General Synthesis of (Z)-Alk-1-en-1-yl Esters *via* Ruthenium-Catalyzed *anti*-Markovnikov *trans*-Addition of Carboxylic Acids to Terminal Alkynes

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The direct addition of carboxylic acids to terminal alkynes in the presence of catalytic amounts of (bis(diphenylphosphino)alkane)Ru(η^3-methallyl)$_2$ complexes provides a novel selective route to (Z)-alk-1-en-1-yl esters. This reaction involves an *anti*-Markovnikov and *trans*-addition to alkynes and gives access to a variety of new (Z)-alkene derivatives from hex-1-yne, phenylacetylene, and (trimethylsilyl)acetylene. The actual catalyst precursors are (bis(diphenylphosphino)alkane)Ru-(η^2-carboxylate)$_2$ complexes formed *in situ* during the reaction.

Enol esters are useful intermediates for carbon–carbon and carbon–heteroatom bond formation. They have been used for the selective generation of enolates,[1] acylation of carbonyl compounds,[2] and *O*- and *N*-acylation[3] under mild conditions. They are also suitable substrates for the access to α-halo ketones[4] and to carbonyl compounds *via* aldol-type reactions in the presence of tin derivatives[5] or palladium catalysts.[6] The carbon–carbon double bond of alkenyl esters has been involved in cyclopropanation,[7] Diels–Alder reactions,[8] [2 + 2] cycloaddition,[9] and 1,3-dipolar cycloaddition.[10] Recently, optically active branched aldehydes have been obtained *via* enantioselective rhodium-catalyzed hydroformylation of enol esters.[11] Vinyl acetate, acetoxystyrenes[12] and vinyl haloacetates[13] are important industrial monomers for the preparation of various polymers and copolymers. Vinyl and isopropenyl acetates have recently found useful applications in enzymatic synthesis.[14]

Alk-1-en-2-yl esters are the most commonly accessible acyclic enol esters *via* acylation of enolates,[15] transvinylation from vinyl or isopropenyl acetate in the presence of mercury(II), ruthenium(II), or palladium(II) catalysts,[13,16] or from vinylmercurials, obtained by acetoxymercuration of alkynes.[17] Moreover, oxidative acetoxylation of olefins catalyzed by palladium(II) derivatives is the basis of industrial processes for the production of enol acetates.[18] A straightforward synthesis of enol esters involves the catalytic addition of carboxylic acids to alkynes. Unsaturated lactones containing an exocyclic double bond have been obtained by cyclization of acetylenic acids in the presence of a variety of metal catalysts, such as mercury(II),[19] silver(I),[20] rhodium(I),[21] and pal-

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(1) (a) House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310. (b) House, H. O.; Auerback, R. A.; Gall, M.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514.

(2) (a) Rothman, E. S.; Moore, G. G. *Tetrahedron Lett.* **1969**, 2553. (b) Rothman, E. S.; Moore, G. G.; Speca, A. N. *Tetrahedron Lett.* **1969**, 5205.

(3) (a) van Melick, J. E. W.; Scheeren, J. W.; Nivard, R. J. F. *Tetrahedron Lett.* **1971**, 2083. (b) van Melick, J. E. W.; Wolters, E. T. M. *Synth. Commun.* **1972**, 83. (c) Kabouche, Z.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1991**, *32*, 5359. (d) Neveux, M.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1197. (e) Neveux, M.; Bruneau, C.; Lécolier, S.; Dixneuf, P. H. *Tetrahedron* **1993**, *49*, 2629. (f) Kita, Y.; Akai, S.; Ajimura, N.; Yoshigi, M.; Tsugoshi, T.; Yasuda, H.; Tamura, Y. *J. Org. Chem.* **1986**, *51*, 4150. (g) Villemin, D.; Labiad, B.; Loupy, A. *Synth. Commun.* **1993**, *23*, 419.

(4) (a) Cort, A. D. *J. Org. Chem.* **1991**, *56*, 6708. (b) Cambie, R. C.; Hayward, R. C.; Jurlina, J. L.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 126. (c) Torii, S.; Inokuchi, T.; Misima, S.; Kobayashi, T. *J. Org. Chem.* **1980**, *45*, 2731. (d) Stavber, S.; Sket, B.; Zajc, B.; Zupan, M. *Tetrahedron* **1989**, *45*, 6003.

(5) (a) Masuyama, Y.; Kobayashi, Y.; Yanagi, R.; Kurusu, Y. *Chem. Lett.* **1992**, 2039. (b) Masuyama, Y.; Kobayashi, Y.; Kurusu, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1123.

(6) (a) Kosugi, M.; Hagiwara, I.; Sumiya, T.; Migita, T. *J. Chem. Soc., Chem. Commun.* **1983**, 344. (b) Kosugi, M.; Hagiwara, I.; Migita, T. *Chem. Lett.* **1983**, 839. (c) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 4713. (d) Masuyama, Y.; Sakai, T.; Kurusu, Y. *Tetrahedron Lett.* **1993**, *34*, 653. (e) Listemann, M. L. U.S. Pat. 5239112, 1993. (f) Masuyama, Y.; Sakai, T.; Kato, T. ; Kurusu, Y. *Bull. Chem. Soc. Jpn* **1994**, *67*, 2265.

(7) (a) Demonceau, A.; Saive, E.; de Froidmont, Y.; Noels, A. F.; Hubert, A. J. *Tetrahedron Lett.* **1992**, *33*, 2009. (b) Motherwell, W. B.; Roberts, L. R. *J. Chem. Soc., Chem. Commun.* **1992**, 1582.

(8) (a) Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4309. (b) Tietze, L. F.; Montenbruck, A.; Schneider, C. *Synlett* **1994**, 509.

(9) Wexler, A.; Balchunis, R. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1975**, 601.

(10) Pirrung, M. C.; Lee, Y. R. *Tetrahedron Lett.* **1994**, *35*, 6231.

(11) (a) Sakai, N.; Nozaki, K.; Mashima, K.; Takaya, H. *Tetrahedron: Asymmetry* **1992**, *3*, 583. (b) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033. (c) Arena, C. G.; Nicolo, F.; Drommi, D.; Bruno, G.; Faraone, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2251.

(12) Monthéard, J. P.; Camps, M.; Seytre, G.; Guillet, J.; Dubois, J. C. *Angew. Makromol. Chem.* **1978**, *72*, 45.

(13) Seidel, A.; Jägers, E.; Bylsma, F. Eur. Pat. 0574 725 A1, 1993.

(14) (a) Menendez, E.; Gotor, V. *Synthesis* **1993**, 72. (b) Larpent, C.; Chasseray, X. *New J. Chem.* **1993**, *17*, 851. (c) Uemura, M.; Nishimura, H.; Yamada, S.; Nakamura, K.; Hayashi, Y. *Tetrahedron Lett.* **1993**, *34*, 6581. (c) Matsumoto, K.; Ohta, H. *Chem. Lett.* **1989**, 1589. (d) Kume, Y.; Ohta, H. *Tetrahedron Lett.* **1992**, *33*, 6367. (e) Lobell, M.; Schneider, M. P. *Tetrahedron: Asymmetry* **1993**, *4*, 1027.

(15) (a) Mao, C. L.; Hauser, C. R. *Org. Synth.* **1971**, *51*, 90. (b) Russell, G. A.; Sabourin, E. T. *J. Org. Chem.* **1969**, 2336. (c) Blanc, P. Y. *Helv. Chim. Acta* **1961**, 1. (d) Kowalski, C.; Creary, X.; Rollin, A. J.; Burke, M. C. *J. Org. Chem.* **1978**, *43*, 2601. (e) Dénes, V. I.; Ciurdaru, G. *J. Chem. Soc., Chem. Commun.* **1970**, 510. (f) Gwynn, B. H.; Degering, E. F. *J. Am. Chem. Soc.* **1942**, *64*, 2216. (g) Rothman, E. S.; Moore, G. G. *Tetrahedron Lett.* **1971**, 1065. (h) Libman, J.; Mazur, Y. *Tetrahedron* **1969**, 1699.

