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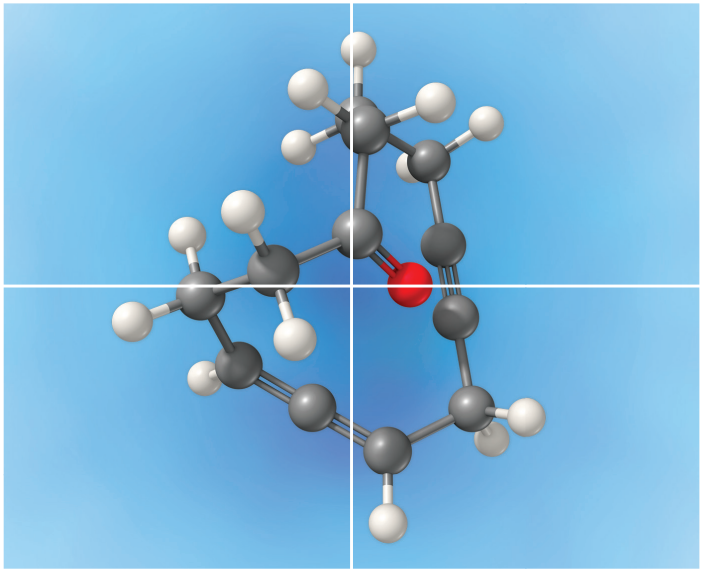

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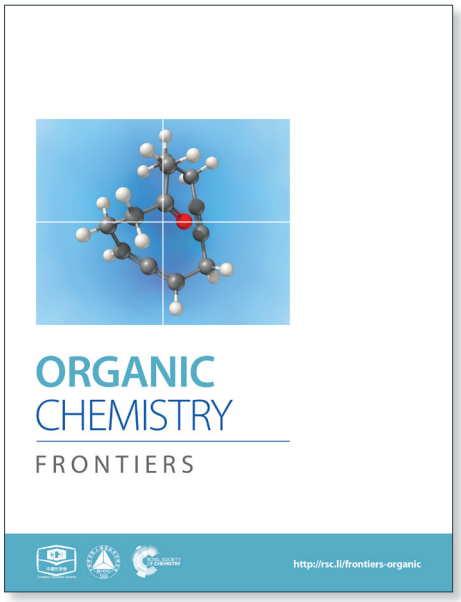

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ARTICLE

Sulfur-containing stable five-membered "cycloallene" complexes: 1-thia-2-zircona- and 1-thia-2-titanacyclopenta-3,4-dienes†

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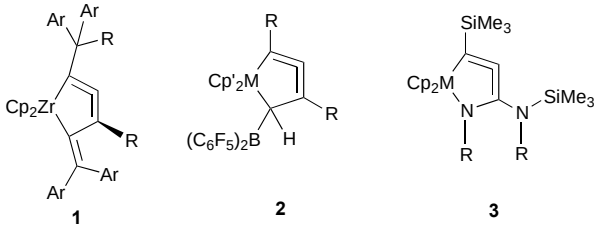
Stable five-membered metallacyclic allenes that contain a sulfur atom were synthesized and structurally characterized. Low-valent zirconocene and titanocene reacted with alkynylthioamides to afford 1-thia-2-metallacyclopenta-3,4-diene compounds in moderate to excellent yields. The molecular structure of the zirconium complexes indicated their cycloallene structure, while an η^2-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-dienes, 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-dienes **3**, by C=N insertion into the Zr–C bond, followed by silyl group-rearrangement.[5]



1 **2** **3**

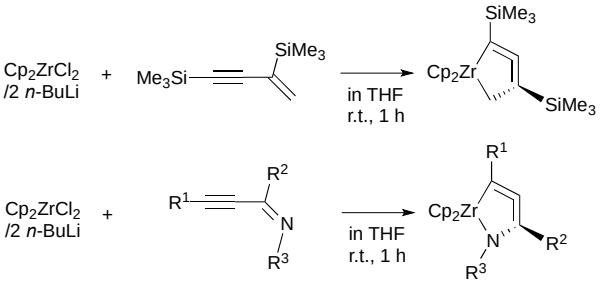
R = Me, Me_3Sn Ar = 4-EtC_6H_4-

$Cp'_2M = Cp_2Hf$, R = $SiMe_3$; $Cp'_2M = Cp_2Hf$, R = *t*-Bu; $Cp'_2M = (C_5H_4Me)_2Zr$, R = $SiMe_3$

M = Ti, R = *i*-Pr; M = Zr, R = Cy, *i*-Pr, *p*-tol

Figure 1. Stable five-membered metallacycloallenes.

