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Rhenium-Catalyzed *anti*-Markovnikov Addition Reaction of Methanetricarboxylates to Unactivated Terminal Acetylenes

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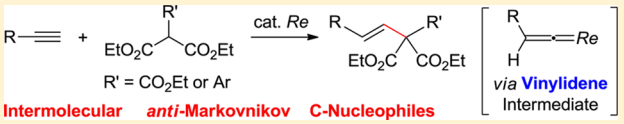
Supporting Information

ABSTRACT: A novel *anti*-Markovnikov addition reaction of methanetricarboxylates with terminal acetylenes under neutral conditions was achieved using a rhenium complex. This transformation represents a rare example of intermolecular *anti*-Markovnikov addition of carbon nucleophiles to unactivated terminal acetylenes. 1,3-Diesters having bulky substituents at the active methylene carbon are also applicable as substrates to provide *anti*-Markovnikov adducts as single regio- and stereoisomers. Preliminary mechanistic studies imply that the rhenium vinylidene species is the key intermediate in the current catalytic cycle.

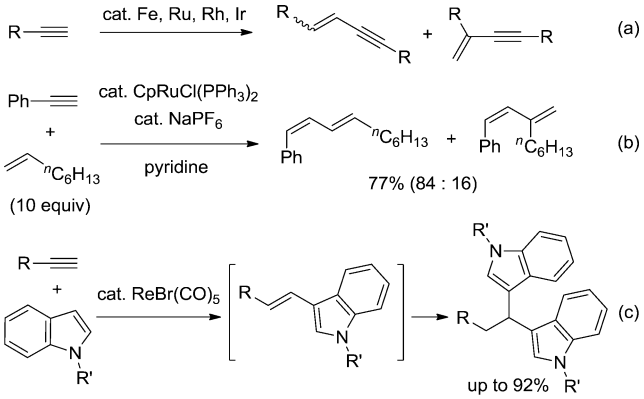


INTRODUCTION

The addition of nucleophiles to carbon−carbon multiple bonds represents one of the most straightforward ways to construct a variety of complex molecules with high atom efficiency.[1] Although considerable success has been achieved in this field by using late transition metals as catalysts, the control of regio- and stereoselectivities in the addition to terminal acetylenes still remains an important challenge.[2] For example, most electrophilic addition reactions of alkynes are known to follow the Markovnikov rule, and the *anti*-Markovnikov addition of carbon nucleophiles to unactivated terminal acetylenes is difficult and remains an unmet challenge.[3,4] Hydroboration followed by cross-coupling provides alternative access to formal *anti*-Markovnikov adducts but requires multistep reaction sequences.[5]

While several intramolecular cyclizations via the *anti*-Markovnikov addition of carbon nucleophiles have been reported,[3] the intermolecular addition for the selective construction of carbon frameworks has been rarely reported. Head-to-head dimerization of acetylenes is a typical example. Several transition-metal complexes (Fe, Ru, Rh, and Ir) are known to be effective for this transformation, although adducts were usually obtained as a mixture of regio- and stereoisomers and the selective cross-dimerization has not been achieved (Scheme 1a).[4a,b,d−g,i] Murakami et al. have reported *anti*-Markovnikov addition of alkenes to alkynes via the [2 + 2]cycloaddition reaction with a catalytic ruthenium vinylidene complex (Scheme 1b).[4c] Both aryl- and alkylacetylenes can be applicable, although the reaction provided a mixture of two regioisomers and excess amount of alkenes were required to avoid the competitive oligomerization of alkynes. Recently, Wang et al. have demonstrated the rhenium-catalyzed synthesis of bisindolylalkanes via the *anti*-Markovnikov addition of indoles to alkynes (Scheme 1c).[4h]

Scheme 1. Intermolecular *anti*-Markovnikov Addition of Carbon Nucleophiles



The present study describes the rhenium-catalyzed *anti*-Markovnikov addition of methanetricarboxylates to unactivated terminal acetylenes. The reaction proceeded with excellent regio- and stereoselectivity under neutral conditions.

