COOR). While studying the chloroesterification, we were surprised to find that Rh–COCOOR species were quite stable against decarbonylation. During previous mechanistic studies of the palladium-catalyzed double carbonylation of aromatic halides affording α-oxo acid derivatives, we and others learned that M–COCOAr species are extremely unstable in respect of decarbonylation even at low temperatures, and concluded that these species are not involved in the double carbonylation catalysis.[3] Pd–COCOOMe species are also known to undergo decarbonylation readily at room temperature.[4] We were therefore encouraged by the unique and unexpected stability of Rh–COCOOR species to explore catalytic addition reactions of Cl–COCOOR with unsaturated organic compounds. We now report the efficient CO-retentive addition of Cl–COCOOEt **2** to alkynes **1** affording γ-chloro-α-oxo-β,γ-unsaturated esters,[5] catalyzed by rhodium complexes [Eq. (1)]. The products are expected to allow a wide range of synthetic elaborations, in view of the high reactivities of γ-chloro, α-oxo, and β,γ-alkene linkages. For instance, γ-organo-α-oxo-β,γ-unsaturated esters, which have proven to



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be useful intermediates in organic synthesis,[6] can be readily synthesized by metal-catalyzed substitution of the γ-chloro group, while their synthesis by conventional methods requires multistep processes.[7]

Results and Discussion

The reaction of 1-octyne to optimize the conditions: In a representative experiment, a solution of [Rh(acac)(CO)(PPh$_3$)] (0.025 mmol), ethoxalyl chloride **2** (0.5 mmol) and 1-octyne **1a** (1.0 mmol) in benzene (0.5 mL) was heated at 60 °C for 20 h. The addition reaction proceeded highly stereo- and regioselectively to give ethyl (*Z*)-4-chloro-2-oxo-3-decenoate **3a** and its regioisomer **3′a** in 91 % total yield with 97 % regioselectivity for **3a** [Eq. (2)] (Table 1, entry 1).

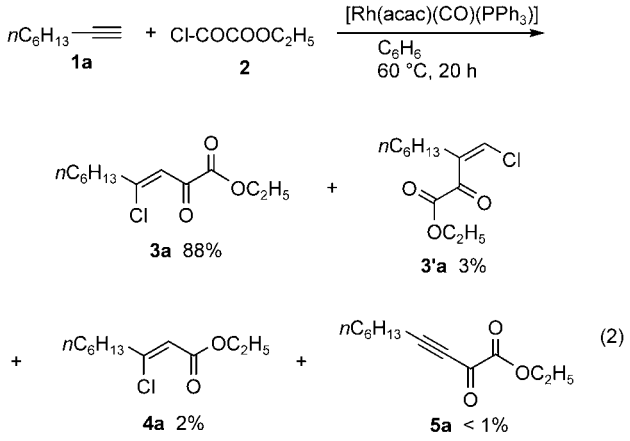


Table 1. Addition to 1-octyne (**1a**) of ethoxalyl chloride (**2**) in the presence of [Rh(acac)(CO)(PPh$_3$)].[a]

Entry	**1a** [mmol]	**2** [mmol]	Yield[b] [%]	
			3a + **3′a**[c]	**4a**
1	1.0	0.5	91 (97)	2
2	0.75	0.5	81 (97)	5
3	0.5	0.5	57 (97)	8
4	0.5	0.75	71 (97)	12

[a] The reactions were carried out at 60 °C for 20 h in 0.5 mL of benzene using 5 mol % catalyst. [b] Yields, relative to the quantity of the limiting starting material (0.5 mmol of **1a** or **2**), were determined by GC. [c] Total yield of **3a** and **3′a**. Values in parentheses are the regioselectivities of **3a** [100 × **3a**/(**3a** + **3′a**)].

Besides **3a** and **3′a**, ethyl (*Z*)-3-chloro-2-nonenoate **4a** (2 %) and ethyl 2-oxo-3-decynoate **5a** (< 1 %) were also detected. The reaction could take place almost as well, even under air; **3a** was obtained in 83 % yield with a similar regioselectivity, but no addition reaction was observed in the absence of the rhodium catalyst.

The structure of **3a** was determined on the basis of its spectroscopic data, which included ^{13}C NMR signals assignable to *C*OCOOC$_2$H$_5$ (δ = 180.2 ppm) and CO*C*OOC$_2$H$_5$ (δ = 162.0 ppm), its intense IR absorption bands at 1734 and 1705 cm^{-1}, its MS, and its elemental analysis. An NOE experiment, which displayed a 9 % enhancement of the olefinic proton signal at δ = 6.95 ppm upon irradiation of the allylic protons, confirmed the *Z* stereochemistry (*cis* addition). The structure of **3** was further confirmed unequivocally by X-ray crystallography in the case of **3u** (vide infra). MS analysis of by-product **3′a** displayed its molecular ion, but no further characterization could be made because it was formed in low yield. However, the structures of **3′e**, **3′h**, and **3′s** were confirmed not only by MS but also by ^{1}H and ^{13}C NMR spectroscopy. The structure of by-products **4a** and **5a** was characterized by comparing their MS and NMR spectroscopic data with those of separately prepared authentic samples.[8]

We normally used a twofold excess of the alkyne, as for the reaction of Table 1, entry 1. Although oligomerization can occur as a side reaction, the necessity for an excess of **1a** in entry 1 was not associated with the possible oligomerization. In practice, approximately 0.5 mmol of **1a** remained unchanged after the reaction of entry 1, suggesting that oligomerization of the alkyne was not extensive. However, the presence of excess alkyne appeared to be beneficial to promote the desired reaction and to suppress the formation of **4a**; for instance, when the quantity of 1-octyne was reduced to 0.75 mmol (Table 1, entry 2) and further to 0.5 mmol (Table 1, entry 3), the total yield of **3a** and **3′a** decreased to 81 and 57 % respectively, whereas that of **4a** increased slightly to 5 and 8 %. When **2** was used in an excess of **1a**, formation of **4a** was more extensive. The formation of **4a** indicates that a slight decarbonylation also occurs under these conditions. We presume that if the insertion of **1a** does not proceed as soon as oxidative addition of ClCOCOOEt has taken place, the intermediate undergoes slight decarbonylation, and that the presence of an excess of **1a** minimizes the decarbonylation. It appears reasonable that an elevated reaction temperature would enhance the decarbonylation. Indeed, from reaction at 80 °C for 10 h (under otherwise the same conditions as in entry 1), a more significant amount of **4a** was formed (9 %) at the expense of the yield of **3a** (85 %). However, no substantial change was observed in the yield of **5a** when the reaction temperature was raised.

Any effect of the solvent on the reactivity was only marginal; the yield of **3a** decreased in the order toluene (88 %) > 1,2-dichloroethane (80 %) > dibutyl ether (73 %).

In the previously reported chloroesterification of alkynes catalyzed by a rhodium complex, the nature of the phosphine ligand and the ligand/Rh ratio affected the yield and regioselectivity significantly,[2r] and the chloroesterification reaction required heating at 110 °C to proceed smoothly. However, various rhodium–phosphine complexes ligated by one or two phosphines performed rather similarly in the reaction of **1a** with **2**; the yield ranged from 74 to 92 % (Table 2, entries 1–12). Even the use of [RhCl(cod)(PMe$_3$)], which had a very low activity in the chloroesterification (at 110 °C), resulted in a respectable yield of 74 % (at 60 °C). In all these reactions the regioselectivity was consistently higher than 80 %. The modest sensitivity of the reaction per-

Table 2. Catalytic activity of rhodium complexes in the addition reaction of **1a** to **2**.[a]