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-yne compounds.[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]

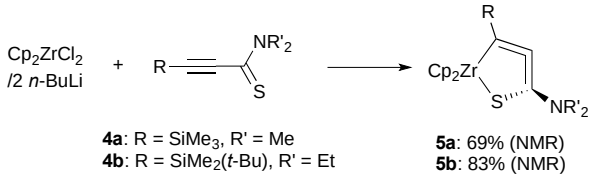


Scheme 1. Simple synthetic protocols for metallacycloallenes.

We have demonstrated in these previous reports that 1-zirconacyclopenta-2,3-diene and 1-aza-2-zirconacyclopenta-3,4-dienes 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-dienes 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.

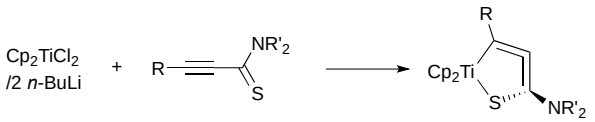
Results and discussion

In our previous study on 1-aza-2-zirconacyclopenta-3,4-dienes, 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 2. Synthesis of 1-thia-2-zirconacyclopenta-3,4-dienes.

We added *N*,*N*-dimethyl-3-(trimethylsilyl)prop-2-ynethioamide (**4a**) to di-*n*-butylzirconocene, Negishi reagent,[10] that was generated in situ from zirconocene dichloride and two equiv of *n*-butyllithium at –78 ℃. After stirring at room temperature for 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**. *N*,*N*-Diethyl-3-(*tert*-butyldimethylsilyl)prop-2-ynethioamide (**4b**) gave **5b** in 83% yield. The molecular structures of **5a** and **5b** were determined by X-ray diffraction analyses, although the quality of the structural data of **5a** was unsatisfactory to discuss its bond lengths and angles in detail.[11] These are the first examples of 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_2TiCl_2 and two equiv of *n*-butyllithium serving as a precursor of "Cp_2Ti(II)" species,[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_6D_6 solution, even under an argon atmosphere.



Scheme 3. Preparation of 1-thia-2-titanacyclopenta-3,4-dienes

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.

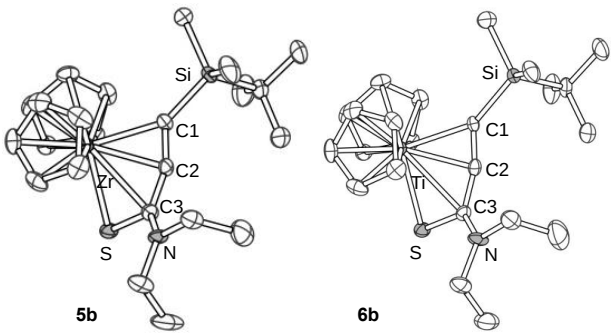


Figure 2. The Molecular structures of **5b** and **6b**. Hydrogen atoms are omitted for clarity. One position of the disordered groups in **5b** is omitted.

The C1–C2 bond distances were 1.27–1.29 Å, showing that these were in the range of short double bonds.[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.[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.[4a,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-κ*S* coordination mode, **Q** (Figure 3). The S-C3 bonds were more than 1.7 Å, and these are closer to C*sp*^{2}–S single bonds than C=S double bonds.[13]

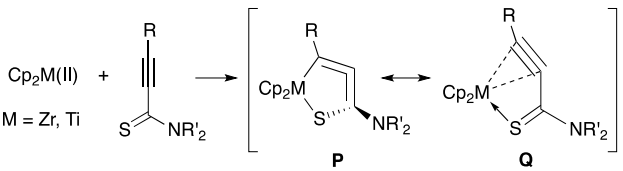


Figure 3. Resonance structures of metallacycloallenes.

