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New sulfur and selenium derivatives of (η^5-cyclopentadienyl) (η^7-cycloheptatrienyl) titanium, and their application in the syntheses of heterobimetallic compounds *

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Abstract

Reactions of (η^5-C_5H_4Li)(η^7-C_7H_6Li)Ti · 2TMEDA with two equivalents of dimethyl disulfide have produced (η^5-$C_5H_4SCH_3$)(η^7-$C_7H_6SCH_3$)Ti (**1**) in 18% yield. Similar reactions of (η^5-C_5H_4Li)(η^7-C_7H_6Li)Ti · 2TMEDA with either diphenyl disulfide or diphenyl diselenide likewise afford the respective bis(phenylthio) and bis(phenylseleno) analogs **4** and **5**, respectively. The corresponding mono-substituted compounds [(η^5-C_5H_5)(η^7-C_7H_6ER) (E = S, R = CH_3, **3**), (E = S, R = C_6H_5, **6**) and (E = Se, R = C_6H_5, **7**)] can be prepared in low yield from reactions of (η^5-C_5H_5)(η^7-C_7H_6Li)Ti with the appropriate organic dichalcogenide. All these new sulfur and selenium derivatives of (η^5-C_5H_5)(η^7-C_7H_7)Ti have been characterized by ^{1}H NMR and mass spectrometry and by elemental analyses. The crystal and molecular structure of **4** have been determined. The C(5) and C(7) rings are essentially coplanar, and the two phenylthio substituents are in a *trans*-orientation. Reactions of **1** with (η^4-norbornadiene)tetracarbonyl-molybdenum and -chromium produce the corresponding heterobimetallic complexes [(η^5-$C_5H_4SCH_3$)(η^7-$C_7H_6SCH_3$)Ti]M(CO)$_4$ (**8**, M = Mo; **9**, M = Cr), respectively. Reaction of **1** with ($C_6H_5CN)_2PtCl_2$ generates a heterobimetallic complex formulated as [(η^5-$C_5H_4SCH_3$)(η^7-$C_7H_6SCH_3$)Ti]PtCl$_2$ (**10**).

Key words: Titanium; Sulfur; Selenium; Cyclopentadienyl; Cycloheptatrienyl; Heterobimetallics; Crystal structure

1. Introduction

Recent studies in our laboratories and elsewhere have shown the applicability of mono- and di-metallation products of the mixed sandwich compound (η^5-C_5H_5)-(η^7-C_7H_7)Ti in the synthesis of alkyl [1], trimethylsilyl [2], carboxy [2], and phosphinyl [3–5] derivatives. The disubstituted phosphinyl derivatives (η^5-$C_5H_4PR_2$)(η^7-$C_7H_6PR_2$)Ti (R = CH_3, C_6H_5) have proven useful as chelating ligands in the synthesis of heterobimetallics [4–6]. As a continuation of this program, the chemistry of sulfur and selenium derivatives of (η^5-C_5H_5)(η^7-C_7H_7)Ti has now been investigated, and is the subject of this paper. Of special interest is the synthesis of disulfide and diselenide derivatives with potential application in the formation of heterobimetallic complexes. Such complexes might be useful in probing electronic and chemical reactions between metal centers held in close proximity [7,8].

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* Dedicated to Professor Dr. Helmut Werner, a good friend and a distinguished organometallic chemist.

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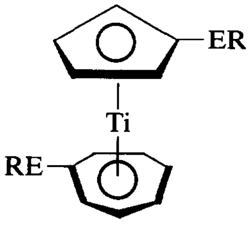
2. Results and discussion

2.1. *Sulfur and selenium derivatives of* $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$*Ti*

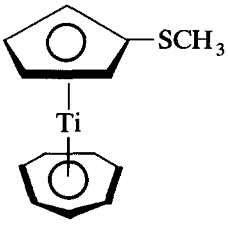
Sulfur, selenium and tellurium derivatives have long played a significant role in the development of ferrocene chemistry. Knox and Pauson [9] demonstrated in 1958 that methylthioferrocene could be formed by the reaction between sodium ferrocenethiolate and dimethyl sulfate. The ferrocenethiol was obtained by reduction of ferrocenesulfonyl chloride, which in turn was obtained from the monosulfonation of ferrocene followed by chlorination. In 1961, Rausch [10] reported a facile synthesis of ferrocenyl aryl sulfides from reactions of iodoferrocene with sodium arenethiolates. A very useful route to sulfur- and selenium-containing ferrocenes involves reaction of 1,1'-dilithioferrocene · TMEDA with an excess of elemental sulfur to produce the corresponding [3] ferrocenophane [11]. Reactions of 1,1'-dilithioferrocene · TMEDA with two equivalents of sulfur or selenium produced directly the reagents $Fe(C_5H_4ELi)_2 \cdot 2THF$ (E = S, Se). These intermediates reacted cleanly with various electrophiles such as alkyl halides to produce new alkylthioferrocene derivatives [12,13]. Herberhold and coworkers reported for the first time the insertion of tellurium into ferrocenyllithium to give $Fe(C_5H_5)(C_5H_4TeLi)$, which is a useful reagent in a variety of reactions with a range of electrophiles [14]. Herberhold *et al.* also reported the synthesis of various acyl derivatives $Fe(C_5H_4ECOR)_2$ (E = S, Se, Te) from reactions of $Fe(C_5H_4ELi)_2$ with the corresponding acyl chloride [15]. 1,3-Ditellura-[3]ferrocenophanes have also been prepared from reactions of $Fe(C_5H_4TeLi)_2$ with an excess of sulfur, selenium, or tellurium, or with one equivalent of CH_2I_2 [16].