Entry	Catalyst	Yield of **3a** + **3′a**[b] [%]	Recovery of **1a** [mmol]
1	[Rh(acac)(CO)(PPh_3)]	91 (97)	0.52
2	[Rh(acac)(CO)(PPh_2Me)]	92 (92)	0.42
3	[Cp*Rh(CO)(PPh_3)]	85 (>99)	n.d.[c]
4	[RhCl(cod)(PPh_3)]	85 (95)	0.51
5	[RhCl(cod)(PPh_2Me)]	90 (93)	0.40
6	[RhCl(cod)($PPhMe_2$)]	86 (92)	0.47
7	[RhCl(cod)(PMe_3)]	74 (85)	0.35
8	[RhCl(CO)(PPh_3)$_2$] (**6d**)	82 (81)	~0.50
9	[RhCl(CO)(PPh_2Me)$_2$] (**6a**)	85 (83)	~0.50
10	[RhCl(CO)($PPhMe_2$)$_2$] (**6b**)	81 (92)	~0.50
11[d]	[RhCl(CO)(dppf)]	83 (>99)	n.d.[c]
12	[RhCl(PPh_3)$_3$]	27 (20)	0.65
13[d]	[[RhCl(CO)$_2$]$_2$] + bisoxaz[e]	66 (99)	n.d.[c]
14	[$Rh_2Cl_2(CO)_4$]	48 (96)	0.4[f]
15	[$Rh_2(acac)_2(CO)_4$]	50 (92)	0.4[f]
16	[Cp*Rh(CO)$_2$]	31 (100)	n.d.[c]
17	[$Rh_2Cl_2(cod)_2$]	36 (89)	0.4[f]

[a] Unless otherwise noted, the reactions were carried out at 60 °C for 20 h, using 1.0 mmol of **1a** , 0.5 mmol of **2**, and 0.025 mmol (in respect of Rh) of catalyst in 0.5 mL benzene. [b] Total GC yield of **3a** + **3′a** based on the amount of **2** used. Values in parentheses are regioselectivities [100×**3a**/(**3a** + **3′a**)]. [c] Not determined. [d] Run in toluene. [e] bisoxaz = bis[(4*S*)-4-phenyl-2-oxazolin-2-yl]methane; Rh/bisoxaz = 1:1. [f] Trimers also were formed.

formance to the nature of the phosphine ligand and the high reactivity of ethoxalyl chloride as compared with chloroformate are presumably associated with the ease of oxidative addition of the Cl–COCOOEt bond, which is envisaged to be the initiation step in the catalytic cycle (vide infra).

In contrast to the mono- and bisphosphine–rhodium complexes, the Wilkinson catalyst, which has three phosphine groups, displayed much lower activity and selectivity (Table 2, entry 12). The catalyst comprising rhodium and chelating bis[(4*S*)-4-phenyl-2-oxozolin-2-yl]methane performed slightly less satisfactorily than the dppf complex (Table 2, entries 13 and 11). Phosphine-free rhodium complexes also promote the reaction with high regioselectivity (Table 2, entries 14–17), but the activity was lower than that of the complexes with only one phosphine ligand. MS analysis revealed that two isomeric octyne trimers were formed in entries 14, 15, and 17.[9] Other complexes such as [Pd(PPh_3)$_4$], [Pt(PPh_3)$_4$], [$RhH_2(CO)(PPh_3)_3$] and [$Co(CO)_3P$*i*Bu_3]$_2$ did not show any catalytic activity under similar conditions.

Scope and limitations of the catalytic reactions: The addition reaction can be applied to a variety of alkynes (Table 3). Most aliphatic alkynes, including 3,3-dimethyl-1-butyne, having a sterically demanding substituent react readily to afford the respective adducts in high yields with high regioselectivities (Table 3, entries 1–4). The reaction of propyne (at atmospheric pressure in a balloon) is rather exceptional in that it is low-yielding and less regioselective, affording a 56:44 isomeric ratio in 45% total yield (Table 3, entry 5). The low yield is associated with extensive oligomerization.[10]

The tolerance of the addition reaction to a wide variety of functional groups is seen clearly in entries 6–13. Thus, chlorinated alkynes having chlorine bonded to a carbon remote from the alkyne linkage react normally in high yields with nearly 100% regioselectivities without interference by the chlorine (Table 3, entries 6, 7). As expected, however, the propargyl chloride reaction gave a complicated mixture, in which two regioisomeric adducts **3h** and **3′h** were formed in only 38% total yield (**3h**/**3′h** = 66:34; Table 3, entry 8) together with other unidentified by-products. Alkynes substituted by cyano, ester, and ether groups also reacted normally (Table 3, entries 9–11), although the product obtained from the reaction of methyl propargyl ether appeared to decompose even at room temperature, resulting in a low yield (Table 3, entry 12). Most notable was the reaction of 3-methyl-1-butyn-3-ol; ester formation between the hydroxy group and ethoxalyl chloride was negligible and the desired adduct could be obtained selectively in a high yield (Table 3, entry 13).

The alkene linkage is totally inert under these conditions. Accordingly the enyne starting materials, such as ethynylcyclohexene and 2-methylbut-1-en-3-yne, undergo the addition exclusively at the triple bond (Table 3, entries 14, 15).

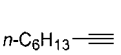
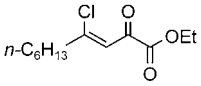
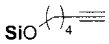
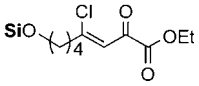
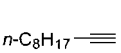
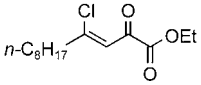
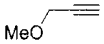
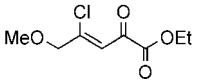
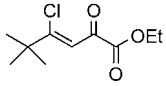
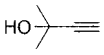
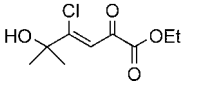
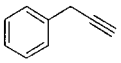
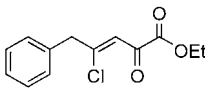
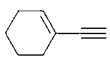
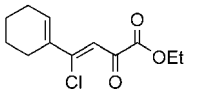
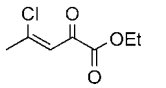
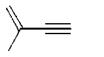
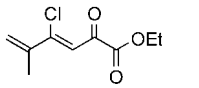
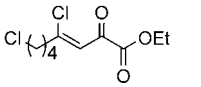
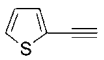
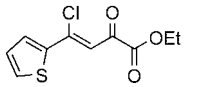
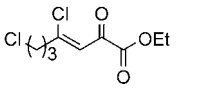
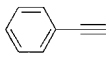
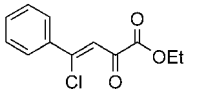
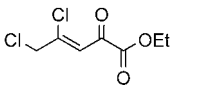
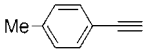
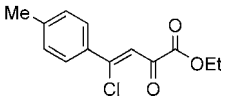
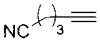
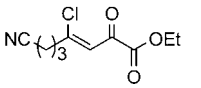
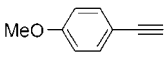
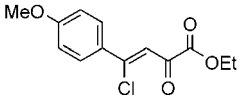
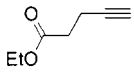
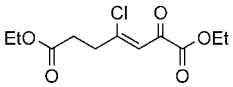
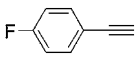
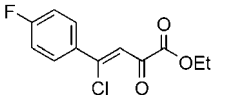
Aromatic and heteroaromatic alkynes also display high reactivity although the regioselectivity is rather low compared with the aliphatic ones (Table 3, entries 16–20). The electronic effect of the substituent on the aromatic ring is not very significant, but electron-releasing *p* substituents appear to enhance the reactivity and slightly decrease the regioselectivity (Table 3, entries 17–20). The reaction of *p*-fluorophenylacetylene afforded **3u** as crystals of good quality, which allowed us to confirm the *Z* configuration unequivocally by X-ray crystallography (Figure 1).

Attempted reactions of internal alkynes such as 4-octyne and dimethyl acetylenedicarboxylate failed, and these alkynes were mostly recovered, suggesting their inertness in the chosen conditions.

Mechanism of the addition reaction: The present catalysis is most likely to proceed through three fundamental processes: oxidative addition of the Cl–C bond of **2** to Rh^I; insertion of an alkyne molecule into the resulting Rh–Cl bond; and subsequent C–C reductive elimination. Our mechanistic proposal (Scheme 1) is substantiated by the observations described below.

