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Sulfur-containing stable five-membered “cycloallene” complexes: 1-thia-2-zircona- and 1-thia-2-titanacyclopenta-3,4-diienes

Noriyuki Suzuki, Takumi Asada, Akiko Kawamura, and Yoshiro Masuyama

Stable five-membered metallacyclic allenes that contain a sulfur atom were synthesized and structurally characterized. Low-valent zirconocene and titanocene reacted with alkynylthioamides to afford 1-thia-2-metallacyclopenta-3,4-diene compounds in moderate to excellent yields. The molecular structure of the zirconium complexes indicated their cycloallene structure, while an η³-alkyne-coordinated structure might be more responsible for the titanium complexes. Hydrolysis of the compounds gave the corresponding (Z)-alkenylthioamides predominantly. Deuterolysis resulted in >99% D incorporation.

Introduction

Allene compounds have attracted organic chemists because they exhibit a variety of reactivity and are versatile for organic synthesis.1 Cyclic allenes are more reactive than linear allenes, and are usually unstable, especially for small ring sizes. Cyclopenta-1,2-diienes, which are five-membered cyclic allenes, have been reported to exist as very short-lived intermediates.2 Cycloallenes can be stabilized by replacing one or more of the ring members with heteroatoms, such as silicon or phosphorus. A few six-membered heterocyclic allenes have been isolated, and their molecular structures have been unambiguously determined.3 Recently, our group and Erker’s group have independently reported the synthesis of metal-containing five-membered cycloallenes (1 and 2, Figure 1). It was surprising that these compounds were very stable despite their highly strained allene structures, and the molecular structures were unambiguously determined.4 Rosenthal and coworkers demonstrated the synthesis of nitrogen-containing five-membered metallacycloallene compounds, 1-aza-2-metallacyclopenta-3,4-diienes 3, by C=N insertion into the Zr–C bond, followed by silyl group-rearrangement.5

![Figure 1. Stable five-membered metallacycloallenes.](image)

However, the preparative methods of these complexes are not generally applicable for the synthesis of a variety of their analogues. We have reported a simpler protocol to prepare 1-metallacyclopenta-2,3-diene complexes from the reaction of a low-valent zirconocene with 1-en-3-ynes.6 Erker and coworkers have described an alternative approach by borane-catalyzed reductive elimination from (σ-alkynyl)(σ-alkenyl)zirconocene complexes.7 Alternative preparative methods for 1-aza-2-zirconacyclopenta-3,4-diene have also been reported.8

![Scheme 1. Simple synthetic protocols for metallacycloallenes.](image)

We have demonstrated in these previous reports that 1-zirconacyclopenta-2,3-diene and 1-aza-2-zirconacyclopenta-3,4-diienes can be prepared from the reaction of low-valent zirconocenes with 1-en-3-ynes and alkynylimines, respectively (Scheme 1). This protocol seems to be applicable to other types of metallacycloallenes. To the best of our knowledge, 1-aza-2-zirconacyclopenta-3,4-diienes are the only examples for reported stable five-membered metallacycloallenes containing a heteroatom. These results prompted us to pursue the possibility of synthesizing sulfur-containing analogues of these compounds as well as other group 4 metal complexes. We herein report the synthesis and structure of sulfur-containing zirconacycloallenes and titanacycloallenes.

Results and discussion

In our previous study on 1-aza-2-zirconacyclopenta-3,4-diienes, we employed alkynylimines as the starting materials. To synthesize the sulfur-analogues, we chose alkynylthioamides as starting compounds because these are rather stable sulfur-derivatives of 1-en-3-ynes.9

Scheme 1. Simple synthetic protocols for metallacycloallenes.
We added $N,N$-dimethyl-3-(trimethylsilyl)prop-2-ynethioamide (4a) to di-$n$-butylzirconocene, Negishi reagent,\textsuperscript{10} that was generated in situ from zirconocene dichloride and two equiv of $n$-butyllithium at $-78$ °C. After 1 h, the formation of 1-thia-2-zirconacyclopenta-3,4-diene 5a was observed by $^1$H NMR spectroscopy (69% yield) (Scheme 2). Two singlets assigned to cyclopentadienyl (Cp) ligands appeared at 5.25 and 5.49 ppm. The methyl groups on the nitrogen atom were observed as a single signal at 2.59 ppm, while the two methyl groups were observed inequivalent for 4a.