Based on similarities between the chemistry of ferrocene and the chemistry of the mixed sandwich complex $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$Ti, the syntheses and reactivities of new sulfur, selenium and tellurium derivatives of the latter compound have been investigated.

It is well-established that the reaction of $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$Ti with two equivalents of *n*-butyllithium · TMEDA in hexane solution produces the dilithio derivative $(\eta^5\text{-}C_5H_4Li)(\eta^7\text{-}C_7H_6Li)Ti \cdot$ 2TMEDA [1,2,4,5]. By analogy with ferrocene chemistry, as described above, the reaction of this dilithio derivative and two equivalents of sulfur should produce a corresponding dithiolate intermediate, which should be converted into $(\eta^5\text{-}C_5H_4SCH_3)(\eta^7\text{-}C_7H_6SCH_3)$Ti (**1**) by treatment with two equivalents of methyl iodide. When we attempted this reaction, however, analysis of the reaction mixture indicated the presence of the desired product **1** in only very low yield (*ca.* 2%), together with extensive decomposition of the starting compound $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$Ti.



E = S E = Se
1, R = CH_3 **5**, R = C_6H_5
4, R = C_6H_5



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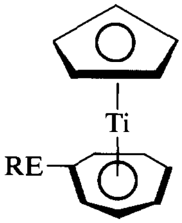


E = S E = Se
3, R = CH_3 **7**, R = C_6H_5
6, R = C_6H_5

Fortunately, an alternate route to ferrocenyl sulfides has been described by Brubaker and coworkers in 1985 [17]. They reported that reactions of $(C_5H_4Li)_2Fe \cdot$ 2TMEDA with two equivalents of dialkyl or diaryl disulfides produced the corresponding ferrocenyl sulfide derivatives in high yields. We subsequently found that, in an analogous manner, the reaction of $(\eta^5\text{-}C_5H_4Li)(\eta^7\text{-}C_7H_6Li)Ti \cdot$ 2TMEDA with two equivalents of dimethyl disulfide in hexane solution resulted in formation of **1** in 18% yield following purification, demonstrating that this is a better route to **1** than that involving elemental sulfur.

The bis(methylthio) derivative **1** was characterized by ^1H NMR, elemental analysis and mass spectrometry. The ^1H NMR spectrum of **1** contains two singlets, at 1.94 and 2.40 ppm, assignable to the methylthio groups on the 5-membered and 7-membered rings, respectively. Two overlapping doublets of doublets (4.97, 5.10 ppm) correspond to the protons on the 5-membered ring at the 3, 4 and 2, 5 positions, respectively. A complex signal is observed at 5.43–5.52 ppm for the protons 3 to 6 on the 7-membered ring. A deshielded complex signal is observed at 5.99–6.12 ppm for the protons at the 2 and 7 positions of the 7-membered ring. The elemental analysis and the mass spectrum corroborate the structure proposed. The mass spectrum of **1** displays a strong molecular ion (*m/e*

296) and a fragmentation pattern consistent with the composition of the compound.

Surprisingly, a 5-membered ring monosubstituted derivative (**2**) was observed as a side product in the synthesis of **1**. Compound **2** was characterized solely spectroscopically because only small amounts were isolated. The ^{1}H NMR spectrum of **2** exhibits a singlet at 1.92 ppm, which corresponds to a methylthio substituent in the 5-membered ring. Two sets of doublets of doublets, at 4.84 and 5.05 ppm, can be assigned to the H(2, 5) and H(3, 4) protons on this ring. A singlet at 5.50 ppm is assigned to the equivalent protons on the 7-membered ring. A related phosphinyl derivative (η^5-$C_5H_4PMe_2$)(η^7-C_7H_7)Ti was previously obtained in very low yield from reactions of the dilithio intermediate with chlorodimethylphosphine in hexane [5,18]. The C_5-monosubstituted derivatives may thus be the result of incomplete dimetalation of (η^5-C_5H_5)(η^7-C_7H_7)Ti under the reaction conditions employed, or possibly of protonation of a (η^5-C_5H_4SMe)(η^7-C_7H_6Li)Ti intermediate.

The selective metalation of the mixed sandwich compound (η^5-C_5H_5)(η^7-C_7H_7)Ti on the 7-membered ring is well documented [1] and has been used successfully for the synthesis of 7-membered ring substituted derivatives [1–5]. A reaction of (η^5-C_5H_5)(η^7-C_7H_7)Ti with one equivalent of *n*-butyllithium in diethyl ether at 0°C produced the monolithio derivative, which reacted with dimethyl disulfide to form (η^5-C_5H_5)(η^7-$C_7H_6SCH_3$)Ti (**3**) in low yield. The ^{1}H NMR spectrum of **3** displays a singlet at 2.42 ppm, which corresponds to the methylthio group attached to the 7-membered ring. A singlet at 5.00 ppm was observed for the protons of the 5-membered ring. A complex multiplet was observed at 5.20–5.43 ppm for protons 3 to 6 of the 7-membered ring, and a deshielded complex signal at 5.96–6.04 for the protons on the 2 and 7 positions of the 7-membered ring. The elemental analysis corroborates the proposed formulation.

One of the features of the reaction of lithium reagents with dichalcogenides is the facile synthesis of aromatic derivatives that would not be accessible through reaction of lithium reagents with elemental sulfur or selenium followed by treatment with aryl halides. Reactions of (η^5-C_5H_4Li)(η^7-C_7H_6Li)Ti · 2TMEDA with two equivalents of diphenyl disulfide or diphenyl diselenide produced the corresponding sulfur (**4**) and selenium (**5**) derivatives in moderate to low yields. The ^{1}H NMR spectra of both **4** and **5** contain apparent triplet resonances near 5.0 and 5.2 ppm assignable to the C(3, 4) and C(2, 5) protons on the C_5-rings, as well as deshielded doublets at 6.05 and 6.18 ppm corresponding to the C(2) and C(7) protons on the C_7-rings. The mass spectra of **4** and **5** both display strong molecular ions at *m/e* 420 and 516, respectively, as well as fragmentation patterns consistent with the formulation adopted.