(16) (a) Mondal, M. A. S.; van der Meer, R.; German, A. L.; Heikens, D. *Tetrahedron* **1974**, 4205. (b) Rothman, E. S.; Serota, S.; Swern, D. *J. Org. Chem.* **1966**, *31*, 629. (c) Murray, R. E. Eur. Pat. 0351603 A2, 1989. (d) Lobell, M.; Schneider, M. P. *Synthesis* **1994**, 375.

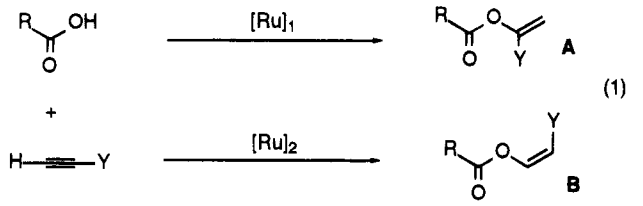
(17) (a) Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966. (b) Bach, R. D.; Woodard, R. A.; Anderson, T. J.; Glick, M. D. *J. Org. Chem.* **1982**, *47*, 3707.

(18) (a) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. In *New Pathways for Organic Synthesis*; Plenum Press: New York, 1985; p 350. (b) Nicoleau, I.; Colling, P.; Johnson, L. Int. Pat. WO 94/08714, 1994.

(19) (a) Yamamoto, M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 582. (b) Jellal, A.; Grimaldi, J.; Santelli, M. *Tetrahedron Lett.* **1984**, *25*, 3179. (c) Yamamoto, M. *J. Chem. Soc., Chem. Commun.* **1978**, 649. (d) Kraft, G. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5459. (e) Spencer, R. W.; Tam, T. F.; Thomas, E.; Robinson, V. J.; Krantz, A. *J. Am. Chem. Soc.* **1986**, *108*, 5589.

0022-3263/95/1960-7247$09.00/0

ladium(II)[22] derivatives. Carboxylic acids have been added to the internal C(2) carbon atom of terminal alkynes by using metal catalysts based on zinc,[23] mercury,[24] palladium,[25] and rhodium.[26] The best catalytic systems appear to be based on ruthenium, and since the first synthesis of alkenyl esters by direct addition of carboxylic acids to alkynes, catalyzed by $Ru_3(CO)_{12}$,[27] the regioselectivity of the Markovnikov addition has been significantly increased for the production of derivatives of type **A** (eq 1) by using a variety of ruthenium precursors such as (cyclooctadienyl)$_2$Ru,[28] (arene)$RuCl_2(PR_3)$,[29] or $(Ru(O_2CR)(CO)_2(PR_3))_2$[30] for functional carboxylic acids and $((arene)RuCl_2)_2$[31] for ethoxyacetylene.

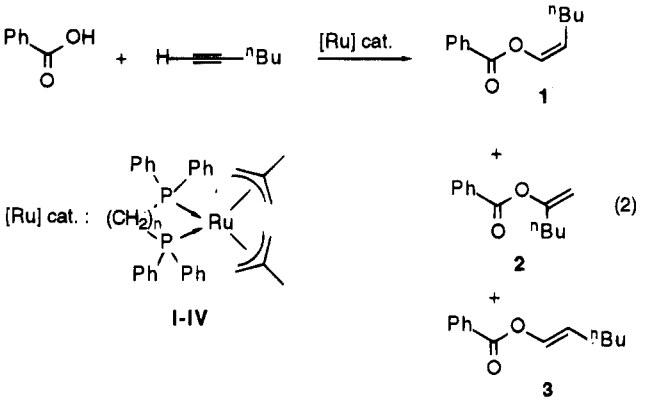


Among these methods, no general preparation of alk-1-en-1-yl esters corresponding to an *anti*-Markovnikov addition of the carboxylic acid to the triple bond was discovered. Despite their usefulness in synthetic chemistry as masked aldehydes, only scarce examples have been described, all of them prepared by stoichiometric transformation of organometallics: by reaction of acyl chlorides with chromium carbenes,[32] elimination of a trimethylsilyl group from β-hydroxy silanes,[33] and acetoxylation of vinylmercurials.[17a] We now report that the modification of the active ruthenium(II) center by coordination of a chelating diphosphine and labile allylic ligands in complexes $(Ph_2P(CH_2)_nPPh_2)Ru(methallyl)_2$ provides suitable catalyst precursors for the *anti*-Markovnikov addition of carboxylic acids to terminal alkynes to stereoselectively afford (*Z*)-alk-1-en-1-yl esters of type **B** (eq 1). Following our preliminary results,[34] we now show that this reaction, extended to a variety of alkynes and carboxylic acids, stands as a general method for the selective access to functionalized (*Z*)-alkenes and aldehyde precursors and that the catalytic reaction involves the formation of $(Ph_2P(CH_2)_nPPh_2)Ru(O_2CR)_2$ derivatives, which do not transfer their coordinated carboxylate to the alkyne.

Results and Discussion

Selective Synthesis of (*Z*)-Alk-1-en-1-yl Esters. Our studies of ruthenium(II) as catalyst precursor for electrophilic activation of alkynes[29,30,35] suggested that to increase their catalytic activity under mild conditions and to reverse the regioselectivity of nucleophilic addition very labile ligands as compared to chlorides should be introduced to provide an easy access to vacant sites on the ruthenium center. We decided to study the $(Ph_2P(CH_2)_nPPh_2)Ru(\eta^3\text{-}CH_2C(Me)=CH_2)_2$ complexes that, in addition to the easily removable methallyl ligands, contain a chelating diphosphine, more able to stabilize a catalytic metal site than monodentate phosphines. The influence of the chelating ligand on the ruthenium site can be modulated by modification of the chain linking the two PPh_2 groups.

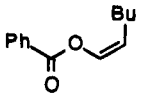
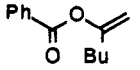
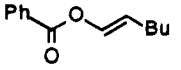
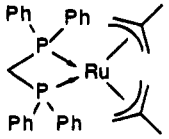
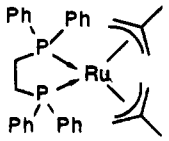
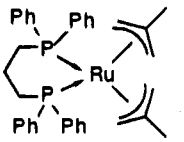
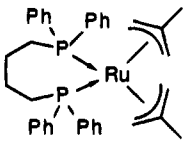
Benzoic acid readily reacted with hex-1-yne in the presence of a catalytic amount of [bis(diphenylphosphino)alkane][bis(2-methylpropenyl)]ruthenium complexes **I–IV**[36] (1 mol %) in toluene at 65 °C to afford hexenyl benzoates **1–3** (eq 2, Table 1).



