concentration of dissolved organic carbon ultimately limit organic carbon richness in marine sediments.

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Isolation and Structural Characterization of 1-Zirconacyclopent-3-yne, Five-Membered Cyclic Alkynes

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Stable five-membered cyclic alkynes were synthesized, isolated, and fully characterized. Divalent zirconium species, bis(cyclopentadienyl)zirconium(II) equivalent, reacted with (*Z*)-1,4-disubstituted 1,2,3-butatrienes [(*Z*)-R-CH=C=C=CH-R, 1a: R = $(CH_3)_3Si$-, 1b: R = *tert*-C_4H_9-] to give 1-zirconacyclopent-3-yne compounds (2a-b) in good yields. X-ray diffraction analysis revealed their five-membered cyclic structure with a sufficiently short triple bond to regard this compound as a metallacyclopentyne.

Synthesis of small cyclic alkynes long has challenged organic chemists because of structural limitation *(1–3)*. The C–C≡C–C moiety is normally linear, and cyclization creates highly strained and often labile species. Cyclopentynes, five-membered cyclic alkynes, have not been isolated yet because they are extremely reactive and unstable. Although several preparative methods of cyclopentynes have been reported *(4–6)*, their existence was confirmed only spectroscopically in a matrix *(7)* or as trapped compounds by reactions such as [2+2] cycloaddition *(8)* or metal complexation *(9–11)*. The resulting trapped compounds, however, no longer have C≡C triple bonds. The products of [2+2] cycloaddition are cyclopentene compounds. In the metal-coordinated cyclopentynes, the C≡C triple bond is elongated because of its coordination to the metal, and its length is in a range of double bonds. 3,3,7,7-Tetramethylcycloheptyne, which contains a seven-membered ring, is the smallest hydrocarbyl cyclic alkyne isolated to date *(12)*. Heterocyclic compounds that have longer heteroatom-carbon bonds are expected to give more stable cyclic alkynes. Indeed, silacycloheptynes are less reactive than hydrocarbyl analogs *(1, 13)*. A silacyclic system even allowed isolation of a six-membered cyclic alkyne as 1,2,3,4-tetrasilacylohex-5-yne, although the ring contains four silicon atoms and only the triple bond consists of carbon atoms *(14)*. With regard to a five-membered ring, the preparation of a thiacyclopentyne was reported *(15)*. However, it was a short-lived species and isolation of a heterocyclic pentyne has not been successful. Organometallic compounds that contain metal-carbon bonds have allowed the isolation of small cyclic unsaturated compounds, such as metallacyclic cumulenes *(16, 17)*. We reasoned that metallacyclic compounds may give stable small cyclic alkynes. We report here the synthesis and structural characterization of 1-zirconacyclopent-3-yne compounds that are stable and isolable and that can be fully characterized as five-membered cyclic alkynes.

Dichlorobis(cyclopentadienyl)zirconium (Cp_2ZrCl_2, Cp = η^5-C_5H_5) reacts with 2 equivalents of *n*-butyllithium or *n*-butyl Grignard reagent to form divalent zirconocene equivalent "Cp_2Zr" (Negishi reagent) *(18)*. When we reacted this species with (*Z*)-1,4-bistrimethylsilyl-1,2,3-butatriene (**1a**) *(19)*, 1-zirconacyclopent-3-yne (**2a**) was obtained in 89% yield after stirring at room temperature (rt) for 1 hour (Scheme 1) *(20)*. Complex **2a** was an 83/17 mixture of cis and trans form at this stage. The cis-isomer gradually isomerized to trans at rt and gave a 36/64 mixture of *cis*/*trans*-**2a** that is in equilibrium after 48 hours. These compounds were very stable in solution at rt and were fully characterized by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Two signals for the cyclopentadienyl (Cp) ligands were observed for the cis-isomers, whereas the Cp ligands are magnetically equivalent in the trans-isomers. A butatriene with *tert*-butyl groups, (*Z*)-2,2,7,7-tetramethyl-3,4,5-octatriene (**1b**) *(21)*, also gave the zirconacyclopentyne **2b** after 1 hour at rt (yield 90% by ^1H NMR, cis/trans = 66/34), and the cis/trans ratio reached 12/88 after 48 hours.