Unexpectedly, reactions between the dilithio intermediate with two equivalents of diphenyl ditelluride at room temperature or at reflux did not produce the desired disubstituted tellurium analog. Approximately 25% of the diphenyl ditelluride and *ca.* 10% of (η^5-C_5H_5)(η^7-C_7H_7)Ti were recovered. Probably, the reaction did not take place, and the presence of the mixed sandwich compound could be due to incomplete metalation or partial hydrolysis on the chromatographic column.

In a procedure analogous to that used for the synthesis of the mono-methylthio derivative **3**, reactions of (η^5-C_5H_5)(η^7-C_7H_6Li)Ti with one equivalent of diphenyl disulfide or diphenyl diselenide produced the corresponding sulfur (**6**) and selenium (**7**) derivatives. The ^{1}H NMR spectra of both compounds contained singlets for the 5-membered ring protons near 5.0 ppm and low-field doublets for the C(2, 7) protons of the substituted C_7-ring near 6.0 ppm. Compounds **6** and **7** exhibited strong molecular ions in their mass spectra at *m/e* 312 and 360, respectively, and both gave satisfactory elemental analyses.

2.2. Molecular structure of (η^5-Phenylthiocyclopentadienyl)(η^7-phenylthiocycloheptatrienyl)titanium (4)

The molecular structure and atom labeling scheme for compound **4** are presented in Fig. 1. Bond distances and angles are given in Table 1. Compound **4** has a sandwich structure similar to that of the parent compound (η^5-C_5H_5)(η^7-C_7H_7)Ti [19] and the bis(diphenylphosphinyl) analog (η^5-$C_5H_4PPh_2$)(η^7-$C_7H_6PPh_2$)Ti [4]. The cyclopentadienyl and cycloheptatrienyl rings are essentially planar, with the largest deviations of 0.03 Å for η^5-C_5H_4SPh and 0.05 Å for η^7-C_7H_6SPh. The most important aspect of the structure of **4** is the *trans* orientation of the phenylthio groups, which point away from the rest of the molecule. Similar structural features were observed for the bis(diphenylphosphinyl) analog [4].

The electronic and steric nature of **4** does not greatly affect the basic structure. The average Ti–C(η^5) and Ti–C(η^7) separations (2.30(2) and 2.17(3) Å) are similar to those in the bis(diphenylphosphinyl) analog (2.34(7) and 2.19(5) Å) [4] and the parent compound (2.32 and 2.19 Å) [19]. We would expect stronger Ti–C(η^5) and Ti–C(η^7) interactions owing to stronger electron donation by the rings caused by the phenylthio substituents, but the large esd's do not permit us to see such detail. The Cent(η^5)–Ti–Cent(η^7) angle for **4** is 176.8°, which is similar to the parent compound (177.8°) [19]. The cyclopentadienyl and cycloheptatrienyl rings

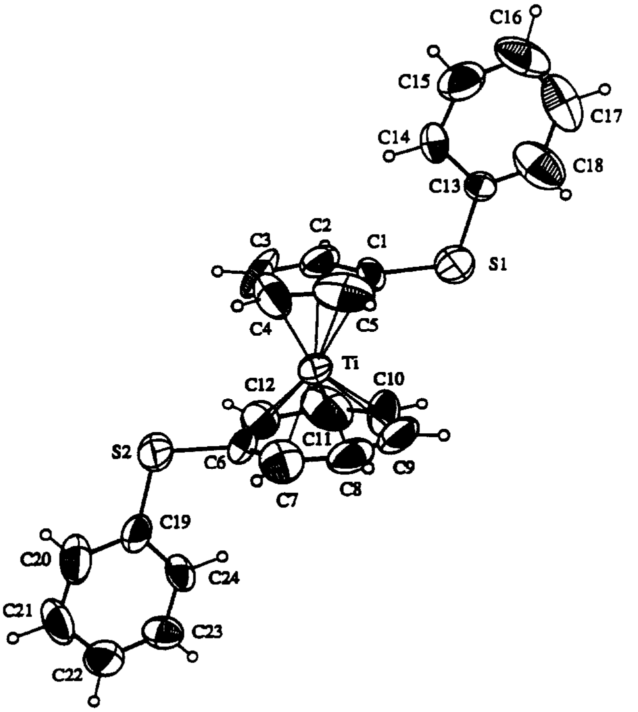


Fig. 1. Molecular structure and atom numbering for $(\eta^5\text{-}C_5H_4SPh)(\eta^7\text{-}C_7H_6SPh)Ti$ (4).

in **4** are essentially parallel with a dihedral angle of 3.5°.

2.3. Heterobimetallic derivatives of $(\eta^5$-methylthiocyclopentadienyl$)(\eta^7$-methylthiocycloheptatrienyl$)$titanium (1)

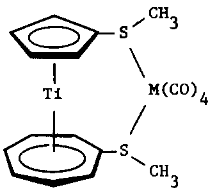
Given the availability of the disubstituted sulfur derivative $(\eta^5\text{-}C_5H_4SCH_3)(\eta^7\text{-}C_7H_6SCH_3)Ti$ **1**, several reactions were examined in the hope of producing heterobimetallic complexes with chromium and molybdenum, in procedures analogous to those used for the corresponding ferrocene [20] and ruthenocene [21] species.

