Regioselective Hydroformylation of Enynes Catalyzed by a Zwitterionic Rhodium Complex and Triphenyl Phosphite

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The reaction of aliphatic 1-en-3-ynes with synthesis gas in the presence of the zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(1,5-COD) and triphenyl phosphite affords formyl dienes in high stereoselectivity. This catalytic system provides a useful method for the hydroformylation of both nonfunctionalized and functionalized conjugated enynes under mild conditions, affording formyl dienes in moderate to good yields.

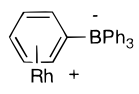
Introduction

The hydroformylation of alkenes is an important industrial process which has been extensively investigated for many years.[1] In contrast, the hydroformylation of alkynes to give α,β-unsaturated aldehydes has attracted less attention until recently, since past research resulted in poor product yields and selectivities.[2]

In 1995, Buchwald and co-workers[3] reported an effective hydroformylation catalyst composed of $Rh(CO)_2$acac (acac = acetylacetonate) and a sophisticated bisphosphite ligand. This catalyst system enabled the hydroformylation of internal alkynes to occur under mild conditions and with good selectivity. Last year, Hidai and co-workers[4] reported a heterobimetallic catalyst to hydroformylate internal acetylenes. The conditions used by Hidai and co-workers were not as mild as those of Buchwald, although the conversion and selectivity were good. The Hidai group described the hydroformylation of the conjugated enyne (*Z*)-1,4-diphenyl-1-buten-3-yne to form (2*E*,4*Z*)-2,5-diphenyl-2,4-pentadienal as the exclusive hydroformylation product in 80% conversion and 39% isolated yield. Doyama and others[5a,b] noted that when an alkyne is conjugated to an alkene, the triple bond is more reactive toward hydroformylation. Conjugated enynes undergo hydroformylation giving formyl dienes in either a linear or branched fashion.

Enynes find practical use in the preparations of polymers[6a] and substituted benzenes[6b] and in enediyne antibiotics.[7] The catalytic hydroformylation of conjugated enynes is an attractive synthetic route for the preparation of formyl dienes, an interesting subgroup of substituted dienes used in the preparation of cyclized materials and as chain extensions.[8] Enynes may be prepared through a variety of methods including the reaction of an alkyne with various organometallic species, affording acetylenes bearing alkyl, vinyl, aryl, or heteroaryl groups α to the triple bond.[9a] More recent methods have been developed using palladium and tris(2,6-dimethoxyphenyl)phosphine to self-couple terminal alkynes or cross-couple terminal alkynes to functionalized internal alkynes.[9b]

The use of rhodium-based catalysts for the hydroformylation of alkenes is well documented. In recent years, the zwitterionic complex (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(1,5-COD) (**1**) has been shown to be capable of hydrogenating imines,[10] hydroformylating alkenes,[11] germylformylating and silylformylating terminal alkynes,[12,13] and polymerizing phenyl acetylene.[14]



1

We now describe the use of catalytic quantities of **1**, in the presence of triphenyl phosphite, to attain the

(1) (a) Trost, B. M.; Fleming, I. In *Comprehensive Organic Synthesis*; Perganon: Oxford, 1991; Vol. 4, pp 913−950. (b) Elschenbroich, C.; Salzer, A. In *Organometallics: A Concise Introduction*, 2nd ed.; VCH Publishers: New York, 1992; pp 434−437. (c) Cornils, B.; Herrmann, W. A. In *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH Publishers: 1996; Vol. 1, pp 29−111.

(2) (a) Fell, B.; Beutler, M. *Tetrahedron Lett.* **1972**, 3455−3456. (b) Botteghi, C.; Salomon, C. *Tetrahedron Lett.* **1974**, 4285−4288. (c) Greenfield, H.; Wotiz, J. H.; Wender, I. *J. Org. Chem.* **1957**, *22*, 542. (d) Wuts, P. G. M.; Ritter, A. R. *J. Org. Chem.* **1989**, *54*, 5180−5182. (e) Campi, E. M.; Jackson, W. R.; Nilsson, Y. *Tetrahedron Lett.* **1991**, *32*, 1093−1094. (f) Nombel, P.; Lugan, N.; Mulla, F.; Lavigne, G. *Organometallics* **1994**, *13*, 4673.