First, ethoxalyl chloride reacts readily with Rh^I; the reactivity of this oxidative addition is higher than with chloroformates. Initial attempts to confirm this oxidative addition were made using [Rh(acac)(CO)(PPh_3)] with **2** at room temperature. For instance, when a suspension of [Rh(acac)(CO)(PPh_3)] in [D_6]benzene was treated with two equivalents of **2**, the reaction mixture became a homogeneous yellow solution immediately. ^1H and ^{31}P NMR spectroscopy suggested that a complex mixture of transient species was generated within 10 min. After this initial 10 min

Table 3. Rhodium-catalyzed addition reactions of ethoxalyl chloride to alkynes.[a]

Entry	Alkyne	Adduct	Yield of **3** + **3′**[b] [%]	Entry	Alkyne	Adduct	Yield of **3** + **3′**[b] [%]
1[c]			**3a**: 91 (97) [86]	11[e,f]			**3k**: 87 (96) [80]
2[c]			**3b**: 90 (96) [81]	12			**3l**: 34 (100) [24]
3[c]			**3c**: 93 (99) [86]	13			**3m**: 80 (100) [61]
4			**3d**: 87 (92) [73]	14			**3n**: 89 (90) [84]
5			**3e**: 45 (57) [32][d]	15			**3p**: 49 (82) [41]
6[c]			**3f**: 87 (100) [76]	16			**3q**: 94 (85) [85]
7[c]			**3g**: 90 (100) [80]	17[g]			**3r**: 85 (87) [81]
8			**3h**: 38 (66) [18][d]	18			**3s**: 93 (88) [87][d]
9			**3i**: 81 (100) [76]	19			**3t**: 97 (83) [93]
10			**3j**: 78 (90) [62]	20			**3u**: 83 (95) [79]

[a] Unless otherwise noted, the reactions were carried out with alkyne (4.0 mmol), ethoxalyl chloride (2.0 mmol), and catalyst [Rh(acac)(CO)(PPh_3)] (0.1 mmol) in toluene (2.0 mL) at 60 °C for 20 h. [b] Total yield of **3** and **3′** by GC analysis based on the amount of ethoxalyl chloride used. The regioselectivities for **3** [100 × [**3**]/(**3** + **3′**)] are in parentheses and isolated yields are in brackets. [c] Benzene was used as solvent. [d] Obtained as a mixture of regioisomers. [e] **Si** = *tert*-butyldimethylsilyl. [f] [RhCl(cod)(PPh_3)] was used as catalyst. [g] [RhCl(CO)(PPh_2Me)$_2$] (**6a**) was used as catalyst.

Figure 1. Molecular structure of ethyl (*Z*)-4-chloro-4-(*p*-fluorophenyl)-2-oxo-3-butenoate.

period, precipitation of a yellow powder, which was sparingly soluble in $CDCl_3$ and could not be characterized, started.

The reaction of [RhCl(CO)(PR_3)$_2$] (**6**; PR_3 = PPh_2Me (**6a**), $PPhMe_2$ (**6b**), PMe_3 (**6c**)) with **2** [Eq. (3)] appeared to be much cleaner. Thus, **6a** reacts readily with 1.5 equivalents of ethoxalyl chloride in toluene at 60 °C to afford [$RhCl_2$(CO)(PPh_2Me)$_2$($COCOOC_2H_5$)] **7a** (88 %, pale yellow powder) in 15 min. The P–Me moiety in **7a** displayed a single doublet ($J_{P,Rh}$ = 86.5 Hz) in ^{31}P NMR spectroscopy and a virtual triplet in ^{1}H NMR spectroscopy, both suggesting that the two phosphine ligands are in mutually *trans* positions. IR (1725, 1697 cm^{-1}) and ^{13}C NMR (δ = 213.0 and

Scheme 1. A plausible mechanism for the catalytic nondecarbonylative addition.

$$[RhCl(CO)(PR_3)_2] \;(\mathbf{6}) + Cl\text{-}COCOOC_2H_5 \xrightarrow{\text{at 60 °C or RT}} [RhCl_2(CO)(PR_3)_2(COCOOC_2H_5)] \quad (3)$$

7a $PR_3 = PPh_2Me$, 88 %
7b $PR_3 = PPhMe_2$, 81 %
7c $PR_3 = PMe_3$, 93 %

160.7 ppm) spectra both suggest the existence of an ethoxalyl group. These and previous observations with related rhodium complexes such as $[RhCl_2(CO)(PPh_2Me)_2(COOC_2H_5)]$[2r] led us to presume that **7a** adopts the configuration shown in Scheme 1. Careful recrystallization of **7a** from CH_2Cl_2–CH_3CN furnished pale yellow crystals, allowing unequivocal confirmation of the structure by X-ray crystallography (Figure 2 and Table 4).

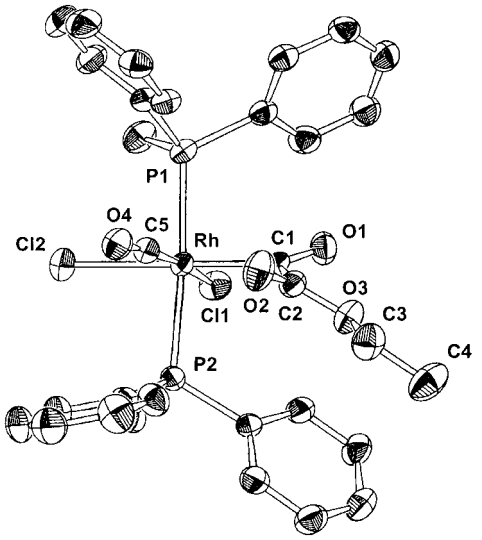


Figure 2. Molecular structure of $[RhCl_2(CO)(PPh_2Me)_2(COCOOC_2H_5)]$ (**7a**) drawn at the 50 % probability level. Hydrogen atoms and solvated $0.5\,CH_2Cl_2$ are omitted for clarity.

Table 4. Selected structural parameters for **7a**.

bond lengths [Å]			
Rh–P1	2.377(1)	Rh–P2	2.394(1)
Rh–Cl1	2.386(1)	Rh–Cl2	2.504(1)
Rh–C1	2.029(4)	Rh–C5	1.881(4)
C1–O1	1.198(4)	C5–O4	1.135(4)
C1–C2	1.544(5)	C2–O2	1.188(5)
bond angles [°]			
P1-Rh-P2	173.62(3)	Cl1-Rh-C5	173.5(1)
Cl2-Rh-C1	177.1(1)	P1-Rh-C5	90.0(1)
P2-Rh-C5	93.4(1)	Cl1-Rh-Cl2	91.58(4)
C5-Rh-Cl2	82.1(1)	C5-Rh-C1	95.0(2)
Cl1-Rh-C1	91.3(1)	Rh-C1-O1	124.5(3)
Rh-C5-O4	171.2(3)	C1-C2-O3	109.9(3)

As expected from the NMR data, the coordination geometry at the rhodium center is octahedral with diphenylmethylphosphine ligands in *trans* positions. The other *trans* ligand pairs in the coordination sphere are a chlorine and ethoxalyl, and the other chlorine and carbonyl. The Rh–Cl2 bond is much longer than the Rh–Cl1 one, suggesting that the ethoxalyl ligand exerts a stronger *trans* influence than that of the terminal CO; this agrees with the general *trans* influence trend of acyl > CO.[11]

The complexes $[RhCl(CO)(PPhMe_2)_2]$ (**6b**) and $[RhCl(CO)(PMe_3)_2]$ (**6c**) are even more reactive in the oxidative addition, presumably because of the higher electron-donating abilities of $PPhMe_2$ and PMe_3. Complex **6b** reacts with two equivalents of ethoxalyl chloride in dichloromethane at room temperature for 60 min leading to isolation of $[RhCl_2(CO)(PPhMe_2)_2(COCOOC_2H_5)]$ **7b** as pale yellow needles in 81 % yield, while **6c**, upon treatment with 1.5 equivalents of ethoxalyl chloride in toluene (room temperature, 60 min), also afforded 93 % yield of $[RhCl_2(CO)(PMe_3)_2(COCOOC_2H_5)]$ **7c** as pale yellow crystals. These complexes also displayed NMR spectroscopic features similar to those of **7a**.