TABLE 1. Selected bond distances (Å) and angles (deg) for $(\eta^5\text{-}C_5H_4SPh)(\eta^7\text{-}C_7H_6SPh)Ti$ (4)

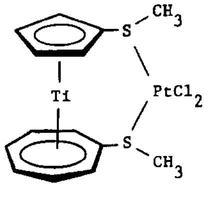
Distance			
Ti–C(1)	2.28(1)	Ti–C(2)	2.33(2)
Ti–C(3)	2.32(2)	Ti–C(4)	2.29(2)
Ti–C(5)	2.30(2)	Ti–C(6)	2.20(2)
Ti–C(7)	2.13(2)	Ti–C(8)	2.12(2)
Ti–C(9)	2.20(2)	Ti–C(10)	2.18(2)
Ti–C(11)	2.19(2)	Ti–C(12)	2.17(2)
S(1)–C(1)	1.74(1)	S(1)–C(13)	1.75(2)
S(2)–C(6)	1.77(2)	S(2)–C(19)	1.76(2)
Cent1 [a]–Ti	1.97	Cent2 [a]–Ti	1.46
Angle			
C(1)–S(1)–C(13)	106.6(7)	C(6)–S(2)–C(19)	103.6(7)
Cent1–Ti–Cent2	176.8		

[a] Cent1 is the centroid of the C_5-ring; Cent2 is the centroid of the C_7-ring.

A reaction between **1** and one equivalent of $(\eta^4$-norbornadiene)molybdenum tetracarbonyl in refluxing hexane produced the heterobimetallic derivative tetracarbonyl-[$(\eta^5$-methylthiocyclopentadienyl$)(\eta^7$-methylthiocycloheptatrienyl)-titanium]molybdenum (**8**) in 13% yield.



8, M = Mo
9, M = Cr



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Complex **8** was characterized spectroscopically by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectrum of **8** displays two singlets at 2.09 and 2.53 ppm, which correspond to the methylthio groups on the 5- and 7-membered rings, respectively. Both signals are shifted downfield relative to the starting ligand **1**. The deshielding, as expected, is due to the electron donation of the sulfur atoms to the molybdenum atom. Two apparent triplets at 4.55 and 5.02 ppm correspond to the protons on the 3, 4 and 2, 5 positions of the 5-membered ring, respectively. Two complex groups of signals between 5.26–5.30 ppm and 5.64–5.70 ppm are assigned to the protons on the 3 to 6 as well as 2 and 7 positions of the 7-membered ring, respectively. The presence of carbonyl groups in **8** was demonstrated by IR spectroscopy (2027, 1915 and 1861 cm^{-1}). These absorptions are typical of *cis*-metal tetracarbonyl complexes and are similar to those reported for the ferrocene [20] and ruthenocene [21] analogs.

Analogously, the reaction between **1** and one equivalent of $(\eta^4$-norbornadiene)chromium tetracarbonyl produced the corresponding heterobimetallic complex (**9**) in very low yield (9%). Complex **9** was characterized by its ^{1}H NMR and IR spectra, both of which were similar to those of the molybdenum analog **8**.

Sulfide derivatives of ferrocene have been reported to produce heterobimetallic complexes with palladium and platinum dihalides [17,22]. In an attempt to extend this approach to titanium species, the bis(methylthio) derivative **1** was stirred at room temperature in benzene solution with one equivalent of bis(benzonitrile)platinum dichloride. A yellow product, believed to be the heterobimetallic complex (**10**) was obtained, but solubility limitations hindered its characterization by ^1H NMR spectroscopy. An elemental analysis of the insoluble product suggests the presence of 10, possibly contaminated with bis(benzonitrile)-platinum dichloride.

3. Experimental section

All operations were carried out under argon using standard Schlenk and glove box techniques. The argon was deoxygenated with BTS catalyst and dried with molecular sieves and P_2O_5. Diethyl ether and THF were predried over sodium wire, and distilled under argon from sodium-potassium alloy. Pentane, hexane, benzene and toluene were distilled under argon directly from sodium-potassium alloy. Dichloromethane was distilled under argon from calcium hydride. Silica was obtained from M. Woelm and activated by heating with a heating gun *in vacuo* for 2 h, and kept under argon in a Schlenk flask. Column chromatography was by the dry-pack technique under an inert atmosphere. The Schlenk-type chromatography column was modified with a jacketed system to allow cooling with circulating cold water. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was obtained from Aldrich, and was distilled from calcium hydride. Bis(benzonitrile)platinum dichloride was obtained from Strem Chemicals. Dimethyl disulfide, diphenyl disulfide and diphenyl diselenide were obtained from Aldrich. (η^5-Cyclopentadienyl) (η^7-cycloheptatrienyl)titanium [3], diphenyl ditelluride [23], (η^4-norbornadiene)molybdenum tetracarbonyl [24], and (η^4-norbornadiene)chromium tetracarbonyl [24] were made by literature procedures.

^1H NMR spectra were recorded in C_6D_6 solution, with a JEOL FX-90Q, Varian XL-200 or Varian XL-300 spectrometer with tetramethylsilane or residual solvent signals as internal standards. Infrared spectra were obtained on a Perkin-Elmer FT spectophotometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA. Electron impact mass spectra were obtained at 70 eV on a Varian CH7 mass spectrometer at the University of Bayreuth.