(3) Johnson, J. R.; Cuny, G. D.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1760−1761.

(4) Ishii, Y.; Miyashita, K.; Kamita, K.; Hidai, M. *J. Am. Chem. Soc.* **1997**, *119*, 6448−6449.

(5) (a) Doyama, K.; Joh, T.; Takahashi, S. *Tetrahedron Lett.* **1996**, *27*, 4497−4500. (b) Doyama, K.; Joh, T.; Shiohara, T.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4353−4360. (c) Campi, E. M.; Jackson, W. R. *Aust. J. Chem.* **1989**, *42*, 471−478.

(6) (a) Xu, W.; Alper, H.; *Macromolecules* **1996**, *29*, 6695−6699. (b) Gevorgyan, V.; Takeda, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11313−11314.

(7) Stang, P. J.; Diederich, F. Chapter 7. In *Modern Acetylene Chemistry*; VCH Publishers: New York, 1995.

(8) (a) O′Shea, D. F.; Sharp, J. T. *J. Chem. Soc., Perkins Trans. 1*, **1997**, 3025−3034. (b) Kimura, M.; Ezoc, A.; Shibata, K.; Tamaru, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4033−4034. (c) Barluenga, J.; Canteli, R. M.; Flórez, J.; Gutiérrez-Rodriquez, A.; Martin, E. *J. Am. Chem. Soc.* **1998**, *120*, 2514−2522.

(9) (a) Sauvêtre, R.; Normant, J. F. *Tetrahedron Lett.* **1982**, *23*, 4325−4328. (b) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698−708.

(10) Zhou, Z.; James, B. R.; Alper, H. *Organometallics* **1995**, *14*, 4. 4209−4212.

(11) (a) Alper, H.; Zhou, J. Q. *J. Org. Chem.* **1992**, *57*, 3729−3731. (b) Totland, K.; Alper, H. *J. Org. Chem.* **1993**, *58*, 3326−3329. (c) Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1990**, *112*, 3674−3676. (d) Lee, C. W.; Alper, H. *J. Org. Chem.* **1995**, *60*, 499−503.

(12) Monteil, F.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1601−1602.

(13) Zhou. J. Q.; Alper, H. *Organometallics* **1994**, *13*, 1586−1591.

(14) Goldberg, Y.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1209−1210.

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Table 1. Hydroformylation of 2,7-Dimethyl-1-octen-3-yne (3a) with CO/H_2 Using Different Catalyst Systems and Solvents[a]

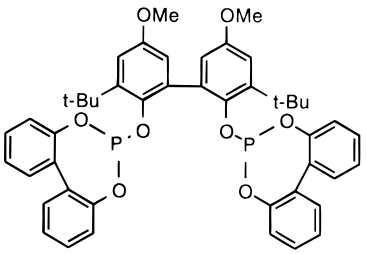
entry	rhodium catalyst	ligand	solvent	reactn time (h)	convn (%)[b]	product ratio (**4**/**5**)[c]	isolated yield of **4a** (%)[d]
1	**1**	$(PhO)_3P$	CH_2Cl_2	48	>95	10:1	52
2	**1**	$(PhO)_3P$[e]	CH_2Cl_2	48	50	10:1	26
3	**1**	$(PhO)_3P$[f]	CH_2Cl_2	24[g]	100	3:1	37
4	**1**	$(PhO)_3P$	Et_2O	48	<10	only **4a**	
5	**1**	$(PhO)_3P$	benzene	48	100	4:1	42
6	**1**	$(PhO)_3P$	THF	48	60	20:1	39
7	**1**	Ph_3P	CH_2Cl_2	48	50	2 (:1)[h]	16
8	**1**	dppb[i]	CH_2Cl_2	48	<10	undefined[j]	
9	**1**	2[k]	CH_2Cl_2	8[l]	80	10:1	51
10	$Rh(CO)_2acac$	$(PhO)_3P$	CH_2Cl_2	48	67	5:1	33
11	$CO(PPh_3)_2RhCl$	$(PhO)_3P$	CH_2Cl_2	48	<5	only **4a**	