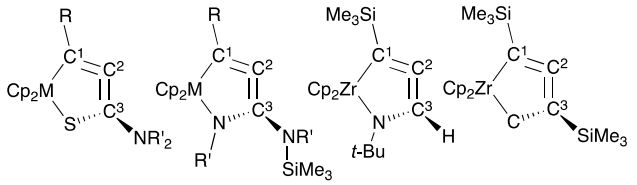
The Zr–C1 (2.308 Å) and Zr–C2 (2.344 Å) bond distances in **5b** were significantly longer than those reported for Zr-η^2-alkyne complexes, where the Zr–C bond distances are 2.18–2.26 Å.[14] The reported Zr–S covalent bond lengths in zirconium thiolates are 2.5–2.6 Å, while Zr←S dative bonds are typically 2.7–2.8 Å.[15] Thus, the Zr–S bond in **5b** (2.588 Å) can be regarded a covalent bond. These suggest that the zirconium compounds **5** should be described with the structure **P**.
On the other hand, the Ti–C1 and Ti–C2 distances (2.245 and 2.254 Å, respectively) in **6b** were not much longer than those reported for Ti-η^2-alkyne complexes, where the Ti–C distances are 2.10-2.27 Å.[16] The C1–C2 bond in **6b** was slightly shorter than that in the zirconium complex **5b**. The Ti–S bond in **6b** was 2.535 Å, which is significantly longer than the reported Ti–S bonds in titanium thiolates, where typically observed values are 2.3–2.4 Å.[17] These results are consistent with the fact that the Ti–C1 and Ti–S bonds are shorter than the Zr–C1 and Zr–S bonds by only 0.05–0.06 Å, although titanium has a smaller atomic radius than zirconium by more than 0.1 Å (Ti: 1.324 Å,

Zr: 1.454 Å).[18] These facts suggest that the contribution of **Q** is more responsible in titanium complexes **6**. The shorter S–C3 bond corresponds to this idea.

Table 1. Selected bond lengths (Å) and angles (deg) of **5b** and **6b**.

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

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



5: M = Zr
6: M = Ti
7: M = Zr
8: M = Ti
9
10

	5a	**5b**	**6a**	**6b**	**7**	**8**	**9**	**10**
R	TMS	TBDMS	TMS	TBDMS	TMS	TMS	–	–
R'	Me	Et	Me	Et	*i*-Pr	*i*-Pr	–	–
M	Zr	Zr	Ti	Ti	Zr	Ti	Zr	Zr
C1	140.7	136.9	142.5	138.1	106.8	110.6	134.6	119.2
C2	136.7	137.8	138.2	136.1	134.2	145.9	122.5	135.1
C3	126.6	124.6	119.9	120.0	111.0	117.9	97.6	79.5
ref.	This work				5a	5a	8	6a

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, $^{1}J_{CSi}$ = 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 $^{1}J_{CC}$ = 68.2 and 88.5 Hz, respectively. These are similar values to those observed in our previous study on zirconacycloallene,[4a] 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).[19] The chemical shifts for the "allene" moieties in **5** and **6** were observed in the same range as those of known metallacycloallenes.[5a,6a,8] 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 were observed at higher field compared with η^2-coordinated trimethylsilylalkyne groups in titanium complexes (196–220 ppm),[16a,20] 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 ℃. These coalesced at 40 ℃ and then sharpened at 60 ℃. 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 ℃. 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 η^2-alkyne-κ*S*-structure (**Q**) has a higher contribution in the titanium complexes.

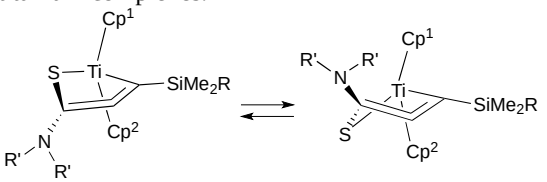
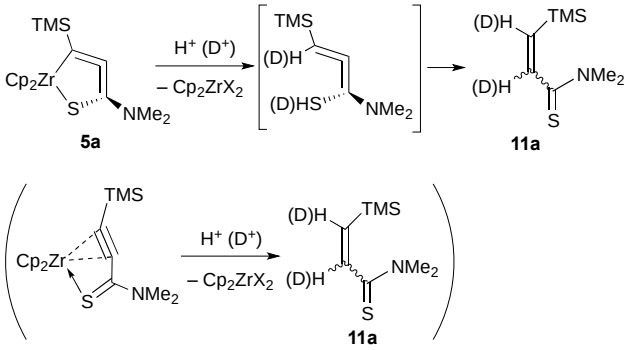


Figure 4. "Ring flipping" in the titanium complex **6**.

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.[4b,c]

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.[10a,21] The deuteolysis 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.



Scheme 4. Hydrolysis of **5a**.