Substituents. We tried to synthesize an alkynyl thioamides with $R$ = phenyl group, but the reactions gave a complex mixture. The yield was improved when two equiv of titanium was used at room temperature under an inert atmosphere. For example, they degraded within a day at room temperature in a stable five-membered metallacycloallenes that contain a sulfur atom. These complexes are considerably stable at room temperature under an inert atmosphere. For example, crystals of 5b can be kept at room temperature for a month under argon. Trialkylsilyl groups were found to be suitable as R substituents. We tried to synthesize an alkynyl thioamides with $R$ = phenyl group, but the reactions gave a complex mixture.

Starting from Cp$_2$TiCl$_2$ and two equiv of $n$-butyllithium serving as a precursor of “Cp$_2$Ti(II)” species,\textsuperscript{12} the titanium analogues 6a and 6b were also synthesized in moderate yields (Scheme 3). The yield was improved when two equiv of titanium was used in the reaction (6b, 58%). Titanium complexes were rather unstable compared with their zirconium analogues. For example, they degraded within a day at room temperature in a dry $C_8D_8$ solution, even under an argon atmosphere.

The zirconium complex 5b and the titanium complex 6b showed similar molecular structures (Figure 2). It is noteworthy that these two have almost same cell parameters, indicating that they are nearly isostructural. Selected bond lengths and angles are summarized in Table 1.

The C1–C2 bond distances were 1.27–1.29 Å, showing that these were in the range of short double bonds.\textsuperscript{13} The C2–C3 bond lengths were 1.37–1.38 Å. The metallacycle structures are not planar and bent at the M–C3 bonds. These showed similar structural features to the aza-analogues.\textsuperscript{5a,8} The angle C1–C2–C3 was 159° for the zirconium complex 5b, and was 164° for the titanium complex 6b, showing that the allene moieties are bent from 180°. Note that the M–C3 distance was significantly longer than the reported 1-zirconacyclopenta-2,3-dienes and 1-aza-2-metallacyclopenta-3,4-dienes.\textsuperscript{5a,5,7} Two possible structures, P and Q, may contribute to 5 and 6, the 1-thia-2-metallacyclopenta-3,4-diene structure, P, and the η$^2$-alkyne-S coordination mode, Q (Figure 3). The S-C3 bonds were more than 1.7 Å, and these are closer to Csp$^2$–S single bonds than C=S double bonds.\textsuperscript{13}
Table 1. Selected bond lengths (Å) and angles (deg) of 5b and 6b.

<table>
<thead>
<tr>
<th></th>
<th>5b (M = Zr)</th>
<th>6b (M = Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–S</td>
<td>2.5875(12)</td>
<td>2.5348(17)</td>
</tr>
<tr>
<td>M–C1</td>
<td>2.306(2)</td>
<td>2.245(4)</td>
</tr>
<tr>
<td>M–C2</td>
<td>2.342(2)</td>
<td>2.254(4)</td>
</tr>
<tr>
<td>M–C3</td>
<td>2.655(3)</td>
<td>2.671(5)</td>
</tr>
<tr>
<td>C1–C2</td>
<td>1.286(3)</td>
<td>1.271(6)</td>
</tr>
<tr>
<td>C2–C3</td>
<td>1.377(3)</td>
<td>1.381(5)</td>
</tr>
<tr>
<td>S–C3</td>
<td>1.745(2)</td>
<td>1.718(4)</td>
</tr>
<tr>
<td>Si–C1</td>
<td>1.860(2)</td>
<td>1.850(4)</td>
</tr>
<tr>
<td>N–C3</td>
<td>1.394(3)</td>
<td>1.375(5)</td>
</tr>
<tr>
<td>C1–C2–C3</td>
<td>158.8(2)</td>
<td>164.1(4)</td>
</tr>
<tr>
<td>S–C3–C2</td>
<td>115.9(2)</td>
<td>113.3(3)</td>
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<tr>
<td>M–C1–C2</td>
<td>75.53(12)</td>
<td>74.0(2)</td>
</tr>
<tr>
<td>M–S–C3</td>
<td>72.65(7)</td>
<td>75.08(16)</td>
</tr>
<tr>
<td>S–M–C1</td>
<td>94.87(8)</td>
<td>96.22(12)</td>
</tr>
<tr>
<td>S–C3–N</td>
<td>122.8(2)</td>
<td>124.5(3)</td>
</tr>
<tr>
<td>N–C3–C2</td>
<td>119.7(2)</td>
<td>121.2(3)</td>
</tr>
</tbody>
</table>

Table 2. The $^{13}$C NMR chemical shifts of the metallacyclic compounds.