The results in Table 1 show that complexes **I–IV** are efficient catalyst precursors for the activation of C–C triple bonds toward the addition of carboxylic acids as the conversion of the alkyne is complete. Complexes **I–IV** make possible the addition of benzoic acid to hex-1-yne at 65 °C, which is a very mild temperature as compared to that required with other ruthenium(II) catalysts precursors[28–30] which mainly led to enol ester **2**. It is noteworthy that the rate and regioselectivity of the addition strongly depend on the nature of the diphosphine ligand coordinated to the ruthenium(II) center. Complex **IV**, containing the 1,4-bis(diphenylphosphino)butane ligand, leads to 95% of isolated enol benzoates containing 98% of the (Z)-alk-1-en-1-yl benzoate **1**. Precursor **IV** thus appears as the first catalyst

(20) (a) Jong, T. T.; Williard, P. G.; Porwoll, J. P. *J. Org. Chem.* **1984**, *49*, 735. (b) Dalla, V.; Pale, P. *Tetrahedron Lett.* **1994**, *35*, 3525. (c) Castaner, J.; Pascual, J. *J. Chem. Soc.* **1958**, 3962. (d) Pale, P.; Chuche, J. *Tetrahedron Lett.* **1987**, *28*, 6447.
(21) (a) Marder, T. B.; Chan, D. M. T.; Fultz, W. C.; Calabrese, J. C.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1885. (b) Chan, D. M. T.; Marder, T. B.; Milstein, D.; Taylor, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 6385.
(22) (a) Lambert, C.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 5323. (b) Yanagihara, N.; Lambert, C.; Iritani, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 2753. (c) Kundu, N. G.; Pal, M. *J. Chem. Soc., Chem. Commun.* **1993**, 86. (d) Tsuda, T.; Ohashi, Y.; Nagahama, N.; Sumiya, R.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 2650. (e) Bouyssi, D.; Goré, J.; Balme, G. *Tetrahedron Lett.* **1992**, *33*, 2811. (f) Arcadi, A.; Burini, A.; Cacchi, S.; Delmastro, M.; Marinelli, F.; Pietroni, B. R. *J. Org. Chem.* **1992**, *57*, 976.
(23) Rothman, E. S.; Hecht, S. S.; Pfeffer, P. E.; Silbert, L. S. *J. Org. Chem.* **1972**, *37*, 3551.
(24) Hudrlik, P. F.; Hudrlik, A. M. *J. Org. Chem.* **1973**, *38*, 4254.
(25) Lu, X.; Zhu, G.; Ma, S. *Tetrahedron Lett.* **1992**, *33*, 7205.
(26) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Bruneau, C.; Dixneuf, P. H. *Organometallics* **1990**, *9*, 1155.
(27) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689.
(28) (a) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1566. (b) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1986**, *27*, 2125. (c) Hori, Y.; Mitsudo, T.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *321*, 397. (d) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *J. Org. Chem.* **1987**, *52*, 2230.
(29) (a) Ruppin, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1986**, *27*, 6323. (b) Ruppin, C.; Dixneuf, P. H.; Lécolier, S. *Tetrahedron Lett.* **1988**, *29*, 5365. (c) Bruneau, C.; Neveux, M.; Kabouche, Z.; Ruppin, C.; Dixneuf, P. H. *Synlett* **1991**, 755.
(30) Neveux, M.; Seiller, B.; Hagedorn, F.; Bruneau, C.; Dixneuf, P. H. *J. Organomet. Chem.* **1993**, *451*, 133.
(31) Kita, Y.; Maeda, H.; Onari, K.; Okuno, T.; Tamura, Y. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2999.
(32) Söderberg, B. C.; Turbeville, M. J. *Organometallics* **1991**, *10*, 3951.
(33) (a) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993.
(34) Doucet, H.; Höfer, J.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 850.
(35) Höfer, J.; Doucet, H.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1991**, *32*, 7409.
(36) Höfer, J.; Doucet, H.; Bruneau, C.; Dixneuf, P. H. To be published.

Table 1. Synthesis of Hex-1-en-1-yl Benzoates from Hex-1-yne and Benzoic Acid. Influence of the Nature of the Ru(η^3-methallyl)$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_2$ Catalyst Precursor[a]

run	catalyst precursor		reaction time (h)	enol esters distribution (%)[b]		
						
				1	**2**	**3**
1		**I**	3	16	80	4
2		**II**	24	72	7	21
3		**III**	24	69	25	6
4		**IV**	2.5	98	0	2

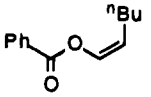
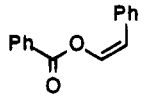
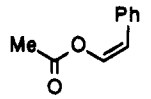
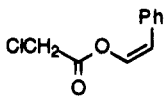
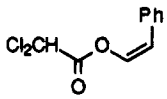
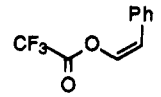
[a]Reactions were carried out by using 10 mmol of benzoic acid, 10 mmol of hex-1-yne and 0.1 mmol of catalyst in 5 ml of toluene at 65 °C under an inert atmosphere. [b]Determined by VPC after complete conversion of the starting products.

precursor leading to regio- and stereoselective *anti*-Markovnikov addition to terminal alkynes. The catalytic addition of benzoic acid to hex-1-yne at 100 °C in the presence of complex **IV** led to a complete conversion of the starting materials in 1.7 h but with a drastic loss of regioselectivity since the isomers **1** and **2** were obtained in the ratio **1**/**2** = 20/78 (Table 2, run 6). However, the addition of benzoic acid to phenylacetylene was less sensitive to temperature. In the presence of catalyst precursor **IV**, the (*Z*)-styryl benzoate **4** was obtained as the major enol ester in 96 and 98% selectivity at 100 and 60 °C, respectively (Table 2). The loss of selectivity observed with hex-1-yne, due to the increase of the reaction temperature, can be overcome by adding small amounts of triphenylphosphine or tertiary amine to the catalytic system. Thus, by addition of 1 mol % of PPh_3 or 4 mol % of NEt_3 to 1 mol % of catalyst **IV**, the addition of benzoic acid to hex-1-yne at 100 °C became regio- and stereoselective, leading respectively to 95 and 96% of (*Z*)-hexenyl benzoate. The rate of the reaction was slightly decreased in the presence of triphenylphosphine: the complete conversion of the reactants was obtained in 4.5 h, whereas only 1.5 h was needed in the presence of NEt_3 at 100 °C or without additive at 65 °C. The effect of the addition of phosphine to complex **IV** is opposite to that observed with the catalytic system based on bis(η^5-cyclooctadienyl)ruthenium/maleic anhydride, where the addition of PBu_3 regioselectively orientates the addition at C(2) carbon of the triple bond to produce geminal alkenyl esters of type **A**.[28d] This observation confirms the importance of the bidendate diphosphine ligand in the regioselectivity of the addition. These results on the addition of benzoic acid to phenylacetylene and hexyne show that the bulkyness of the alkyne becomes an important factor in the regioselectivity of the addition as the reaction temperature is increased.

The steric effect of the carboxylic acid has also been studied. At 60 °C, after complete conversion of the acid and phenylacetylene into styryl esters, acetic acid led to a 90% yield of acetates containing 76% of (*Z*)-styryl acetate (**5**), whereas benzoic acid gave 92% of styryl benzoates containing 98% of the (*Z*)-isomer **4** (Table 2), suggesting that the regioselectivity increased with the size of the carboxylic acid. The acidity of the carboxylic acid had a drastic influence on the reaction temperature: the lower the pK_a of the acid, the lower the reaction temperature. Thus, strong acids requiring lower temperature led to higher regio- and stereoselectivities. This important feature made possible the synthesis of (*Z*)-alkenyl esters **6**, **7**, and **8** from strong carboxylic acids such as chloro-, dichloro-, and trifluoroacetic acids under very mild conditions (below room temperature) (Table 2). At 0 °C, trifluoroacetic acid led to a 100% yield of (*Z*)-styryl trifluoroacetate whereas at 20 °C it gave only a mixture of isomers containing 60% of the (*Z*)-isomer **8**. Finally, we have shown that in each case the lower the reaction temperature, the higher the stereoselectivity, but a minimum temperature had to be found in the range (0−80 °C) to obtain a reasonable reaction rate.