[a] Reaction conditions: enyne (**3a**), 3 mmol; rhodium catalyst, 0.12 mmol; triphenyl phosphite, 0.48 mmol; CH_2Cl_2, 10 mL; CO, 6 atm; H_2, 6 atm; 60 °C. [b] The percent conversion was determined by the loss of the olefin ^1H NMR signal at 5.17 ppm. [c] The ratio of **4**/**5** was determined by the ratio of their aldehyde ^1H NMR signals. The saturated aldehyde (**5**) proton signal appeared as a doublet approximately 0.10 ppm downfield from the unsaturated aldehyde (**4**). [d] The product was isolated by Kugelrohr distillation followed by column chromatography using pentane:ether (90:10) as eluant. [e] The reaction temperature was 50 °C. [f] The reaction temperature was 70 °C. [g] After 24 h a pressure drop of 80 psi was observed, and the reaction was stopped; this was consistent with a completed reaction. [h] A cyclopentenone was identified by an olefin ^1H NMR signal at 5.90 ppm in the crude mixture, it had a ratio of 1:2 to **4a**. Campi and Jackson identified this proton signal as being due to the cyclopentenone.[5c] [i] A 2:1 ratio of dppb:**1** was used. [j] The reaction gave multiple products in the ^1H NMR region of 9−10 ppm. [k] A 1.5:1 ratio of **2**/**1** was used. [l] After 8 h a pressure drop of 80 psi was observed, and the reaction was stopped.

hydroformylation of both simple and functionalized enynes in good conversions, selectivities, and yields.

Results and Discussion

The phosphite skeleton of the ligand used by Buchwald and co-workers (**2**),[3] when applied in conjunction with a rhodium catalyst, enables the hydroformylation of internal alkynes to be carried out under very mild conditions.



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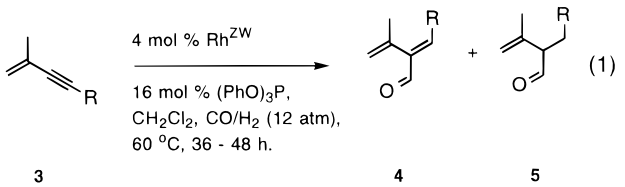
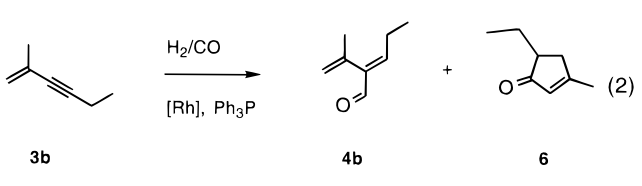
It was envisaged that this catalytic system could also be used to carry out the hydroformylation of enynes under mild conditions as well. We reasoned that a much simpler phosphite such as triphenyl phosphite could be used for the hydroformylation of enynes. Indeed, the catalytic system of **1** with triphenyl phosphite gives preferential hydroformylation of the triple bond in conjugated enynes affording unsaturated aldehydes in high selectivity (eq 1).



