1.45, 1.48)). We assumed that the changes in structure in the AI would be similar, and the HF/STO-3G results were then scaled accordingly. This gave the following stretching parameters (bond, r_0 (Å), force constant (mdyn/Å)): (C–C, 1.470, 5.88), (C–N, 1.520, 5.43), (N–N, 1.553, 1.42). The bending and torsional parameters were modeled after cyclopropane parameters.

Acknowledgment. We thank Exxon for a fellowship, the Friedman bag company for additional support (F.J.), and the Alexander von Humboltstiftung for a Senior Scientist Award (C.S.F.). This work was supported by NSF Grant No. CHE83-11804. We thank Prof. E. Clennan for helpful discussions and a prepublication copy of his manuscript.

Supplementary Material Available: Listing of all nonstandard parameters used in the force-field calculations (3 pages). Ordering information is given on any current masthead page.

Transition-Metal-Catalyzed Cyclization of Alkynoic Acids to Alkylidene Lactones

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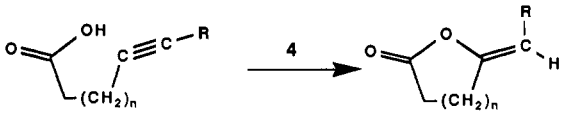
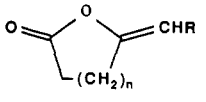
Abstract: Alkynoic acids I–IV can be effectively cyclized to the corresponding exocyclic enol lactones with a new Rh(I) complex, $[(cycphos)RhCl]_2$ (**4**) (cycphos = 1,2-bis(dicyclohexylphosphino)ethane), that we have developed. The high-yield lactonizations can be performed at room temperature, and methylene chloride appears to be the best solvent for the cyclization. Exclusive



I R=H, n=1
II R=CH_3, n=1
III R=Ph, n=1
IV R=H, n=2

formation of *Z*-olefinic isomers was observed, i.e., trans addition of the carboxylate OH across the triple bond. There is also a strong preference for the formation of five- vs six-membered rings in the substituted pentynoic acid systems. Other electron-rich group VIII transition-metal complexes and mercuric salts were tested for catalytic activity under similar reaction conditions and were found to be less effective. The proposed mechanism involves initial OH activation by the metal center followed by nucleophilic attack of carboxylate anion on the metal-coordinated alkyne of the intermediate, and subsequent reductive elimination from the resulting hydrido–vinyl complex releases the lactone product and regenerates the catalyst.

Interest in the chemistry of exocyclic enol lactones **1** has emerged in recent years because of the biological activities of a number of natural products shown to contain this moiety.[1-3] For example, compounds such as obtusilactone (**2**)[4] and cyanobacterin (**3**)[5] are reported to possess cytotoxic and antibiotic properties.



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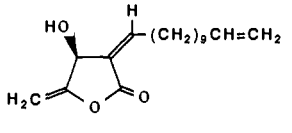

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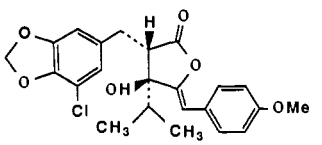

3

Due to their ready availability, the cyclization of α,ω-acetylenic acid precursors represents one of the most effective synthetic approaches to these enol lactone systems (eq 1). Indeed, the

(1)

cyclizations of 4-pentynoic acids to alkylidenebutyrolactones catalyzed by conventional Lewis acids such as silver nitrate,[6] mercuric acetate,[2,7a] mercuric trifluoroacetate,[7b-d] and mercuric oxide[3] have been reported. However, the utility of these catalysts