The above reaction can be applied to the production of (*Z*)-alk-1-en-1-yl carboxylates from a variety of carboxylic acids (Table 3). The addition of the saturated acetic and

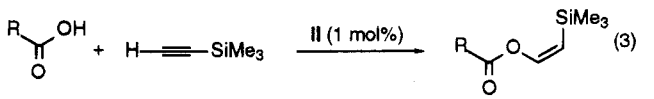
Table 2. Synthesis of (Z)-Alk-1-en-1-yl Esters from Terminal Alkynes. Influence of Temperature and Acidity of the Carboxylic Acid[a]

run	acid	alkyne	temp. °C	time h	product		yield[b] %	selectivity[c] %
5	$PhCO_2H$	hex-1-yne	65	2.5		**1**	95	98
6	"	"	100	1.7	**1**(20), **2**(78), **3**(2)		95	20
7	"	phenylacetylene	100	3		**4**	97	96
8[d]	"	"	60	18	"	**4**	92	98
9	CH_3CO_2H	"	60	4		**5**	90	76
10	"	"	45	4	"	**5**	90	99
11	CH_2ClCO_2H	"	20	24		**6**	90	99
12	$CHCl_2CO_2H$	"	20	21		**7**	78	100
13	CF_3CO_2H	"	0	6		**8**	61	100

[a]Reactions were carried out by using 10 mmol of carboxylic acid, 10 mmol of alkyne and 0.1 mmol of complex **IV** in 5 ml of toluene (runs 5-8, 11-13) or hexane (runs 9, 10) under nitrogen. [b]Isolated yield. [c]((Z)-isomer/total enol esters)x100. [d]50 mmol of benzoic acid and 50 mmol of phenylacetylene.

valeric acids to hex-1-yne in the presence of complex **IV** gave enol esters **9** and **10** in moderate isolated yields but with good regio- and stereoselectivities (91 and 98%, respectively). The bulkier diphenylacetic or 2,6-difluorobenzoic acid reacted regioselectively at higher temperature (65 °C) to give esters **11** and **12**. The reaction with *N*-protected amino acids was highly stereoselective: (*Z*)-hexenyl esters **13** and **14** were obtained at 65 °C in 71 and 97% respective yields from Boc-alanine and Boc-phenylalanine with 94 and 100% stereoselectivity and without racemization of the acid moiety, as shown by the regeneration of the enantiopure amino acid after hydrolysis. The utilization of phenylacetylene gave access to (*Z*)-styryl esters in very good yields and high stereoselectivity (>97%). Saturated aliphatic acids (runs 20 and 21) reacted under mild conditions (T < 65 °C) to provide esters **15** and **16** in high selectivity. From unsaturated aliphatic acids, (*Z*)-styryl acrylate (**17**) and crotonate (**18**), new monomers able to polymerize or copolymerize, were produced in high selectivity. Benzoic acid gave (Z)-styryl benzoate (**4**) in 92% yield and 98% stereoselectivity at 60 °C (Table 2), whereas the functional 2-hydroxybenzoic and 2-acetoxybenzoic acids led to esters **20** and **21** at 80 °C. The addition of *N*-protected alanine led to the optically pure (*Z*)-styryl alaninate in quantitative yield. These catalytic reactions tolerated a variety of organic solvents like toluene, pentane, or tetrahydrofuran.

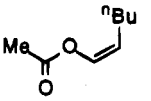
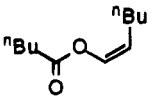
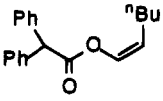
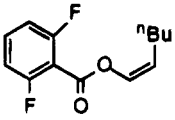
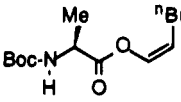
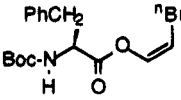
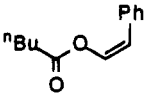
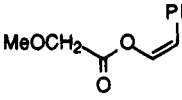
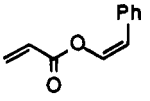
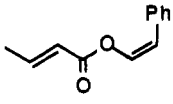
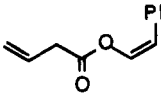
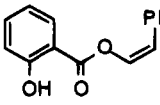
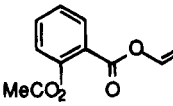
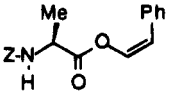
Stereoselective Synthesis of Silylated (Z)-Alk-1-en-1-yl Esters. The mild reaction conditions, especially the low temperature, made possible the use of thermosensitive reagents such as (trimethylsilyl)acetylene. However, the addition of benzoic acid in the presence of $(Ph_2P(CH_2)_4PPh_2)Ru(2\text{-methylpropenyl})_2$ (**IV**) was very slow since after 24 h, even though the reaction was regio- and stereoselective, only a 34% yield of (*Z*)-alkenyl ester was obtained (Table 4). The catalyst precursor $(Ph_2P(CH_2)_2PPh_2)Ru(2\text{-methylpropenyl})_2$ (**II**) appeared to be much more efficient in gaining access to a variety of silylated (*Z*)-enol esters in good yields (eq 3, Table 4).



(3)

Thus, a variety of (*Z*)-2-(trimethylsilyl)alk-1-en-1-yl esters were selectively obtained in 71−96% yields from aliphatic **24** and **25**, aromatic **23**, and functional carboxylic acids **26** and **27** (Table 4). These new silylated enol esters are precursors of β-silylated aldehydes which have recently been isolated for the first time.[37]

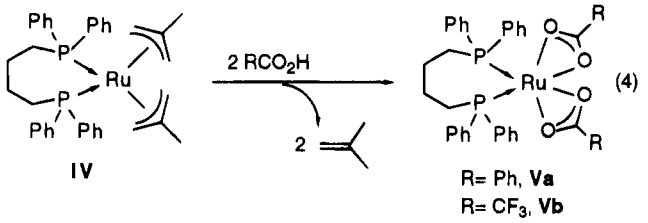
Table 3. Synthesis of (Z)-Alk-1-en-1-yl Esters from Terminal Alkynes and Carboxylic Acids[a]

run	acid	alkyne	temp. °C	time h	enol ester		yield[b] %	selectivity[c] %
14	acetic acid	hex-1-yne	40	4		**9**	35	91
15	valeric acid	"	"	22		**10**	35	98
16	diphenylacetic acid	"	65	20		**11**	97	100
17	2,6-difluorobenzoic acid	"	65	2		**12**	94	96
18[d]	Boc-alanine	"	65	24		**13**	71	94
19[d]	Boc-phenylalanine	"	65	20		**14**	97	100
20	valeric acid	phenyl acetylene	45	1.5		**15**	92	99
21	methoxyacetic acid	"	65	3		**16**	96	97
22	propenoic acid	"	45	5		**17**	65	99
23	(*E*)-but-2-enoic acid	"	45	6		**18**	85	99
24	3-butenoic acid	"	40	20		**19**	84	97
25	2-hydroxybenzoic acid	"	80	24		**20**	94	100
26	2-acetoxybenzoic acid	"	80	20		**21**	98	100
27[e]	Z-alanine	"	65	24		**22**	98	100

[a]Reactions were carried out by using 10 mmol of carboxylic acid, 10 mmol of alkyne and 0.1 mmol of complex **IV** in toluene (runs 16-19, 21, 22, 24-27), pentane (runs 14-15, 21) or THF (run 23) under nitrogen. [b]Isolated yield. [c]((Z)-isomer/total enol esters)x100. [d]Boc : *tert*-butoxycarbonyl. [e]Z : benzyloxycarbonyl.

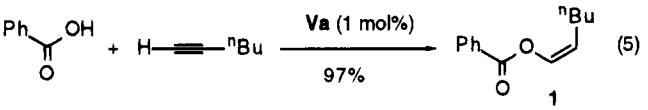
Mechanism

The mechanism of this catalytic reaction was investigated on the basis of complex **IV**, which appeared to be the most efficient catalyst. Although it is not possible to demonstrate the catalytic cycle, several observations can be made. In the presence of carboxylic acid at the reaction temperature, a ligand exchange took place from complex **IV**. The reaction of **IV** with benzoic and trifluoroacetic acids led to the isolation of (bis(diphenylphosphino)butane)Ru(η^2-$O_2CR)_2$ complexes **Va** and **Vb**,[38] respectively, according to eq 4.