The C–Cl bond in ethoxalyl chlorides is known to react at or below room temperature with palladium(0) and platinum(0) complexes to yield ethoxalyl complexes *trans*-$[MCl(COCOOC_2H_5)L_2]$ (M = Pd, Pt; L = PPh_3, PPh_2Me, PEt_3).[4] The resulting complexes, particularly palladium ones, readily undergo decarbonylation resulting in the corresponding alkoxycarbonyl complexes. For instance, decarbonylation of *trans*-$[PdCl(COCOOMe)(PPh_3)_2]$ dissolved in $CHCl_3$ at room temperature is approximately half complete in 10 min and nearly complete in 20 min. However, as the high-yield synthesis of **7a** at 60 °C has already suggested, the rhodium complex is much more stable than the palladium complexes although slight decarbonylation can occur, as evidenced by the formation of minor by-product **4** in the catalytic reaction. Also, the rhodium ethoxalyl complexes are thermally more stable to reductive elimination than the corresponding alkoxycarbonyl complexes, which can be generated in solution upon treatment of Vaska-type rhodium complexes with ClCOOR at 80 °C. However, handling of the complex products in solution must be carried out in the presence of free chloroformates; otherwise, they undergo Cl–C reductive elimination even at room temperature to regenerate ClCOOR and the initial Rh^I complex. The thermal stabilities of the ethoxalyl complexes, to both decarbonylation and reductive elimination, are the key features that make the present catalysis successful.

As mentioned earlier, ethoxalyl chloride is more reactive in the oxidative addition chemistry than chloroformate. The latter required heating at 80 °C, while the former can react even at room temperature, depending on the structure of the phosphine ligand. The thermal stability of the ethoxalyl complexes at higher temperatures was examined by observing thermolysis of the adducts **7** at 60 °C in [D_6]benzene in an NMR tube (Table 5). In general, the major products are three rhodium complexes and diethyl oxalate [Eq. (4)].

In the thermolysis of **7c** ligated by PMe_3, most of the complex (94 %) remained, even after heating for 30 h, but it

$[RhCl_2(CO)(PR_3)_2(COCOOC_2H_5)]$ 60 °C
0.1 M of complex **7** in C_6D_6

- $[RhCl_2(CO)(PR_3)_2(COOEt)]$ **9**
- $[RhCl_3(CO)(PR_3)_2]$ **10**
- $[RhCl(CO)(PR_3)_2]$ **6**
- EtOOCCOOEt

(4)

Table 5. Thermolysis of $[RhCl_2(CO)(PR_3)_2(COCOOC_2H_5)]$ **7**.

Starting complex	Temp [°C]	Duration [h]	Quantity in the mixture [%][a]				
			7	**9**	**10**	**6**	$(COOC_2H_5)_2$
7a (R = PPh_2Me)	60	2	66	5	13	16	–
		8	13	10	39	38	–
		12	4	8	45	41	–
		16	0	7	48	42	65[b]
		30	0	7	48	42	–
7b (R = $PPhMe_2$)	60	30	88	2	6	4	–
		672	0	16	48	41	50[c]
7c (R = PMe_3)	60	30	94	0	3	3	–
		672[d]	0	28	>32[e]	20	64[f]
7d (R = PPh_3)[g]	25	24	–	–	–	–	22
		96	0	0	>89[h]	0	77

[a] Estimated by ^1H NMR spectroscopy. [b] Three more OC_2H_5-containing organic species were found in an approximately 1:1:1 ratio (total ~20%). None of these was diethyl carbonate. [c] One more OC_2H_5-containing organic species (16%) was found. [d] Besides **6**, **7**, **9**, and **10**, another rhodium species of unknown structure was also detected (~6%). [e] Partially insoluble. [f] Two more OC_2H_5-containing species were found in an approximately 1:1 ratio (approximately 12% in total). [g] Since **7d** was extremely thermally unstable, the experiment was carried out starting with a mixture of $[RhCl(CO)(PPh_3)_2]$ and two equivalents of $ClCOCOOC_2H_5$ without isolation of **7d**. [h] Yield of isolated product.

eventually disappeared after 28 days, affording rhodium species **6c**, **9c**, and **10c** (>80% in total), diethyl oxalate (64%), and other unidentified C_2H_5O-containing species. Complex **7b** behaved in much the same way in the thermolysis as **7c** but appeared slightly less stable. However, **7a** with PPh_2Me was much less stable; the complex had already decomposed completely after 16 h to afford $[RhCl_3(CO)(PPh_2Me)_2]$ (**10a**) (48%) and $[RhCl(CO)(PPh_2Me_3)_2]$ (**6a**) (42%) and diethyl oxalate (65%) in large quantities. Decarbonylation product **9a** was also found as a minor transient species (5–10% over 2–30 h). Furthermore, it was not possible to generate $[RhCl_2(CO)(PPh_3)_2(COCOOC_2H_5)]$ (**7d**) cleanly or isolate it, due to its instability. To gain qualitative information about its thermal decomposition for comparison with the other complexes, **7a**–**7c** and **7e**–**7u**, however, we examined the time course of the reaction of $[RhCl(CO)(PPh_3)_2]$ (**6d**) with **2** (2 equiv) at *room temperature*. As expected, even in the very early stage of the reaction, we were unable to detect **7d** formed in the mixture. by ^1H NMR spectroscopy However, after 24 h diethyl oxalate was already formed in 22% NMR yield, and after 96 h $[RhCl_3(CO)(PPh_3)_2]$ and diethyl oxalate were obtained in 89% (isolated) and 77% (NMR) yields, respectively. A fair comparison of the thermolysis of **7d** with those of **7a**–**c** cannot be made, however, because the procedure was different and because two equivalents of **2** was used. Nevertheless, we can safely conclude that the stability of **7** depends significantly on the electronic nature of the phosphine ligand; more electron-donating ones stabilize the ethoxalyl complex, and in the case of PPh_3 the corresponding complex appears to decompose rapidly at higher temperatures as soon as it is generated, unless insertion of an alkyne molecule follows.

The second fundamental process involved is the insertion of the alkyne linkage. We presume, as in the chloroesterification of alkynes, that insertion into the Cl–Rh bond takes place, forming an intermediate such as **8**, which eventually undergoes C–C reductive elimination. To confirm this route, we carried out the reaction of **7a** with 2.5 equiv of **1a** in $[D_6]$benzene. At room temperature **7a** did not dissolve completely. The mixture was still a suspension even after 18 h and by ^1H and ^{31}P NMR spectroscopic inspection we observed that nothing new appeared to have been generated. When heated at 60 °C, however, the mixture developed a homogeneous yellow solution, in which, after 2.5 h, adduct **3a** was formed in 44% yield along with the Rh^I complex $[RhCl(CO)(PPh_2Me)_2]$ (**6a**, 62%), $[RhCl_3(CO)(PPh_2Me)_2]$(**10a**, 13%), and **7a** recovered in 24% yield (determined by ^1H and ^{31}P NMR spectroscopy in $[D_6]$benzene) [Eq. (5)]. A similar reaction of **7b** with 1-hexyne (5 equiv) did not proceed even at 60 °C (4 h) and the majority of the initial rhodium complex remained unreacted. However, heating at 80 °C (4 h) afforded approximately 20% of the corresponding adduct (**3**, R = *n*-C_4H_8) together with $[RhCl(CO)(PPhMe_2)_2]$ (**6b**). Heating continued at 80 °C for an additional 36 h afforded the adduct and **6b**, both in 50% yield. Complex **7b** remained partially in the mixture (35%). These reactivities of **7a** and **7b** with alkynes are consistent with the mechanism depicted in Scheme 1, although the experiments neither suggest the involvement of intermediate species such as **8** nor provide other details of the insertion process.