RESULTS AND DISCUSSION

Recently, we reported the rhenium-catalyzed intermolecular *anti*-Markovnikov hydroamination of cyclic amides.[6] In connection with our continued interest in development of group 7 transition-metal complexes as valuable catalysts to promote innovative organic reactions,[7] we initiated this work using rhenium catalysts for the intermolecular *anti*-Markovnikov addition of carbon nucleophiles to unactivated acetylenes. First, the reaction of triethyl methanetricarboxylate **2a** with 2 equiv of 1-dodecyne **1a** was carried out as a model reaction in

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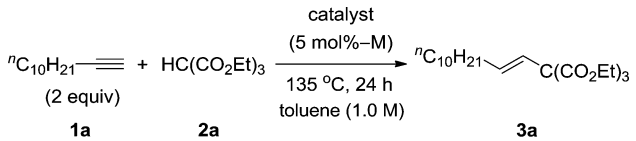
toluene at 135 °C in the presence of various transition-metal catalysts. Preliminary studies revealed that the *anti*-Markovnikov addition of **1a** proceeded in the presence of a catalytic amount of $Re_2(CO)_{10}$ (Table 1, entry 1). Notably, addition

Table 1. Effect of Catalyst



entry	catalyst	yield of **3a**[a] (%)
1	$Re_2(CO)_{10}$	48
2	$[ReBr(CO)_3(thf)]_2$	0
3	$[HRe(CO)_4]_n$	53
4	$Mn_2(CO)_{12}$	0
5	$Ru_3(CO)_{12}$	0

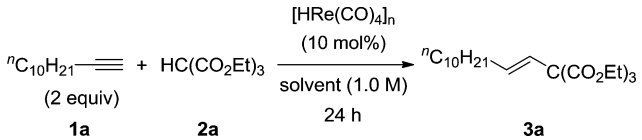
[a]Determined by ^1H NMR.

occurred selectively at the terminal carbon of the alkyne to produce *E*-olefin **3a** in 48% yield as a single regio- and stereoisomer without forming the corresponding Markovnikov adduct. In contrast, $[ReBr(CO)_3(thf)]_2$, which was the best catalyst for the addition of 1,3-diketones to acetylenes reported by our group, was completely ineffective (entry 2).[8] Among the catalysts screened, $[HRe(CO)_4]_n$ showed the highest catalytic efficiency to yield **3a** in 53% yield (entry 3). Other transition-metal complexes including $Mn_2(CO)_{10}$, $MnBr(CO)_5$, $W(CO)_6$, $Ir_4(CO)_{12}$, and $AuCl_3$ were found to be totally ineffective, and **2a** was recovered intact (entry 4). In sharp contrast to the previous *anti*-Markovnikov addition of oxygen or nitrogen nucleophiles to terminal acetylenes, ruthenium catalysts including $Ru_3(CO)_{12}$, $[RuCl_2(p\text{-cymene})]_2$, and $RuCl_3$-nH_2O did not promote the desired reaction at all (entry 5).[9]

With the optimized catalyst, $[HRe(CO)_4]_n$, in hand, examination of other parameters such as solvent, temperature, and concentration was next carried out (Table 2). The reaction occurred efficiently in chlorobenzene, octane, and 1,2-dichloroethane to afford the expected *anti*-Markovnikov adduct **3a** in slightly lower yields compared with that obtained in toluene (entries 1–3). More polar solvents including 1,4-dioxane and DMF could be used, although the reaction conducted in MeCN was very slow to give **3a** in low yield (entries 4–6). The reaction proceeded even without the solvent (entry 7). Note that *anti*-Markovnikov adduct **3a** was obtained selectively without producing its regio- and stereoisomers under the all the reaction conditions examined. These studies revealed the best yield was achieved in toluene. Thus, $[HRe(CO)_4]_n$ and toluene were chosen as the best catalyst and solvent, respectively, for further optimization. The yield was decreased when the reaction was carried out at 100 °C, and the best yield was obtained from the reaction at 135 °C (entries 8–11). Decreasing the concentration from 1.0 to 0.125 M to prevent the competitive formation of uncharacterized oligo- or polymeric compounds of 1-dodecyne led to an increased yield of up to 64% (entry 12). Finally, **3a** was isolated in 80% yield (81% NMR yield) when 0.5 equiv of 1-dodecyne was added at the beginning and additional 1-dodecyne (0.5 equiv each) was added three times at 2 h intervals (entry 13).[10]