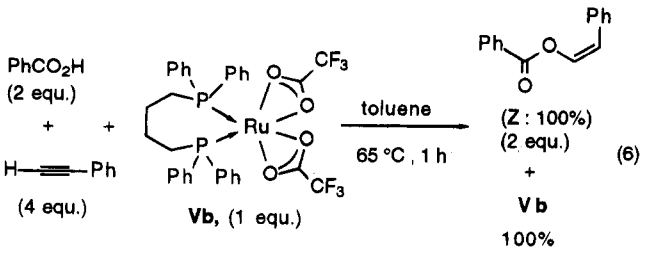
(4)

The addition of benzoic acid to hexyne (10 mmol), carried out at 65 °C for 3 h in the presence of 1 mol % of complex **Va** as catalyst precursor, led to a complete conversion of the starting materials and formation of (*Z*)-hex-1-en-1-yl benzoate **1** in 97% selectivity (eq 5). Moreover, complex **Va** was recovered at the end of the reaction and thus appeared to be the actual catalyst precursor or the catalyst itself.



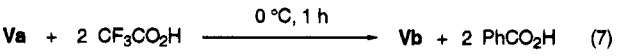
(5)

Coupling of the alkyne with the carboxylate could occur according to two different pathways: either insertion of the triple bond into a (carboxylato)O–Ru bond or coordination of the alkyne followed by addition of an external carboxylate. The former proposal was ruled out by performing a stoichiometric reaction according to eq 6. The reaction of 2 equiv of benzoic acid with 4 equiv of phenylacetylene at 65 °C for 1 h in the presence of 1 equiv of (bis(diphenylphosphino)butane)Ru(η^2-$O_2CCF_3)_2$ (**Vb**) led to the formation of (*Z*)-styryl benzoate without any trace of styryl trifluoroacetate, and the starting complex **Vb** was recovered unchanged. This experiment showed that the coordinated carboxylate group ($CF_3CO_2^-$) did not add to the alkyne but only to the external free carboxylic acid $PhCO_2H$.



(6)

A stoichiometric reaction of 2 equiv of trifluoroacetic acid with 1 equiv of complex **Va** at 0 °C gave **Vb** in quantitative yield within 1 h. This showed that the coordination of the trifluoroacetate is favored with respect to that of the benzoate ligand (eq 7).



(7)

Indeed, the parallel experiment to that of eq 6, but carried out at 0 °C, with 4 equiv of phenylacetylene and 2 equiv of trifluoroacetic acid in the presence of 1 equiv of complex **Va** led to a fast ligand exchange as complex **Vb** was formed quantitatively within 1 h, and the complete conversion of the freed benzoic acid into only (*Z*)-styryl benzoate was observed after 5 h.

On the basis of these observations, we propose that the first step is the ligand substitution of the allylic groups by the carboxylates with elimination of isobutene to produce complex **V** (Scheme 1). A rearrangement of the (η^2-carboxylate) into (η^1-carboxylate) ligands (**VI**) would make possible the coordination of the alkyne to give intermediate **VII**. From this intermediate, several resonance forms (**VIIb,c**) and the vinylidene tautomer **VIIa** can be postulated, depending on the ancillary bidentate ligands. The external addition of the carboxylate to the electrophilically activated C(1) of the alkyne might then take place to form the intermediate **VIII**. On subsequent protonolysis of the Ru–C bond, or protonation of the ruthenium center followed by reductive elimination, the alkenyl ester is liberated. The regioselectivity of the reaction may depend on the electron deficiency of the coordinated triple bond. Its polarization according to **VIIb** with a positive charge at the unsubstituted carbon atom of the alkyne due to electronic effects of the diphosphine ligand, or the formation of the tautomeric ruthenium–vinylidene moiety **VIIa**, easily formed from a terminal alkyne and ruthenium(II) complexes,[39] would favor the addition of the carboxylate at the electrophilic C(1) of the terminal alkyne. The selective formation of (*Z*)-isomers suggests a ruthenium intermediate of type **VIII**, which on protonation would lead to a formal *trans*-addition of the acid to the triple bond. The rate of the addition of carboxylic acids to (trimethylsilyl)acetylene is lower with catalyst **IV** than with **II**. This might be due to steric interactions between the phenyl groups of the diphosphine ligand and the bulky $SiMe_3$ group.

Conclusion

Our study has shown that the catalytic addition of carboxylic acids to terminal alkynes in the presence of ($Ph_2P(CH_2)_nPPh_2$)Ru(η^3-$CH_2C(Me)=CH_2)_2$ precursors provides a new general access,[40] under mild conditions (0–65 °C), to (*Z*)-alk-1-en-1-yl esters derivatives *via* a regio- and stereoselective *anti*-Markovnikov and *trans*-addition reaction. This reaction offers potential for the selective transformation of terminal alkynes into (*Z*)-alkene derivatives or masked aldehydes. It has been established that the more efficient ruthenium precursors are ($Ph_2P(CH_2)_4PPh_2$)Ru(η^3-$CH_2C(Me)=CH_2)_2$ (**IV**) and, for the addition to the bulky HC≡$CSiMe_3$, ($Ph_2P(CH_2)_2PPh_2$)Ru-

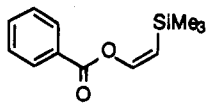
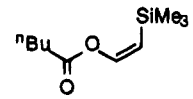
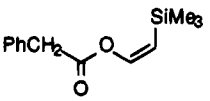
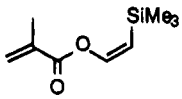
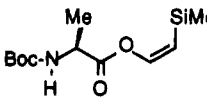
(37) Duhamel, L.; Gralak, J.; Bouyanzer, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1763.

(38) Complexes **Va** and **Vb** were prepared and characterized separately. Selected data: **Va**, IR (KBr) ν 1630, 1540, 1380, 695; ^{31}P NMR (CD_2Cl_2) δ 60.75 (s); ^{1}H NMR (CD_2Cl_2) δ 1.75 (m, 4H, $PCH_2(CH_2)_2CH_2P$), 2.50 (m, 4H, CH_2P), 7.00–7.60 (m, 30H, Ph); ^{13}C NMR (CD_2Cl_2) δ 23.89 (s, $PCH_2(CH_2)_2CH_2P$), 28.70 (d, J = 26 Hz, CH_2P), 182.26 (s, O_2C). **Vb**, IR (KBr) ν 1700, 1435, 1200, 695; ^{31}P NMR (CD_2Cl_2+CD_3OD) δ 53.97 (s); ^{1}H NMR (CD_2Cl_2) δ 1.60 (m, 4H, $PCH_2(CH_2)_2CH_2P$), 2.40 (m, 4H, CH_2P), 7.20–7.60 (m, 20H, Ph).

(39) (a) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768. (b) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579. (c) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132.

(40) The addition of carboxylic acids to functional alkynes such as enynes and propargylic ethers under similar conditions also takes place and is under investigation.

Table 4. Synthesis of (Z)-2-(Trimethylsilyl)alk-1-en-1-yl Esters from Carboxylic Acids and Trimethylsilylacetylene[a]

run	acid	solvent	temp °C	time h	product		yield[b] %	selectivity[c] %
28[d]	benzoic acid	toluene	60	24		**23**	34	100
29	benzoic acid	"	"	3	"	**23**	88	100
30	valeric acid	hexane	"	3.5		**24**	71	98
31	phenylacetic acid	toluene	"	18		**25**	96	100
32	2-methylpropenyl acid	hexane	50	24		**26**	76	100
33[e]	Boc-alanine	toluene	"	24		**27**	75	100

[a]Reactions were carried out by using 10 mmol of carboxylic acid, 10 mmol of trimethylsilylacetylene and 0.1 mmol of complex **II** in toluene (runs 28, 29, 31, 33) or hexane (runs 30, 32) under nitrogen. [b]Isolated yields. [c]((Z)-isomer/total enol esters)x100. [d]Complex **IV** was used. [e]Boc : *tert*-butoxycarbonyl.