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(1) Kupchan, S. M.; Britto, R. W.; Ziegler, M. P.; Gilmore, C. J.; Restivo, R. G.; Bryan, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 1335, and references cited therein.
(2) Amos, R. A.; Katzenellenbogen, J. A. *J. Org. Chem.* **1978**, *43*, 560.
(3) Yamamoto, M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 582. Jellal, A.; Grimaldi, J.; Santelli, M. *Tetrahedron Lett.* **1984**, 3179.
(4) Niwa, M.; Iguchi, M.; Yamamura, S. *Tetrahedron Lett.* **1975**, 1539. Niwa, M.; Iguchi, M.; Yamamura, S. *Chem. Lett.* **1975**, 655. Niwa, M.; Iguchi, M.; Yamamura, S. *Tetrahedron Lett.* **1975**, 4395.
(5) Mason, C. P.; Edwards, K. R.; Carlson, R. E.; Pignatello, J.; Gleason, F. K.; Wood, J. M. *Science (Washington, D.C.)* **1982**, *215*, 400.
(6) Castaner, J.; Pascual, J. *J. Chem. Soc.* **1958**, 3962. Williard, P. G.; Jong, T. T.; Porwoll, J. P. *J. Org. Chem.* **1984**, *49*, 736.
(7) (a) Amos, R. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5459. (b) Rollinson, S. W.; Amos, R. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4114. (c) Sofia, M. J.; Katzenellenbogen, J. A. *J. Org. Chem.* **1984**, *50*, 2331. (d) Spencer, R. W.; Tam, T. F.; Thomas, E.; Robinson, V. J.; Krantz, A. *J. Am. Chem. Soc.* **1986**, *108*, 5589 and references therein.

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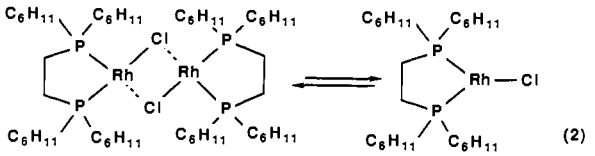
sometimes suffers from limited scope, drastic conditions, and poor stereo- and regioselectivity.

Recent reports of Pd(II)-catalyzed cyclization of alkynoic acids in the presence of added base[8] prompt us to report herein our findings that a new rhodium(I) complex is an excellent catalyst *in the absence of any external reagents.*

We reasoned that an electron-rich metal complex will activate the acid moiety via oxidative addition, and the intermediate should cyclize because the oxidized metal can now function as a Lewis acid. A reductive elimination of the hydrido–vinyl intermediate regenerates the catalyst. Indeed we observed that low-valent group VIII metal–phosphine complexes such as Wilkinson's catalyst ($[(PPh_3)_3RhCl]$) and $[(PPh_3)_4Pd]$ promote lactonization in simple unsubstituted systems, e.g., lactonization of 4-pentynoic acid to γ-methylidene-γ-butyrolactone. However, all complexes we examined either gave unsatisfactory yields or were not effective at all with substituted systems and higher homologues (vide infra). Thus with this mechanistic working hypothesis in mind, we set out to design a new catalytic system.

We chose a rhodium(I) system because of its well-known catalytic chemistry. The use of bulky alkylphosphine ligands should enhance metal basicity and catalyst selectivity. In addition, a very unsaturated complex, e.g., a 14-electron Rh(I) species, should be more efficient than a 16-electron analogue in that intermediate transformations and final reductive elimination processes are expected to be much more facile. Furthermore, this catalyst should be easy to prepare in good yield, well characterized, stable at room temperature, and soluble in common organic solvents.

Preparation and Structural Characterization of $[(cycphos)RhCl]_2$ (4). The compound that satisfies all of the above criteria is $[(cycphos)RhCl]_2$[9] (**4**), a new Rh(I) complex developed in our laboratory. This complex is readily formed by the addition of 2 equiv of the cycphos ligand to $[(cyclooctene)_2RhCl]_2$[10] (**5**) in THF. Recrystallization of the crude material from methylene chloride and nitromethane furnishes complex **4** in 83% yield. Although **4** as a dimer is formally a 16-electron species, its reaction chemistry is dominated by chloride bridge cleavage reactions,[11] possibly proceeding via equilibrium 2. It seems likely that the 14-electron monomer **4'** is responsible for the catalytic properties of **4**.