These zirconacyclopentyne complexes **2a** and **2b** are so stable that the trans-isomers formed good crystals suitable for x-ray diffraction analysis. The molecular structure of *trans*-**2a** (Fig. 1) shows that the compound has a strained five-membered cyclic structure *(22)*. The Zr atom and the four C atoms (C1-C4) in the cyclopentyne ring are coplanar.

Although there are several examples of butatriene complexes of transition metals *(23, 24)*, no metallacyclopentyne complexes have been reported so far. In most of these complexes, a butatriene coordinates to the metal in η^2-fash-

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ion such as **3** (*25*) (Fig. 2). The structure of **2** is obviously different from those of known η^2-butatriene-metal π-complexes, and the addition of trimethylphosphine to **2** did not change the metallacyclopentyne structure to a η^2-π complex like **3**.

The bond length of C2-C3 in *trans*-**2a** is 1.206 ± 0.007 Å. In comparison with the reported larger cyclic alkynes, this value is similar to those of cyclononyne (*26*), thiacycloheptyne (*27*) (1.21 Å), and cyclooctyne (*28*) (1.23 Å). Triple bonds in small cyclic alkynes are slightly longer than those in acyclic C≡C bonds (1.167 to 1.197 Å) (*29*) because of ring strain. The C–C≡C angles in **2a**, 156.2 ± 0.6° and 155.9 ± 0.7°, are near those observed in cyclooctyne (158.5°) but larger than those in thiacycloheptyne (145.8°) (*30*). The bond lengths C1-C2 and C3-C4 are 1.415 ± 0.007 and 1.400 ± 0.006 Å, respectively. These are slightly shorter than normal Csp^3-Csp^1 single bonds (1.436 to 1.481 Å), although they are obviously much longer than usual nonconjugated C=C double bonds (1.280 to 1.347 Å). Distances Zr-C1 and Zr-C4 are 2.50 Å, whereas Zr-C2 and Zr-C3 are 2.29 Å. The former are slightly longer than those observed in typical Zr-Csp^3 σ bonds [e.g., 2.28 Å in $Cp_2Zr(CH_3)_2$] (*31*). The molecular structure of *trans*-**2b** was similar to *trans*-**2a**, although two enantiomers are randomly packed in the crystal and this disorder made detailed analysis difficult (*20*).

In the reported metal-coordinated cyclopentyne complex (**4**, Fig. 2), the length of the formal C–C triple bond was 1.295 Å, which is in the expected range for a double bond (*9*). It is generally observed in zirconocene-alkyne complexes that the lengths of coordinated triple bonds are much longer than normal triple bonds, typically 1.31 Å (*32*), and the C–C≡C bonds bend away from the metal by 30° to 45°. Thus, such compounds are often described as a zirconacyclopropene (**5**).

The relatively short distances of Zr-C2 and Zr-C3 raise the possibility that the triple bond coordinates to the metal and that it should be illustrated as a metallacyclopentene. However, the bond length of C2-C3 in *trans*-**2a** was short enough (1.206 Å) that it is reasonable as a cyclic triple bond (see above). In ^{13}C NMR spectroscopy, chemical shifts of C2 (=C3) at the triple bond are 102.92 parts per million (ppm) for cis and 103.59 ppm for the trans-isomer of **2a**, and 102.42 and 105.75 ppm for *cis*-**2b** and *trans*-**2b**, respectively (*20*). It was reported that the acetylenic carbon appears at lower field as ring strain increased (*1*, *14*). For instance, it appears at 100 to 110 ppm in cycloheptynes, 91 to 100 ppm in cyclooctynes, 82 to 90 ppm in cylononynes, and 80.9 ppm in *acyclic* 3-hexyne. Considering that the angles C1-C2-C3 and C2-C3-C4 are similar to those for cyclooctyne, the chemical shifts for C2 and C3 in **2** are best attributed to a triple bond in a strained ring. In the reported zirconium-alkyne complexes, acetylenic carbons of coordinated alkynes appear as far downfield such as 170 to 220 ppm (*33*) because the coordinated alkyne probably functions as a four-electron donor, which is not likely to be the case of **2**. Infrared (IR) spectroscopy of **2** (KBr) showed weak to moderate C≡C stretching bands at 2014 (**2a**) and 2011 cm^{-1} (**2b**). These are in a sharp contrast with a Zr-alkyne complex [**5**, R = Me_3Si, R′ = *t*-Bu, L = thf

