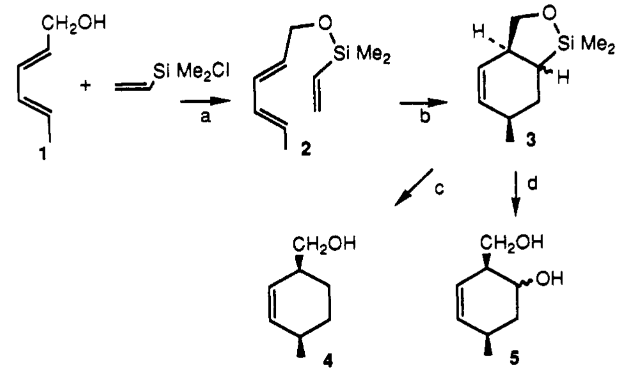
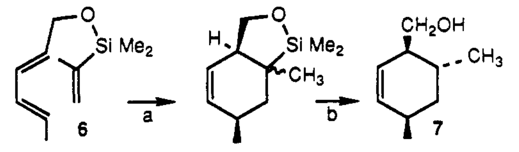
Scheme I[a]



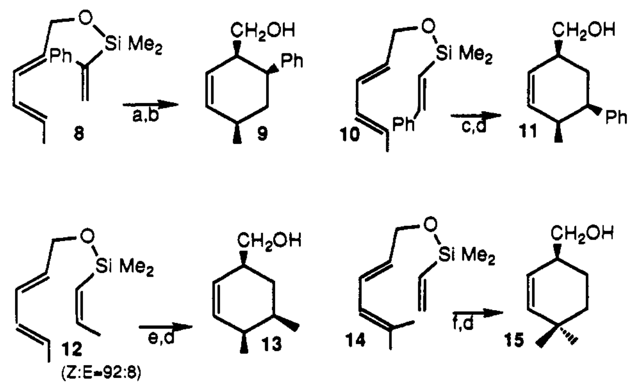
[a] Conditions: (a) Et_3N-THF; (b) 160 °C,[2] 3.5 h; 70%; (c) 4 equiv of TBAF-DMF, 75 °C, 4 h; 75%; (d) 1 equiv of TBAF-DMF, 10 equiv of 30% H_2O_2, 55 °C, 2 h; 85% (cis-1,2:trans-1,2 = 70:30).

Scheme II[a]



[a] Conditions: (a) 160 °C, 5 h; 80%, 2 isomers (60:40); (b) as in **3** → **4**; 65% (1 isomer; see footnote 7).

Scheme III[a]

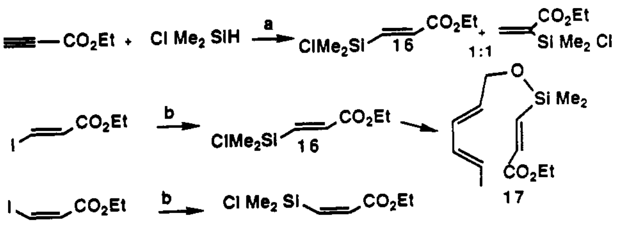


[a] Conditions: (a) 160 °C, 4 h; 75%; (b) TBAF-DMF; 85%; (c) 180 °C, 10 h; 80%; (d) TBAF-DMF, 85% (cis-4,5:trans-4,5 = 85:15); (e) 200 °C, 10 h; 45% (cis-4,5:trans-4,5 = 81:19); (f) 200 °C, 30 h; 50-60%.

context. This proved very successful. We were able to prepare the (*E*)-(chlorosilyl)acrylate **16** in two different ways, as shown in Scheme IV: as a component of a 1:1 mixture of regioisomers[11] or, regiospecifically, from (*E*)-ethyl 3-iodoacrylate.[12,13] Addition of **16** to **1** then gave the silicon-tethered acrylate **17** (50% from the iodoacrylate).