3.1. (η^5-Methylthiocyclopentadienyl)(η^7-methylthiocycloheptatrienyl)titanium (1)

A suspension of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)titanium (0.96 g, 4.7 mmol) in 50 ml of hexane was added with stirring during 10 min to a solution of 5.9 ml of n-butyllithium (9.4 mmol) and 2.2 ml of TMEDA (15 mmol) in 50 ml of hexane. Within minutes, the mixture darkened and gas was evolved. Stirring was continued for 12 h at room temperature to produce a dark green-black suspension. The mixture was cooled to 0°C and a solution of 0.90 ml of dimethyl disulfide (10 mmol) in 10 ml of hexane was added dropwise with vigorous stirring. The color changed to light green-brown, and the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the dark brown residue was chromatographed on silica. Elution with pentane produced a small blue band, identified as $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ by ^1H NMR spectroscopy, followed by a second small green band, identified as $(\eta^5\text{-}C_5H_4SCH_3)(\eta^7\text{-}C_7H_7)Ti$ (**2**) (*vide infra*). A third wide green band was also collected. The solvent was reduced to *ca.* 50 ml under vacuum and the solution cooled to −20°C. Aggregates of green crystals of **1** formed (0.25 g, 18%). Anal. Found: C, 57.22; H, 5.44. $C_{14}H_{16}S_2Ti$ calc.: C, 56.75; H, 5.44%. ^1H NMR (C_6D_6): δ 1.94 (s, 3H), 2.40 (s, 3H), 4.97 (m, 2H), 5.10 (m, 2H), 5.43–5.52 (m, 4H), 5.99–6.12 (m, 2H). MS: m/e 296 $(M)^+$, 281 $(M-CH_3)^+$, 266 $(M-2CH_3)^+$, 249 $(M-SCH_3)^+$, 234 $(M-S-2CH_3)^+$, 204 $(M-2SCH_3)^+$, 144 $(C_5H_4STi)^+$, 137 $(C_7H_6SCH_3)^+$, 48 $(CH_3SH)^+$.

Compound **1** was also obtained from the reaction of elemental sulfur and $(\eta^5\text{-}C_5H_4Li)(\eta^7\text{-}C_7H_6Li)Ti$, which was produced from 0.96 g (4.7 mmol) of $(\eta^5\text{-}C_5H_5)\text{-}(\eta^7\text{-}C_7H_7)Ti$ and 5.9 ml (9.4 mmol) of *n*-butyllithium/TMEDA (2.2 ml, 15 mmol). A solution of 0.31 g (9.7 mmol) of yellow sulfur in 100 ml of THF was added dropwise to the dilithium derivative at 0°C. The dark mixture was stirred for 12 h at room temperature and then treated with 0.60 ml (9.6 mmol) of methyl iodide. After stirring for 1 h, the solvents were removed under reduced pressure and the dark residue was chromatographed on silica. A small blue band identified as $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ by ^1H NMR was detected, followed by a small green band which contained *ca.* 0.03 g of **1** (*ca.* 2% yield) as identified by its ^1H NMR spectrum.

3.2. (η^5-Methylthiocyclopentadienyl)(η^7-cycloheptatrienyl)titanium (2)

During the synthesis of compound **1**, a small green band was eluted after the starting material in the chromatographic separation of the products from the reaction. The green band was collected, the solvent was reduced to *ca.* 20 ml, and the solution was cooled to −20°C. Compound **2** separated as a blue-green crystalline solid (*ca.* 0.1 g, 0.4%). ^1H NMR (C_6D_6): 1.92 (s, 3H), 4.84 (dd, 2H), 5.05 (dd, 2H), 5.50 (s, 7H).

3.3. (η^5-Cyclopentadienyl)(η^7-methylthiocycloheptatrienyl)titanium (3)

A slurry of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)titanium (1.10 g, 5.39 mmol) in 100 ml of diethyl ether was cooled to 0°C. n-Butyllithium (3.4 ml, 5.4

mmol) was then added slowly from a syringe. The mixture was stirred for 5 h at 0°C. The original blue color disappeared to give a dark brown suspension. A solution of methyl disulfide (0.50 ml, 5.6 mmol) in 50 ml of diethyl ether was added dropwise (1 h) to the brown suspension at 0°C with vigorous stirring. The color changed to light green-brown, and the mixture was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure and the oily brown residue was chromatographed on silica. Elution with pentane yielded a wide blue band. The solvent was reduced under vacuum to *ca.* 50 ml and the solution cooled to −20°C to produce a blue precipitate. The solid was separated, stirred with 50 ml of pentane, and filtered off. The residual blue material was identified as $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$Ti by ^{1}H NMR. The clear deep blue solution was cooled to −20°C to produce dark blue crystals of **3** (0.10 g, 7.4%), which were recrystallized from pentane. Anal. Found: C, 62.46; H, 5.56. $C_{13}H_{14}STi$ calc.: C, 62.40; H, 5.64%. ^{1}H NMR (C_6D_6): δ 2.42 (s, 3H), 5.00 (s, 5H), 5.20–5.43 (m, 4H), 5.96–6.04 (m, 2H).

3.4. $(\eta^5$-*Phenylthiocyclopentadienyl*$)(\eta^7$-*phenylthiocycloheptatrienyl*$)$*titanium (4)*