Treatment of enynes (**3**) (3−6 mmol) with 4 mol % **1**, 16 mol % triphenyl phosphite, and 12 atm of CO/H_2 (total pressure) in CH_2Cl_2 affords one formyl diene in all cases. The branched formyl diene (**4**) is the major product, with the nonconjugated unsaturated aldehyde (**5**) as a byproduct in all reactions. Unidentified polymeric material was also formed, in accord with similar behavior for 2,2-disubstituted olefins.[15]

Reaction Optimization. The optimization of this process was effected using 2,7-dimethyl-1-octen-3-yne (**3a**) as the model substrate. The hydroformylation process is temperature, solvent, ligand, and catalyst dependent (Table 1). The highest isolated yield of **4a** resulted using the conditions described in the previous paragraph (Table 1, entry 1). Decreasing the temperature by 10 °C (60 to 50 °C) leads to only 50% conversion of the enyne (**3a**) after 48 h (Table 1, entry 2). Increasing the temperature by 10 °C (60 to 70 °C) leads to completion of the reaction in 24 h. An undesirable consequence of the increased reactivity is the substantial increase in the formation of **5a** (Table 1, entry 3). Use of benzene, THF, or ether as the solvent results in lower yields of **4a** (Table 1, entries 4−6). Mono- (Ph_3P) and bidentate (dppb) phosphorus ligands give inferior results when compared with $(PhO)_3P$ (Table 1, entries 7 and 8). Ligand **2** affords results comparable to those of $(PhO)_3P$ (Table 1, entry 9). The substituents present on **2** have a significant influence on the rate of the reaction, resulting in a 6-fold rate increase. $Rh(CO)_2acac$ and $CO(Ph_3P)_2RhCl$ are inferior to **1** (Table 1, entries 10 and 11).

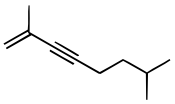
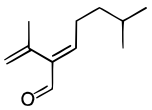
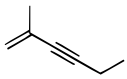
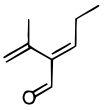
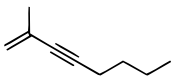
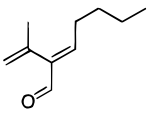
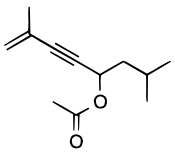
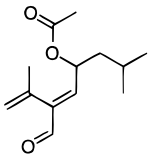
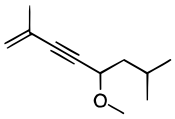
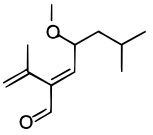
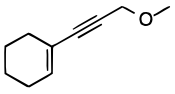
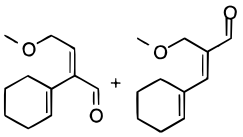
Hydroformylation of Enynes. The hydroformylation of **3b** (Table 2) was reported previously by Campi and Jackson[5c] using carbonylhydridotris(triphenylphosphine)-rhodium(I) and excess triphenylphosphine as the catalytic system at 80 °C and 26 atm of synthesis gas in benzene. The formyl diene **4b** and the cyclopentenone **6**



were formed in 20% and 10% yields, respectively (eq 2). Under the conditions described herein, the formyl diene (**4b**) was obtained in 50% isolated yield (Table 2).

(15) Stevens, M. P. In *Polymer Chemistry: An Introduction*, 2nd ed.; Oxford University Press: New York, 1990; Chapter 6.

Table 2. Hydroformylation of Enynes (3) with CO/H_2 Using Zwitterionic Rhodium (1) and $(PhO)_3P$[a]

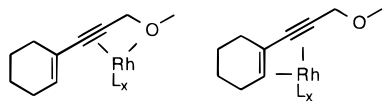
Substrate	Reaction Time (h)	Conversion (%)[b]	Product Ratio (**4**/**5**)[c]	Major Product	Isolated Yield of **4** (%)[d]
 **3a**	48	>95	9.7/1	 **4a**	55
 **3b**	36	100	8.2/1	 **4b**	50
 **3c**	48	>95	8.6/1	 **4c**	55
 **3d**	48	100	7.5/1	 **4d**	51
 **3e**	48	100	8.8/1	 **4e**	50
 **3f**	24	100	14.3/1	 **4f:4f′, 2:1**	70

[a] Reaction conditions: enyne (**3**), 6 mmol; **1**, 0.24 mmol; triphenyl phosphite, 0.96 mmol; CH_2Cl_2, 10 mL; CO, 6 atm; H_2, 6 atm; 60 °C; 36−48 h. [b] The percent conversion was determined by the loss of the olefin ^{1}H NMR signal at 5.17 ppm. [c] The ratio of **4**/**5** was determined by the ratio of their aldehyde ^{1}H NMR signals. The saturated aldehyde (**5**) proton signal appeared as a doublet approximately 0.10 ppm downfield from the unsaturated aldehyde (**4**). [d] The product was isolated by Kugelrohr distillation followed by column chromatography using pentane:ether (90:10) as eluant.