![Chemical structure](image_url)

The chemical shifts in $^{13}$C NMR spectroscopy for 5 and 6 are shown in Table 2 with other metallacycloallenes 7-10 for comparison. A coupling between C1 and the silicon atom was observed (for example, $^1$JCS = 67 Hz for 5a). To assign the other quaternary carbon atoms C2 and C3, two dimensional INADEQUATE measurement was carried out on 5a. The central carbon atom of “allene” (C2) appeared at 136.7 ppm, and the coupling constants for C1–C2 and C2–C3 were $^1$JCC = 68.2 and 88.5 Hz, respectively. These are similar values to those observed in our previous study on zirconacycloallene, but are smaller than typical values of acetylene (170 Hz), and are in between the range of ethylene (68 Hz) and allenes (99–103 Hz). The chemical shifts for the “allene” moieties in 5 and 6 were observed in the same range as those of known metallacycloallenes. For example, signals for C2 atoms appeared at 136–138 ppm, although the central carbon atoms of most linear allenes are observed at around 200 ppm.

A contribution of the structure Q to the titanium complexes 6 was suggested based on our X-ray diffraction analyses. Nevertheless, the $^{13}$C NMR chemical shifts of C1 and C2 in 6 were in the range 136–143 ppm, and it was observed at higher field compared with $\eta^2$-coordinated trimethylsilylalkyne groups in titanium complexes (196–220 ppm), indicating that contribution from the structure P cannot be ruled out.

In the titanium complexes 6, the Cp groups were observed as broad signals at room temperature, as well as methyl/methylene protons on the nitrogen atoms. The Cp signals appeared as two sharp singlets at 40 °C. These coalesced at 40 °C and then sharpened at 60 °C. For the zirconium complex 5b, however, the Cp ligands appeared as two sharp singlets at room temperature, and these did not broaden even at 100 °C. This indicates that the titanacyclic structures flip faster than the corresponding zirconacycles. The two Cp rings are inequivalent because of the enantiotopic structure of the allene, and a fast epimerization leads to a broadening of their $^1$H NMR signals (Figure 4). The ring flipping must formally involve a bond cleavage of the ring structure, and it is proposed that the $\eta^2$-alkyne-κS-structure (Q) has a higher contribution in the titanium complexes.

![Figure 4](image_url)

Figure 4. “Ring flipping” in the titanium complex 6.

Erker and coworkers have reported on hafnium and zirconium cycloallene complexes, where diastereoisomerization by ring flipping was faster for the zirconacycle than for the hafnacycle. Hydrolysis of 5a with dil. HCl gave the corresponding Z-alkene 11a in an 86:14 Z/E ratio (76% combined yield, Scheme 4). It has been reported that hydrolysis of zirconium-alkyne complexes affords the corresponding Z-alkenes. The deuterolysis of 5a using a diethyl ether solution of DCl gave the dideuterated alkene with >99% incorporation of deuterium. Complex 5b also gave 11b after hydrolysis.
Hydrolysis might have occurred at the 1,4-position of the metallocycles to give 11. Another possibility is that hydrolysis took place at the 3,4-position, i.e., the alkyl carbons, to afford the alkene. Part of the Z-alkene might have isomerized into the trans-alkene. Further investigation on the synthesis of the analogues, reactivity of the complexes is now in progress.

**Experimental**

**General.** All manipulations involving organometallic compounds were conducted under an inert atmosphere using a standard Schlenk technique or a glove box. The anhydrous tetrahydrofuran was purchased from Kanto Chemical Co., Inc., degassed and kept under argon. n-Butyllithium (hexane solution) was purchased from Kanto Chemical Co., Inc. Dichlorobis(η⁵-cyclopentadienyl)zirconium was purchased from Tokyo Chemical Industry Co., Ltd. Zirconacyclopentadienyl (dehydrated grade) were purchased from Kanto Chemical Co., Inc. and purified with Glass Contour Solvent System (SG Water USA). Hexane and toluene (dehydrated grade) were purchased from Wako Pure Chemical Industries Ltd. Hexane and toluene were obtained from Wako Pure Chemical Industries Ltd. and cooled at –30 °C. Another possibility is that hydrolysis have occurred at the 1,4 position of the alkenes.