With the optimized reaction conditions in hand, the scope of terminal acetylenes and functional group tolerance was examined. The series of acetylenes having linear and cyclic

Table 2. Effect of Solvent and Temperature

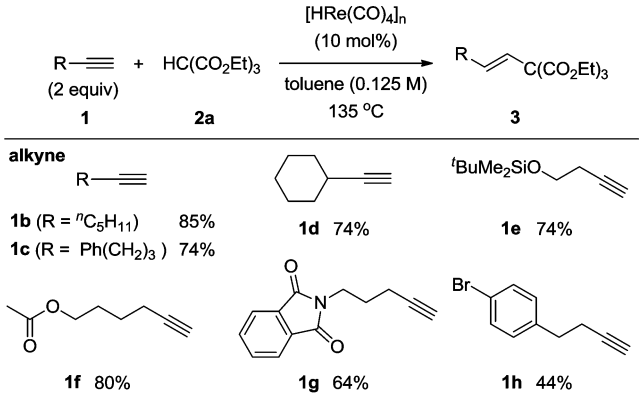


entry	solvent	temperature (°C)	yield of **3a**[a] (%)
1	C_6H_5Cl	135	46
2	octane	135	50
3	CH_2ClCH_2Cl	135	48
4	dioxane	135	52
5	MeCN	135	23
6	DMF	135	49
7	neat	135	49
8	toluene	100	44
9	toluene	120	51
10	toluene	135	53
11	toluene	150	52
12[b]	toluene	135	64
13[b,c]	toluene	135	81 (80)

[a]Determined by ^1H NMR. A value in parentheses is the isolated yield. [b]In toluene (0.125 M). [c]0.5 equiv of 1-dodecyne **1a** was added at the beginning, and additional **1a** was added three times (0.5 equiv each) at the interval of 2 h.

alkyl chains shown in Table 3 was successfully reacted with methanetricarboxylate **2a** to furnish the *anti*-Markovnikov

Table 3. Re-Catalyzed *anti*-Markovnikov Addition of Methanetricarboxylate 2a with Alkynes 1[a]



[a]0.5 equiv of alkyne **1** was added at the beginning, and additional **1** was added three times (0.5 equiv each) at the interval of 2 h.

adducts as single regio- and stereoisomers in all cases. Reactions with 1-heptyne **1b** and 5-phenyl-1-pentyne **1c** provided the corresponding adducts **3b** and **3c** in 85% and 74% yields, respectively. The corresponding *anti*-Markovnikov adduct **3d** was obtained, even when sterically congested cyclohexylacetylene **1d** was used as a substrate. Silyl and acetyl groups in **1e** and **1f** as protecting groups of the hydroxy group were well-tolerated under the current reaction conditions. The high chemoselectivity was also demonstrated in the reaction of alkynes **1f** and **1g** having coordinating functionalities, such as acetyl and amidocarbonyl groups. The reaction proceeded without affecting these functional groups to furnish the corresponding adducts **3f** and **3g** in moderate to good yields with complete regio- and stereoselectivities. Moreover, the

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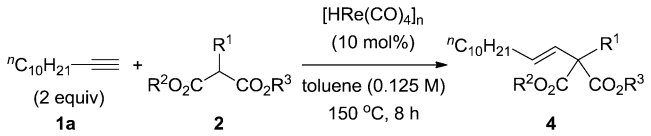
bromide group in **1h**, which can be further employed in various cross-coupling reactions, was tolerated, thereby showing the potential utility of the present reaction in various organic syntheses. Unfortunately, arylacetylenes (4-anisyl, phenyl, and 4-trifluoromethylphenyl acetylenes) as well as trimethylsilyl acetylene did not afford the expected adducts, and most of **2a** was recovered intact under the current reaction conditions. These results can be ascribed to the rapid oligomerization of aryl- and trimethylsilyl acetylene under the current rhenium-catalyzed reaction conditions.[11]