Hydrolysis might have occurred at the 1,4-position of the metallacycles to give a formal "allenylaminothiol" followed by tautomerization into **11**. Another possibility is that hydrolysis took place at the 3,4-position, i.e., the alkyne carbons, to afford the alkene. Part of the *Z*-alkene might have isomerized into the trans-alkene.[22] 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. and purified with Glass Contour Solvent System™ (SG Water USA). Hexane and toluene (dehydrated grade) were purchased from Kanto Chemical Co., Inc., degassed and kept under argon. *n*-Butyllithium (hexane solution) were purchased from Kanto Chemical Co., Inc. Dichlorobis(η^5-cyclopentadienyl)zirconium, *N*,*N*-diethylthiocarbamoyl chloride were purchased from Sigma-Aldrich Corp. Trimethylsilylacetylene was purchased from Tokyo Chemical Industry Co., Ltd. *N*,*N*-Dimethylthiocarbamoyl chloride, *tert*-butyldimethylsilylacetylene, were obtained from Wako Pure Chemical Industries Ltd. These chemicals were used as received unless otherwise mentioned. *N*,*N*-dimethyl-3-(trimethylsilyl)prop-2-ynethioamide (**4a**) was prepared according to a literature method.[9a] The INADEQUATE measurement was recorded on a JNM-ECA 600 spectrometer equipped with an UltraCOOL probe (JEOL RESONANCE). The other NMR spectra were recorded on JNM-ECX 300 and ECA 500 spectrometers (JEOL), and NMR yields were determined using anhydrous toluene as an internal standard. Infrared spectra were recorded on Shimadzu FT-IR 8300. EI-MS spectra were recorded on a Shimadzu GCMS QP-5050 instrument or on a JEOL JMS-700 instrument. ESI-MS spectra were recorded on a JEOL JMS-T100LC instrument or on a Thermo Exactive spectrometer. Elemental analyses were measured on Perkin Elmer PE2400 Series II CHNS/O.

Preparation of 3-(*tert*-butyldimethylsilyl)-*N*,*N*-diethylprop-2-ynethioamide (4b). The title compound was prepared in a similar manner to **4a** according to the literature.[9a] In a Schlenk tube (100 mL) filled with argon, $PdCl_2(PPh_3)_2$ (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*-butyldimethylsilyl)acetylene (1.40 g, 10 mmol), and diethylthiocarbamoyl chloride (1.52 g, 10 mmol) in this order. The mixture was stirred at 90 ℃ 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 and cooled at –30 ℃. The title compound was obtained as black crystals (1.60 g, 63%). ^{1}H NMR (C_6D_6, Me_4Si, 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). ^{13}C NMR (C_6D_6, Me_4Si, 125.8 MHz): δ –5.10 (*C*H$_3$Si), 11.23 (*C*H$_3$), 13.45 (*C*H$_3$), 17.00 (q, *C*Si), 26.18 ((*C*H$_3$)$_3$C), 44.99 (*C*H$_2$N), 48.51 (*C*H$_2$N), 99.59 (*C*≡C), 102.08 (*C*≡C), 176.73 (*C*=S). IR (KBr): 2858 , 2932 , 2149 , 1655 , 1628 , 1489 , 1423, 1277, 1123, 1007, 779, 671 cm^{-1}. Anal. Calcd. for $C_{13}H_{25}NSSi$, C 61.11, H 9.86, N 5.48, S 12.55; found C 60.77, H 9.79, N 5.58, S 12.39.

Synthesis of 2,2-bis(η^5-cyclopentadienyl)-3-trimethylsilyl-5-dimethylamino-1-thia-2-zirconacyclopenta-3,4-diene (5a). Typically, to a solution of dichlorobis(η^5-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 ℃. After stirring at –78 ℃ for 1 h, *N*,*N*-dimethyl-3-(trimethylsilyl)prop-2-ynethioamide (**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 ^{1}H 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 ℃. The title compound was obtained as orange needles accompanied by small amount of lithium salts (47 mg, 23% crude). ^{1}H NMR (C_6D_6, Me_4Si, 300 MHz): δ 0.33 (s, 9H), 2.59 (s, 6H), 5.25 (s, 5H), 5.49 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si, 75.6 MHz): δ 1.98 (*C*H$_3$Si), 40.37 (*C*H$_2$N), 105.81 (Cp), 106.39 (Cp), 126.59 (q, $^1J_{CC}$ = 88.5 Hz, *C*N), 136.67 (q, $^1J_{CC}$ = 88.5, 68.2 Hz, C=*C*=C), 140.70 (q, $^1J_{CC}$ = 68.2 Hz, $^1J_{CSi}$ = 67 Hz, *C*SiMe$_3$). IR (KBr): 664 , 849 , 1092 , 1261, 1801 cm^{-1}. High resolution mass spectrometry: calcd. for $C_{18}H_{25}NSSiZr+H^+$ [M+H]$^+$, 406.0602, found, 406.0603.

