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Synthesis of Alkynechalcogenolato Complexes of Titanocene(IV) and Samarocene(III) and Formation of a Ti_2Ni Trinuclear Cluster $[Cp_2Ti(\mu\text{-}SC{\equiv}CPh)_2]_2Ni$

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Reactions between $(C_5H_4R')_2TiCl_2$ and 2 equiv of $LiEC{\equiv}CR$ generated a series of alkynethiolato and alkyneselenolato complexes of titanocene(IV), $(C_5H_4R')_2Ti(EC{\equiv}CR)_2$ in high yields (**1**, R = Ph, R′ = H, E = S; **2**, R = *p*-$C_6H_4CH_3$, R′ = H, E = S; **3**, R = ^tBu, R′ = H, E = S; **4**, R = Ph, R′ = Me, E = S; **5**, R = Ph, R′ = H, E = Se). Complex **1** reacted with $^1/_2$ equiv of $Ni(cod)_2$ to give a linear Ti_2Ni trimetallic complex, $[Cp_2Ti(\mu\text{-}SC{\equiv}CPh)_2]_2Ni$ (**6**), in which the Ni atom links two $Cp_2Ti(SC{\equiv}CPh)_2$ units through interactions with thiolate sulfur bridges. Treatment of $Cp^*{}_2Sm(\mu\text{-}Cl)_2Li(OEt_2)_2$ with 2 equiv of $LiSC{\equiv}CPh$ and TMEDA resulted in $[Li(tmeda)_2][Cp^*{}_2Sm(SC{\equiv}CPh)_2]$ (**7**). The structures of complexes **4**, **5**, **6**, and **7** were determined by X-ray diffraction analysis.

Introduction

Transition metal complexes of alkoxides, thiolates, selenolates, and tellurolates constitute an important domain in inorganic chemistry.[1] Although it is well recognized that redox-active chalcogenolate ligands play significant roles in modulation of electronic properties of transition metals, they are often regarded as reactively inert and have been used as innocent spectator ligands. For instance, chalcogenolates carrying bulky substituents have facilitated isolation of coordinatively unsaturated transition metal complexes.[2] Chelates containing both a chalcogen (E)-donor and a P-donor (or an N-donor) have also appeared, and the E−P (or N) hybrid ligands have contributed to expansion of the scope of chalcogenolate chemistry.[3,4] On the other hand, the most notable reaction of thiolate ligands on transition metals is perhaps C−S bond cleavage, which has frequently been observed for alkanethiolate complexes.[5]

As an extension of our study on transition metal thiolates,[6] we began to investigate the behavior of alkynethiolates and

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alkyneselenolates bound to transition metals. Having a carbon−carbon triple bond in close proximity to a chalcogen atom, alkynechalcogenolate ligands may exhibit structural diversity and unusual reactivity upon coordination to transition metals. As the first report of our study of alkynechalcogenolate complexes, we describe here the synthesis and characterization of a series of titanocene(IV) alkynethiolate and alkyneselenolate complexes as well as a samarocene(III) alkynethiolate, which are the first fully characterized transition metal alkynechalcogenolate complexes. Also reported is the reaction of $Cp_2Ti(SC{\equiv}CR)_2$ (Cp = η^5-C_5H_5) with $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) to give $[Cp_2Ti(SC{\equiv}CR)_2]_2Ni$.

While alkali metal salts of alkynechalcogenolate have been known for some time,[7] there are only a few examples of their transition metal complexes. Alkynethiolate complexes, $CpRu(SC{\equiv}CR)L_2$ and $L_2Pt(SC{\equiv}CR)_2$ were prepared from reactions of $LiSC{\equiv}CR$ (R = Ph, $SiMe_3$, $(C_5H_5)Fe(C_5H_4)$) with $CpRuClL_2$ (L = PPh_3, PMe_3) and L_2PtCl_2 (L = PPh_3, $^1/_2$ dppe), respectively, while the Fisher-type carbene complexes $M(CO)_5\{{=}CPh(OEt)\}$ (M = Cr, W) were found to react with $LiEC{\equiv}CPh$ and gaseous HCl to give $M(CO)_5\{E{=}CHC(Ph){=}C(OEt)Ph\}$ (E = S, Se).[8,9] Interestingly the treatment of $[(\mu\text{-}S_2)Fe_2(CO)_6]$ with $LiC{\equiv}CR$ and subsequent addition of alkyl halide or acyl halide gave rise to alkynethiolate complexes, $[(\mu\text{-}SC{\equiv}CR)(\mu\text{-}SR')Fe_2(CO)_6]$ (R = Ph, n-C_4H_9, n-C_5H_{11}, $SiMe_3$; R′ = Me, Et, $PhCH_2$, $CH_2C(O)CH_3$, $CH_3C(O)$, $(CH_3)_3CC(O)$).[10] However, crystal structures of these alkynechalcogenolate complexes have not been determined. The cadmium complex, $[Cd(SeC{\equiv}CPh)_2(tmeda)]_2$, is the sole example of structurally characterized alkynechalcogenolate complex, which was synthesized by the reaction between $Cd(C{\equiv}CPh)_2$ and metallic Se.[11]

Experimental Section

General. The standard Schlenk techniques were used for all manipulations. The solvents (THF, Et_2O, hexane, and toluene) were distilled from sodium/benzophenone ketyl under an Ar atmosphere. Deuterated solvents were dried over Na (C_6D_6) or CaH_2 ($CDCl_3$ and CD_3CN) and then vacuum-transferred prior to use. The 4-aryl-1,2,3-thiadiazole,[7c] Cp_2TiCl_2,[7g] and $Cp^*{}_2Sm(\mu\text{-}Cl)_2Li(OEt_2)_2$[7h] were prepared based on the literature with a slight modification. The NMR spectra were recorded on a Varian Unity Inova 500 spectrometer operating at 500 MHz for ^1H, at 126 MHz for ^{13}C. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS by using the residual protons or carbons of deuterated solvents (^1H: C_6D_6, δ 7.2 ppm; CD_3CN, δ 1.97 ppm. ^{13}C: C_6D_6, δ 128.5 ppm). Some $^{13}C\{^1H\}$ NMR spectra were measured under the presence of $Cr(acac)_3$ as a relaxation reagent to detect the alkynyl ^{13}C resonances. IR and UV−vis spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer and a JASCO V-500 spectrometer, respectively. Elemental analyses were performed on a LECO CHNS-932 microanalyzer.