$[RhCl_2(CO)(PPh_2Me)_2(COCOOC_2H_5)]$ (**7a**) + 1-octyne **1a** (2.5 equiv) $\xrightarrow[C_6D_6]{60\ °C,\ 2.5\ h}$

3a 44% + **7a** 24% + $[RhCl(CO)(PPh_2Me)_2]$ **6a** 62% + $[RhCl_3(CO)(PPh_2Me)_2]$ **10a** 13% (5)

An alternative possibility for the formation of **3** is C–Cl reductive elimination from a chloro(β-ethoxalylalkenyl)rhodium species, which arises if an alkyne molecule is inserted

into the rhodium–carbon bond of **7** (ethoxalylrhodation). However, this possibility can be ruled out in view of the following relevant observations, reported previously. First, the C–Cl reductive elimination from chloro(organo)rhodium complexes normally requires very high temperatures. For example, $[RhCl(CO)(PPh_3)_2]$-catalyzed decarbonylation of aromatic acid chlorides and desulfonylation of aromatic sulfonyl chlorides, both of which proceed by C–Cl reductive elimination to form aromatic chlorides, take place only at temperatures of approximately 170 °C or higher.[12] Second, the reaction of cinnamoyl chloride with $[RhCl(PPh_3)_3]$ at 85 °C, which proceeds through $[RhCl_2(\beta\text{-styryl})(CO)(PPh_3)_2]$, has been reported to form β-styryltriphenylphosphonium chloride, but not β-chlorostyrene, an expected product of olefinic C–Cl reductive elimination.[13] Attempted decarbonylation of cinnamoyl chloride using $[\{RhCl(cod)\}_2]$ with PPh_3 ($Rh/PPh_3 = 2:1$) at 140 °C did not give β-chlorostyrene either.[2q] Thus, in our catalytic reactions at 60 °C the insertion is envisaged to proceed through chlororhodation. The ethoxalylrhodation pathway, which must experience the difficulty of C–Cl reductive elimination in the final stage of the catalytic cycle, is highly unlikely. More detailed mechanistic aspects, such as the possible necessity of ligand dissociation before alkyne insertion, remain to be further clarified.

Conclusion

We have described a novel rhodium-catalyzed addition reaction of ethoxalyl chloride with terminal alkynes which, in most cases, proceeds regio- and stereoselectively under relatively mild conditions. A wide range of functional groups are tolerated, and γ-chloro-α-oxo-β,γ-unsaturated esters obtained are expected to serve as versatile intermediates in organic synthesis. The catalysis is initiated by facile oxidative addition of ethoxalyl chloride forming $[RhCl_2(CO)(PR_3)_2(COCOOC_2H_5)]$, which undergoes alkyne insertion into its Rh–Cl bond. Application of the products to develop new synthetic methodologies will be reported soon.

Experimental Section

General: All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk tube techniques. Benzene and toluene were refluxed over sodium wire under nitrogen and distilled before use. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker ARX-300 spectrometer (^1H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121.5 MHz) in $CDCl_3$ or [D$_6$]benzene solution and referenced to $SiMe_4$ (^1H), appropriate solvent resonances (^{13}C), and 85 % H_3PO_4 (^{31}P). Infrared spectra were measured on a JASCO FT/IR-5000 spectrometer. MS was run on a Shimadzu GC-17 A/QP-5000 mass spectrometer, using the EI technique (70 eV). High-resolution mass spectra were obtained with a JEOL JMS-BU20 mass spectrometer at an ionization potential of 70 eV. Melting points were measured on a Yanagimoto Micro Melting Point apparatus and were uncorrected. Elemental analysis was performed at the Analytical Center of the National Institute of Materials and Chemical Research (Japan).

$[Rh_2(cod)_2Cl_2]$,[14] $[RhCl(cod)(PR_3)]$[15] (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3), $[RhCl(CO)(PR_3)_2]$[16] (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3), $[Rh(acac)(CO)(PR_3)]$[17] (PR_3 = PPh_3, PPh_2Me), and $[Cp^*Rh(CO)(PPh_3)]$[18] were prepared according to the literature. [RhCl(CO)(dppe)], [RhCl(CO)(dppp)], [RhCl(CO)(dppb)], and [RhCl(CO)(dppf)] were prepared from $[Rh_2Cl_2(CO)_4]$ and chelating phosphine ligand (Rh/P = 1:2) in toluene, similarly to the preparation of $[RhCl(CO)(PR_3)_2]$. The other metal complexes were commercial products and used as received. Ethoxalyl chloride was a commercial product and was used after distillation. Most of the alkynes were obtained from commercial sources, dried over 4 Å molecular sieves and degassed before use. Ethyl 4-pentynoate was obtained by esterification of 4-pentynoic acid.[19]

General procedure for the catalytic addition of ethoxalyl chloride to alkynes: The following procedure for 1-octyne is representative. Into a flask (20 mL) equipped with a three-way stopcock and a magnetic stirring bar were placed [Rh(acac)(CO)(PPh_3)] (49.2 mg, 0.1 mmol), ethoxalyl chloride (224 μL, 2.0 mmol), 1-octyne (587 μL, 4.0 mmol), and benzene (2.0 mL) under nitrogen. The mixture was stirred at 60 °C for 20 h and docosane ($C_{22}H_{46}$, 252 mg) was added as a GC internal standard. After GC analysis of **3a**, **4a**, and **5a** present in the reaction mixture, volatiles were removed under reduced pressure (ca. 100 Torr). The residue was subjected to silica gel column chromatography. Elution with hexane, followed by a diethyl ether–hexane mixture (3–5:100) afforded **3a** as a yellow oil in 86 % yield.

Ethyl (*Z*)-4-chloro-2-oxo-3-decenoate (3a): ^1H NMR ($CDCl_3$): δ = 6.95 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.51 (t, J = 7.4 Hz, 2H), 1.64 (m, 2H), 1.37–1.28 (m, 9H), 0.87 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.2, 162.0, 156.2, 118.6, 62.6, 42.0, 31.4, 28.2, 27.3, 22.4, 14.0, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1734, 1705 cm^{-1} (C=O); MS: *m/z* (%): 246 (0.1) $[M]^+$, 211 (1), 173 (100), 109 (16), 95 (11), 81 (18), 67 (53), 55 (46); elemental analysis calcd (%) for $C_{12}H_{19}ClO_3$: C 58.42, H 7.71; found: C 58.21, H 7.72.

Ethyl (*Z*)-3-chloro-2-nonenoate (4a): ^1H NMR ([D$_6$]benzene): δ = 5.85 (s, 1H), 4.00 (q, J = 7.1 Hz, 2H), 2.02 (t, J = 7.4 Hz, 2H), 1.31 (m, 2H), 1.21–0.96 (m, 9H), 0.81 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ([D$_6$]benzene): δ = 163.3, 150.0, 116.8, 60.0, 41.1, 31.6, 28.3, 27.2, 22.7, 14.2, 14.1 ppm; IR (neat): $\tilde{\nu}$ = 1734 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{11}H_{19}ClO_2$: C 60.43, H 8.70; found: C 60.82, H 8.87.

Ethyl 2-oxo-3-decynoate (5a): ^1H NMR ($CDCl_3$): δ = 4.34 (q, J = 7.1 Hz, 2H), 2.46 (t, J = 7.0 Hz, 2H), 1.66–1.27 (m, 11H), 0.88 ppm (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 169.7, 159.3, 102.6, 79.7, 63.1, 31.1, 28.4, 27.3, 22.4, 19.4, 14.0, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 2211, 1741, 1681 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{18}O_3$: C 68.57, H 8.57; found: C 68.35, H 8.81.

Ethyl (*Z*)-4-chloro-2-oxo-3-dodecenoate (3b): Isolated yield: 81 %, yellow oil. ^1H NMR ($CDCl_3$): δ = 6.95 (s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.50 (t, J = 7.4 Hz, 2H), 1.62 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.26 (m, 10H), 0.83 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.2, 162.0, 156.2, 118.6, 62.2, 42.0, 31.7, 29.2, 29.0, 28.5, 27.3, 22.6, 14.0, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1735, 1708 cm^{-1} (C=O); MS: *m/z* (%): 239 (1) $[M-Cl]^+$, 201 (100), 165 (2), 147 (2), 115 (7), 95 (34), 81 (57), 67 (36), 55 (65); elemental analysis calcd (%) for $C_{14}H_{23}ClO_3$: C 61.20, H 8.38; found: C 61.42, H 8.36.