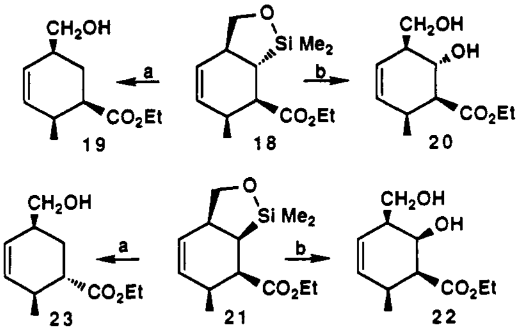
Cyclization of **17** readily (4-6 h, 80 °C) gave **18** (see Scheme V), the product of endo addition, in 90% yield. A similar sequence starting with (*Z*)-ethyl 3-iodoacrylate[12] gave the corresponding product of endo addition, as judged by its conversion to **22**. In this particular case, however, the initial, unstable, all-cis adduct **21** was epimerized by fluoride ion in the course of the desilylation process, with the formation of **23**.

Scheme IV[a]



[a] Conditions: −100 °C; then 1 equiv of acetyl chloride.

Scheme V[a]



[a] Conditions: (a) 2 equiv of TBAF; DMF, 60 °C, 4 h; 75%; (b) as in **3** → **5**; 80%.

The important feature of *controlled regiochemistry* which the temporary silicon connection can afford in the context of 4 + 2 cycloadditions is particularly well illustrated by the syntheses of **20** and **22**, in which, in addition, four new asymmetric centers are generated stereospecifically. Regiocontrol is also notable in the syntheses of **9** and **11**, inter alia.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their support of this work.

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[11] Both isomers can be successfully used in silicon-tethered 4 + 2 cycloadditions, e.g., to **1**.

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[13] Use of chlorosilyl rather than (dimethylamino)silyl derivatives is necessary when electrophilic olefins are involved to avoid conjugate addition of the dimethylamine released during silyl ether formation.

New Preparation of α-Methylene-γ-butyrolactones Mediated by (Iodomethyl)zinc Iodide

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A number of α-methylene-γ-butyrolactones display significant biological activity, and many syntheses of this class of molecules have been described.[2] We report a new stereoselective one-pot

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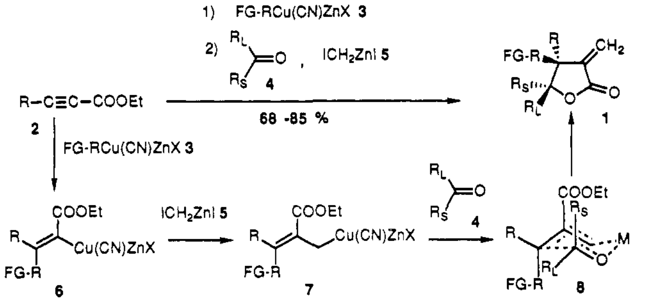
Table I. α-Methylene-γ-butyrolactones **1** Prepared by the Reaction of an Acetylenic Ester **2**, (FG-R)Cu(CN)ZnX **3**, a Carbonyl Compound **4**, and (Iodomethyl)zinc Iodide (**5**)

entry	R	FG-R	R_L	R_S	product **1**	cis:trans ratio[b]	yield (%)[a]
1	H	Bu	c-Hex	H	**1a**	80:20	76
2	H	$PhCH_2$	Ph	H	**1b**	92:8	78
3	H	$NC(CH_2)_3$	Ph	H	**1c**	90:10	75
4	H	$BuC{\equiv}C(CH_2)_2$	Ph	H	**1d**	95:5	76
5	H	$EtO_2C(CH_2)_3$	Ph	H	**1e**	95:5[c]	85
6	H	$EtO_2C(CH_2)_3$	$(CH_2)_5$		**1f**		68
7	H	$Cl(CH_2)_4$	Ph	CH_3	**1g**	100:0[c]	82
8	EtO_2C	$EtO_2C(CH_2)_3$	$PhCH_2CH_2$	H	**1h**	85:15	86
9	EtO_2C	$NC(CH_2)_3$	c-Hex	H	**1i**	95:5	93
10	Bu	c-Hex	Ph	H	**1j**	75:25	60
11	c-Hex	Bu	Ph	H	**1j**	98:2[c]	67
12	Bu	Ph	Ph	H	**1k**	60:40	78
13	Ph	Bu	Ph	H	**1k**	98:2	85

[a] All yields refer to isolated yields of analytically pure products. [b] Crude GC ratios. [c] Relative stereochemistry determined by ^{1}H NMR NOE experiments or X-ray analysis (see supplementary material).