Synthesis of 2,2-bis(η^5-cyclopentadienyl)-3-*tert*-butyldimethylsilyl-5-diethylamino-1-thia-2-zirconacyclopenta-3,4-diene (5b). To a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (146 mg, 0.5 mmol) in THF (5 mL) was added dropwise *n*-butyllithium (1.6 M hexane solution, 1.0 mmol) at –78 ℃. After stirring at –78 ℃ for 1 h, *N*,*N*-diethyl-3-(*tert*-butyldimethylsilyl)prop-2-ynethioamide (**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 ^{1}H 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 ℃. The title compound was obtained as orange needles (67 mg, 28%). ^{1}H NMR (C_6D_6, Me_4Si, 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). ^{13}C NMR (C_6D_6, Me_4Si, 75.6 MHz): δ –3.05 ($^1J_{CSi}$ = 53 Hz, *C*H$_3$Si), –2.63 ($^1J_{CSi}$ = 53 Hz, *C*H$_3$Si), 13.82 (*C*H$_3$CH$_2$N), 18.48 (q, $^1J_{CSi}$ = 58 Hz, *C*Si), 27.14 (*C*H$_3$C), 44.03 (br, *C*H$_2$N), 105.34 (Cp), 105.75 (Cp), 124.55 (q, *C*N), 136.91 (q, $^1J_{CSi}$ = 64 Hz, *C*Si), 137.88 (q, C=*C*=C). IR (KBr): 799, 1015, 1088, 1231, 1493, 1628 , 1674, 1805, 3086, 3807 cm^{-1}. Elemental analysis, calcd. for $C_{23}H_{35}NSSiZr$, C 57.92, H 7.40, N 2.94, S 6.72; found C 57.93, H 7.41, N 2.91, S 6.72.

Synthesis of 2,2-bis(η^5-cyclopentadienyl)-3-trimethylsilyl-5-dimethylamino-1-thia-2-titanacyclopenta-3,4-diene (6a). To a solution of dichlorobis(η^5-cyclopentadienyl)titanium (125 mg, 0.5 mmol) in THF (5 mL) was added dropwise *n*-butyllithium (1.6 M hexane solution, 1.0 mmol) at –78 ℃. After stirring at –78 ℃ for 1 h, *N*,*N*-dimethyl-3-(trimethylsilyl)prop-2-ynethioamide (**4a**) (92 mg, 0.5 mmol) was added, and the reaction mixture was warmed up to –10 ℃. The mixture was stirred at that temperature for 1 h. ^{1}H NMR

observation suggested the formation of the title compound in 38% yield. ^{1}H NMR (rt, C_6D_6, Me_4Si, 300 MHz): δ 0.42 (s, 9H, CH_3Si), 2.78 (br, 6H, CH_3N), 5.25 (br, 10H, Cp). ^{13}C NMR (rt, C_6D_6, Me_4Si, 125.8 MHz): δ 1.84 (*C*H_3Si), 39.14 (*C*H_3N), 105.21 (br, Cp), 119.94 (q, *C*N), 138.15 (q, C=*C*=C), 142.52 (q, $^1J_{CSi}$ = 73 Hz, *C*Si).

Synthesis of 2,2-bis(η^5-cyclopentadienyl)-3-*tert*-butyldimethylsilyl-5-diethylamino-1-thia-2-titanacyclopenta-3,4-diene (6b). The title compound was prepared similarly to **6a** using *N*,*N*-diethyl-3-(*tert*-butyldimethylsilyl)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 ℃. The title compound was obtained as red crystals (57 mg, 26%). ^{1}H NMR (rt, C_6D_6, Me_4Si, 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). ^{13}C NMR (rt, C_6D_6, Me_4Si, 125.8 MHz): δ –2.80 (*C*H_3Si), 14.00 (*C*H_3CH$_2$N), 18.42 (q, $^1J_{CSi}$ = 57.6 Hz, *C*Si), 26.86 ((*C*H_3)$_3$C), 41.69 (*C*H_2N), 103.91 (Cp), 105.38 (Cp), 119.96 (q, *C*N), 136.09 (q, C=*C*=C), 138.05 (q, $^1J_{CSi}$ = 70 Hz, *C*Si).