A suspension of $(\eta^5$-cyclopentadienyl$)(\eta^7$-cycloheptatrienyl)titanium (1.05 g, 5.14 mmol) in 50 ml of hexane was added with stirring during 10 min to a solution of 7.5 ml of n-butyllithium (12 mmol) and 2.2 ml of TMEDA (15 mmol) in 50 ml of hexane. Within minutes the mixture had darkened and gas was evolved. Stirring was continued for 12 h at room temperature to produce a dark green-black suspension. The mixture was cooled to 0°C and a solution of 2.2 g of diphenyl disulfide (10 mmol) in 10 ml of toluene was added with vigorous stirring. The color changed to light green-brown, and the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the dark brown residue was chromatographed on silica. Elution with pentane produced a small blue band identified as $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$Ti by NMR spectroscopy, followed by a second wide green band. The solvent was evaporated under vacuum and the green residue was dissolved in 50 ml of a mixture of 1 : 1 toluene-hexane. When the solution was cooled −20°C, emerald-green crystals of **4** were formed (0.72 g, 33%). The product was recrystallized from toluene-hexane at −20°C. Anal. Found: C, 68.73; H, 4.81. $C_{24}H_{20}S_2Ti$ calc.: C, 68.56; H, 4.79%. ^{1}H NMR (C_6D_6): δ 4.97 (t, 2H), 5.23 (t, 2H), 5.41–5.47 (m, 2H), 5.49–5.55 (m, 2H), 6.05 (d, 2H), 6.81–7.01 (m, 8H), 7.24 (d, 2H). MS: *m/e* 420 $(M)^+$, 330 $(M - C_7H_6)^+$, 296 $(M - C_6H_5 - Ti)^+$, 253 $(M - C_7H_6 - C_6H_5)^+$, 199 $(C_7H_6SC_6H_5)^+$, 144 $(C_5H_4STi)^+$.

3.5. $(\eta^5$-*Cyclopentadienyl*$)(\eta^7$-*phenylthiocycloheptatrienyl*$)$*titanium (6)*

A slurry of $(\eta^5$-cyclopentadienyl$)(\eta^7$-cycloheptatrienyl)titanium (1.20 g, 5.88 mmol) in 100 ml of diethyl ether was cooled to 0°C and n-butyllithium (3.7 ml, 5.9 mmol) was slowly added from a syringe. The mixture was stirred for 5 h at 0°C. The original blue color disappeared to give a dark brown suspension. A solution of phenyl disulfide (1.29 g, 5.87 mmol) in 50 ml of diethyl ether was added dropwise (1 h) to the brown suspension at 0°C with vigorous stirring. The color changed to dark green and the mixture was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure and the oily brown residue was chromatographed on silica. Elution with hexane yielded a small blue band, identified as $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$Ti by ^{1}H NMR, closely followed by a wide blue band. The solvent was reduced under vacuum to *ca.* 50 ml and the solution was cooled to −20°C to produce a blue precipitate. The solid was separated and recrystallized twice at −20°C from 1 : 1 toluene-hexane. Dark blue crystals of **6** formed (0.57 g, 31%). Anal. Found: C, 69.24; H, 5.02. $C_{18}H_{16}STi$ calc.: C, 69.23; H, 5.16%. ^{1}H NMR (C_6D_6): δ 4.99 (s, 5H), 5.33–5.43 (m, 4H), 6.00 (d, 2H), 6.84–7.02 (m, 3H), 7.32 (d, 2H). MS: *m/e* 312 $(M)^+$, 278 $(M - H_2S)^+$, 234 $(M - C_6H_6)^+$, 199 $(C_7H_6SC_6H_5)^+$, 109 $(C_6H_5S)^+$.

3.6. $(\eta^5$-*Phenylselenocyclopentadienyl*$)(\eta^7$-*phenylselenocycloheptatrienyl*$)$*titanium (5)*

A suspension of $(\eta^5$-cyclopentadienyl$)(\eta^7$-cycloheptatrienyl)titanium (1.00 g, 4.90 mmol) in 50 ml of hexane was added with stirring during 10 min to a solution of 11.0 ml of n-butyllithium (11.2 mmol) and 2.2 ml of TMEDA (15 mmol) in 50 ml of hexane. Within minutes, the mixture darkened and gas was evolved. Stirring was continued for 12 h at room temperature to produce a dark green-brown suspension. The mixture was cooled to 0°C and 3.06 g of diphenyl diselenide (9.80 mmol) dissolved in 10 ml of toluene was added dropwise with vigorous stirring. The color changed to light green-brown and the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the dark brown residue was chromatographed on silica. Elution with pentane produced a small blue first band (identified as $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$Ti by ^{1}H NMR spectroscopy) followed by a wide green band. The solvent was evaporated under vacuum and the green residue was dissolved in 50 ml of a mixture of 1 : 1 toluene-hexane. The solution was cooled to −20°C to produce emerald green crystals of **5** (0.25 g, 10%), which were recrystallized from toluene-hexane at −20°C. Anal. Found: C, 55.94; H, 4.04. $C_{24}H_{20}Se_2Ti$ calc.: C, 56.06; H, 3.92%.

^{1}H NMR (C_6D_6) δ 4.94 (t, 2H), 5.27 (t, 2H), 5.34–5.40 (m, 2H), 5.45–5.50 (m, 2H), 6.18 (d, 2H), 6.86–6.95 (m, 6H), 7.17 (d, 2 H), 7.45 (d, 2H). MS: *m/e* 516 (M)$^+$, 362 M − $2C_6H_5)^+$, 314 ($[C_6H_5Se]_2)^+$, 247 (C_7H_6Se-$C_6H_5)^+$, 222 ($C_5H_4SeC_6H_5)^+$, 167 ($C_7H_6C_6H_5)^+$, 157 ($C_6H_5Se)^+$, 91 ($C_7H_7)^+$, 78 ($C_6H_6)^+$.