Preparation of $LiSC{\equiv}C^tBu$. A hexane solution of ^nBuLi (1.6 M, 6.2 mL, 9.92 mmol) was added to an Et_2O (20 mL) solution of $^tBuC{\equiv}CH$ (1.25 mL, 10.2 mmol) at 0 °C, and the reaction mixture was stirred for 1 h at room temperature, which was then added dropwise to a cold Et_2O (20 mL, −80 °C) suspension of S_8 (320 mg, 1.25 mmol) by syringe. The reaction mixture was warmed to room temperature and was stirred for 4 h. The volatiles were removed under reduced pressure. The white powder was dissolved into THF (20 mL) and was stored in Schlenk flask as a ca. 0.5 M solution of $LiSC{\equiv}C^tBu$. ^1H NMR (CD_3CN, 500 MHz, 20 °C): δ 1.10 (s, 9H, $C(CH_3)_3$). IR (KBr, Nujol mull (cm^{-1})): 2132 (s, $\nu(C{\equiv}C)$).

Preparation of $LiSC{\equiv}CR$ (R = Ph, p-$C_6H_4CH_3$). A THF solution of $LiN(SiMe_3)_2$ (1.0 M, 2.1 mL, 2.1 mmol) was added to a cold THF (10 mL) solution of 4-phenyl-1,2,3-thiadiazole (357 mg, 2.2 mmol) at 0 °C and were stirred for 1.5 h. The volatiles were removed under reduced pressure. The residue was washed with hexane (10 mL) and was dried in vacuo to give $LiSC{\equiv}CPh$ as a white powder. The analogous treatment of 4-p-tolyl-1,2,3-thiadiazole with 1 equiv of $LiN(SiMe_3)_2$, gave $LiSC{\equiv}C(p\text{-}C_6H_4CH_3)$ as a white powder.

Synthesis of $(C_5H_4R')_2Ti(SC{\equiv}CR)_2$ (1, R = Ph, R′ = H; 2, R = p-$C_6H_4CH_3$, R′ = H; 3, R = ^{t}Bu, R′ = H; 4, R = Ph, R′ = Me). A series of alkynethiolate complexes of titanocene were synthesized in a similar manner, and only the preparation of **1** is described here. A THF (40 mL) solution of $LiSC{\equiv}CPh$ (2.1 mmol, prepared as described above) was added to a THF (20 mL) solution of Cp_2TiCl_2 (249 mg, 1.0 mmol) at 0 °C. The dark green reaction mixture was stirred for 4 h at room temperature before the solvent was removed in vacuo. The residue was extracted with toluene (70 mL) and centrifuged to remove LiCl, and the toluene was evaporated to leave a dark green solid. This crude product was recrystallized from THF/hexane to give **1** as dark green crystals in 93% yield.

1, dark green crystals, yield 93%. ^1H NMR (C_6D_6, 500 MHz, 20 °C): δ 5.89 (s, 10H, C_5H_5), 6.98−7.04 (m, 6H, o,p-C_6H_5), 7.53 (m, 4H, m-C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 20 °C, with $Cr(acac)_3$): δ 94.2 (SC_2Ph), 108.3 (SC_2Ph), 115.5 (C_5H_5), 126.9 (C_6H_5), 127.7 (C_6H_5), 129.0 (C_6H_5), 131.8 (C_6H_5). IR (Nujol mull, KBr (cm^{-1})): 2144 (m, $\nu(C{\equiv}C)$). UV−vis (THF, λ_{max} (nm), ϵ_{max} (M^{-1} cm^{-1})): 595 (3.9×10^3), 450 (2.6×10^3), 398 (2.7×10^3), 289 (2.1×10^4). Anal. Calcd for $C_{26}H_{20}S_2Ti$: C, 70.26; H, 4.54; S, 14.43. Found: C, 70.22; H, 4.62; S, 13.94.

2, dark green crystals, yield 83%. ^1H NMR (C_6D_6, 500 MHz, 20 °C): δ 2.06 (s, 6H, $C_6H_4CH_3$), 5.91 (s, 10H, C_5H_5), 6.87 (d, 4H, o-$C_6H_4CH_3$, J_{om} = 7.7 Hz), 7.50 (d, 4H, m-$C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 20 °C, with $Cr(acac)_3$): δ 21.8 ($C_6H_4CH_3$), 93.5 ($SC_2C_6H_4CH_3$), 108.8 ($SC_2C_6H_4CH_3$), 115.5 (C_5H_5), 124.0 ($C_6H_4CH_3$), 129.8 ($C_6H_4CH_3$), 131.8 ($C_6H_4CH_3$), 137.5 ($C_6H_4CH_3$). IR (Nujol mull, KBr (cm^{-1})): 2143 (m, $\nu(C{\equiv}C)$). UV−vis (THF, λ_{max} (nm), ϵ_{max} (M^{-1} cm^{-1})): 599 (8.2×10^3), 457 (5.6×10^3), 391 (5.8×10^3), 287 (4.5×10^4). Anal. Calcd for $C_{28}H_{24}S_2Ti$: C, 71.17; H, 5.12; S, 13.57. Found: C, 70.81; H, 5.42; S, 13.47.