In our investigation we examined three types of conjugated enynes: internal acetylenes, terminal acetylenes, and functionalized internal acetylenes at the position β to the triple bond. In the first case (Table 2) only one unsaturated aldehyde was obtained in 50−55% yield (**4a**, **4b,** and **4c**). In the second group, terminal acetylenes, a multiple number of products were observed from 1-ethynylcyclohexene after 12 h. In this situation there was no selectivity, possibly due to the lack of any steric interaction with the "R" substituent, as in the internal acetylene case.

Placement of a methyl ether in the position β to the triple bond, i.e., **3f**, affords a second isomer of the formyl diene (**4f'**) in a ratio of 1:2 relative to the usual product **4f**.[16] In contrast, only one product (**4e**) was formed when 2,7-dimethyl-5-methoxy-1-octen-3-yne (**3e**) was the substrate. The appearance of the minor product **4f'** from **3f**

(16) 1-(3-Methoxy-2-propynyl)cyclohexene, **3f**, was prepared by the reaction of 1-ethynylcyclohexene with *n*-butyllithium followed by chloromethyl methyl ether. After hydroformylation under the same conditions as for the nonfunctionalized enynes, a mixture of two hydroformylated products was obtained, **4f** and **4f'**. The spectral data for **4f** are as follows: IR ν(CO) 1690 cm $^{-1}$; ^{1}H NMR δ 9.32 (s, 1H), 6.40 (t, 1H, J = 5.8 Hz), 5.34 (m, 1H), 4.13 (d, 2H, J = 5.8 Hz), 3.28 (s, 3H), 2.36 (m, 1H), 2.17 (m, 1H), 1.98 (m, 2H), 1.56 (m, 4H); ^{13}C NMR δ 194.2. The spectral data for **4f'** are as follows: IR ν(CO) 1690 cm $^{-1}$; ^{1}H NMR δ 9.32 (s, 1H), 6.78 (s, 1H), 6.29 (m, 1H), 4.09 (s, 2H), 3.23 (s, 3H), 2.36 (m, 1H), 1.98 (m, 4H), 1.56 (m, 4H); ^{13}C NMR δ 195.4. Mixture: EI MS (*m*/*e*) 180 [M$^+$]; EI HRMS calculated for $C_{11}H_{16}O_2$ [M$^+$] 180.11503, found 180.11510.



7 **8**

Figure 1. Rhodium coordination prior to hydroformylation.

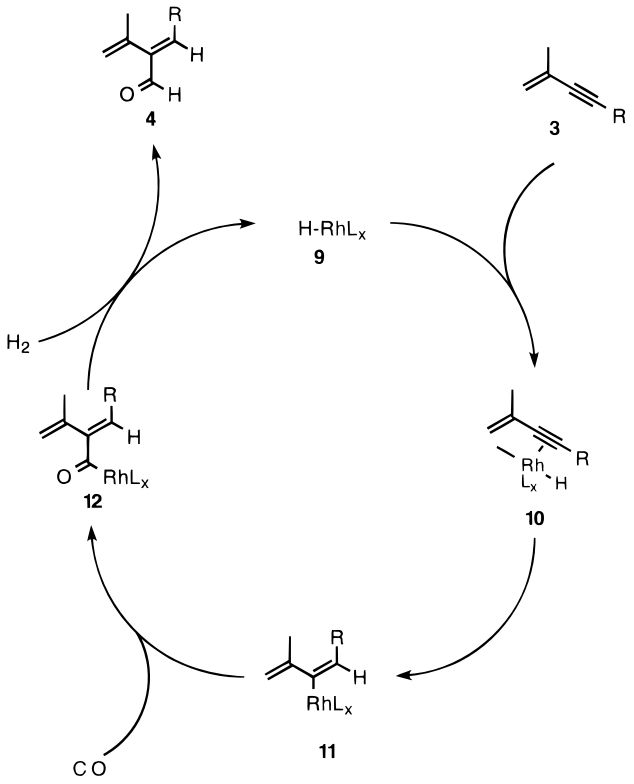


Figure 2. Proposed mechanism.