The substrate scope for the carbon nucleophile was next investigated with 1-dodecyne under the optimized reaction conditions (Table 4). Trimethyl methanetricarboxylate **2b**

Table 4. Re-catalyzed *anti*-Markovnikov Addition of Carbon Nucleophiles 2 with 1-Dodecyne 1a



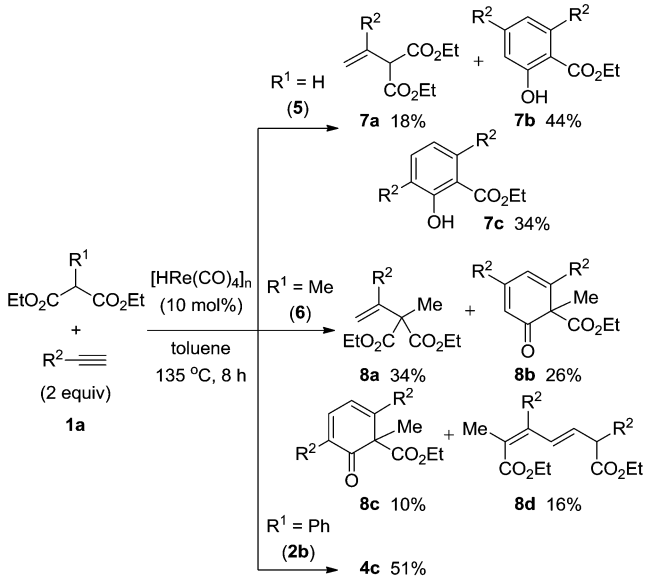
entry	Carbon Nucleophile 2	Product 4
1[a]	**2b**	**4b** 92%
2	**2c** (R = H)	**4c** 51%
3	**2d** (R = OMe)	**4d** 50%
4	**2e** (R = CF_3)	**4e** 49%
5	**2f**	**4f** 24%
6	**2g** (R^1 = NO_2) **2h** (R^1 = CN) **2i** (R^1 = Br)	0%
7	**2j**	0%

[a]0.5 equiv of 1-dodecyne **1a** was added at the beginning, and additional **1a** was added three times (0.5 equiv each) at the interval of 2 h at 135 °C.

reacted efficiently to produce the expected adduct **4b** in higher yield compared with that for **2a** (entry 1). It was soon found that the structure of the carbon nucleophiles required the diester moiety, otherwise the reactions did not proceed at all. When one of the ethoxycarbonyl groups of **2a** was replaced by a phenyl group, the corresponding adduct **4c** was obtained in 51% yield by increasing the reaction temperature up to 150 °C (entry 2). Formation of the *anti*-Markovnikov adduct was predominant again, and its regio- and stereoisomers were not detected at all. To confirm the electronic effect of the substituents, the reactions with 1,3-diesters **2d** and **2e** having electron-donating and -withdrawing groups were next carried out (entries 3 and 4). The corresponding adducts **4d** and **4e** were obtained in almost similar yields. Note that these *anti*-Markovnikov adducts **4c**−**4e** were formed in 12% (for **4c**), 6% (for **4d**), and 25% (for **4e**) yields in 5 min, indicating that the influence of the pK_a value of the proton at the active methylene carbon was significant (See Figure S1 in Supporting Information).[12,13] Although a cyclic 1,3-diester **2f** can be applied as a substrate, the expected adduct **4f** with a quaternary carbon center was obtained in low yield (entry 5). Unfortunately, the reaction with diesters **2g** and **2h** having other electron-withdrawing groups, such as nitro and cyano groups, did not afford any adducts, and the most of diesters were recovered (entry 6).[14] Diester **2i** having bromide group and **2j** prepared from Meldrum's acid were decomposed under the current reaction conditions (entries 6 and 7).