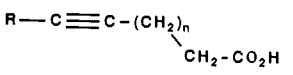


(2)

4 **4'**

The dimeric and steric nature of this complex in the solid state (Figure 1) is confirmed by a single-crystal X-ray diffraction study.[11]

Cyclization Studies. To determine the effectiveness of complex **4** as a catalyst for the intramolecular lactonization, we used four alkynoic acids: 4-pentynoic acid (4PA; R = H, n = 1), 4-hexynoic



acid (4HA; R = CH_3, n = 1), 5-phenyl-4-pentynoic acid (5-P-4PA; R = Ph, n = 1), and 5-hexynoic acid (5HA; R = H, n = 2) as substrates. The substrates were chosen in order to probe the stereoselectivity (*E*- vs *Z*-olefinic isomer) and regioselectivity (ring size) of the cyclizations. For comparison, we have also examined the use of other low-valent group VIII transition-metal complexes and mercuric salts as catalysts under similar reaction conditions. The results are summarized in Table I.

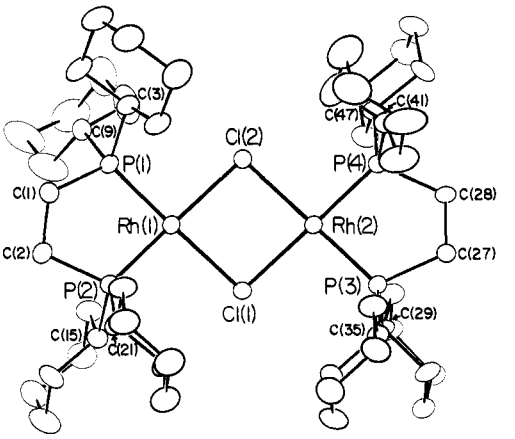
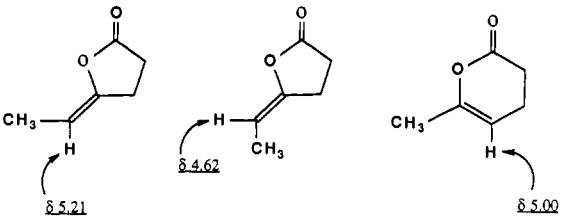


Figure 1. ORTEP view of **4** with hydrogens omitted for clarity. Full details of the structural analysis will be published elsewhere.[11]

For the cyclization, a mixture of the substrate and 3–5 mol % of the catalyst was stirred at room temperature (with the exception of entry 12) in the stated solvent under nitrogen. The products can be easily isolated by solvent evaporation followed by Kügelrohr distillation. All the cyclization products (lactones **6–13**) are known compounds and the spectral properties of our isolated materials are identical with the reported values. In most cases, however, the reaction mixture was directly analyzed by GC to determine yield and product ratio. In the analysis of the product mixture from the 4-hexynoic acid cyclization, high-field proton NMR was used to determine the product ratio via the signal intensity of the vinyl protons of compounds **7**, **8**, and **9**. This proton assignment was based on similar compounds in the literature.[7a,12] The ratio of lactones **10–12** was determined by GC.



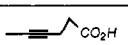
7 **8** **9**

Discussion. In general, the five-membered exocyclic methylene lactone **6** was the sole product when 4-pentynoic acid was used as the substrate regardless of the catalyst. Similarly, with the homologue 5-hexynoic acid, only the six-membered exocyclic methylene lactone **13** was observed. However, with the substituted 4-pentynoic acids, the ring size and stereoselectivity depend critically on the catalytic system. Indeed $[(cycphos)RhCl]_2$ (**4**) is uniquely effective in these transformations with high yields and good regio- and stereoselectivity (entries 1, 10, 14, and 16). The catalyst **4** can also be generated in situ from the reaction of the dimer **5** with 2 molar equiv of cycphos (entries 8 and 9). The complex $[(PPh_3)_4Pd]$ is effective only in the case of 4-pentynoic acid (4PA) and failed in substituted systems and with 5-hexynoic acid (entries 4, 11, and 17). Wilkinson's catalyst ($[(PPh_3)_3RhCl]$) behaves similarly. We have also examined other low-valent transition-metal complexes such as $[(PPh_3)_2Rh(CO)Cl]$, $[(PPh_3)_3(CO)_2Ru]$, $[Co_2(CO)_8]$, and $[(PEt_3)_3IrCl]$. They are not effective as lactonization catalysts even in the 4PA cyclization. Interestingly, methylene chloride is a better solvent than toluene or THF, giving higher yields and faster rates in both **4**- and $[(PPh_3)_4Pd]$-catalyzed lactonizations of 4PA (entries 1–6). Thus all scouting reactions were conducted in this solvent. Mercuric salts, catalysts used traditionally in these lactonizations, are not effective and/or give poor mixtures of products in systems other than 4PA (entries 12, 13, and 15).