may be explained by prior coordination of the rhodium catalyst with the oxygen atom of the methyl ether and the triple bond (**7**) followed by subsequent hydroformylation (see Figure 1). This same double coordination is possible between the alkene and the alkyne in the conjugated enyne prior to hydroformylation (**8**). Depending on the coordinating ability of the group β to the alkyne, different ratios of products are possible. Preference for one product is observed when there is a large sterically hindered group at the opposite side of the enyne.

A possible mechanism for the hydroformylation of enynes is outlined in Figure 2. The initial step may involve coordination of the rhodium with the double and triple bonds (**10**). This step is followed by the intramolecular addition of the rhodium hydride to the triple bond of the enyne affording the (*E*) isomer (**11**). In the case of the ether substituent, the initial coordination is between the rhodium catalyst, the triple bond, and the ether oxygen. This complexation governs the selectivity of the resulting unsaturated product. Carbonyl insertion (**12**), and regeneration of the rhodium catalyst by hydrogen (**9**), releases the formyl diene (**4**).

In conclusion, the catalyst system of the zwitterionic rhodium conplex (**1**) and triphenyl phosphite is of value for the hydroformylation of conjugated enynes. The use of a readily available phosphite ligand under mild conditions makes this process of considerable commercial promise. Hydroformylation in the presence of an ether or an ester linkage allows ready access to products with the potential for further interesting chemistry.

Experimental Section

Materials. All chemicals were purchased from commercial sources. The zwitterionic rhodium complex $(\eta^6\text{-}C_6H_5BPh_3)^-Rh^+$-(1,5-COD) **1** was prepared as described by Schrock and Osborn.[17] All solvents were distilled under nitrogen prior to use.

Hydroformylation of Unfunctionalized Conjugated Enynes. Into a 45 mL autoclave with a glass liner and stirring bar were placed the zwitterionic rhodium catalyst **1** (0.24 mmol), triphenyl phosphite (0.96 mmol), the conjugated enyne **3** (6 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide and pressurized to 6 atm, and then hydrogen was introduced up to a total pressure of 12 atm. The autoclave was placed in an oil bath at 60 °C for 48 h and then allowed to cool to room temperature. The autoclave was depressurized, and the solvent was removed by rotary evaporation. The resulting yellow residue was separated from the catalyst and polymeric material (if formed) by Kugelrohr distillation to give a clear colorless liquid. Product **4** was further purified by silica gel chromatography using pentane:ether (90:10) as the developer to give the formyl dienes **4a**−**c**.

(*E*)-2-(1-Methylethenyl)-6-methyl-2-hepten-1-al (4a): colorless liquid; IR ν(CO) 1690 cm^{-1}; ^1H NMR δ 9.32 (s, 1H), 6.43 (t, 1H, J = 7.4 Hz), 5.15 (d, 1H, J = 1.0 Hz), 4.68 (d, 1H, J = 1.0 Hz), 2.34 (quintet, 2H, J = 7.4 Hz), 1.80 (s, 3H), 1.54 (m, 1H), 1.30 (quartet, 2H, J = 7.0 Hz), 0.83 (d, 6H, J = 6.6 Hz); ^{13}C NMR δ 194.4, 155.8, 146.9, 138.9, 117.2, 38.5, 28.4, 28.1, 23.2, 22.9; EI MS (*m*/*e*) 166 [M^+]; EI HRMS calculated for $C_{11}H_{18}O$ [M^+] 166.13576, found 166.13541.