The result obtained in Table 4 implies that the choice of substituents on the active methylene carbon is crucial for the achievement of current *anti*-Markovnikov addition. This selectivity is in sharp contrast to our previous report, in which [2+2+2] cycloaddition occurred selectively without forming the corresponding *anti*-Markovnikov adducts by the reaction of 1,3-diesters with alkynes.[15] In fact, treatment of diethyl malonate **5** or 2-methylmalonate **6** with 1-dodecyne **1a** gave a regioisomeric mixture of ethyl salicylates **7b** and **7c** or cyclic *β*-keto ester **8b** and **8c** with the Markovnikov adduct **7a**, **8a**, and **8d** under the current reaction conditions (Scheme 2).[16]

Scheme 2. Re-catalyzed Reactions of Several Diethylmalonates with 1-Dodecyne 1a (R^2 = $^nC_{10}H_{21}$)



In this reaction, we proposed the rhenacyclopentene species as one of the most plausible key intermediates, which were formed via the oxidative cycloaddition between a 1,3-diester **5** or **6**, an alkyne **1**, and a rhenium catalyst. **8b** and **8c** were obtained through the insertion of a second equivalent of 1-dodecyne **1a** into the rhenium−carbon bond followed by the reductive elimination of the rhenium complex and the elimination of ethanol (Scheme 3). **8d** was produced by carbon−carbon bond cleavage via the *retro*-Dieckmann reaction.[17] Although factors affecting these reactivity differences remain to be elucidated, one possible explanation is that malonates **2** with bulky substituents (CO_2R or Ar) at the active methylene carbon may interrupt the coordination with rhenium complex and prevent the formation of rhenacyclopentene intermediates, which lead to the Markovnikov addition or [2+2+2] cycloaddition reaction.[18,19]

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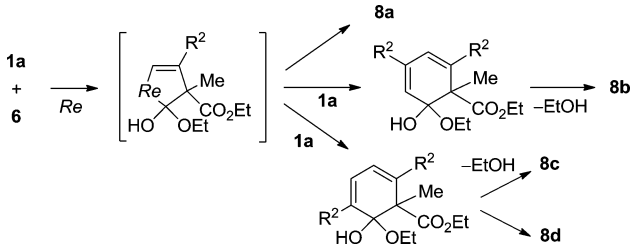
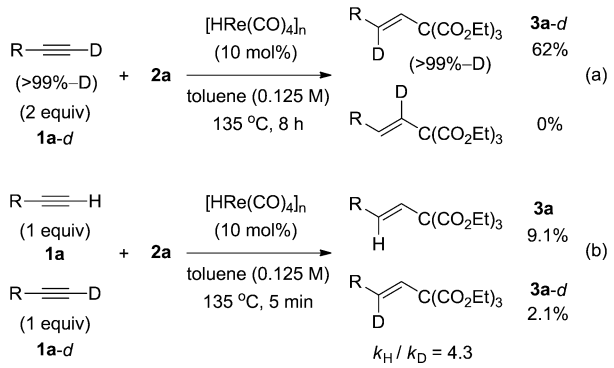
Scheme 3. Proposed Reaction Mechanism for the Formation of 8a-8d (R^2 = $^nC_{10}H_{21}$)



To gain insight into the reaction mechanism, several controlled experiments were carried out. When the reaction was carried out using a deuterated 1-dodecyne, deuterated **3a**-*d* was obtained exclusively in 62% yield without forming its isomer under the standard reaction conditions (Scheme 4a).

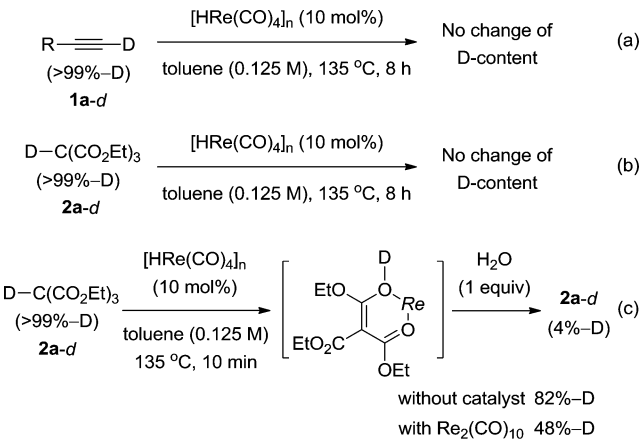
Scheme 4. Deuterium Labeling Experiments (R = $^nC_{10}H_{21}$)