3, red-purple plates, yield 97%. ^1H NMR (C_6D_6, 500 MHz, 20 °C): δ 1.37(s, 18H, $C(CH_3)_3$), 5.88 (s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 20 °C): δ 30.5 ($C(CH_3)_3$), 32.4 ($C(CH_3)_3$), 82.0 ($SC{\equiv}C$), 115.2 (C_5H_5), 117.7 ($SC{\equiv}C$). IR (Nujol mull, KBr (cm^{-1})): 2145 (w,

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ν(C≡C)). UV−vis (THF, λ_{max} (nm), ϵ_{max} (M^{-1} cm^{-1})): 574 (6.1 × 10^3), 415 (4.1 × 10^3), 292 (1.8 × 10^4). Anal. Calcd for $C_{22}H_{28}S_2Ti$: C, 65.33; H, 6.98; S, 15.86;. Found: C, 63.53; H, 6.96; S, 15.42.

4, dark green crystals, yield 75%. ^{1}H NMR (C_6D_6, 500 MHz, 20 °C): δ 1.91 (s, 6H, $C_5H_4CH_3$), 5.82 (t, 4H, $C_5H_4CH_3$, J = 2.58 Hz), 6.00 (t, 4H, $C_5H_4CH_3$), 6.97−7.03 (m, 6H, *o,p*-C_6H_5), 7.53 (m, 4H, *m*-C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 20 °C, Cr(acac)$_3$): δ 16.3 ($C_5H_4CH_3$), 94.4 (SC_2Ph), 107.0 (SC_2Ph), 116.2 ($C_5H_4CH_3$), 116.5 ($C_5H_4CH_3$), 117.3 ($C_5H_4CH_3$), 127.0 (C_6H_5), 127.6 (C_6H_5), 129.0 (C_6H_5), 131.9 (C_6H_5). IR (Nujol mull, KBr (cm^{-1})): 2141 (m, ν(C≡C)). UV−vis (THF, λ_{max} (nm), ϵ_{max} (M^{-1} cm^{-1})): 589 (4.4 × 10^3), 450 (3.2 × 10^3), 401 (3.6 × 10^3), 288 (2.7 × 10^4). Anal. Calcd for $C_{28}H_{24}S_2Ti$: C, 71.17; H, 5.12; S, 13.57. Found: C, 70.87; H, 5.04; S, 13.46. Crystals suitable for X-ray analysis of **4** were grown from toluene/hexane at ambient temperature.

Preparation of LiSeC≡CPh. A hexane solution of ^{n}BuLi (1.6 M, 4 mL, 6.4 mmol) was added to a THF (10 mL) solution of PhC≡CH (0.75 mL, 6.8 mmol) at 0 °C and was stirred for 1 h at room temperature. This resultant THF solution of LiC≡CPh was added dropwise to a THF (30 mL) suspension of gray Se (514 mg, 6.5 mmol) at −80 °C, and the resultant mixture was stirred for 4 h at room temperature. The solvents were evaporated to dryness, and the residue was washed with hexane (10 mL) to give a white powder. The crude product was recrystallized from toluene to give PhC≡CSeLi(thf)$_x$ in 95% yield as white micro crystals, where x was estimated to be 1.5 according to the ^{1}H NMR spectrum in CD_3CN.

Synthesis of $Cp_2Ti(SeC{\equiv}CPh)_2$ (5). This compound was synthesized in a manner analogous to that described for the corresponding thiolate species, using 249 mg (1.0 mmol) of Cp_2TiCl_2 and 2.05 mmol of LiSeC≡CPh. The reaction mixture was stirred for 3 h, and a standard work up gave **5** as dark green microcrystals in 85% yield. ^{1}H NMR (C_6D_6, 500 MHz, 20 °C): δ 5.87 (s, 10H, C_5H_5), 6.98−7.01 (m, 6H, *o,p*-C_6H_5), 7.56 (m, 4H, *m*-C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 20 °C, with Cr(acac)$_3$): δ 82.9 (SC_2Ph), 113.5 (SC_2Ph), 114.0 (C_5H_5), 126.4 (C_6H_5), 128.0 (C_6H_5), 129.0 (C_6H_5), 132.2 (C_6H_5). IR (KBr pellet (cm^{-1})): 2133 (m, ν(C≡C)). UV−vis (THF, λ_{max} (nm), ϵ_{max} (M^{-1} cm^{-1})): 631 (8.2 × 10^3), 453 (5.4 × 10^3), 299 (4.8 × 10^4). Anal. Calcd for $C_{26}H_{20}Se_2Ti$: C, 58.02; H, 3.75. Found: C, 57.97; H, 3.72. Crystals suitable for X-ray analysis of **5** were grown from toluene/hexane at ambient temperature.