(*E*)-2-(1-Methylethenyl)-2-penten-1-al (4b): colorless liquid; IR ν(CO) 1690 cm^{-1}; ^1H NMR δ 9.29 (s, 1H), 6.40 (t, 1H, J = 7.6 Hz), 5.10 (d, 1H, J = 1.0 Hz), 4.64 (d, 1H, J = 1.0 Hz), 2.30 (quintet, 2H, J = 7.6 Hz), 1.77 (s, 3H), 1.01 (t, 3H, J = 7.6 Hz); ^{13}C NMR δ 194.4, 156.8, 146.5, 138.8, 117.1, 23.5, 23.1, 13.9; EI MS (*m*/*e*) 124 [M^+]; EI HRMS calculated for $C_8H_{12}O$ [M^+] 124.08882, found 124.08891.

(*E*)-2-(1-Methylethenyl)-2-hepten-1-al (4c): colorless liquid; IR ν(CO) 1690 cm^{-1}; ^1H NMR δ 9.33 (s, 1H), 6.44 (t, 1H, J = 7.6 Hz), 5.14 (d, 1H, J = 1.0 Hz), 4.67 (d, 1H, J = 1.0 Hz), 2.34 (quintet, 2H, J = 7.2 Hz), 1.80 (s, 3H), 1.35 (m, 4H), 0.86 (t, 3H, J = 6.8 Hz); ^{13}C NMR δ 194.4, 155.7, 147.1, 138.9, 117.3, 31.5, 29.9, 23.2, 23.0, 22.9, 14.4; EI MS (*m*/*e*) 152 [M^+]; EI HRMS calculated for $C_{10}H_{16}O$ [M^+] 152.12012, found 152.12311.

Hydroformylation of 5-Acetyl-2,7-dimethyl-1-octen-3-yne (3d). Enyne **3d** was prepared from 2,7-dimethyl-7-octen-5-yn-4-ol by the following procedure. A solution of 2.8 mL (2.0 g, 20 mmol) of triethylamine in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of 1.52 g (10 mmol) of 2,7-dimethyl-7-octen-5-yn-4-ol, 1.43 mL (1.57 g, 20 mmol) of acetyl chloride, and 0.12 g (1.0 mmol) of 4-(dimethylamino)pyridine in CH_2Cl_2 (25 mL). After 2 h the reaction mixture was treated with CH_2Cl_2 (50 mL), washed with 10% HCl, saturated $NaHCO_3$, and brine, and then dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation to afford a light yellow solution. The ester was further purified by silica gel chromatography using CH_2Cl_2 as eluant (R_f = 0.75) to give **3d** as a colorless liquid (90% isolated yield): IR ν(CO) 1744 cm^{-1}; ^1H NMR δ 5.50 (t, 1H, J = 7.4 Hz), 5.25 (d, 1H, J = 1.0 Hz), 5.20 (d, 1H, J = 1.0 Hz), 2.07 (s, 3H), 1.85 (s, 3H), 1.80−1.58 (m, 3H), 0.90 (d, 6H, J = 7.0 Hz); ^{13}C NMR δ 170.6, 126.6, 123.2, 86.3, 63.7, 44.3, 25.4, 23.8, 23.1, 22.9, 21.6; MS (*m*/*e*) 194 [M^+]; EI HRMS calculated for $C_{12}H_{18}O_2$ [M^+] 194.13068, found 194.13074.

The hydroformylation of **3d** was effected as described above to give **4d**.

(17) Schrock, P. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339−2343.