**Preparation of 3-(tert-butyldimethylsilyl)-N,N-diethyлprop-2-yethioamide (4b).** The title compound was prepared in a similar manner to 4a according to the literature. In a Schlenk tube (100 mL) filled with argon, PdCl₂(PPh₃)₂ (7.0 mg, 0.01 mmol) and CuI (3.7 mg, 0.02 mmol) were dissolved in triethylamine (10 mL). To this solution was added tert-butyldimethylsilylacetylene (1.40 g, 10 mmol), and diethylthiocarbamoyl chloride (1.52 g, 10 mmol) in this order. The mixture was stirred at 90 °C for 6 h. Volatiles were removed in vacuo from the dark brown solution, and the residue was dissolved in diethyl ether and filtered. The filtrate was concentrated at –30 °C. The title compound was obtained as black crystals (1.60 g, 63%). ¹H NMR (C₆D₆, Me₆Si, 300 MHz): δ 0.05 (s, 6H), 0.82 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H), 0.94 (s, 9H), 3.34 (q, J = 7.2 Hz, 2H), 3.59 (q, J = 7.2 Hz, 2H). ¹³C NMR (C₆D₆, Me₆Si, 125.8 MHz): δ = –5.10 (CH₃Si), 11.23 (CH₃), 13.45 (CH₄), 17.00 (q, C = Si), 26.18 ((CH₂)₃C), 44.99 (CH₂N), 48.51 (CH₂N), 99.59 (C=O), 102.08 (C=O), 176.73 (C=O). IR (KBr): 2858, 2932, 2149, 1655, 1628, 1489, 1423, 1277, 1123, 1077, 779, 671 cm⁻¹. Anal. Calcd. for C₃H₆N₂Si, C 61.11, H 9.86, N 5.48, S 12.55. Found: C 61.11, H 9.86, N 5.48, S 12.55.

**Synthesis of 2,2-bis(η⁵-cyclopentadienyl)-3-tertbutyldimethylsilyl-5-diethyлamino-1-thia-2-zirconacyclopenta-3,4-diene (5a).** To a solution of dichlorobis(η⁵-cyclopentadienyl)zirconium (146 mg, 0.5 mmol) in tetrahydrofuran (THF, 5 mL) was added dropwise n-butyllithium (1.6 M hexane solution, 1.0 mmol) at –78 °C. After stirring at –78 °C for 1 h, N,N-diethyl-3-(tert-butylimethylsilyl)prop-2-yethioamide (4a) (92.5 mg, 0.5 mmol) was added dropwise, and the reaction mixture was warmed up to rt. The mixture was stirred at rt for 1 h, and observed by ¹H NMR to determine the yield (up to 69%). Volatiles were removed in vacuo and the residue was dissolved in toluene and filtered. The filtrate was concentrated and kept at –30 °C. The title compound was obtained as orange needles accompanied by small amount of lithium salts (47 mg, 23% crude). ¹H NMR (C₆D₆, Me₆Si, 300 MHz): δ = 0.33 (s, 9H), 2.59 (s, 6H), 5.25 (s, 5H), 5.49 (s, 5H). ¹³C NMR (C₆D₆, Me₆Si, 75.6 MHz): δ = 1.98 (CH₃Si), 40.37 (CH₃N), 105.81 (Cp), 106.39 (Cp). After stirring at 78 °C for 1 h, N,N-diethyl-3-(tert-butylimethylsilyl)prop-2-yethioamide (4b) (128 mg, 0.5 mmol) was added, and the reaction mixture was warmed up to rt. The mixture was stirred at rt for 1 h, and observed by ¹H NMR to determine the yield with toluene as internal standard (83%). Volatiles were removed in vacuo and the residue was dissolved in toluene and filtered. The filtrate was concentrated and kept at –30 °C. The title compound was obtained as orange needles (67 mg, 28%). ¹H NMR (C₆D₆, Me₆Si, 300 MHz): δ = 0.27 (s, 3H), 0.29 (s, 3H), 1.03 (t, J = 7.2 Hz, 6H), 1.13 (s, 9H), 3.13 (q, J = 7.2 Hz, 4H), 5.33 (s, 5H), 5.52 (s, 5H). ¹³C NMR (C₆D₆, Me₆Si, 75.6 MHz): δ = –3.05 (JC₆D₆ = 53 Hz, CH₃Si), –2.63 (JC₆D₆ = 53 Hz, CH₃Si), 13.82 (CH₂N), 18.48 (JC₆D₆ = 58 Hz, CH₃), 27.14 (CH₃C), 44.03 (br, CH₂N), 105.34 (Cp), 105.75 (Cp), 124.55 (Cq, CH₃), 136.91 (JC₆D₆ = 64 Hz, CH₂N), 137.88 (JC₆D₆ = 64 Hz, C=C=). IR (KBr): 799, 1015, 1088, 1231, 1493, 1628, 1674, 1805, 3086, 3807 cm⁻¹. Elemental analysis, calcd. for C₅H₂₀N₂Si, C 57.93, H 7.41, N 2.91, S 6.72. The mixture was stirred at that temperature for 1 h. ¹H NMR
observation suggested the formation of the title compound in 38% yield. 1H NMR (rt, CDCl3, Me2Si, 300 MHz): δ 0.42 (s, 9H, CH3Si), 2.78 (br, 6H, CH2N), 5.25 (br, 10H, Cp). 13C NMR (rt, CDCl3, Me2Si, 125.8 MHz): δ 1.84 (CH3Si), 39.14 (CH3N), 105.21 (br, Cp), 119.94 (q, CN), 138.15 (q, Ce=C=C), 142.52 (q, JCSi = 73 Hz, CSi).