(η^3-$CH_2C(Me)=CH_2)_2$ (**II**) and that they lead to the *in situ* formation of the corresponding $(Ph_2P(CH_2)_nPPh_2)Ru(\eta^2$-$O_2CR)_2$ intermediates acting as catalyst precursors.

We have shown the crucial influence of the nature of the chelating phosphine on the ruthenium active species to provide both activation and regioselectivity with respect to the nature of the alkyne substrate. This observation teaches us that for the search of both activity and regio- or stereoselectivity of catalytic reactions, it is necessary to modulate step by step the nature of the chelating ligands to reach the best conditions.

Experimental Section

Preparation of Complexes I–IV. Complexes **I–IV** were prepared[36] by displacement of cyclooctadiene from bis(2-methylpropenyl)(cycloocta-1,5-diene)ruthenium by 1 equiv of the appropriate diphosphine according to methods reported for phosphites[41] and chiral diphosphines.[42]

General Procedure for the Preparation of (Z)-Alk-1-en-1-yl Esters. Carboxylic acid (10 mmol), 10 mmol of alkyne, and 0.1 mmol of bis(2-methylpropenyl)(bis(diphenylphosphino)-alkane)ruthenium were stirred in 5 or 10 mL of solvent under an inert atmosphere of nitrogen. After treatment with $NaHCO_3$ and evaporation of the solvent, (Z)-enol esters were isolated by distillation under reduced pressure or by silica gel chromatography.

(Z)-Hex-1-en-1-yl benzoate (1). Benzoic acid (1.22 g, 10 mmol), 1.2 mL (10 mmol) of hex-1-yne, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 65 °C for 2.5 h. The product was purified by silica gel chromatography to afford 1.94 g (95%) of ester **1** as a colorless liquid: IR (neat) ν 1660, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3H, J = 7.0 Hz), 1.38 (m, 4H), 2.25 (m, 2H), 5.01 (dt, 1H, J = 6.3 and 7.5 Hz), 7.25 (d, 1H, J = 6.3 Hz), 7.40–8.10 (m, 5H); MS, *m/z* 204 (M^+). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.11; H, 7.82.

(Z)-β-Styryl Benzoate (4). Benzoic acid (6.10 g, 50 mmol), 5.5 g (55 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 20 mL of toluene were stirred at 60 °C for 18 h. The product was purified by silica gel chromatography to afford 10.30 g (92%) of ester **4** as a white solid: IR (neat) ν 1651, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.88 (d, 1H, J = 7.3 Hz), 7.24 (d, 1H, J = 7.3 Hz), 7.3–8.2 (m, 10H); MS, *m/z* 224 (M^+). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.59; H, 5.46.

(Z)-β-Styryl Acetate (5). Acetic acid (0.60 g, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of hexane were stirred at 45 °C for 4 h. The product was purified by distillation to afford 1.45 g (90%) of ester **5** as a colorless liquid: IR (neat) ν 1652, 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3H), 5.72 (d, 1H, J = 7.3 Hz), 7.2–7.5 (m, 6H); MS, *m/z* 162 (M^+). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.32; H, 6.30. Found: C, 74.06; H, 6.21.

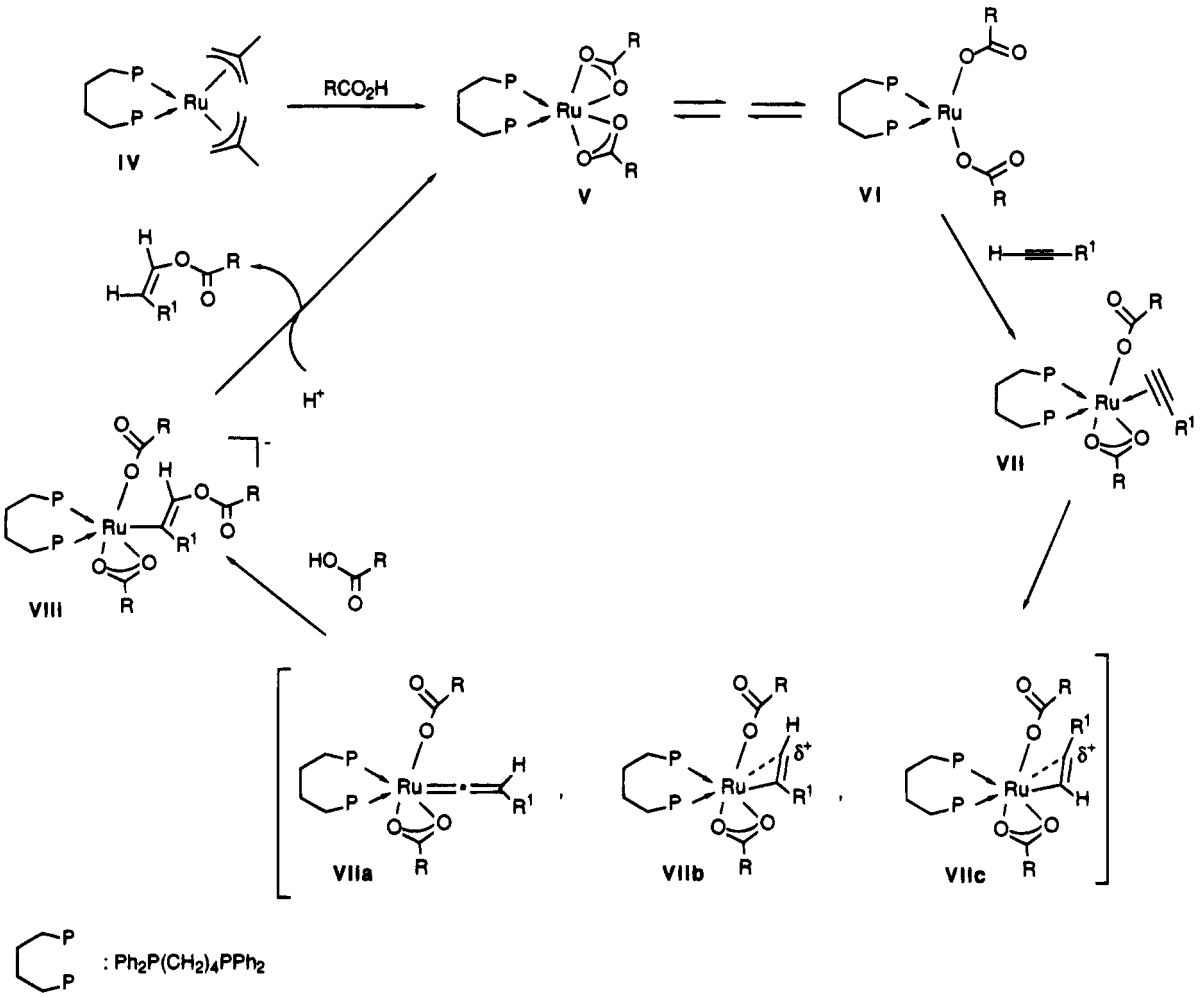
(Z)-β-Styryl Chloroacetate (6). Chloroacetic acid (0.94 mL, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 20 °C for 24 h. The product was purified by distillation to afford 1.77 g (90%) of ester **6** as a colorless liquid: IR (neat) ν 1660, 1775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.22 (s, 2H), 5.81 (d, 1H, J = 7.1 Hz), 7.31–7.37 (m, 6H); Anal. Calcd for $C_{10}H_9ClO_2$: C, 61.08; H, 4.61. Found: C, 60.89; H, 4.85.