(*E*)-4-Acetyl-2-(1-methylethenyl)-6-methyl-2-hepten-1-al (4d): colorless liquid; IR ν_1(CO) 1742 cm^{-1} and ν_2(CO) 1695 cm^{-1}; ^1H NMR δ 9.37 (s, 1H), 6.22 (d, 1H, $J = 8.4$ Hz), 5.66 (t, 1H, $J = 8.4$ Hz), 5.21 (d, 1H, $J = 1.0$ Hz), 4.78 (d, 1H, $J = 1.0$ Hz), 2.01 (s, 3H), 1.87 (s, 3H), 1.71 (m, 2H), 1.28 (m, 1H), 0.90 (d, 3H, $J = 6.6$ Hz), 0.88 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR δ 193.9, 170.8, 150.3, 146.70, 138.8, 118.8, 70.3, 43.7, 25.1, 23.8, 22.8, 22.4, 21.6; FAB MS (*m*/*e*) 225.1413 $[M + H]^+$, calculated for $C_{13}H_{20}O_3$ $[M + H]^+$ 225.1413.

Hydroformylation of 5-Methoxy-2,7-dimethyl-1-octen-3-yne (3e). Enyne **3e** was prepared from 2,7-dimethyl-7-octen-5-yn-4-ol by the following procedure. A solution of 1.52 g (10 mmol) of the alcohol in pyridine (25 mL) was cooled to 0 °C and treated with 4 g (20 mmol) of *p*-toluenesulfonyl chloride. The reaction solution became brown with white crystals (pyridinium chloride). After the reaction was complete the mixture was added to 150 mL of ice−water. The tosylate appeared oily and was taken up in ether. The aqueous layer was extracted three times with additional portions of ether. The collected fractions of ether were further washed with 10% HCl, distilled water, and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a pale yellow solution of the tosylate.

Sodium (0.7 g, 30 mmol) was dissolved in 50 mL of anhydrous methanol at 0 °C. A solution of the above tosylate in 5 mL of anhydrous methanol was added slowly and was allowed to react for 2 h. The solution was poured into 150 mL of ice−water, extracted with ether, and dried over anhydrous $MgSO_4$. Evaporation of the ether afforded a clear yellow liquid. The liquid was further purified by silica gel chromatography using CH_2Cl_2 as eluant ($R_f = 0.85$) to give **3e** as a clear colorless liquid in 80% isolated yield: ^1H NMR δ 5.25 (d, 1H, $J = 1.0$ Hz), 5.17 (d, 1H, $J = 1.0$ Hz), 4.08 (t, 1H, $J = 8.4$ Hz), 3.38 (s, 3H), 1.87 (s, 3H), 1.58 (m, 2H), 1.22 (m, 1H), 0.90 (d, 6H); ^{13}C NMR δ 127.0, 122.2, 87.8, 70.6, 66.7, 45.2, 25.2, 24.0, 23.2, 23.0; MS (*m*/*e*) 166 $[M^+]$; EI HRMS calculated for $C_{11}H_{18}O$ $[M^+]$ 166.13576, found 166.13570.

The hydroformylation of **3e** follows the same procedure used for the acetyl ester (**3d**).

(*E*)-4-Methoxy-2-(1-methylethenyl)-6-methyl-2-hepten-1-al (4e): colorless liquid; IR ν(CO) 1695 cm^{-1}; ^1H NMR δ 9.43 (s, 1H), 6.27 (d, 1H, $J = 9.0$ Hz), 5.22 (d, 1H, $J = 1.0$ Hz), 4.74 (d, 1H, $J = 1.0$ Hz), 4.18 (td, 1H, $J_d = 4.4$ Hz, $J_t = 9.0$ Hz), 3.25 (s, 3H), 1.87 (s, 3H), 1.60 (m, 2H), 1.19 (m, H), 0.89 (d, 6H, $J = 6.6$ Hz); ^{13}C NMR δ 194.0, 154.2, 147.9, 138.6, 118.0, 76.5, 57.7, 44.8, 25.0, 24.0, 23.4, 22.6; EI MS (*m*/*e*) 196 $[M^+]$; EI HRMS calculated for $C_{12}H_{20}O_2$ $[M^+]$ 196.14633, found 196.14782.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of **3d**−**f** and **4a**−**f** . This material is available free of charge via the Internet at http://pubs.acs.org.

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