Ethyl (*Z*)-4-chloro-5,5-dimethyl-2-oxo-3-hexenoate (3c): Isolated yield: 86 %, yellow oil. ^1H NMR ($CDCl_3$): δ = 6.95 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.26 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 181.5, 164.5, 162.3, 116.3, 62.5, 41.1, 28.6, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1729, 1704 cm^{-1} (C=O); MS: *m/z* (%): 218 (0.1) $[M]^+$, 183 (1), 145 (81), 109 (81), 81 (100), 67 (20), 53 (18); elemental analysis calcd (%) for $C_{10}H_{15}ClO_3$: C 54.92, H 6.87; found: C 54.96, H 6.93.

Ethyl (*Z*)-4-chloro-5-phenyl-2-oxo-3-pentenoate (3d): Isolated yield: 73 %, yellow oil. ^1H NMR ($CDCl_3$): δ = 7.38–7.22 (m, 5H), 6.95 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.82 (s, 2H), 1.35 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.4, 161.8, 153.8, 134.9, 129.3, 128.9, 127.7, 119.8, 62.7, 47.9, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1733, 1698 cm^{-1} (C=O); MS: *m/z* (%): 252 (0.4) $[M]^+$, 217 (6), 179 (87), 144 (66), 115 (100), 90 (12), 65 (12), 57 (13); elemental analysis calcd (%) for $C_{13}H_{13}ClO_3$: C 61.78, H 5.15; found: C 61.94, H 5.15.

Ethyl (*Z*)-4-chloro-2-oxo-3-pentenoate (3e) and ethyl (*Z*)-4-chloro-3-methyl-2-oxo-3-butenoate (3′e): The addition reaction of propyne (1 atm) with ethoxalyl chloride gave two adducts in a ratio of 57:43, which were isolated as a mixture in 32% yield. Elemental analysis calcd (%) for $C_7H_9ClO_3$ (mixture of adducts): C 47.59, H 5.10; found: C 47.49, H 5.16. A careful separation by preparative TLC (silica gel, eluted with hexane/diethyl ether (9:1)) gave pure isomers. **3e** (major isomer: 0.34 mmol, 17%): ^{1}H NMR ($CDCl_3$): δ = 7.00 (q, J = 1.0 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.36 (d, J = 1.0 Hz, 3H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.0, 161.8, 151.5, 119.3, 62.6, 29.1, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1731, 1702 cm^{-1} (C=O); MS: *m/z* (%): 176 (0.1) $[M]^+$, 141 (7), 103 (100), 75 (14), 67 (6). **3′e** (minor isomer: 0.22 mmol, 11%): ^{1}H NMR ($CDCl_3$): δ = 7.18 (q, J = 0.8 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.65 (d, J = 0.8 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.0, 161.2, 159.4, 121.2, 62.8, 25.0, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 1731, 1702 cm^{-1} (C=O); MS: *m/z* (%): 176 (0.3) $[M]^+$, 141 (9), 103 (100), 75 (14), 67 (7).

Ethyl (*Z*)-4,8-dichloro-2-oxo-3-octenoate (3f): Isolated yield: 76%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 6.99 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.54 (t, J = 5.8 Hz, 2H), 2.56 (t, J = 6.7 Hz, 2H), 1.86–1.80 (m, 4H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.0, 161.8, 154.8, 119.0, 62.7, 44.2, 41.1, 31.2, 24.6, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1733, 1707 cm^{-1} (C=O); MS: *m/z* (%): 217 (2) $[M-Cl]^+$, 179 (100), 143 (4), 115 (13), 89 (18), 79 (42), 67 (14), 53 (19); elemental analysis calcd (%) for $C_{10}H_{14}Cl_2O_3$: C 47.43, H 5.53; found: C 47.23, H 5.57.

Ethyl (*Z*)-4,7-dichloro-2-oxo-3-heptenoate (3g): Isolated yield: 80%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.06 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.56 (t, J = 6.2 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H), 2.14 (m, 2H), 1.37 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 179.9, 161.6, 153.4, 119.6, 62.6, 43.2, 28.8, 29.8, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1734, 1705 cm^{-1} (C=O); MS: *m/z* (%): 203 (2) $[M-Cl]^+$, 165 (100), 129 (8), 101 (20), 75 (16), 65 (71); elemental analysis calcd (%) for $C_9H_{12}Cl_2O_3$: C 45.19, H 5.04; found: C 45.23, H 5.11.

Ethyl (*Z*)-4,5-dichloro-2-oxo-3-pentenoate (3h) and ethyl (*Z*)-4-chloro-3-chloromethyl-2-oxo-3-butenoate (3′h): The addition reaction of propargyl chloride to ethoxalyl chloride gave two adducts in a ratio of 66:34. A mixture of the two adducts (72:28) was isolated in 18% yield as a yellow oil after silica-gel column chromatography (eluent: hexane and then hexane containing 3–5% diethyl ether) followed by preparative TLC (twice, silica gel, eluted with hexane/diethyl ether (5:1)). **3h** (major product): ^{1}H NMR ($CDCl_3$): δ = 7.40 (t, J = 0.7 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 4.28 (d, J = 0.7 Hz, 2H), 1.37 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 179.8, 161.0, 147.2, 120.1, 63.0, 47.5, 13.9 ppm; MS: *m/z* (%): 175 (11) $[M-Cl]^+$, 137 (100), 109 (21), 102 (9), 83 (7), 73 (7), 67 (16). **3′h** (minor product): ^{1}H NMR ($CDCl_3$): δ = 6.80 (t, J = 0.7 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 4.24 (d, J = 0.7 Hz, 2H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 185.4, 157.9, 141.2, 126.0, 63.1, 47.4, 13.9 ppm; MS: *m/z* (%): 175 (35) $[M-Cl]^+$, 137 (100), 109 (69), 101 (13), 83 (19), 73 (42), 67 (28); IR of the 72:28 mixture of the two products (neat): $\tilde{\nu}$ = 1731, 1708 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_7H_8Cl_2O_3$ (a mixture of **3h** and **3′h** in a 2:1 ratio): C 39.81, H 3.79; found: C 40.36, H 3.95.

Ethyl (*Z*)-4-chloro-7-cyano-2-oxo-3-heptenoate (3i): Isolated yield: 76%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.06 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.69 (t, J = 7.3 Hz, 2H), 2.41 (t, J = 7.0 Hz, 2H), 2.04 (m, 2H), 1.35 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 179.8, 161.4, 152.1, 120.0, 118.5, 62.8, 40.1, 23.0, 16.1, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1729, 1702 cm^{-1} (C=O); MS: *m/z* (%): 194 (1) $[M-Cl]^+$, 156 (100), 128 (13), 115 (39), 101 (13), 87 (14), 65 (20), 54 (35); elemental analysis calcd (%) for $C_{10}H_{12}ClNO_3$: C 52.29, H 5.23, N 6.10; found: C 52.21, H 5.23, N 6.01.

Ethyl (*Z*)-4-chloro-6-ethoxycarbonyl-2-oxo-3-hexenoate (3j): Isolated yield: 62%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.05 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.84 (t, J = 7.3 Hz, 2H), 2.65 (t, J = 7.3 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.24 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 179.9, 171.3, 161.6, 153.1, 119.4, 62.7, 60.9, 36.9, 31.7, 14.1, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1731, 1702 cm^{-1} (C=O); MS: *m/z* (%): 227 (2) $[M-Cl]^+$, 189 (99), 161 (83), 143 (46), 133 (39), 116 (49), 97 (47), 81 (21), 67 (18), 53 (100); elemental analysis calcd (%) for $C_{11}H_{15}ClO_5$: C 50.29, H 5.71; found: C 50.29, H 5.76.

Ethyl (*Z*)-8-tert-butyldimethylsiloxy-4-chloro-2-oxo-3-octenoate (3k): Isolated yield: 80%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 6.97 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.62 (t, J = 6.1 Hz, 2H), 2.56 (t, J = 7.3 Hz, 2H), 1.73–1.51 (m, 4H), 1.36 (t, J = 7.1 Hz, 3H), 0.88 (s, 9H), 0.04 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): δ = 180.2, 161.9, 155.9, 118.7, 62.6, 62.4, 41.7, 31.5, 25.9, 23.9, 18.3, 13.9, −5.34 ppm; IR (neat): $\tilde{\nu}$ = 1735, 1714 cm^{-1} (C=O); MS: *m/z* (%): 348 (2) $[M]^+$, 255 (44), 227 (14), 211 (100), 151 (25), 75 (68), 59 (18); elemental analysis calcd (%) for $C_{16}H_{29}ClO_4Si$: C 55.09, H 8.32; found: C 55.15, H 8.51.