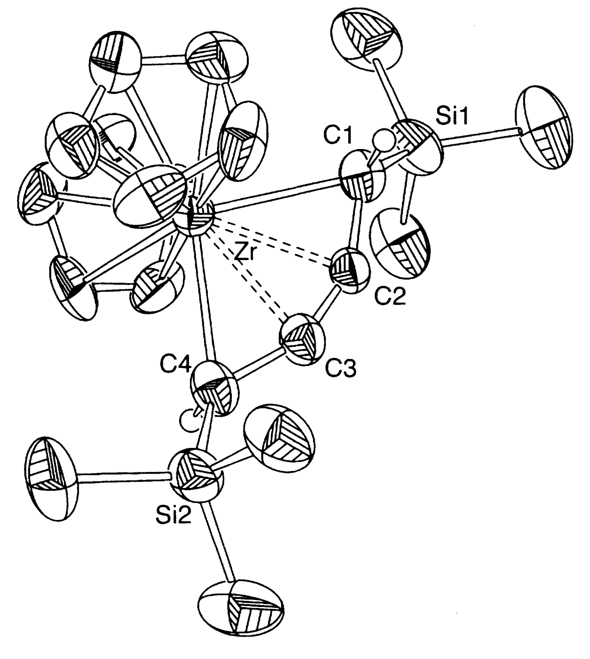
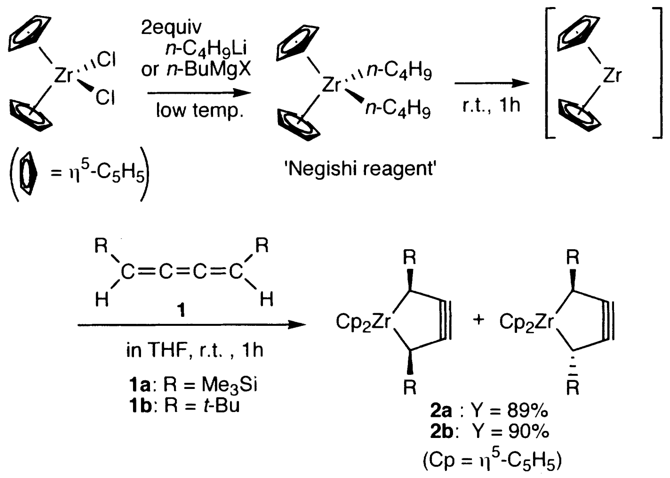
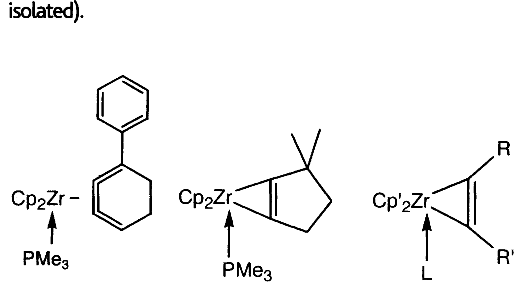


Fig. 1. Molecular structure of *trans*-**2a**. Drawn with 50% probability. Hydrogens are partly omitted for clarity. Selected bond lengths (Å) and angles (°): C1-C2: 1.415 ± 0.007 Å, C2-C3: 1.206 ± 0.007 Å, C3-C4: 1.400 ± 0.006 Å; C1-C2-C3: 155.9° ± 0.7°, C2-C3-C4: 156.2° ± 0.6°.