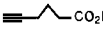
(8) Lambert, C.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, 5323.
(9) Cycphos = 1,2-bis(dicyclohexylphosphino)ethane, available from Strem Chemical Co.
(10) Ent, A. v. d.; Onderdelinden, A. L. *Inorg. Synth.* **1976**, *14*, 92.
(11) Marder, T. B.; Calabrese, J. C.; Chow, P. A.; Taylor, N. J., manuscript in preparation. This paper will describe the structures and stoichiometric reactions of cycphos complexes of Rh and Ir.
(12) Wineberg, J. P.; Abrams, C.; Swern, D. *J. Heterocycl. Chem.* **1975**, *12*, 749.

Table I. Metal-Catalyzed Lactonization of Alkynoic Acid

entry	alkynoic acid	catalyst	solvent (time)	product, % yield **6**
1		**4**	CH_2Cl_2 (24 h)	93
2		**4**	THF (24 h)	48
3		**4**	toluene (20 h)	77
4		$(PPh_3)_4Pd$	CH_2Cl_2 (6 h)	81
5		$(PPh_3)_4Pd$	THF (24 h)	6
6		$(PPh_3)_4Pd$	toluene (50 h)	39
7		$(PPh_3)_3RhCl$	CH_2Cl_2 (72 h)	48
8		**5**	CH_2Cl_2 (216 h)	15
9		**5** + 2 equiv of cycphos	CH_2Cl_2 (20 h)	71

entry	alkynoic acid	catalyst	solvent (time)	**7**	**8**	**9**
10		**4**	CH_2Cl_2 (80 h)	76	none	15
11		$(PPh_3)_4Pd$	CH_2Cl_2 (68 h)	traces	traces	traces
12		HgO	none (110 °C, 2 h)	39	7	33
13		$Hg(TFA)_2$	CH_2Cl_2 (68 h)	30	13	47

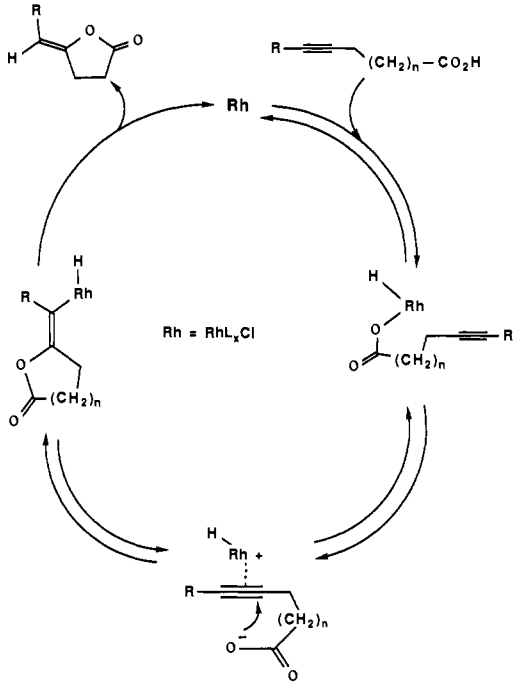
entry	alkynoic acid	catalyst	solvent (time)	**10**	**11**	**12**
14		**4**	CH_2Cl_2 (200 h)	85	none	none
15		$Hg(TFA)_2$	CH_2Cl_2 (48 h)	24	3	63

entry	alkynoic acid	catalyst	solvent (time)	**13**
16		**4**	CH_2Cl_2 (50 h)	85
17		$(PPh_3)_4Pd$	CH_2Cl_2 (24 h)	4
18		$Hg(OAc)_2$	CH_2Cl_2 (48 h)	3