This result and the fact that the use of 6-dodecyne in place of 1-dodecyne **1a** did not produce any adducts clearly support that the rhenium vinylidene species was generated during the reaction. Next, the competition reaction of **1a** vs **1a**-*d* with **2a** in the same flask resulted in the formation of a mixture of *anti*-Markovnikov adducts **3a** and **3a**-*d* in 2.1% and 9.1% yields in 5 min, respectively (Scheme 4b). The parallel reactions of **1a** and **1a**-*d* were also performed separately to afford **3a** and **3a**-*d* in a similar ratio. Thus, the competition and parallel kinetic isotope effect values (k_H/k_D) were both 4.3, indicating that vinylidene formation was involved in the rate-determining step.

Stoichiometric reaction of triester **2a**-*d* having a deuterium atom at the active methylene carbon with $[HRe(CO)_4]_n$ resulted in the no change of its deuterium content (Scheme 5a). Similarly, H–D scrambling of deuterated 1-dodecyne **1a**-*d* with $[HRe(CO)_4]_n$ was not observed under identical conditions.[20] These results are consistent with the previous reports by Huggins et al., in which they mentioned that H–D scrambling between D_2O and $[HRe(CO)_4]_n$ did not occur.[21] However, hydrogen–deuterium scrambling of **2a**-*d* with H_2O was found to be accelerated by $[HRe(CO)_4]_n$ catalyst (Scheme 5c). Deuterium content was decreased from >99% to 4% in the presence of $[HRe(CO)_4]_n$ catalyst, whereas 17% loss (from >99% to 82%) was observed in the absence of the catalyst. Since this H–D exchange should occur between enol form of **2a**-*d* and H_2O, the result clearly suggested that keto–enol tautomerization of **2a**-*d* was accelerated by the coordination of $[HRe(CO)_4]_n$ complex to **2a**-*d*. On the other hand, deuterium content was decreased to 48% when $Re_2(CO)_{10}$ was employed as a catalyst. These results imply that the difference of catalytic

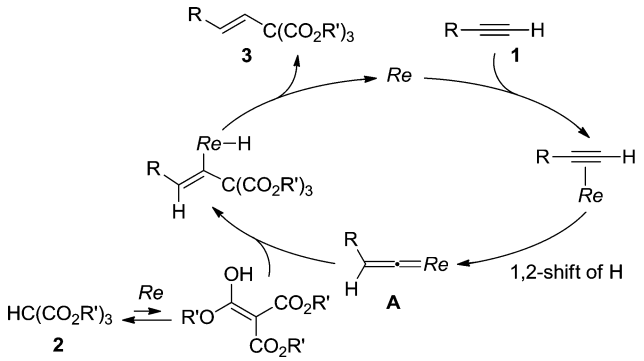
Scheme 5. Attempted H–D Exchange of 1a-*d* or 2a-*d* in the Presence of $[HRe(CO)_4]_n$



activity between $Re_2(CO)_{10}$ and $[HRe(CO)_4]_n$ observed in Table 1 (entries 1 vs 3) is derived from their slightly different Lewis acidity.[22]

On the basis of the above results and our previous reports,[6] we propose the following mechanism for the present reaction, using the reaction with methanetricarboxylate **2** as an example (Scheme 6). The transformation initiates with the generation of

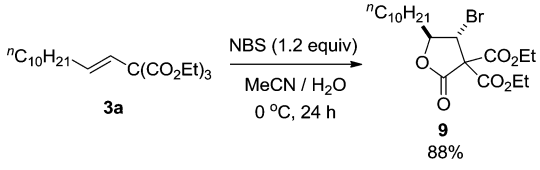
Scheme 6. Proposed Reaction Mechanism



the rhenium vinylidene intermediate **A**[23] via 1,2-migration of the terminal hydrogen atom of **1**, which is facilitated by the coordination of the carbon–carbon triple bond to the rhenium center.[24] Nucleophilic addition of triester **2** occurs selectively at the central carbon affords the corresponding *anti*-Markovnikov adduct **3** together with regeneration of the rhenium catalyst. The complete stereoselectivity can be explained by considering that the intermolecular nucleophilic attack of **2** occurs preferentially to minimize the steric repulsion of **2** and substituent R of the acetylene.