Synthesis of $[Cp_2Ti(\mu\text{-}SC{\equiv}CPh)_2]_2Ni$ (6). A toluene (30 mL) solution of Ni(cod)$_2$ (65 mg, 0.24 mmol) was added to a toluene (30 mL) solution of **1** (210 mg, 0.47 mmol). The dark green solution immediately became purple. After it had been stirred for 2 days at room temperature, the reaction mixture was centrifuged to remove insoluble material. Concentration and cooling of the solution afforded $[Cp_2Ti(\mu\text{-}SC{\equiv}CPh)_2]_2Ni$ (**6**) in 33% yield as black purple microcrystals.^{1}H NMR (C_6D_6, 500 MHz, 20 °C): δ 5.75 (s, 20H, C_5H_5), 6.96−7.01 (m, 12H, *o,p*-C_6H_5), 7.64 (m, 8H, *m*-C_6H_5). IR (KBr pellet (cm^{-1})): 2150 (m, n(C≡C)). UV−vis (toluene, λ_{max} (nm), ϵ_{max} (M^{-1} cm^{-1})): 730 (3.0 × 10^3), 530 (9.4 × 10^3), 391 (1.6 × 10^4), 348 (2.0 × 10^4). Anal. Calcd for $C_{59}H_{49}S_4Ti_2Ni$ (as **6**·toluene): C, 68.09; H, 4.75; S, 12.32. Found: C, 68.17; H, 4.57; S, 12.61. Crystals suitable for X-ray analysis of **6** were grown from a toluene/hexane solution at room temperature.

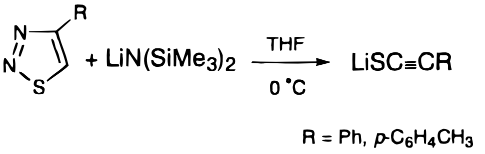
Synthesis of $[Li(tmeda)_2][Cp^*{}_2Sm(SC{\equiv}CPh)_2]$ (7). To a THF (20 mL) solution of $Cp^*{}_2Sm(\mu\text{-}Cl)_2Li(OEt_2)_2$ (406 mg, 0.63 mmol), a THF (20 mL) solution of LiSC≡CPh (1.36 mmol) was added. The yellow orange reaction mixture was stirred for 4 h at room temperature and the solvent was removed in vacuo. The residue was extracted with Et_2O (40 mL). After removal of LiCl by centrifugation, TMEDA (1 mL) was added to the supernatant liquid to form the microcrystals. The volatiles were removed under reduced pressure. The resulted residue was recrystallized from toluene (5 mL) to give the pure materials of **7** as orange crystals in 42% yield. ^{1}H NMR (C_6D_6, 500 MHz, 20 °C): δ 1.67 (s, 30H, $C_5(CH_3)_5$, $\nu_{1/2}$ = 13.4 Hz), 2.01 (s, 8H, $(CH_3)_2NCH_2$, $\nu_{1/2}$ = 5.0 Hz), 2.04 (s, 24H, $(CH_3)_2NCH_2$, $\nu_{1/2}$ = 9.4 Hz), 6.56 (brs, 4H, C_6H_5, $\nu_{1/2}$ = 64.2 Hz), 6.76 (brs, 6H, C_6H_5, $\nu_{1/2}$ = 25.5 Hz). IR (KBr, Nujol mull (cm^{-1})): 2133 (s, ν(C≡C)). UV−vis (THF, λ_{max} (nm), ϵ_{max} (M^{-1} cm^{-1})): 357 (2.5 × 10^4). Anal. Calcd for $C_{48}H_{72}N_4S_2LiSm$: C, 62.22; H, 7.83; N, 6.05; S, 6.92. Found: C, 62.02; H, 8.19; N, 5.89; S, 6.91. Crystals suitable for X-ray analysis were grown from toluene at 0 °C.

X-ray Crystallographic Study. X-ray-quality crystals of **4**, **5**, **6**, and **7** were obtained as described above. The crystals were manipulated and mounted in capillaries in Schlenk tubes. Diffraction data were collected at room temperature on a Rigaku AFC 7R diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The crystal system and cell parameters were initially determined from 20 machine-centered reflections (6° < 2θ < 13°) elected by an automated peak search routine. Refined cell dimensions and their standard deviations were obtained by least-squares refinements of 25 higher-angle reflections (20° < 2θ < 25°). Three standard reflections were recorded every 150 reflections, which showed no significant decay over the duration of the data collections. The diffraction data were corrected for Lorentz and polarization effects, and absorption corrections based on y-scans were applied. The data were processed using the TEXSAN package. The metal atom positions of **4**, **5**, and **6** along with some heavy atom positions were located unambiguously by direct methods with a SHELLX-86 program, while the structure of **7** was solved by the Patterson method with a DIRDIF92 PATTY program. In each case, the remaining non-hydrogen atoms were found in subsequent difference Fourier maps, and the structures were refined by full-matrix least-squares based on the reflections with $I > 3\sigma(I)$. All metal and chalcogene atoms were refined using anisotropic thermal parameters. The number of anisotoropically refined carbon atoms was set so as to maintain a reasonable data/variable ratio for each structure. Thus, phenyl carbons of **4** and **7**, TMEDA carbons of **7**, and solvent molecules of **6**·2toluene were refined isotropically. All hydrogen atoms were put at idealized positions. Crystallographic data and final R indices are summarized in Table 1, and complete crystallographic details are given in the Supporting Information.

Results and Discussion

There are two different synthetic routes to lithium alkynethiolates. One is the reaction of a preformed lithium alkynide with elemental sulfur in an appropriate polar solvent (eq 1). The other makes use of an N_2 elimination reaction of 1,2,3-thiadiazoles with $LiN(SiMe_3)_2$ in THF (eq 2).[7] For the synthesis of lithium alkyneselenolates, eq 1 can be modified by replacing S_8 with gray selenium (eq 3).

$$LiC{\equiv}C^tBu + 1/8\,S_8 \xrightarrow[-80\ ^\circ C\ -\ r.t.]{Et_2O} LiSC{\equiv}C^tBu \qquad (1)$$



(2)

$$LiC{\equiv}CPh + Se \xrightarrow[-80\ ^\circ C\ -\ r.t.]{THF} LiSeC{\equiv}CPh \qquad (3)$$