With our rhodium catalyst **4**, only the *Z*-olefinic isomer was detected, i.e., *trans addition of the carboxylate OH across the triple bond*, in all cases where a substituted acetylenic acid was used (entries 10 and 14). We also observed a strong preference for the formation of five- vs six-membered rings in the pentynoic acid systems. The selectivities are thus parallel to that of Lewis acid catalysis.[3,6] Increase in size of the substituent on the acetylenic moiety (i.e., from hydrogen to phenyl) greatly decreases the rate of reaction (entries 1, 10, and 14), indicating that the coordination of the triple bond to the metal center plays an important role in these cyclizations. On the basis of the above observations, we propose a mechanism that involves an initial OH activation by the low-valent metal complex (Scheme I).[13] Nucleophilic attack of the carboxylate on the coordinated acetylene followed by reductive elimination gives the lactone and regenerates the catalyst. The use of "phosphine-deficient" electron-rich complexes such as **4** as catalyst enhances the rate of the intermediate conversions, which often require ligand dissociation.[14]

Recently, a Pd(II)-catalyzed lactonization was reported;[8] however, these reactions require elevated temperatures and the presence of triethylamine as a cocatalyst. The use of highly basic metal species in our studies eliminates the requirement of external base. Evidence for the proposed catalytic cycle and mechanistic studies, including structural characterization of model intermediates, will be the subject of subsequent reports.[15]

Scheme I. Proposed Mechanism for Lactone Formation



Experimental Section

General Methods. All room temperature catalytic reactions were performed under anhydrous conditions in a nitrogen-filled drybox (Vacuum Atmospheres). Solvents were distilled before use: methylene chloride (CH_2Cl_2), nitromethane, and pentane from calcium hydride, and toluene ($PhCH_3$) and tetrahydrofuran (THF) from sodium benzophenone ketyl. The term in vacuo refers to the removal of solvent on a Büchi–Brinkmann rotoevaporator at water-aspirator pressure. Gas chromatography was performed on a Hewlett-Packard Model 5790 with an FID

(13) For simplicity, we only considered the Rh(I) system.
(14) For example, see: Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221 and references cited therein.
(15) Marder, T. B.; Chan, D. M. T.; Fultz, W. C.; Calabrese, J. C.; Milstein, D. *J. Chem. Soc., Chem. Commun.*, in press.

Table II. Experimental Details for Metal-Catalyzed Lactonization of Alkynoic Acid

entry	alkynoic acid (weight, mg; mmol)	catalyst (weight, mg; mol %[f])	solvent (vol, mL; time, h)	product compound(s) (weight, mg; or (GC) yield)
1a	4-PA (1000; 10.2)	**4** (112; 2.0)	dichloromethane (20; 24)	**6** (93, 93%)
1b	4-PA (400; 4.1)	**4** (101; 4.3)	dichloromethane (15; 24)	**6** (93% (GC))
2	4-PA (400; 4.1)	**4** (99; 4.3)	THF, (15; 24)	**6** (48% (GC)[a])
3	4-PA (400; 4.1)	**4** (99; 4.3)	toluene (15; 20)	**6** (77% (GC))
4a	4-PA (1000; 10.2)	$(PPh_3)_4Pd$ (354; 3.0)	dichloromethane (30; 16)	**6** (720, 72%)
4b	4-PA (400; 4.1)	$(PPh_3)_4Pd$ (190; 4.0)	dichloromethane (15; 16)	**6** (81% (GC))
5	4-PA (400; 4.1)	$(PPh_3)_4Pd$ (192; 4.0)	THF (15; 24)	**6** (6% (GC)[b])
6	4-PA (403; 4.1)	$(PPh_3)_4Pd$ (190; 4.0)	toluene (15; 50)	**6** (39% (GC)[c])
7	4-PA (400; 4.1)	$(PPh_3)_3RhCl$ (150; 4.0)	dichloromethane (15; 72)	**6** (48% (GC)[d])
8	4-PA (400; 4.1)	**5** (57; 4.0)	dichloromethane (15; 216)	**6** (15% (GC))
9	4-PA (400; 4.1)	**5** (57; 4.0) cycphos (67; 4.0)	dichloromethane (15; 40)	**6** (71% (GC))
10	4-HA (399; 3.56)	**4** (98; 4.9)	dichloromethane (10; 80)	**7** (76%), **9** (15%[e])
11	4-HA (399; 3.56)	$(PPh_3)_4Pd$ (197; 4.8)	dichloromethane (10; 68)	**7**, **8**, **9** (traces (GC)[f])
12	4-HA (500; 4.46)	HgO (67; 7.0)	none (2[g])	**7** (39%), **8** (6.5%), **9** (33%)[e]
13	4-HA (400; 3.57)	mercuric trifluoroacetate (60; 4.0)	dichloromethane (13; 68)	**7** (30%), **8** (13%), **9** (47%)[e]
14	5-P-4PA (300; 1.72)	**4** (40; 4.0)	dichloromethane (7; 200)	**10** (255, 85%)
15	5-P-4PA (300; 1.72)	mercuric trilfuoroacetate (30; 3.7)	dichloromethane (7; 48)	**10** (24%), **11** (3%), **12** (63% (GC))
16a	5-HA (1000; 8.93)	**4** (200; 4.0)	dichloromethane (20; 44)	**13** (750, 75%)
16b	5-HA (400; 3.57)	**4** (80; 4.0)	dichloromethane (13; 50)	**13** (85% (GC))
17	5-HA (400; 3.57)	$(PPh_3)_4Pd$ (160; 4.0)	dichloromethane (13; 24)	**13** (4% (GC)[f])
18	5-HA (400; 3.57)	$Hg(OAc)_2$ (44; 4.0)	dichloromethane (13; 48)	**13** (3% (GC)[h])