**Synthesis of 2,2-bis(n^2 -cyclopentadienyl)-3-tert-butylidimethylsilyl-5-dithiylamino-1-thia-2-titanacyclohexa-3,4-diene (6b).** The title compound was prepared similarly to 6a using N,N-diethyl-3-(tert-butylidimethylsilyl)prop-2-ynethioamide (4b) (127 mg, 0.5 mmol) instead of 4a (39%). Volatiles were removed in vacuo and the residue was dissolved in hexane and filtered. The filtrate was concentrated and kept at −30 °C. The title compound was obtained as red crystals (57 mg, 26%). 1H NMR (rt, CDCl3, Me2Si, 500 MHz): δ 0.32 (s, 6H), 1.06 (t, J = 6.9 Hz, 6H), 1.12 (s, 9H), 3.25 (br, 4H), 5.17 (br, 5H), 5.36 (br, 5H). 13C NMR (rt, CDCl3, Me2Si, 125.8 MHz): δ −2.80 (CH3Si), 14.00 (CH2CH2N), 18.42 (q, JCSi = 57.6 Hz, CSi), 26.86 (CH2N), 103.91 (Cp), 105.38 (Cp), 119.96 (q, CN), 136.09 (q, Ce=C=C), 138.05 (q, JCSi = 70 Hz, CSi).

**Hydrolysis of 5 (11).** Typically, THF (5 mL) solution of complex 5a was prepared as described above starting from dichlorobis(n^3 -cyclopentadienyl)zirconium (0.5 mmol) in 70% yield. To this solution diluted hydrochloric acid (1 N) was added and stirred for 5 min. The mixture was extracted with diethyl ether and washed with brine. The organic layer was then evaporated to give brown liquid. This crude product was purified with column chromatography (silica gel, hexane/ethyl acetate) to afford 11a as a mixture of E- and Z-isomers (1:1 ratio) in 76% combined yield (based on 5a).

Recrystallization from hexane solution gave colorless platelet crystals of (Z)-11a. The molecular structure of (Z)-11a was determined by X-ray diffraction analysis (see the supporting information).

X-ray diffraction analyses of the 1-thia-2-zirconacyclohexa-3,4-diene 5b. Crystals were obtained from a toluene solution. An orange platelet crystal (0.4 × 0.3 × 0.02 mm) was mounted on a polyamide film, MicroMounts™ (Mitegen), and coated with paraffin. All data were collected on a Rigaku Mercury 70 CCD area detector with graphite monochromated Mo-Kα radiation at 153 K. The structure was solved by direct methods and expanded using Fourier techniques. The disordered diethylamino group was modeled over two positions. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 5501 observed reflections and 251 variable parameters. All calculations were performed using the CrystalStructure software except for refinement, which was performed using SHELXL97. Crystallographic data are summarized in table S (in the supporting information). CIF data were deposited in Cambridge Structural Database (CCDC-1023317).

**Conclusions**

Low-valent zirconocene and titanocene reacted with alkynylthioamides to give “1-thia-2-metallacyclohexa-3,4-diene” compounds. X-ray diffraction analyses showed that the zirconium complexes have a sulfur-containing cycloallene structure, while an n^2-alkyne-coordinated structure might have more contribution to the titanium complexes. Hydrolysis of the compounds gave the corresponding (Z)-alkenylthioamides as major products.

**Acknowledgements**

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**Notes and references**