Weigand and Raubenheimer prepared LiEC≡CR (E = S, Se; R = Ph, $SiMe_3$, etc.) using the method analogous to eq 1 for the reactions with $CpRuClL_2$ (L = PPh_3, PMe_3), L_2PtCl_2 (L = PPh_3, $^1/_2$dppe), and carbene complexes of chromium and tungsten.[8,9] However the lithium alkynechalcogenolates obtained from one-pot reactions of equimolar amounts of alkyne, ^{n}BuLi, and $^1/_8S_8$ or Se was used for the subsequent reactions without isolation of LiEC≡CR. Therefore, we reexamined preparation of lithium alkynechalcogenolates, to find that LiSC≡C^{t}Bu and LiSeC≡CPh were readily obtained as white solids from the reactions of the corresponding lithium alkynides with S_8 and gray selenium, respectively. However, in the case of the treatment of LiC≡CPh with S_8, the product was strongly reddish orange colored. Although recrystallization from toluene/hexane

Table 1. Crystal Data for **4**, **5**, **6**·2toluene, and **7**

	4	**5**	**6**·2toluene	**7**
empirical formula	$C_{28}H_{24}S_2Ti$	$C_{26}H_{20}Se_2Ti$	$C_{66}H_{56}S_4Ti_2Ni$	$C_{48}H_{72}N_4S_2LiSm$
fw	472.52	538.26	1131.91	926.58
space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1$ (#4)
a, Å	12.474(2)	10.489(6)	13.203(2)	18.077(4)
b, Å	12.153(3)	12.595(7)	16.596(9)	13.904(4)
c, Å	16.072(3)	9.901(8)	25.794(4)	20.516(5)
α, deg		106.53(5)		
β, deg	102.67(1)	112.26(5)	93.19(1)	96.98(2)
γ, deg		99.67(5)		
V, Å^3	2377.1(8)	1103(1)	5643(3)	5118(2)
Z	4	2	4	4
d_{calcd}, g/cm^3	1.320	1.620	1.332	1.202
μ, cm^{-1}	5.49	36.98	7.95	12.64
$2\theta_{max}$, deg	50.0	50.0	45.0	55.0
transm factors	0.90−1.00	0.51−1.00	0.87−1.00	0.70−1.00
no. of indep rflns	4402	4117	7708	12249
no. obsd rflns	1893	2151	4478	6798
no. of refined params	220	262	588	759
R^a	0.053	0.042	0.043	0.042
R$_W$^{b}	0.054	0.042	0.047	0.042
GOF^c	1.91	1.54	2.20	1.80
max. and min. residual	0.30	0.57	0.41	0.74
peak in final diff. map, e$^-$/Å^3	−0.24	−0.36	−0.25	−0.40

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_W = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(M - N)]^{1/2}$, where M = number of reflections and N = number of parameters.

resulted in gradual decoloration, we could not isolate LiSC≡CPh of satisfactory quality. On the other hand, the method based on eq 2 produced LiSC≡CPh successfully as white powders after standard workup. We also prepared LiSC≡C(p-$C_6H_4CH_3$) by a similar procedure. Thus we were able to isolate a series of lithium salts of alkynechalcogenolates in a preparative scale by choosing proper synthetic routes, and they were used for the subsequent syntheses of transition metal complexes reported in this paper.

We have carried out the reactions of $(C_5H_5)_2TiCl_2$ and $(C_5H_4Me)_2TiCl_2$ with 2 equiv of LiSC≡CPh, LiSC≡C(p-$C_6H_4CH_3$), and LiSC≡C^{t}Bu in THF. In either case, the reaction proceeded smoothly with the color change from red to dark green for **1**, **2** and **4**, or to red purple for **3**, and the standard work up afforded bis-alkynethiolate complexes as dark green crystals for **1**, **2**, and **4**, and as red purple plates for **3**.

$$(C_5H_4R')_2TiCl_2 + 2LiSC{\equiv}CR \xrightarrow{THF} (C_5H_4R')_2Ti(SC{\equiv}CR)_2 \quad (4)$$

1, R = Ph, R' = H, 93 %, dark green
2, R = p-$C_6H_4CH_3$, R' = H , 83 %, dark green
3, R = ^{t}Bu, R' = H, 97 %, red purple
4, R = Ph, R' = Me, 75 %, dark green

It has been known that treatment of LiSC≡CR with electrophiles E^+ tends to produce an appreciable amounts of high-boiling residues, which may in part result from further reactions of preformed thioketenes, RC(E)=C=S.[7a] Although the acidic Ti(IV) center could act as an electrophile, the reactions of LiSC≡CR with $(C_5H_4R')_2TiCl_2$ at room temperature generated a series of bis-alkynethiolate complexes in high yields, and the side reactions due to the formation of thioketenes were not observed.

The analogous reaction between Cp_2TiCl_2 and 2 equiv of LiSeC≡CPh also went smoothly, generating the bis-alkyneselenolato complex $Cp_2Ti(SeC{\equiv}CPh)_2$ (**5**) in 84% yield. The IR spectra of **1**, **2**, **3**, and **4** are featured by a common sharp band arising from the C≡C stretching vibration, which appears at 2144, 2143, 2145 and 2141 cm^{-1}, respectively. These bands are similar to those of the known η^1-(S) alkynethiolate complexes, $CpRu(SC{\equiv}CR)L_2$ and $L_2Pt(SC{\equiv}CR)_2$ (R = Ph, $SiMe_3$, $(C_5H_5)Fe(C_5H_4)$; L = PPh_3, PMe_3, $^1/_2$dppe) (2127−2142 cm^{-1}).[8]

$$Cp_2TiCl_2 + 2LiSeC{\equiv}CPh \xrightarrow{THF} Cp_2Ti(SeC{\equiv}CPh)_2 \quad (5)$$