[a] 56% conversion. [b] 30% conversion. [c] 50% conversion. [d] 68% conversion. [e] Isolated yield; product ratio determined by proton NMR (see text for details). [f] Starting material polymerized. [g] Reaction performed at 110 °C.[3] [h] 36% conversion. [i] For dimeric catalysts **4** and **5**, mol % refers to the mol % Rh monomer.

detector and helium as the carrier gas.

Proton NMR spectra were recorded in the stated solvent on a Nicolet NR-360 instrument. ^{31}P NMR spectra were recorded on a Nicolet NT-300 spectrometer. Chemical shifts are reported in δ; ^1H shifts are referenced to residual solvent protons and ^{31}P shifts are referenced to external H_3PO_4. Microanalyses were performed by Mikroanalytisches Laboratorium.

Preparation of Alkynoic Acid Substrates. 4-Pentynoic acid (4PA) was purchased from Aldrich Chemical Co. and recrystallized from benzene and heptane prior to use. 4-Hexynoic acid (4HA)[16] and 5-phenyl-4-pentynoic acid (5P-4HA)[3,17] were prepared according to literature methods, and the known 5-hexynoic acid (5-HA)[7a] was prepared by Jones oxidation of the corresponding alkynol.

Preparation of *m*-Dichlorobis[1,2-bis(dicyclohexylphosphino)ethane]dirhodium (4). In a drybox a 300-mL one-neck flask equipped with an addition funnel was charged with *m*-dichlorotetrakis(cyclooctene)dirhodium(I) (**5**) (4.0 g, 5.6 mmol) and tetrahydrofuran (125 mL). To the stirring suspension at room temperature was added dropwise a solution of 1,2-bis(dicyclohexylphosphino)ethane (4.8 g, 11.2 mmol) in tetrahydrofuran (63 mL). The resulting clear, deep red solution was stirred for 17 h and concentrated to approximately 100 mL. Addition of pentane (150 mL) to the reaction produced a yellow precipitate. Suction filtration followed by pentane washing gave 5.3 g (83%) of complex **4** as a yellowish crystalline solid, which can be further purified by recrystallization with a 1:1 mixture of methylene chloride and nitromethane: mp >210 °C (dec); $^{31}P\{^1H\}$ NMR (121 MHz, dichloromethane-d_2) δ 95.18 (d, J_{Rh-P} = 200 Hz); ^{13}C NMR (75 MHz, dichloromethane-d_2) δ 35.63 (t, J = 11.6 Hz), 28.80 (d, J = 43.9 Hz), 26.91 (d of t, J = 22.6, 6.0 Hz), 26.10 (s), 21.95 (t of d, J = 21.6, 6.0 Hz). Anal. Calcd for $C_{26}H_{96}Cl_2P_4Rh_2$: C, 55.67; H, 8.62; Cl, 6.32; P, 11.0; Rh, 18.3. Found: C, 55.60; H, 8.64; Cl, 6.38; P, 11.3; Rh, 18.6.