3.7. (η^5-Cyclopentadienyl)(η^7-phenylselenocycloheptatrienyl)titanium (7)

A slurry of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)titanium (1.10 g, 5.39 mmol) in 100 ml of diethyl ether was cooled to 0°C and n-butyllithium (3.4 ml, 5.4 mmol) was then slowly added from a syringe. The mixture was stirred for 5 h at 0°C. The original blue color disappeared to give a dark brown suspension. A solution of diphenyl diselenide (1.68 g, 5.38 mmol) in 50 ml of diethyl ether was added dropwise (1 h) to the brown suspension at 0°C with vigorous stirring. The color changed to dark green, and the mixture was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure and the oily brown residue was chromatographed on silica. Elution with hexane yielded a small blue band (identified as (η^5-C_5H_5)(η^7-C_7H_7)Ti by ^{1}H NMR spectroscopy), closely followed by a wide blue band. The solvent was reduced under vacuum to *ca.* 50 ml and the solution was cooled to −20°C to produce a blue precipitate. The solid was separated and recrystallized at −20°C from 1 : 1 toluene-hexane. Dark blue crystals of **7** formed (0.20 g, 10%). Anal. Found: C, 60.09; H, 4.57. $C_{18}H_{16}SeTi$ calc.: C, 60.19; H, 4.49%. ^{1}H NMR (C_6D_6) δ 4.97 (s, 5H), 5.25–5.32 (m, 2H), 5.38–5.45 (m, 2H), 6.10 (d, 2H), 6.91–6.95 (m, 3H), 7.47 (d, 2H). MS: *m/e* 360 (M)$^+$, 314 ($[C_6H_5Se]_2)^+$, 270 (M − $C_7H_6)^+$, 167 ($C_7H_6C_6H_5)^+$, 157 ($C_6H_5Se)^+$, 113 ($C_5H_5Ti)^+$.

3.8. Attempted synthesis of (η^5-phenyltellurocyclopentadienyl)(η^7-phenyltellurocycloheptatrienyl)titanium

A suspension of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)titanium (1.05 g, 5.14 mmol) in 50 ml of hexane was added with stirring during 10 min to a solution of 7.5 ml of n-butyllithium (12 mmol) and 2.2 ml of TMEDA (15 mmol) in 50 ml of hexane. Within minutes the mixture darkened and gas was evolved. Stirring was continued for 12 h at room temperature to produce a dark green-black suspension. The mixture was cooled to 0°C and a solution of 4.1 g of diphenyl ditelluride (10 mmol) in 50 ml of toluene was added dropwise with vigorous stirring. The color changed to dark brown and the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the dark brown residue was chromatographed on silica. Elution with hexane produced a dark yellow band (*ca.* 1.0 g, identified as phenyl ditelluride by ^{1}H NMR spectroscopy); followed closely by a blue band (*ca.* 0.1 g, identified as (η^5-C_5H_5)(η^7-C_7H_7) by ^{1}H NMR). Elution with more polar solvents including toluene and toluene-THF produced only a dark tarry material that could not be characterized.

An analogous reaction conducted at reflux for 4 h produced only extensive decomposition and none of the desired product.

3.9. Tetracarbonyl[(η^5-methylthiocyclopentadienyl)(η^7-methylthiocycloheptatrienyl)titanium]molybdenum (8)

A solution of (η^5-methylthiocyclopentadienyl)(η^7-methylthiocycloheptatrienyl)titanium **1** (0.45 g, 1.5 mmol) and (η^4-norbornadiene)molybdenum tetracarbonyl (0.45 g, 1.5 mmol) in 50 ml of hexane was refluxed under an inert atmosphere for 12 h. The color changed from yellow-green to dark brown. The mixture was then cooled and the solvent was removed under reduced pressure. The resulting dark brown residue was chromatographed on silica. A green band was eluted with hexane and identified as (η^5-C_5H_4-SCH_3)(η^7-$C_7H_6SCH_3$)Ti (**1**). Elution with 1 : 1 hexane-toluene produced a yellow-green band which was collected. The solvent was removed under reduced pressure and the green residue was dissolved in 50 ml of 1 : 1 hexane-toluene. Cooling of the solution to −20°C gave green crystals of **8** (0.10 g, 13%). Anal. Found: C, 43.17; H, 2.99. $C_{18}H_{16}MoO_4S_2Ti$ calc.: C, 42.87; H, 3.20%. ^{1}H NMR (C_6D_6): δ 2.09 (s, 3H), 2.53 (s, 3H), 4.55 (t, 2H), 5.02 (t, 2H), 5.26–5.30 (m, 4H), 5.64–5.70 (m, 2H). IR (CH_2Cl_2): 2027s, 1915br, 1861br cm^{-1}.

3.10. Tetracarbonyl[(η^5-methylthiocyclopentadienyl)(η^7-methylthiocycloheptatrienyl)titanium]chromium (9)

A solution of (η^5-methylthiocyclopentadienyl)(η^7-methylthiocycloheptatrienyl)titanium (0.37 g, 1.3 mmol) and (η^4-norbornadiene)chromium tetracarbonyl (0.33 g, 1.3 mmol) in 50 ml of hexane was refluxed under an inert atmosphere. The color changed from yellow-green to dark brown. Workup and purification on a silica column as described above for **8** produced **9** as green crystals (0.05 g, 9%). ^{1}H NMR (C_6D_6) δ 2.09 (s, 3H), 2.53 (s, 3H), 4.55 (t, 2H), 5.10 (t, 2H), 5.28–5.34 (m, 4H), 5.6--5.8 (m, 2H). IR (CH_2Cl_2): 2020s, 1937, 1912br, 1863br cm^{-1}.