Ethyl (*Z*)-4-chloro-5-methoxy-2-oxo-3-pentenoate (3l): Isolated yield: 24%, pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.30 (t, J = 1.5 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 4.12 (d, J = 1.5 Hz, 2H), 3.44 (s, 3H), 1.37 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.2, 161.5, 150.1, 117.2, 75.5, 62.7, 59.0, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1731, 1704 cm^{-1} (C=O); MS: *m/z* (%): 171 (7) $[M^+-Cl]$, 133 (100), 105 (98), 67 (15), 55 (29); elemental analysis calcd (%) for $C_8H_{11}ClO_4$: C 46.49, H 5.33; found: C 46.30, H 5.30.

Ethyl (*Z*)-4-chloro-5-hydroxy-5-methyl-2-oxo-3-hexenoate (3m): Isolated yield: 61%, pale yellow powder after being washed with hexane, m.p. 44–45 °C. ^{1}H NMR ($CDCl_3$): δ = 7.45 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.50 (s, 1H), 1.53 (s, 6H), 1.36 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 181.1, 161.8, 160.2, 116.0, 75.3, 62.7, 28.4, 13.9 ppm; IR (KBr): $\tilde{\nu}$ = 1733, 1700 cm^{-1} (C=O); MS: *m/z* (%): 147 (92) $[M-COOC_2H_5]^+$, 131 (11), 111 (100), 91 (4), 89 (10), 83 (16), 69 (12), 59 (20); elemental analysis calcd (%) for $C_9H_{13}ClO_4$: C 48.98, H 5.90; found: C 49.42, H 5.88.

Ethyl (*Z*)-4-chloro-4-(1-cyclohexenyl)-2-oxo-3-butenoate (3n): Isolated yield: 84%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.02 (s, 1H), 6.95 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.31–2.29 (m, 4H), 1.74–1.59 (m, 4H), 1.37 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 181.3, 162.4, 150.8, 139.8, 134.0, 114.7, 62.5, 26.7, 26.2, 22.3, 21.3, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1731, 1718 cm^{-1} (C=O); MS: *m/z* (%): 242 (6) $[M]^+$, 213 (4), 207 (8), 169 (100), 151 (10), 141 (14), 105 (60), 91 (26), 77 (45), 51 (23); elemental analysis calcd (%) for $C_{12}H_{15}ClO_3$: C 59.38, H 6.18; found: C 59.12, H 6.28.

Ethyl (*Z*)-4-chloro-5-methyl-2-oxo-3-hexadienoate (3p): Isolated yield: 41%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.13 (s, 1H), 6.05 (s, 1H), 5.56 (s, 1H), 4.34 (q, J = 7.1 Hz, 2H), 2.08 (s, 3H), 1.37 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 181.2, 162.0, 149.5, 139.9, 125.2, 117.6, 62.7, 20.3, 13.9 ppm; IR (neat): $\tilde{\nu}$ = 1731, 1689 cm^{-1} (C=O); MS: *m/z* (%): 202 (2) $[M]^+$, 187 (2), 174 (3), 129 (84), 101 (54), 65 (100); elemental analysis calcd (%) for $C_9H_{11}ClO_3$: C 53.33, H 5.43; found: C 53.31, H 5.43.

Ethyl (*Z*)-4-chloro-2-oxo-4-(2-thienyl)-3-butenoate (3q): Isolated yield: 85%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.69 (d, J = 3.7 Hz, 1H), 7.53 (m, 2H), 7.10 (m, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.38 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 179.5, 161.9, 143.0, 141.1, 131.5, 131.4, 128.7, 114.1, 62.7, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 1729, 1687 cm^{-1} (C=O); MS: *m/z* (%): 244 (5) $[M]^+$, 209 (1), 171 (100), 143 (16), 108 (41), 69 (6), 58 (5); elemental analysis calcd (%) for $C_{10}H_9ClO_3S$: C 49.08, H 3.68; found: C 49.64, H 3.63.

Ethyl (*Z*)-4-chloro-2-oxo-4-phenyl-3-butenoate (3r): Isolated yield: 81%, yellow oil. ^{1}H NMR ($CDCl_3$): δ = 7.79–7.76 (m, 2H), 7.56 (s, 1H), 7.51–7.41 (m, 3H), 4.47 (q, J = 7.1 Hz, 2H), 1.39 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.2, 162.0, 150.6, 136.7, 131.7, 128.8, 127.6, 117.7, 62.8, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 1729, 1697 cm^{-1} (C=O); MS: *m/z* (%): 238 (0.2) $[M]^+$, 203 (0.5), 165 (100), 137 (16), 102 (71), 71 (17), 63 (10); elemental analysis calcd (%) for $C_{12}H_{11}ClO_3$: C 60.38, H 4.61; found: C 60.57, H 4.67.

Ethyl (*Z*)-4-chloro-2-oxo-4-*p*-tolyl-3-butenoate (3s) and ethyl (*Z*)-4-chloro-2-oxo-3-*p*-tolyl-3-butenoate (3′s): Isolated yield: 87%, yellow oil. Elemental analysis calcd (%) for $C_{13}H_{13}ClO_3$ (mixture of adducts): C 61.78, H 5.15; found: C 62.20, H 5.25. A pure sample of the major adduct **3s** was obtained by preparative TLC (silica gel, eluted with hexane/diethyl ether (9:1)). **3s**: ^{1}H NMR ($CDCl_3$): δ = 7.68 (d, J = 8.2 Hz, 2H), 7.53

(s, 1H), 7.23 (d, J = 8.2 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.38 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.2, 162.1, 150.8, 142.6, 133.9, 129.5, 127.6, 116.6, 62.7, 21.4, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 1725, 1695 cm^{-1} (C=O); MS: m/z (%): 252 (2) $[M]^+$, 217 (0.5), 179 (100), 151 (6), 143 (3), 115 (67), 89 (10), 63 (6). Minor adduct **3′s** (72% purity in a mixture with **3s**) was also obtained from the preparative TLC. **3′s**: ^{1}H NMR ($CDCl_3$): δ = 7.37 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.01 (s, 1H), 4.03 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.21 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 181.3, 161.7, 155.7, 141.9, 133.2, 129.1, 128.9, 122.4, 62.5, 21.5, 13.7 ppm; MS: m/z (%): 252 (1) $[M]^+$, 179 (39), 151 (2), 143 (100), 115 (37), 89 (13), 63 (12).

Ethyl (*Z*)-4-chloro-4-(4-methoxyphenyl)-2-oxo-3-butenoate (3t): Isolated yield: 93%, yellow crystals (recrystallized from hexane at −10°C), m.p. 42–43°C. ^{1}H NMR ($CDCl_3$): δ = 7.76 (d, J = 8.8 Hz, 2H), 7.49 (s, 1H), 6.92 (d, J = 8.2 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.38 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.1, 162.7, 162.3, 150.6, 129.5, 128.8, 115.4, 114.2, 62.6, 55.5, 14.0 ppm; IR (KBr): $\tilde{\nu}$ = 1720, 1685 cm^{-1} (C=O); MS: m/z (%): 195 (100) $[M-COOC_2H_5]^+$, 167 (20), 132 (24), 117 (13), 89 (18), 63 (11); elemental analysis calcd (%) for $C_{13}H_{13}ClO_4$: C 58.10, H 4.84; found: C 58.10, H 4.81.

Ethyl (*Z*)-4-chloro-4-(*p*-fluorophenyl)-2-oxo-3-butenoate (3u): Isolated yield: 79%, yellow crystals (recrystallized from hexane at −10°C), m.p. 39–40°C. ^{1}H NMR ($CDCl_3$): δ = 7.81–7.76 (m, 2H), 7.52 (s, 1H), 7.15–7.10 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 1.38 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 180.0, 164.8 (d, $^1J_{C,F}$ = 254.2 Hz), 161.9, 149.3, 132.9 (d, $^4J_{C,F}$ = 3.3 Hz), 129.9 (d, $^3J_{C,F}$ = 9.0 Hz), 117.4, 116.0 (d, $^2J_{C,F}$ = 22.1 Hz), 62.8, 14.0 ppm; IR (KBr): $\tilde{\nu}$ = 1729, 1695 cm^{-1} (C=O); MS: m/z (%): 256 (1) $[M]^+$, 221 (1), 183 (100), 155 (18), 120 (59), 99 (8), 74 (9), 50 (7); elemental analysis calcd (%) for $C_{12}H_{10}FClO_3$: C 56.14, H 3.90; found: C 56.14, H 3.73.