General Procedure for Metal-Catalyzed Lactonization of Alkynoic Acid (Table II). A flask equipped with a magnetic stirring bar was charged with the catalyst (3–5 mol %) in a nitrogen-filled drybox. The alkynoic acid substrate (approximately 4 mmol), tridecane (50 μL, an internal standard for GC analysis), and 15 mL of solvent were added. The resulting solution was then stirred at room temperature. The progress of the reaction was followed by analyzing 1–2-μL aliquots of the solution by GC (10% methylsilicone capillary column, 25 m × 0.32 mm, 0.52-mm-thick film). To determine the GC conversion and yield, the response factors of the components were calculated by using a mixture of known amounts of starting material, isolated authentic products, and 50 μL of tridecane as the internal standard.

For product isolation and determination of isolated yields, the reactions were performed similarly at 2–3 times the scale and no tridecane was added. The workup method entailed filtration of the reaction solution through a short column of silica gel (to remove the catalyst) and elution with ether (100–150 mL). The eluate was concentrated in vacuo and the residue was purified by Kügelrohr distillation. A typical run is illustrated in the synthesis of 5-methylidenetetrahydro-2-furanone (γ-methylidene-γ-butyrolactone).

Synthesis of 5-Methylidenetetrahydro-2-furanone (6). A solution of 4-pentynoic acid (1.0 g, 10.2 mmol) and **4** (112 mg, 0.1 mmol) in methylene chloride (20 mL) was stirred under nitrogen at room temperature for 24 h. The reaction mixture was filtered through a short column of silica gel, eluting with 150 mL of ether. The solvent was then removed in vacuo and the product was isolated by Kügelrohr distillation (50–60 °C (2 mmHg)) to give 0.93 g (93%) of the title compound as a clear colorless oil. The spectral data were identical with the literature values.[7a]

5-Ethylidenetetrahydro-2-furanones (7 and 8) and 6-Methyl-3,4-dihydro-2-pyrone (9). These three lactones are characterized as a mixture, with spectral assignment based on similar compounds:[3] ^1H NMR ($CDCl_3$) δ 5.21 (q of t, J = 8, 2 Hz, **8**), 5.00 (t, J = 5 Hz, **9**), 4.62 (q of t, J = 8, 2 Hz, **7**), 2.84–2.25 (m), 1.89 (d, J = 2 Hz, **9**), 1.67 (d of t, J = 8, 2 Hz, **7**), 1.58 (d of t, J = 8, 2 Hz, **8**); IR 1793, 1711, 1130, 993 cm^{-1}; mass spectrum, *m/e* (%) 112 (M^+, 17), 55 (10), 43 (100). Calcd for $C_6H_8O_2$: 112.0524. Found: 112.0531. The ratio of isomers was determined by integration of the olefin signals.

5-Benzylidenetetrahydro-2-furanones (10 and 11) and 6-Phenyl-3,4-dihydro-2-pyrone (12). The spectral data of these lactones were identical with the literature values.[3] The ratio of isomers were determined by GC.

6-Methylidenetetrahydro-2-pyrone (13). The spectral data of **13** are identical with the literature values.[7a]

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(16) Gravestock, M. B.; Johnson, W. S.; McCarry, B. E.; Parry, R. J.; Ratcliffe, B. E. *J. Am. Chem. Soc.* **1978**, *100*, 4274.

(17) Prepared by Jones oxidation of the corresponding aldehyde: Johnson, W. S.; Hughes, L. R.; Kloek, J. A.; Niem, T.; Shenvi, A. *J. Am. Chem. Soc.* **1979**, *101*, 1279.