Scheme I



synthesis of highly functionalized α-methylene-γ-butyrolactones **1** starting from an acetylenic ester **2**, a readily prepared zinc–copper reagent[3] **3**, an aldehyde or a ketone **4**, and (iodomethyl)zinc iodide[4] (**5**) (Scheme I and Table I).

The carbocupration of acetylenic esters[5] **2** with (FG-R)Cu(CN)ZnX (FG = functional group) provides stereoselectively the alkenylcopper **6** (THF, −50 °C, 3 h). The reaction mixture is then treated with a mixture of a carbonyl compound **4** (0.7 equiv) and (iodomethyl)zinc iodide in THF (2 equiv). The vinylic copper reagent **6** is not reactive enough to add to an aldehyde or ketone **4**; however, it is readily homologated (−30 to 0 °C) by a methylene unit[6] with (iodomethyl)zinc iodide (**5**), affording in situ a highly reactive polyfunctional allylic zinc and copper species **7**, which reacts stereoselectively with the carbonyl compound **4**, giving, after workup, the α-methylene-γ-butyrolactone **1**. The groups R of the alkyne, FG-R of the zinc–copper organometallic, and R_L of the aldehyde can bear a wide range of functionalities (ester, nitrile, halide, triple bond), allowing a unique approach to new α-methylene-γ-butyrolactones[7] **1**. A cis relationship is always found between the substituents R_L and FG-R in the major diastereoisomer[8] of **1**, which is compatible with the chair transition state[9] **8**. The stereochemistry of lactone **1** depends on the stereochemistry of the vinylic copper **6**. If the carbocupration can be performed at low temperature (below −30 °C), the resulting syn-adduct **6** is configurationally stable at this reaction temperature and affords, after methylene homologation and reaction with a carbonyl compound, the cis lactone as the major diastereoisomer (entries 1–9). Thus, the addition of BuCu(CN)Li to ethyl 3-cyclohexylpropiolate provides stereospecifically the alkenyl copper **6j** (R = c-Hex, FG-R = Bu), as confirmed by low-temperature iodolysis (−30 °C) giving only (*E*)-ethyl 3-cyclohexyl-2-iodo-2-heptenoate. The methylene homologation of **6j** followed by reaction with PhCHO gives the lactone **1j** (cis:trans, 98:2; entry 11). However, if the alkenylcopper **6j** obtained as described previously is allowed to warm to −10 °C, a mixture of (*E*)- and (*Z*)-alkenyl iodides is obtained after iodolysis (*E*:*Z* = 75:25). Also the carbocupration of ethyl 2-heptynoate with c-HexCu(CN)ZnI·2LiCl occurs only above −10 °C and leads under these reaction conditions to the same *E*/*Z* mixture of the alkenylcopper **6j** (*E*:*Z* = 75:25 as shown by iodolysis). After methylene homologation and reaction with benzaldehyde, the butyrolactone **1j** is produced as a 75:25 cis–trans mixture (entry 10). Similar behavior is observed in the addition of PhCu(CN)Li and BuCu(CN)Li respectively to ethyl 2-heptynoate (entry 12) and ethyl 3-phenylpropiolate (entry 13).

The intramolecular version of the reaction is also possible, and the addition of the keto-substituted copper[10] reagent **9** to ethyl propiolate and diethyl acetylenedicarboxylate provides, after the addition of $(ICH_2)_2Zn$[11] and benzaldehyde (THF, −35°, 0.5 h), the bicyclic α-methylene lactones **10a** and **10b** in respectively 76% and 83% yields (eq 1).