Oxidative addition of ethoxalyl chloride to [RhCl(CO)(PR$_3$)$_2$]

[RhCl$_2$(CO)(PPh$_2$Me)$_2$(COCOOC$_2$H$_5$)] (7a): A mixture of [RhCl(CO)(PPh$_2$Me)$_2$] (85.1 mg, 0.15 mmol) and $ClCOCOOC_2H_5$ (26 μL, 0.23 mmol) in toluene (2.0 mL) was heated at 60°C for 15 min under nitrogen. After removal of volatiles, the residue was washed with hexane and dried in vacuo. Complex **7a** was obtained in 88% yield (93.2 mg, 0.132 mmol) as a pale yellow solid. ^{1}H NMR ($CDCl_3$): δ = 7.86–7.15 (m, 20H, 4C$_6$H$_5$), 3.78 (q, J = 7.1 Hz, 2H, CH_2), 2.43 (virtual t, J_{P-H} = 4.2 Hz, 6H, 2PCH$_3$), 0.94 ppm (t, J = 7.1 Hz, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 213.0 (dt, J = 30.1 Hz, J = 5.5 Hz, $COCOOC_2H_5$), 182.1 (dt, J = 67.2 Hz, J = 9.9 Hz, CO), 160.7 (apparent q, J = 3.6 Hz, CO$COOC_2H_5$), 133.1–132.7 (m, PPh), 131.0 (s, PPh), 130.9 (s, PPh), 128.5–128.4 (m, PPh), 62.6 (s, CH_2), 13.6 (s, CH_3CH_2), 13.4 ppm (virtual t, J = 18.7 Hz, PCH$_3$); ^{31}P NMR ($CDCl_3$): δ = 8.0 ppm (d, $J_{P,Rh}$ = 86.5 Hz); IR (KBr): $\tilde{\nu}$ = 2090, 1725, 1697 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{31}H_{31}Cl_2O_4P_2Rh$: C 52.92, H 4.41; found: C 53.30, H 4.43.

[RhCl$_2$(CO)(PPhMe$_2$)$_2$(COCOOC$_2$H$_5$)] (7b): Prepared similarly to **7a** by treating [RhCl(CO)(PPhMe$_2$)$_2$] in CH_2Cl_2 with $ClCOCOOC_2H_5$ (2 equiv) at room temperature for 60 min. Isolated in 81% yield; pale yellow needles. ^{1}H NMR ($CDCl_3$): δ = 7.72–7.65 (m, 4H, aromatic), 7.41–7.39 (m, 6H aromatic), 3.92 (q, J = 7.1 Hz, 2H, CH_2), 2.15 (virtual t, J_{P-H} = 4.2 Hz, 6H, 2PCH$_3$), 1.98 (virtual t, J_{P-H} = 4.2 Hz, 6H, 2PCH$_3$), 1.08 ppm (t, 3H, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 213.4 (dt, J = 30.0 Hz, J = 6.2 Hz, $COCOOC_2H_5$), 181.1 (dt, J = 67.8 Hz, J = 9.8 Hz, C=O), 161.3 (apparent q, J = 3.5 Hz, CO$COOC_2H_5$), 133.8 (virtual t, J = 24.8 Hz, PPh), 130.8 (s, PPh), 130.1 (virtual t, J = 5.0 Hz, PPh), 128.7 (virtual t, J = 4.8 Hz, PPh), 62.4 (CH_2), 13.8 (CH_3CH_2), 12.9 (virtual t, J = 18.7 Hz, PCH$_3$), 11.7 ppm (virtual t, J = 17.6 Hz, PCH$_3$); ^{31}P NMR ($CDCl_3$): δ = 0.43 ppm (d, $J_{P,Rh}$ = 84.0 Hz); IR (KBr): $\tilde{\nu}$ = 2082, 1731, 1694 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{21}H_{27}Cl_2O_4P_2Rh$: C 43.54, H 4.67; found: C 43.58, H 4.68.

[RhCl$_2$(CO)(PMe$_3$)$_2$(COCOOC$_2$H$_5$)] (7c): Prepared similarly to **7a** by treating [RhCl(CO)(PMe$_3$)$_2$] in toluene with $ClCOCOOC_2H_5$ (1.5 equiv) at room temperature for 60 min. Isolated in 93% yield; nearly colorless–pale yellow crystals. ^{1}H NMR ($CDCl_3$): δ = 4.22 (q, J = 7.1 Hz, 2H, CH_2), 1.75 (virtual t, J_{P-H} = 4.0 Hz, 18H, 2PMe$_3$), 1.30 (t, J = 7.1 Hz, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 217.1 (dt, $J_{Rh,C}$ = 28.9 Hz, $J_{P,C}$ = 6.3 Hz, $COCOOC_2H_5$), 180.9 (dt, $J_{Rh,C}$ = 73.2 Hz, $J_{P,C}$ = 10.7 Hz, C=O), 162.3 (apparent q, J = 3.2 Hz, CO$COOC_2H_5$), 61.9 (CH_2), 14.5 (virtual t, J_{P-C} = 17.8 Hz), 14.2 ppm (CH_3CH_2); ^{31}P NMR ($CDCl_3$): δ = −4.62 ($J_{P,Rh}$ = 83.4 Hz); IR (KBr): $\tilde{\nu}$ = 2080, 1735, 1714 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{11}H_{23}Cl_2O_4P_2Rh$: C 29.01, H 5.05; found: C 29.44, H 5.11.

X-ray crystallography: Single crystals of **3u** were obtained by recrystallization from hexane and crystals of **7a** were obtained by recrystallization from CH_2Cl_2–CH_3CN. Single crystals were mounted on glass fibers. All the measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71069 Å) and a rotating anode generator. The unit cells were determined and refined by a least-squares method using the setting angles of 25 carefully centered reflections in the range 29.8° < 2θ < 30.00°. The data were collected at about −70°C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structures were solved by direct methods and expanded Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystal structure analysis of **3u**: $C_{12}H_{10}ClFO_3$, M_r = 256.66, yellow, needles, 0.20×0.20×0.60 mm^3. Triclinic crystal system, space group $P\bar{1}$ (no. 2). Cell parameters: a = 11.892(2) Å, b = 15.515(2) Å, c = 7.0181(6) Å, α = 94.193(10)°, β = 106.935(8)°, γ = 68.755(9)°, V = 1153.7(2) Å^3; Z = 4, ρ_{calcd} = 1.478 g cm^{-3}, R = 0.093, R_w = 0.119, $R1$ = 0.036. Crystal structure analysis of **7a**: $C_{31}H_{31}Cl_2O_4P_2Rh\cdot 0.5CH_2Cl_2$, M_r = 745.81, yellow, needles, 0.15×0.05×0.50 mm^3. Triclinic crystal system, space group $P\bar{1}$ (no. 2). Cell parameters: a = 10.119(5), b = 17.134(2), c = 9.962(2) Å, α = 97.84(1), β = 108.87(2), γ = 79.70(2)°, V = 1602.3(9) Å^3; Z = 2, ρ_{calcd} = 1.546 g cm^{-3}, R = 0.069, R_w = 0. 108, $R1$ = 0.039. CCDC-254019 (**3u**) and CCDC-254020 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[9] MS (70 eV) for one of the isomers: *m/z* (%): 330 (M^+, 22), 260 (82), 189 (35), 175 (53), 119 (61), 105 (100), 91 (53), 55 (37). For the other isomer: *m/z* (%): 330 (M^+, 26), 259 (24), 245 (26), 189 (100), 175 (49), 119 (63), 105 (84), 91 (80), 55 (57).

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