Scheme 1. Preparation of 1-zirconacyclopent-3-ynes. Typical procedure for preparation of zirconacyclopentynes **2** is as follows. We added *n*-butylmagnesium chloride (0.9 M THF solution, 2.0 mmol) and (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene (**1a**, 196 mg, 1.0 mmol) at −78°C to a solution of dichlorobis(cyclopentadienyl)zirconium (292 mg, 1.0 mmol) in THF (5 ml). The mixture was warmed up to room temperature and stirred for 1 hour. ^1H NMR observation showed the formation of **2a** (yield 89% by NMR). The volatiles were removed in vacuo, and the residue was extracted with diethyl ether and filtered. The filtrate was concentrated and the trans-isomer was recrystallized at −30°C (pale-yellow needle, yield 60%). **2b** was prepared similarly using **1b** (yield 90% by NMR, 57% isolated).



3 **4** **5**

Fig. 2. A zirconocene-butatriene π complex (**3**), a Zr-cyclopentyne (**4**), and a Zr-alkyne complex (**5**).

(*33*)] that shows a band in the region for a double bond (1611 cm^{-1}).

In a few zirconocene-alkyne complexes, the weakly coordinated triple bond has shorter bond distances (1.203 to 1.211 Å) (*34*, *35*). In these complexes, the Zr metal is electron-deficient (d^0) and there is no π-back donation to the alkyne that would increase its bond distance. The ^{13}C resonances of the weakly coordinated alkynes appeared slightly downfield (106 and 114 ppm) (*34*). IR bands for C≡C stretching in **2** appeared at slightly lower frequencies than known cyclic alkynes (2100 to 2200 cm^{-1}). The possibility of weak interaction between the triple bond and the metal in **2** cannot be ruled out, but, even so, it would not be inconsistent with the metallacyclopentyne structure.

Interconversion between a η^4-diene-zirconocene complex and a zirconacyclopentene was proposed in the zirconocene-1,3-butadiene complexes (*36*, *37*). Also, in the present compound **2**, a zirconacyclopentyne (Fig. 3A) and a η^4 complex (Fig. 3B) seem possible. Generally, a Zr-C σ bond is hydrolyzed by acid to give a Zr salt and hydrocarbons, whereas zirconium-alkene π complexes give the corresponding alkene and/or a reduced alkane after hydrolysis (*18*, *38*). Hydrolysis of **2a** by HCl gave 1,4-bistrimethylsilyl-2-butyne (**6a**) and Cp_2ZrCl_2 exclusively (Scheme 2). No other isomers of **6a**, such as 2-butenes, allenes, or 1,3-butadienes were observed by gas chromatograph, nor was butatriene **1a**. Deuterolysis with DCl afforded a 1,4-dideutero-2-butyne (**7a**), where D atoms were incorporated with >99% probability. Hydrolysis of **2b** also gave 2,2,7,7-tetramethyl-4-octyne (**6b**) in good yield (80% isolated). These results show that C1 and C4 had attached to the metal with a σ bond in spite of their slightly longer bond lengths, supporting the structure A for compound **2**.

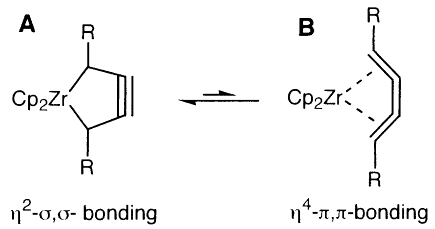


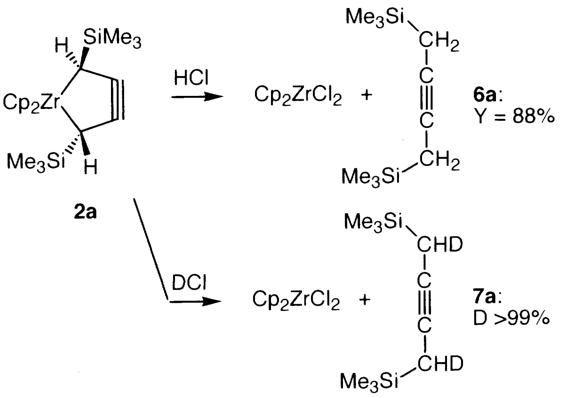
Fig. 3. Possible coordination modes: a zirconacyclopentyne or a zirconocene-butatriene complex.