(Z)-β-Styryl Dichloroacetate (7). Dichloroacetic acid (0.83 mL, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 20 °C for 21 h. The product was purified by distillation to afford 1.80 g (78%) of ester **7** as a colorless liquid: IR (neat) ν

(41) Cooke, M.; Goodfellow, R. J.; Green, M.; Parker, G. *J. Chem. Soc A* **1971**, 16.

(42) Genet, J. P.; Mallart, S.; Pinel, C.; Juge, S.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1991**, *2*, 43.

Scheme 1



1658, 1793 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.91 (d, 1H, J = 7.0 Hz), 6.14 (s, 1H), 7.25–7.65 (m, 6H).

(Z)-β-Styryl Trifluoroacetate (8). Trifluoroacetic acid (0.77 mL, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 0 °C for 6 h. The product was purified by distillation to afford 0.85 g (61%) of ester **8** as a colorless liquid: IR (neat) ν 1650, 1793 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.00 (d, 1H, J = 7.0 Hz), 7.25 (d, 1H, J = 7.0 Hz), 7.30–7.60 (m, 5H); MS, *m/z* 216 (M^+).

(Z)-Hex-1-en-1-yl Acetate (9). Acetic acid (1.14 mL, 10 mmol), 1.2 mL (10 mmol) of hex-1-yne, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of pentane were stirred at 40 °C for 6 h. The product was purified by distillation to afford 1.00 g (35%) of ester **9** as a colorless liquid: IR (neat) ν 1670, 1758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (m, 3H), 1.35 (m, 4H), 2.05 (m, 2H), 2.15 (s, 3H), 4.85 (dt, 1H, J = 6.4 and 7.5 Hz), 6.97 (dt, 1H, J = 6.4 and 1.6 Hz); MS, *m/z* 142 (M^+),

(Z)-Hex-1-en-1-yl Valerate (10). Valeric acid (1.08 mL, 10 mmol) 1.2 mL (10 mmol) of hex-1-yne, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of pentane were stirred at 40 °C for 20 h. The product was purified by distillation to afford 0.65 g (35%) of ester **10** as a colorless liquid: IR (neat) ν 1670, 1754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (m, 6H), 1.35 (m, 6H), 1.65 (m, 2H), 2.12 (m, 2H), 2.35 (t, 2H, J = 7.5 Hz), 4.85 (dt, 1H, J = 6.5 and 7.5 Hz), 6.95 (dt, 1H, J = 6.5 and 1.5 Hz); MS, *m/z* 184 (M^+). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.73; H, 10.86. Found: C, 71.50; H, 10.74.

(Z)-Hex-1-en-1-yl Diphenylacetate (11). Diphenylacetic acid (2.12 g, 10 mmol), 1.2 mL (10 mmol) of hex-1-yne, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 65 °C for 20 h. The product was purified by distillation to afford 2.85 g (97%) of ester **11** as a colorless liquid: IR (neat) ν 1668, 1748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, J = 7.0 Hz), 1.20–1.40 (m, 4H), 2.06 (dtd, 2H, J = 7.5, 7.2 and 1.4 Hz), 4.90 (dt, 1H, J = 6.4 and 7.5 Hz), 5.16 (s, 1H), 7.12 (dt, 1H, J = 6.4 and 1.4 Hz), 7.25–7.40 (m, 10H); MS, *m/z* 294 (M^+). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.40; H, 7.57. Found: C, 81.60; H, 7.53.

(Z)-Hex-1-en-1-yl Difluorobenzoate (12). 2,6-Difluorobenzoic acid (1.54 g, 10 mmol), 1.2 mL (10 mmol) of hex-1-yne, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 65 °C for 2 h. The product was purified by silica gel chromatography to afford 2.25 g (94%) of ester **12** as a colorless liquid: IR (neat) ν 1671, 1745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3H, J = 7.0 Hz), 1.36 (m, 4H), 2.21 (dtd, 2H, J = 7.4, 7.2, and 1.3 Hz), 5.05 (dt, 1H, J = 6.3 and 7.4 Hz), 7.21 (dt, 1H, J = 6.3 and 1.3 Hz), 6.90–7.10 (m, 2H), 7.40–7.50 (m, 1H); MS, *m/z* 240 (M^+). Anal. Calcd for $C_{13}H_{14}F_2O_2$: C, 64.99; H, 5.87. Found: C, 65.14; H, 6.01.

(Z)-Hex-1-en-1-yl *N*-(*tert*-butyloxycarbonyl)alaninate (13). Boc-alanine (1.89 g, 10 mmol), 1.2 mL (10 mmol) of hex-1-yne, and 64 mg (0.1 mmol) of catalyst **IV** in 10 mL of toluene were stirred at 65 °C for 24 h. The product was purified by silica gel chromatography to afford 1.51 g (71%) of ester **13** as a white solid, mp 62 °C: IR (neat) ν 1665, 1720, 3350 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H, J = 7.0 Hz), 1.29 (m, 4H), 1.39 (d, 3H), 1.40 (s, 9H), 2.10 (dtd, 2H, J = 7.5, 7.3, and 1.4 Hz), 4.36 (m, 1H), 5.07 (s, 1H), 4.90 (dt, 1H, J = 6.4 and 7.5 Hz), 6.95 (dt, 1H, J = 6.4 and 1.4 Hz).

(Z)-Hex-1-en-1-yl *N*-(*tert*-butyloxycarbonyl)phenylalaninate (14). Boc-phenylalanine (2.65 g, 10 mmol), 1.2 mL (10 mmol) of hex-1-yne, and 64 mg (0.1 mmol) of catalyst **IV** in 10 mL of toluene were stirred at 65 °C for 20 h. The product was purified by silica gel chromatography to afford 3.55 g (97%) of ester **14** as a white solid: IR (neat) ν 1673, 1720, 1755, 3375 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H, J = 6.8 Hz), 1.30 (m, 4H), 1.40 (s, 9H), 2.05 (m, 2H), 3.10 (d, 2H, J = 5.8 Hz), 4.64 (dt, 1 H, J = 8.2 and 5.8 Hz), 4.91 (dt, 1H, J = 7.4 and 7.5 Hz), 5.03 (d, 1H, J = 8.2 Hz). 6.95 (d, 1 H, J = 7.4 Hz), 7.0–7.4 (m, 5H).

(Z)-β-Styryl Valerate (15). Valeric acid (1.08 mL, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of hexane were stirred at 45 °C for 1.5 h. The product was purified by distillation to afford 1.90 g (93%) of ester **15** as a colorless liquid: IR (neat) ν 1659, 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, 3H, J = 7.5 Hz), 1.40 (qt, 2H, J = 7.5 and 7.3 Hz), 1.70 (tt, 2H, J = 7.5 and 7.3 Hz), 2.55 (t, 2H, J = 7.5 Hz), 5.70 (d, 1H, J = 7.25 Hz), 7.20–7.40 (m, 5H), 7.58 (d, 1H, J = 7.25 Hz); MS, m/z 204 (M^+). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.50; H, 7.80. Found: C, 76.31; H, 7.90.

(Z)-β-Styryl Methoxyacetate (16). Methoxyacetic acid (0.90 g, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 65 °C for 3 h. The product was purified by distillation to afford 1.84 g (96%) of ester **16** as a colorless liquid: IR (neat) ν 1660, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.50 (s, 3H), 4.24 (s, 1H), 5.76 (d, 1H, J = 7.3 Hz), 7.26 (d, 1H, J = 7.3 Hz), 7.2–7.5 (m, 5H). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.58; H, 6.34.