5
84 %, dark green

The alkyneselenolate complex **5** also exhibits a sharp C≡C stretching band at 2133 cm^{-1} in the IR spectrum, which is comparable to that observed for $[Cd(SeC{\equiv}CPh)_2(tmeda)]_2$ (2130 cm^{-1}).[11] In the ^1H NMR spectra of **1**−**5**, the relative intensity of the proton signals of cyclopentadienyl and alkynethiolate or alkyneselenolate is consistent with their formulation. In the $^{13}C\{^1H\}$ NMR spectra of **1**−**4**, two alkynyl carbon resonances appeared at δ 94.2 and 108.3 for **1**, δ 93.5 and 108.8 for **2**, δ 82.0 and 117.7 for **3**, and δ 94.4 and 107.0 for **4**. They are shifted to lower fields compared with the corresponding ^{13}C resonances of RC≡CH (R = Ph, δ 77.1 and 83.6; R = p-$C_6H_4CH_3$, δ 76.4 and 83.8; R = ^{t}Bu, δ 66.4 and 93.1). The $^{13}C\{^1H\}$ NMR spectrum of **5** exhibits the alkynyl carbon resonances at δ 82.9 and 113.5, and the difference of the chemical shifts between the two alkynyl carbons is larger than those of the alkynethiolate complexes **1**−**4**.

The crystal structures of **4** and **5** were determined by X-ray analysis, and their molecular views are shown in Figures 1 and 2, respectively. The selected structural parameters of **4** and **5** are summarized in Table 2. The two structures are very much alike, and alkynyl groups of both thiolato and selenolato ligands are syn oriented in the crystals. The two phenyl rings in each structure are situated perpendicular to each other with the dihedral angles 118.8° for **4** and 104.4° for **5**. The intramolecular p−p stacking of these phenyl groups did not occur. The Ti−S bond distances of 2.448(2) and 2.427(2) Å) for **4** are close to those of $Cp_2Ti(SPh)_2$ (2.4395(8) and 2.424(8) Å), while the S−Ti−S angle of 95.79(8) ° is slightly smaller than that of Cp$_2$-

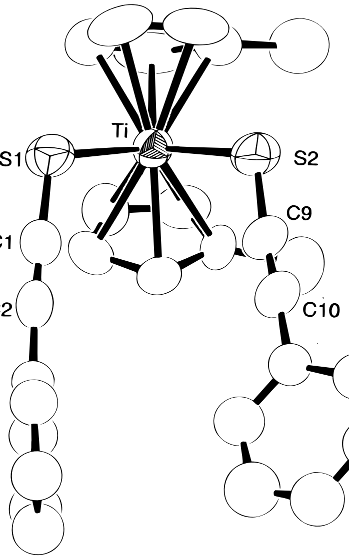


Figure 1. Structure of $MeCp_2Ti(SC{\equiv}CPh)_2$ (**4**).

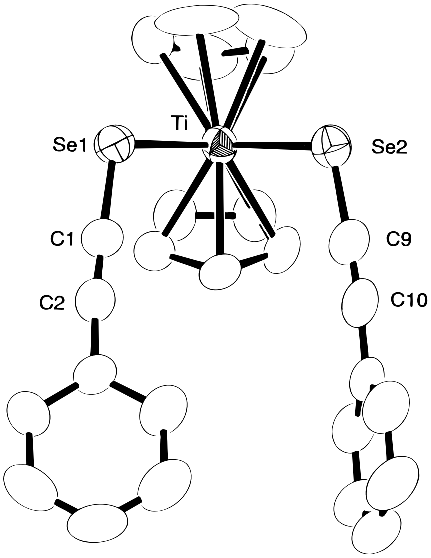


Figure 2. Structure of $Cp_2Ti(SeC{\equiv}CPh)_2$ (**5**).

Table 2. Selected Structural Parameters of Complexes **4** and **5**

4		**5**	
Bond Distances (Å)			
Ti−S1	2.448(2)	Ti−Se1	2.588(2)
Ti−S2	2.427(2)	Ti−Se2	2.563(2)
S1−C1	1.684(8)	Se1−C1	1.838(8)
S2−C9	1.687(7)	Se2−C9	1.857(9)
C1−C2	1.188(8)	C1−C2	1.195(10)
C9−C10	1.178(8)	C9−C10	1.17(1)
Bond Angles (deg)			
S1−Ti−S2	95.79(8)	Se1−Ti−Se2	96.71(5)
Ti−S1−C1	109.0(2)	Ti−Se1−C1	107.2(2)
Ti−S2−C9	112.5(2)	Ti−Se2−C9	107.8(3)
S1−C1−C2	179.4(7)	Se1−C1−C2	176.7(8)
S2−C9−C10	174.8(7)	Se2−C9−C10	178.0(8)
Dihedral Angles (deg)			
Ph(ring)−Ph(ring)	118.8		104.4

$Ti(SPh)_2$ (99.3(1)°). It appears that alkynethiolate is sterically less demanding than benzenethiolate.[12] The Ti−Se bond distances (2.588(2) and 2.563(2) Å) of **5** resemble those of $(MeCp_2Ti)_2Se_4$ (2.563(1) and 2.542(1) Å).[13] The geometric parameters of the SC≡CPh and SeC≡CPh groups are normal. The C≡C distances for **4** and **5** fall in the normal range of carbon−carbon triple bonds and the both S−C−C and Se−C−C bonds are practically linear. Therefore, the contribution from the thio- or selenoketenyl resonance structures is negligible. The averaged Ti−S bond length is 0.14 Å shorter than the Ti−Se bond, which reflects the difference in ionic radii of S^{2-} (1.84 Å) and Se^{2-} (1.98 Å).[14] The Ti−S−C angles of 109.0(2) and 112.5(2)° are understandably greater than the Ti−Se−C angles of 107.2(2) and 107.8(3)°.