The methine carbons adjacent to Zr in *cis*- and *trans*-**2a** appeared at 2.19 and 2.15 ppm in ^1H NMR, respectively, and 38.91 and 39.48 in ^{13}C NMR. These chemical shifts are similar to those observed in the oxazirconacyclopentane compound with a trimethylsilyl group (^1H: 2.45 ppm; ^{13}C: 43.37 ppm) (*39*). On the other hand, they are different from the vinylsilane-π complex (^1H: −0.82 ppm; ^{13}C: 17.67 ppm) (*39*). These results also support the sp^3 character of C1 and C4 in the zirconacyclopentyne (*20*).

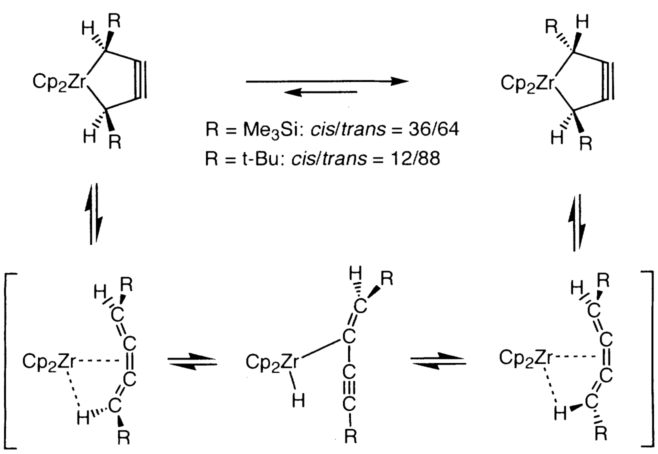
We note that the isomerization of (*Z*)-**1a** to (*E*)-**1a** proceeded in the presence of only catalytic amount of zirconium species. It possibly involves β-hydrogen elimination and reinsertion (*40*) (Scheme 3). This implies that π coordination of butatriene (form **B**) might contribute to the metallacyclopentyne structure to some extent, particularly in solution.

Stability of the triple bond in **2** was preliminarily studied. It has been known that acetylenic carbons in cyclopentynes readily undergo [2+2] cycloaddition with alkenes (*6*). When **2a** was mixed with 3-hexene (*cis*/*trans* mixture) in tetrahydrofuran (THF), however, no reactions took place, and **2a** remained stable after 24 hours at room temperature. It seems reasonable because the ring strain of **2a** is similar to cyclooctyne that is not so reactive toward [2+2] cycloaddition with unactivated internal alkenes. It was pointed that 3,3,7,7-tetramethylcyclohept-1-yne is more stable than nonsubstituted cycloheptyne because of methyl substituents on the carbons adjacent to the triple bond. Bulky substituents such as trimethylsilyl or *tert*-butyl groups in **2a** and **2b** may participate in stabilization of the metallacyclopentyne structure.

Scheme 2. Hydrolysis of metallacyclopentyne.



Scheme 3. Possible mechanism for isomerization of **2**.



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Hydrophobicity at a Janus Interface

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Water confined between adjoining hydrophobic and hydrophilic surfaces (a Janus interface) is found to form stable films of nanometer thickness whose responses to shear deformations are extraordinarily noisy. The power spectrum of this noise is quantified. In addition, the frequency dependence of the complex shear modulus is a power law with slope one-half, indicating a distribution of relaxation processes rather than any dominant one. The physical picture emerges that whereas surface energetics encourage water to dewet the hydrophobic side of the interface, the hydrophilic side constrains water to be present, resulting in a flickering, fluctuating complex.