3.11. Attempted synthesis of dichloro[(η^5-methylthiocyclopentadienyl)(η^7-methylthiocycloheptatrienyl)]platinum (10)

A solution of (η^5-methylthiocyclopentadienyl)(η^7-methylthiocycloheptatrienyl)titanium (0.40 g, 1.4 mmol)

TABLE 2. X-ray data collection parameters for (η^5-phenylthiocyclopentadienyl)-(η^7-phenylthiocycloheptatrienyl)titanium (4)

Compound	$(\eta^5\text{-}C_5H_4SPh)(\eta^7\text{-}C_7H_6SPh)Ti$
Color/Shape	green/parallelepiped
For. wt.	320.44
Space group	$P2_12_12_1$
Temp., °C	18
Cell Constants [a]	
a, Å	8.130(3)
b, Å	11.569(6)
c, Å	21.694(6)
Cell Vol, Å^3	2040
Formula units/unit cell	4
D_{calc}, g cm^{-3}	1.37
μ_{calc}, cm^{-1}	6.38
Diffractometer/Scan	Enraf-Nonius CAD-4/ω-2θ
Radiation, graphite monochromator	Mo K_α(λ = 0.71073)
Max. crystal dimensions, mm	0.10×0.40×0.50
Scan width	0.80 + 0.35 tan θ
Standard reflections	400; 060; 0, 0, 12
Decay of standards	±2.5%
Reflections measured	2092
2θ range, deg	$2 \leq 2\theta \leq 50$
Range of h, k, l	+9, +13, +25
Reflections observed $[F_0 \geq 5\sigma(F_0)]$ [b]	855
Computer programs [c]	SHELX
Structure solution	SHELXS
No. of parameters varied	244
Weights	$[\sigma(F_o)^2 + 0.0008F_o^2]^{-1}$
GOF	1.53
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.058
R_w	0.067
R inverse configuration	0.058, 0.067
Largest feature final diff. map	0.3 e$^-$Å^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 11°$.

[b] Corrections: Lorentz-polarization.

[c] Neutral scattering factors and anomalous dispersion corrections.

in 25 ml of benzene was mixed with a filtered solution of bis(benzonitrile)platinum dichloride (0.66 g, 1.4 mmol) in 30 ml of benzene (slight warming was necessary to achieve almost complete dissolution). The two solutions were transferred to a third flask via a cannula and the mixture was stirred at room temperature for 12 h. The color changed from yellow-green to dark yellow with a light yellow precipitate. The latter was filtered off, washed twice with 50 ml portions of benzene, twice with 50 ml portions of pentane, and dried under high vacuum for 24 h. The resulting yellow solid (0.20 g, 26%) was too insoluble to obtain a solution ^{1}H NMR spectrum. Anal. Found: C, 28.48; H, 2.41. $C_{18}H_{16}Cl_2PtS_2Ti$ calc.: C, 29.90; H, 2.87%.

3.12. X-ray data collection, structure determination and refinement for (η^5-phenylthiocyclopentadienyl)(η^7-phenylthiocycloheptatrienyl)titanium (4)

A single green crystal of the title compound was mounted in a thin wall capillary under argon and transferred to the goniometer. The space group was determined to be non-centrosymmetric $P2_12_12_1$ from the systematic absences. A summary of data collection parameters is given in Table 2. Least-squares refinement with isotropic thermal parameters led to R = 0.129. The hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The crystals were very weakly diffracting and a severe shortage of data resulted. The thermal parameters for C(3) and C(4) were unusually elongated, but this appears to be a crystallographic artifact. It was not possible to resolve the absolute configuration with the data set obtained, both conformations producing the same R value. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.058 and R_w = 0.067. The final values of the positional parameters are given in Table 3.

TABLE 3. Final fractional coordinates for $(\eta^5\text{-}C_5H_4SPh)(\eta^7\text{-}C_7H_6SPh)Ti$ (4)

Atom	x	y	z	B_{eq} [a]
Ti	0.0022(5)	0.5633(2)	0.1656(1)	3.23
S(1)	−0.3389(7)	0.6181(4)	0.0695(2)	4.16
S(2)	0.3671(6)	0.4640(3)	0.2464(2)	4.33
C(1)	−0.199(2)	0.517(1)	0.0968(8)	2.64
C(2)	−0.052(2)	0.491(2)	0.068(1)	5.02
C(3)	0.024(3)	0.402(2)	0.102(2)	10.51
C(4)	−0.076(3)	0.374(2)	0.155(2)	8.99
C(5)	−0.217(3)	0.443(2)	0.1482(8)	4.90
C(6)	0.223(2)	0.571(1)	0.2246(7)	2.51
C(7)	0.078(2)	0.573(1)	0.2595(9)	4.27
C(8)	−0.063(2)	0.636(2)	0.252(1)	5.44
C(9)	−0.106(3)	0.718(2)	0.208(1)	7.73
C(10)	−0.004(4)	0.751(1)	0.158(1)	6.14
C(11)	0.148(3)	0.716(2)	0.143(1)	5.77
C(12)	0.253(2)	0.625(1)	0.1721(8)	3.84
C(13)	−0.482(2)	0.542(1)	0.0252(6)	3.08
C(14)	−0.470(2)	0.418(1)	0.0187(7)	2.85
C(15)	−0.587(2)	0.372(2)	−0.0173(9)	4.68
C(16)	−0.702(3)	0.429(2)	−0.051(1)	5.82
C(17)	−0.707(3)	0.548(2)	−0.042(1)	6.36
C(18)	−0.596(3)	0.601(2)	−0.0051(9)	5.62
C(19)	0.483(2)	0.532(1)	0.3045(8)	3.98
C(20)	0.579(2)	0.465(1)	0.342(1)	4.55
C(21)	0.676(2)	0.513(1)	0.3864(9)	4.40
C(22)	0.670(3)	0.632(2)	0.3955(8)	4.48
C(23)	0.578(2)	0.701(1)	0.3581(7)	3.36
C(24)	0.483(2)	0.653(1)	0.3145(7)	2.91

[a] $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_3]$.

A complete list of bond distances and angles and a table of thermal parameters have been deposited at the Cambridge Crystallographic Data Center. Structure factors are available from R.D.R. upon request.

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