The current *anti*-Markovnikov adducts can be elaborated by further transformations to illustrate their synthetic utility (Scheme 7). For example, bromolactonization of **3a** by the

Scheme 7. Transformation of the Product



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reaction with NBS furnished the bromolactone **5** as a single stereoisomer in 88% yield.[25] Since γ-lactones are basic structural motifs frequently found in numerous biologically active natural products and pharmaceutical,[26] the selectively functionalized bromolactone **9** might serve as a useful building block for the stereodefined synthesis of this backbone.

CONCLUSION

The novel rhenium-catalyzed intermolecular *anti*-Markovnikov addition of carbon nucleophiles with unactivated terminal acetylenes has been demonstrated. The reaction proceeds under neutral conditions, and does not require the use of external ligands or additives, thus tolerating diverse functional groups. The current methodology represents a powerful diverse catalytic system for the regio- and stereoselective construction of complicated carbon frameworks. Methanetricarboxylates as well as 1,3-diesters having bulky substituents at the active methylene carbon are suitable as substrates, which expands the limited arena of *anti*-Markovnikov addition of carbon nucleophiles.

EXPERIMENTAL SECTION

General Procedure for Rhenium-Catalyzed *anti*-Markovnikov Addition Reaction of Methanetricarboxylates with Terminal Acetylenes. A flame-dried test tube was charged with $[HRe(CO)_4]_n$ (12.0 mg, 0.040 mmol), methanetricarboxylates **1** (0.40 mmol), terminal acetylenes **2** (0.20 mmol), and toluene (3.2 mL), and then the resulting mixture was stirred at 135 °C for 2 h. Additional alkyne was added three times at the interval of 2 h (0.20 mmol × 3). The solvent was removed under the reduced pressure, and the residue was subjected to flash column chromatography on silica gel with hexane/ethyl acetate (v/v = 10/1) as eluents to afford the corresponding *anti*-Markovnikov adducts **3** or **4** as single regio- and stereoisomers in all cases.

*Ethyl 2,2-di(ethoxycarbonyl)tetradec-(E)-3-enoate (**3a**).* A pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3H), 1.18−1.43 (m, 25H), 2.07−2.14 (m, 2H), 4.26 (q, J = 6.9 Hz, 6H), 5.79 (dt, J = 6.6, 15.9 Hz, 1H), 5.86 (d, J = 15.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 14.0, 22.6, 28.7, 28.9, 29.3, 29.4, 29.53, 29.54, 31.8, 32.7, 62.2, 67.7, 122.1, 136.3, 166.3. IR (neat/cm^{-1}): 2981, 2956, 2926, 2854, 1742, 1466, 1368, 1261, 1231, 1055, 966, 862. HRMS (FAB$^+$): calcd for $C_{22}H_{39}O_6$ ([M + H]$^+$) 399.2747; found. 399.2751.