The role of water as a solvent or lubricant in physical situations from biology to geology is almost universally thought to be important, but the details are disputed (*1–19*). In proteins, for example, the side chains of roughly half the amino acids are polar whereas the other half are hydrophobic; the nonmixing of the two is a major mechanism steering the folding of proteins and other self-assembly processes. Similarly, it is an everyday occurrence to observe the beading-up of raindrops, on raincoats or the leaves of plants. Moreover, it has been observed theoretically and experimentally that when the gap between two hydrophobic surfaces becomes critically small, water is spontaneously ejected (*10*, *15–19*), whereas water films confined between symmetric hydrophilic surfaces are stable at comparable spacings (*3*). It is then interesting to consider the antisymmetric situation, with a hydrophilic surface on one side to contain the water and a hydrophobic surface on the other to force it away. This Janus situation is shown in Fig. 1.

The main result of this experimental study is that when water is confined between these two competing tendencies, the result is neither simple wetting nor dewetting. We observe instead giant fluctuations (of the dynamical shear responses) around a well-defined mean. This noise and fluctuation are peculiar to water and are not observed with nonpolar fluids (*20*) or with a polar fluid such as ethanol. Aqueous films in the confined, symmetrically hydrophilic situation also give stable dynamical responses (*21*). The implied spatial scale of fluctuations is enormous compared to the size of a water molecule and lends support to the theoretical prediction that an ultrathin gas gap forms spontaneously when an extended hydrophobic surface is immersed in water (*5*, *10*, *12*).

The atomically smooth clay surfaces used in this study—muscovite mica (hydrophilic) and muscovite mica blanketed with a methyl-terminated organic self-assembled monolayer (SAM) (hydrophobic)—allowed the surface separation to be measured by multiple beam interferometry. Pairs of hydrophilic-hydrophobic surfaces were brought to the spacings described below by means of a surface forces apparatus (*3*) modified for dynamic oscillatory shear (*22*, *23*). A droplet of water was placed between the two surfaces oriented in crossed cylinder geometry. Piezoelectric bimorphs were used to produce and detect controlled shear motions. The deionized water was previously passed through a purification system, Barnstead Nanopure II (control experiments with water containing dissolved salt were similar). In experiments using degassed water, the water was either first boiled, then cooled in a sealed container, or was subjected to vacuum for 5 to 10 hours in an oven at room temperature. The temperature at which the measurements were taken was 25°C.

In order to firmly determine that the findings did not depend on the details of surface preparation, three methods were used to render one surface hydrophobic. In order of increasing complexity, these were (i) atomically smooth mica coated with a SAM of condensed octadecyltriethoxysiloxane (OTE), according to methods described previously (*23*); (ii) mica coated by means of Langmuir-Blodgett methods with a monolayer of condensed OTE; and (iii) a thin film of silver sputtered onto atomically smooth mica, then coated with a self-assembled thiol monolayer. In method (i), the monolayer quality was improved by distilling the OTE before self-assembly. In method (ii), OTE was spread onto aqueous HCl (pH, 2.5), 0.5 hour was allowed for hydrolysis, the film was slowly compressed to the surface pressure π = 20 mN m^{-1} (3 to 4 hours), and the close-packed film was transferred onto mica by the Langmuir-Blodgett technique at a creep-up speed of 2 mm min^{-1}. Finally the transferred films were vacuum-baked at 120°C for 2 hours. In method (iii), 650 Å of silver were sputtered at 1 Å s^{-1} onto mica that was held at room temperature, then octadecanethiol was deposited from 0.5 mM ethanol solution. In this case, atomic force microscopy (AFM) (with a Nanoscope II) showed the root mean square roughness to be 0.5 nm. All three methods led to the same conclusions. The contact angle of water with the hydrophobic surface was θ = 110° ± 2° (OTE surfaces) and θ = 120° ± 2° (octadecanethiol). In shear experiments, the sheared plate held the hydrophobic alkane monolayer.

The starting point was to measure the force-distance profile. The inset of Fig. 1 shows force, normalized by the mean radius of curvature of the crossed cylinders (R ≈ 2 cm), plotted against surface separation (D). Each datum refers to an equilibration of 5 to 10 min. Attraction was observed starting at very large separations, D ≈ 0.5 μm, and the slope of the ensuing

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