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(7) Typical procedure: preparation of 4-(3-cyanopropyl)-4,5-dihydro-3-methylene-5-phenyl-2(3*H*)-furanone (**1c**). A THF solution of 4-iodobutyronitrile (1.38 g, 7.1 mmol in 4 mL of THF) was added at 25 °C to zinc dust (1.3 g, 20 mmol pretreated with 1,2-dibromoethane (0.3 g, 1.5 mmol) and Me_3SiCl (0.1 mL)).[5] An exothermic reaction occurred, and the reaction mixture was stirred for 1.5 h at 40 °C. The excess of zinc was allowed to settle, and the supernatant solution was added to a solution of CuCN (0.635 g, 7.1 mmol) and LiCl (0.6 g, 14 mmol) in THF (10 mL) at −10 °C. After 5 min, the reaction mixture was cooled to −60 °C, ethyl propiolate (0.588 g, 6 mmol) was added, and the mixture was stirred for 4 h between −60 and −40 °C. A solution of PhCHO (0.53 g, 5 mmol) in THF (2 mL) was added, followed by the dropwise addition of a THF solution of (iodomethyl)zinc iodide (ca. 10 mmol) prepared from CH_2I_2 (3.75 g, 14 mmol) and zinc foil (0.91 g, 14 mmol) in THF (8 mL) at 25–26 °C (3 h).[5] The reaction mixture was allowed to warm to 0 °C and was stirred for 0.5 h at this temperature. After the usual workup, the residual oil was purified by flash chromatography, affording **1c** as a cis–trans mixture (90:10, 0.9 g, 75% yield).

(8) The relative stereochemistry of the α-methylene-γ-butyrolactone substituents has been established by comparisons with the literature, ^{1}H NMR NOE experiments, or X-ray structure determinations (**1g** and **1j**; see supplementary material).

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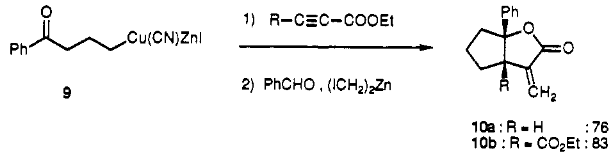

(1)

In conclusion, we have developed a new, efficient one-pot synthesis of polyfunctionalized α-methylene-γ-butyrolactones starting from readily available acetylenic esters, ICH_2ZnI, (FG-R)Cu(CN)ZnX, and an aldehyde or ketone. Applications to the synthesis of natural products are currently underway.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Spectral data for **1a–k** and **10a,b** and X-ray crystallographic analyses of **1g** and **1j** (52 pages). Ordering information is given on any current masthead page.

Preparation, Characterization, and Sequential Transformation of Dicarbide Cluster Compounds with Permetalated Ethyne, Ethene, and Ethane Structures

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The structures and properties of the C_2 ligand incorporated in polymetallic systems have been studied as models for elementary species on a heterogeneous catalyst surface, and several coordination modes have been reported.[1] Although ethynediyldimetal complexes (MC≡CM) are expected to serve as versatile starting compounds, this route has been frustrated by their limited accessibility. We[2a,b] and other groups[3] recently developed a preparative method for MC≡CM via deprotonation of $[M_2(\mu\text{-}C{\equiv}CH)]^+$. Herein we report the utility of Fp*C≡CFp* (**1**)[2a,b] [Fp* = Cp*Fe(CO)$_2$; Cp* = η^5-C_5Me_5] as a building block for a series of *dicarbide* cluster compounds.