Bis-alkynide complexes of late transition metals occasionally undergo C−C bond-forming reactions.[15] On the other hand, the titanocene alkynides, $Cp'_2Ti(C{\equiv}CR)_2$ were reported to react with copper(I) salts to give $Cp'_2Ti(C{\equiv}CR)_2CuX$ (Cp′ = cyclopentadienyl derivatives; R = Ph, $SiMe_3$ etc., X = halogens, SPh, etc.).[16] To examine reactivity of the Ti-bound alkynethiolates, we carried out the reaction of **1** with $^1/_2$ equiv of $Ni(cod)_2$ in toluene. The cod ligands were liberated during this reaction, and a Ti_2Ni cluster $[Cp_2Ti(\mu\text{-}SC{\equiv}CPh)_2]_2Ni$ (**6**) was isolated as dark purple crystals in 33% yield.

$$2\ Cp_2Ti(SC{\equiv}CPh)_2 + Ni(cod)_2 \xrightarrow[\text{toluene}]{} \underset{\substack{\mathbf{6}\\ \text{33 \%, dark purple}}}{[Cp_2Ti(\mu\text{-}SC{\equiv}CPh)_2]_2Ni} \qquad (6)$$

The ^1H NMR spectrum of **6** shows resonances attributable to cyclopentadienyl and phenylethynethiolato fragments in accord with the formulation. The ν(C≡C) band appears at 2150 cm^{-1} in the IR spectrum, which is slightly higher than those of **1**−**4**. The observed frequency is rather close to that found for $[(\mu_2\text{-}SC{\equiv}CR)(\mu_2\text{-}SR')Fe_2(CO)_6]$ (R = Ph, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, $SiMe_3$; R′ = Me, Et, $PhCH_2$, $CH_2C(O)CH_3$, $CH_3C(O)$, $(CH_3)_3CC(O)$) (2164−2201 cm^{-1}),[10] in which the sulfur atom of alkynethiolate bridges two iron centers. In light of the high C≡C stretching frequency, alkynethiolates of **6** are anticipated to bridge the metal atoms at sulfur. This geometrical feature was confirmed by X-ray analysis, and the X-ray-derived molecular structure is shown in Figure 3. Table 3 lists the selected bond distances and angles.

As shown in Figure 3, the cluster complex **6** consists of a linear Ti−Ni−Ti spine, and four alkynethiolate ligands bridge the metal atoms. Alternatively, the cluster can be viewed as a

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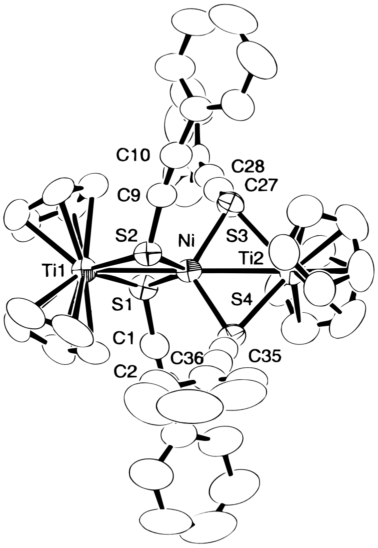


Figure 3. Structure of $[Cp_2Ti(\mu\text{-}SC{\equiv}CPh)_2]_2Ni$ (**6**).

Table 3. Selected Structural Parametrs of **6**

	Bond Distances (Å)		
Ni−Ti1	2.782(1)	Ni−Ti2	2.795(1)
Ti1−S1	2.510(2)	Ti2−S3	2.521(2)
Ti1−S2	2.507(2)	Ti2−S4	2.508(2)
Ni−S1	2.225(2)	Ni−S3	2.209(2)
Ni−S2	2.227 (2)	Ni−S4	2.210(2)
S1−C1	1.688(7)	S3−C27	1.683(6)
S2−C9	1.691(7)	S4−C35	1.689(6)
C1−C2	1.186(8)	C27−C28	1.183(7)
C9−C10	1.193(8)	C35−C36	1.190(7)
	Bond Angles (deg)		
Ti1−Ni−Ti2	179.71(5)		
S1−Ti1−S2	98.86(6)	S3−Ti2−S4	97.64(6)
S1−Ni−S2	117.75(6)	S3−Ni−S4	117.90(6)
Ti1−S1−Ni	71.69(5)	Ti2−S3−Ni	72.11(5)
Ti1−S2−Ni	71.69(5)	Ti2−S4−Ni	72.35(5).
Ti1−S1−C1	116.7(2)	Ti2−S3−C27	117.6(2)
Ti1−S2−C9	116.8(2)	Ti2−S4−C35	116.3(2)
Ni−S1−C1	105.7(2)	Ni−S3−C27	108.5(2)
Ni−S2−C9	104.6(2)	Ni−S4−C35	107.8(2)
S1−C1−C2	174.3(6)	S3−C27−C28	175.2(6)
S2−C9−C10	173.5(6)	S4−C35−C36	174.8(6)

single Ni atom being sandwiched by the two titanocene bis-alkynethiolate complexes **1**. The core structure of **6** resembles that of $[Cp_2Ti(\mu\text{-}SMe)_2]_2Ni$.[17] In each titanocene fragment, two alkynyl groups assume an anti conformation presumably to avoid steric repulsion. Combining two such fragments, four alkynyl groups around the Ti−Ni−Ti bond are staggered. In the formation of **6**, the Ni(0) oxidation state appears to be retained, and the coordination geometry at Ni is approximately tetrahedral. This zerovalent Ni center favors interactions with the thiolate sulfurs, and coordination of the alkyne portion to Ni does not take place. The relatively short Ni−Ti distances (av 2.79 Å), coupled with the acute Ni−S−Ti angles (av 72.0°), suggest a dative bond between d^{10} Ni and d^0 Ti.[18]