Hydrolysis of 5 (11). Typically, THF (5 mL) solution of complex **5a** was prepared as described above starting from dichlorobis(η^5-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 (14/86 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).

(*Z*)-**11a** (major). ^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ 0.12 (s, 9H), 3.31 (s, 3H), 3.44 (s, 3H), 5.73 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si, 125.8 MHz): δ –0.67 (*C*H_3Si), 41.89 (*C*H_3N), 42.74 (*C*H_3N), 131.94 (*C*HSi), 145.26 (*C*H-C=S), 199.48 (q, *C*=S). (*E*)-**11a** (minor): ^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ 0.14 (s, 9H), 3.35 (s, 3H), 3.52 (s, 3H), 6.80 (d, *J* = 18.3 Hz, 1H), 6.96 (d, *J* = 18.3 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$, Me_4Si): δ –1.54 (*C*H_3Si), 42.10 (*C*H_3N), 44.22 (*C*H_3N), 140.55 (*C*HSi), 144.15 (*C*H-C=S), 197.45 (*C*=S). IR (NaCl, *E*/*Z* mixture): 732.9, 983.6, 1199.6, 1350.1, 1454.2, 1593.1, 1643.2, 2954.7. High resolution mass spectrometry (E/Z mixture): [M+H]$^+$ m/z calcd. for $C_8H_{18}NSSi$ 188.0929, found 188.0924.

(*Z*)-**11b** (major). ^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ 0.12 (s, 6H), 0.90 (s, 9H), 1.22 (t, *J* = 6.9 Hz, 3H), 1.30(t, *J* = 6.9 Hz, 3H), 3.66 (q, *J* = 6.9 Hz, 2H), 3.97 (q, *J* = 6.9 Hz, 2H), 5.75 (d, *J* = 15.5 Hz, 1H), 7.00 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si, 125.8 MHz):δ –5.05 (*C*H_3Si), 11.18 (*C*H_3CH$_2$), 12.98 (*C*H_3CH$_2$), 16.66 (q, *C*Si), 26.50 ((*C*H_3)$_3$C), 45.68 (*C*H_2N), 46.88 (*C*H_2N), 128.82 (*C*HSi), 146.07 (*C*HC=S), 198.48 (*C*=S). (*E*)-**11b** (minor). ^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ 0.10 (s, 6H), 0.91 (s, 9H), 1.27 (t, *J* = 6.9 Hz, 3H), 1.30(t, *J* = 6.9 Hz, 3H), 3.65 (q, *J* = 6.9 Hz, 2H), 4.03 (q, *J* = 6.9 Hz, 2H), 6.83 (d, *J* = 18 Hz, 1H), 7.01 (d, *J* = 18 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si, 125.8 MHz): δ –6.27 (*C*H_3Si), 11.35 (*C*H_3CH$_2$), 13.61 (*C*H_3CH$_2$), 16.77 (q, *C*Si), 26.45 ((*C*H_3)$_3$C), 46.54 (*C*H_2N), 48.12 (*C*H_2N), 141.47 (*C*HSi), 141.84 (*C*HC=S), 196.14 (*C*=S). High resolution mass spectrometry (E/Z mixture): [M+H]$^+$ m/z calcd. for $C_{13}H_{28}NSSi$ 258.1712, Found, 258.1741.

X-ray diffraction analyses of the 1-thia-2-zirconacyclopenta-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[23] 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[24] crystallographic software except for refinement, which was performed using SHELXL97.[25] Crystallographic data are summarized in table S (in the supporting information). CIF data were deposited in Cambridge Structural Database (CCDC-1023317).

X-ray diffraction analyses of the 1-thia-2-titanacyclopenta-3,4-diene 6b. Crystals were obtained by recrystallization from a toluene solution. A red platelet crystal (0.15 × 0.07 × 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[23] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 4105 observed reflections and 251 variable parameters. All calculations were performed using the CrystalStructure[24] crystallographic software package except for refinement, which was performed using SHELXL97.[25] Crystallographic data are summarized in table S (in the supporting information). CIF data were deposited in Cambridge Structural Database (CCDC-1023315).

Conclusions

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

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Notes and references

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Electronic Supplementary Information (ESI) available: The NMR spectra for the products, details on X-ray diffraction analyses. See DOI: 10.1039/b000000x/

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