*Transformation of the anti-Markovnikov Adduct **3a**.* To a stirred solution of **3a** (39.9 mg, 0.10 mmol) in MeCN (0.40 mL) and H_2O (0.20 mL) was added *N*-bromosuccinimide (21.4 mg, 0.12 mmol) at 0 °C. After stirring for 24 h, the reaction was quenched with aq. sodium thiosulfate. The residue was dissolved in EtOAc, washed with water, extracted with EtOAc, and then dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 10/1) as eluents to afford 4,5-*trans*-4-bromo-3,3-diethoxycarbonyl-5-dodecyldihydro-2(3H)-furanone **9** as a pale yellow oil (43.7 mg, 0.088 mmol, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 6.3 Hz, 3H), 1.26−1.72 (m, 23H), 1.92−2.03 (m, 1H), 4.23−4.44 (m, 4H), 4.56 (t, J = 8.7 Hz, 1H), 4.75 (d, J = 8.7 Hz, 1H). 13C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 14.1, 22.6, 25.3, 29.1, 29.2 (two peaks overlapped), 29.4, 29.5, 31.7, 31.8, 46.5, 63.4, 63.5, 67.0, 83.6, 162.9, 163.2, 164.8. IR (neat/cm^{-1}): 2982, 2926, 2855, 1802, 1748, 1732, 1466, 1456, 1369, 1302, 1279, 1211, 1113, 1099, 1032, 1013, 912, 860, 733. HRMS (FAB$^+$): calcd for $C_{20}H_{34}BrO_6$ ([M + H]$^+$) 449.1539; found. 449.1529.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Investigation of the reaction time with 10 mol% of $[HRe(CO)_4]_n$ in toluene (0.125 M) at 135 °C. Yield of **3a**: 56% for 0.5 h (recovery of **2a**: 32%); 61% for 1 h (**2a**: 18%); 64% for 2 h (**2a**: 15%); 64% for 24 h (**2a**: 0%).

(11) Even when phenylacetylene was treated with $[HRe(CO)_4]_n$ catalyst in the presence of TEMPO (2,2,6,6-tetramethylpiperidoxyl) or galvinoxyl free radical as radical scavengers, most of phenylacetylene was consumed probably due to its self-oligomerization. This result indicates that oligomerization did not proceed through a radical process. Although the mechanism is unclear at the moment, the oligomerization might proceed via the insertion of alkyne into the rhenacyclopetadiene intermediate, which could be formed from the reaction of $[HRe(CO)_4]_n$ with two equivalents of acetylenes.

(12) As implied by the hydrogen−deuterium exchange experiment shown in Scheme 5c, the reaction mechanism involved keto−enol tautomerization of diesters **2**, which was accelerated by the coordination of the rhenium complex to **2**. Since the enol form is more nucleophilic and the ratio of the enol form increased with the pK_a value of **2**, the initial reaction rate of **4e** might become larger than that of **4d**. Although one of the rate-determining steps should be vinylidene formation as shown in Scheme 4, attack of carbon nucleophiles might proceed slowly and affect the reaction rate.

(13) Diester **2e** having a trifluoromethyl group was partially decomposed at 150 °C probably via the decarbonylation. In contrast, diester **2d** having a methoxy group was stable under the present reaction conditions. This is the reason why the yield of **4d** increased as time goes by, although the initial reaction rate of **2d** was small.

(14) Although the reaction of malononitrile, 2-phenylmalononitrile, 4-nitrophenylacetonitrile, and 3,3,3-trifluoro-1-phenyl-1-propanone having cyano, nitro, and trifluoromethyl groups with 1-dodecyne have also examined, the expected *anti*-Markovnikov adducts were not obtained.

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(18) Too bulky substituents, such as isopropyl group, at the active methylene carbon of diester disrupted the reaction with 1-dodecyne. Because 1-dodecyne was consumed completely, we deduced that the nucleophilic attack of diethyl isopropylmalonate to the rhenium vinylidene intermediate was prevented in this reaction.

(19) Considering the difference of the yield obtained by the reaction with triester **2a** and cyclic diester **2f** despite of their similar steric crowding around the active methylene carbon, the reactivity seems not to be affected by only the steric effect. Because triester **2a** have lower pK_a, the ratio of the more nucleophilic enol form in the solution increases, and the corresponding adduct **4a** might be obtained in higher yield.

(20) When the reaction of **1a**-*d* with $[HRe(CO)_4]_n$ was examined at 135 °C, most of **1a**-*d* was oligomerized, and the recovery of **1a**-*d* was 8% yield. The same reaction carried out at 50 °C to avoid the competitive oligomerization resulted in the quantitative recovery of **1a**-*d*. Both of the recovered **1a**-*d* were obtained without loss of their deuterium contents.

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