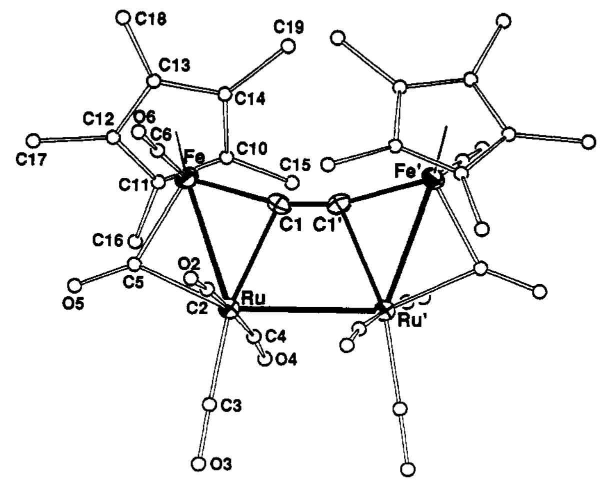


Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Ru–Ru, 2.963 (2); Ru–Fe, 2.733 (2); Ru–C1, 2.204 (7); Fe–C1, 1.946 (7); C1–C1′, 1.24 (1); Fe–Ru–Ru′, 110.61 (4), C1–Ru–Ru′, 66.5 (2); Fe–Ru–C1, 44.9 (2), Ru–Fe–C1, 53.0 (2); Ru–C1–Fe, 82.1 (2); Ru–C1–C1′, 112.0 (2); Fe–C1–C1′, 165.5 (2).

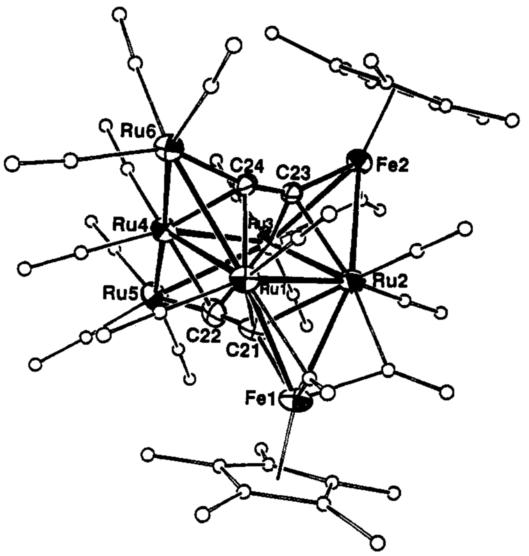
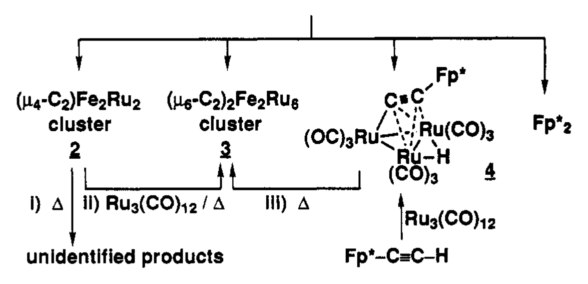


Figure 2. Molecular structure of one of two independent molecules of **3**. Selected bond lengths (Å): Ru–Ru, 2.746 (3)–2.857 (4); Ru–Fe, 2.687 (4)–2.855 (3); C21–C22, 1.35 (4); C23–C24, 1.37 (3); C21–Ru1, 2.25 (2); C21–Ru2, 2.20 (2); C21–Fe1, 1.90 (3); C22–Ru3, 2.15 (2); C22–Ru4, 2.18 (3); C22–Ru5, 1.99 (3); C23–Ru2, 2.18 (2); C23–Ru3, 2.17 (2); C23–Fe2, 1.86 (2); C24–Ru1, 2.15 (2); C24–Ru4, 2.11 (2); Ru6–C24, 2.01 (2).

Scheme I



Treatment of **1** with $Ru_3(CO)_{12}$ in refluxing benzene afforded a mixture of products, from which a tetranuclear dicarbide cluster, $(\mu_4\text{-}C_2)(Cp^*Fe)_2Ru_2(CO)_8(\mu\text{-}CO)_2$ (**2**), and an octanuclear bis-

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