(Z)-β-Styryl Acrylate (17). Acrylic acid (0.70 mL, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 45 °C for 5 h. The product was purified by distillation to afford 1.15 g (65%) of ester **17** as a colorless liquid: IR (neat) ν 1635, 1651, 1742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.76 (d, 1H, J = 7.2 Hz), 6.02 (dd, 1H, J = 1.2 and 10.3 Hz), 6.30 (dd, 1H, J = 10.3 and 17.3 Hz), 6.60 (dd, 1H, J = 1.2 and 17.3 Hz), 7.2–7.6 (m, 6H); MS, m/z 174 (M^+). Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.86; H, 5.74. Found: C, 75.45; H, 5.84.

(Z)-β-Styryl Crotonate (18). Crotonic acid (0.86 g, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of THF were stirred at 45 °C for 6 h. The product was purified by distillation to afford 1.51 g (85%) of ester **18** as a colorless liquid: IR (neat) ν 1651, 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90 (dd, 3H, J = 7.0 and 1.7 Hz), 5.75 (d, 1H, J = 7.3 Hz), 6.02 (dq, 1H, J = 15.5 and 1.7 Hz), 7.20 (dq, 1H, J = 15.5 and 7.0 Hz), 7.25–8.00 (m, 6H).

(Z)-β-Styryl Vinylacetate (19). Vinylacetic acid (0.87 mL, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 40 °C for 20 h. The product was purified by distillation to afford 1.49 g (84%) of ester **19** as a colorless liquid: IR (neat) ν 1659, 1762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.32 (dt, 2H, J = 6.9 and 1.4 Hz), 5.25–5.35 (m, 2H), 5.74 (d, 1H, J = 7.2 Hz), 6.02 (ddt, 1H, J = 17.5, 7.9, and 6.9 Hz), 7.25–7.70 (m, 6H). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.79; H, 6.55.

(Z)-β-Styryl Salicylate (20). Salicylic acid (1.38 g, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 90 °C for 24 h. The product was purified by silica gel chromatography to afford 2.25 g (94%) of ester **20** as a yellow solid: IR (neat) ν 1674, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.93 (d, 1H, J = 7.2 Hz), 6.9–8.0 (m, 10H), 10.50 (s, 1H). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.08; H, 5.11.

(Z)-β-Styryl Acetylsalicylate (21). Acetylsalicylic acid (1.80 g, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 80 °C for 20 h. The product was purified by distillation to afford 2.76 g (98%) of ester **21** as a colorless liquid: IR (neat) ν 1658, 1738, 1768 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3H), 5.34 (d, 1H, J = 7.2 Hz), 7.00–8.15 (m, 9H), 7.46 (d, 1H, J = 7.2 Hz).

(Z)-β-Styryl (Z)-Alaninate (22). Z-Alanine (2.23 g, 10 mmol), 1.1 mL (10 mmol) of phenylacetylene, and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene were stirred at 65 °C for 24 h. The product was purified by silica gel chromatography to afford 3.20 g (98%) of ester **22** as a colorless liquid: IR (neat) ν 1650, 1765, 3388 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (d, 3H, J = 7.2 Hz), 4.52 (dq, 1H, J = 7.2 and 7.3 Hz), 5.12 (d, 1H, J = 12.0 Hz), 5.16 (d, 1H, J = 12.0 Hz), 5.33 (d, 1H, J = 7.0 Hz), 5.77 (d, 1H, J = 7.2 Hz), 7.0–7.6 (m, 11H).

(Z)-2-(Trimethylsilyl)ethen-1-yl Benzoate (23). Benzoic acid (1.22 g, 10 mmol), 1.0 g (10 mmol) of (trimethylsilyl)-acetylene, and 62 mg (0.1 mmol) of catalyst **II** in 5 mL of toluene were stirred at 60 °C for 18 h. The product was purified by silica gel chromatography to afford 2.12 g (95%) of ester **23** as a colorless liquid: IR (neat) ν 1625, 1770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.23 (s, 9H), 5.05 (d, 1H, J = 8.5 Hz), 7.48 (m, 2H), 7.60 (tt, 1H, J = 7.4 and 1.3 Hz), 7.77 (d, 1H, J = 8.5 Hz), 8.09 (m, 2H); MS, m/z 220 (M^+). Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32. Found: C, 65.14; H, 7.41.

(Z)-2-(Trimethylsilyl)ethen-1-yl Valerate (24). Valeric acid (1.08 mL, 10 mmol), 1.0 g (10 mmol) of (trimethylsilyl)-acetylene, and 62 mg (0.1 mmol) of catalyst **II** in 5 mL of hexane were stirred at 60 °C for 3.5 h. The product was purified by silica gel chromatography to afford 1.40 g (71%) of ester **24** as a colorless liquid: IR (neat) ν 1616, 1756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9H), 0.79 (t, 3H, J = 7.3 Hz), 1.23 (m, 2H), 1.51 (m, 2H), 2.24 (t, 2H, J = 7.5 Hz), 4.72 (d, 1H, J = 8.5 Hz), 7.39 (d, 1H, J = 8.5 Hz); MS, m/z 200 (M^+). Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 60.17; H, 9.98.

(Z)-2-(Trimethylsilyl)ethen-1-yl Phenylacetate (25). Phenylacetic acid (1.36 g, 10 mmol), 1.0 g (10 mmol) of (trimethylsilyl)acetylene, and 62 mg (0.1 mmol) of catalyst **II** in 5 mL of toluene were stirred at 60 °C for 18 h. The product was purified by silica gel chromatography to afford 2.25 g (96%) of ester **25** as a colorless liquid: IR (neat) ν 1618, 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H), 3.65 (s, 2H), 4.86 (d, 1H, J = 8.4 Hz), 7.2–7.4 (m, 5H), 7.50 (d, 1H, J = 8.5 Hz); MS, m/z 234 (M^+).

(Z)-2-(Trimethylsilyl)ethen-1-yl Methacrylate (26). Methacrylic acid (0.85 mL, 10 mmol), 1.0 g (10 mmol) of (trimethylsilyl)acetylene, and 62 mg (0.1 mmol) of catalyst **II** in 5 mL of hexane were stirred at 50 °C for 24 h. The product was purified by silica gel chromatography to afford 1.40 g (76%) of ester **26** as a colorless liquid: IR (neat) ν 1616, 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9H), 1.80 (s, 3H), 4.80 (d, 1H, J = 8.5 Hz), 5.50 (s, 1H), 6.03 (s, 1H), 7.40 (d, 1H, J = 8.5 Hz); MS, m/z 184 (M^+).

(Z)-2-(Trimethylsilyl)ethen-1-yl *N*-(*tert*-Butyloxycarbonyl)alaninate (27). Boc-alanine (1.86 g, 10 mmol), 1.0 g (10 mmol) of (trimethylsilyl)acetylene, and 62 mg (0.1 mmol) of catalyst **II** in 10 mL of toluene were stirred at 50 °C for 24 h. The product was purified by silica gel chromatography to afford 2.14 g (75%) of ester **27** as a white solid, mp 66 °C: IR (neat) ν 1620, 1725, 3410 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H), 1.43 (d, 3H, J = 5.5 Hz), 1.44 (s, 9H), 4.36 (m, 1H), 4.93 (d, 1H, J = 8.4 Hz), 5.09 (s, 1H), 7.52 (d, 1H, J = 8.4 Hz). Anal. Calcd for $C_{13}H_{25}NO_4Si$: C, 54.32; H, 4.87. Found: C, 54.66; H, 4.96.

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Supporting Information Available: ^1H NMR (300 MHz, $CDCl_3$) spectra of compounds **7, 8, 9, 13, 14, 18, 21, 22, 25,** and **26** (10 pages). This material is contained in libraries on microfiche, immediatly follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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