We extended our study of alkynechalcogenolate complexes of titanocene(IV) to lanthanides. The reaction of $Cp^*_2Sm(\mu\text{-}Cl)_2Li(OEt_2)_2$ with 2 equiv of $LiSC{\equiv}CPh$ in THF at room-temperature resulted in the formation of a yellow orange solution. After removal of THF, the residue was extracted with Et_2O. Attempts to crystallize a Sm(III)-alkynethiolate complex from this Et_2O solution was unsuccessful. However, addition of TMEDA to the supernatant liquid produced a yellow microcrystalline solid. Recrystallization of the solid from toluene gave $[Li(tmeda)_2][Cp^*_2Sm(SC{\equiv}CPh)_2]$ (**7**) as orange crystals in 42% yield. The ^1H NMR signals of Cp* and phenyl protons appeared as broad peaks due to paramagnetism associated with f^5 Sm(III). The $\nu(C{\equiv}C)$ band, observed at 2133 cm^{-1} in the IR spectrum, is shifted to lower compared with those of **1**−**4**.

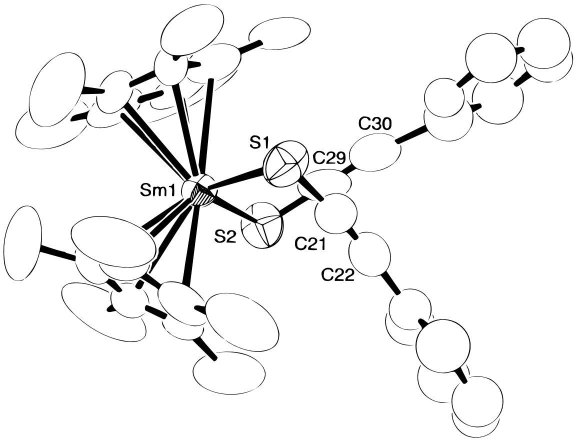
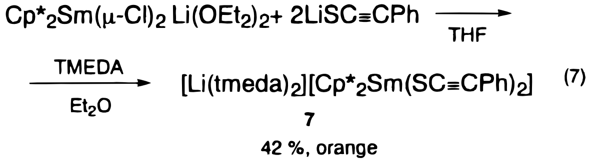


Figure 4. Structure of the anion part of$[Li(tmeda)_2][Cp^*_2Sm(SC{\equiv}CPh)_2]$ (**7**) (molecule 1).

Table 4. Selected Structural Parameters of **7**

molecule **1**		molecule **2**	
	Bond Distances (Å)		
Sm1−S1	2.784(4)	Sm2−S3	2.774 (4)
Sm1−S2	2.803(3)	Sm2−S4	2.813(4)
S1−C21	1.61(1)	S3−C57	1.63(1)
S2−C29	1.53(1)	S4−C65	1.61(1)
C21−C22	1.20(1)	C57−C58	1.18(1)
C29−C30	1.24(1)	C65−C66	1.21(1)
	Bond Angles (deg)		
S1−Sm1−S2	114.25(7)	S3−Sm2−S4	108.01(7)
Sm1−S1−C21	87.3(4)	Sm2−S3−C57	94.0(4)
Sm1−S2−C29	97.7(4)	Sm2−S4−C65	97.6(4)
S1−C21−C22	174.7(10)	S3−C57−C58	175.9(10)
S2−C29−C30	179.3(10)	S4−C65−C66	177(1)



$$\mathrm{Cp^*_2Sm(\mu\text{-}Cl)_2\,Li(OEt_2)_2 + 2LiSC{\equiv}CPh \xrightarrow[THF]{} \xrightarrow[Et_2O]{TMEDA} [Li(tmeda)_2][Cp^*_2Sm(SC{\equiv}CPh)_2]} \quad (7)$$

7

42 %, orange

According to the X-ray analysis, the crystal of **7** consists of discrete $[Li(tmeda)_2]^+$ cations and $[Cp^*_2Sm(SC{\equiv}CPh)_2]^-$ anions, and no interactions between Li and $SC{\equiv}CPh$ can be seen. Being crystallized in noncentrosymmetric $P2_1$ space group, an asymmetric unit contains two crystallographically independent cations and two anions. Although the geometric parameters are somewhat different between the two complex anions, their main structural features are practically the same. Therefore, Figure 4 shows the structure for only one of them, while the metric parameters of the two complex anions are compared in Table 4.

The two alkynyl groups in the structure of **7** exhibit an anti orientation, which contrasts to a syn orientation of **4** and **5**. We do not find particular electronic reasons for the different orientations, and the choice of the two orientations is probably determined by a crystal packing effect. The mean Sm−S

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distance of 2.79 Å is close to the longest end of the known Sm(III)−S single bonds (2.65−2.83 Å).[19] Interestingly, the Sm−S−C angles vary substantially (87.3(4)°, 97.7(4)° for molecule 1 and 94.0(4), 97.6(4)° for molecule 2), and they are all smaller than the Ti−S−C angles of **4** (109.0(2) and 112.5(2)°). The long Sm−S distances indicate an ionic character of the bond, which may lead to the flexible Ti−S−C angles.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **4**, **5**, **6**, and **7** are available on the Internet only. Access information is given on any current masthead page.

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