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Registry No. 1, 82666-28-2; 2, 82666-29-3; 3, 82666-30-6; 4, 82666-31-7; 5, 82666-32-8; 6, 82678-93-1; 7, 82666-34-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes and equations of planes and dihedral angles (Table S1) and a drawing of the unit cell packing (Figure S1) (18 pages). Ordering information is given on any current masthead page.

Contribution from the School of Chemical Sciences,
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Template Syntheses of 1,2-Alkene Dichalcogenide Chelates via the Addition of Activated Acetylenes to Dicyclopentadienyltitanium Pentachalcogenides

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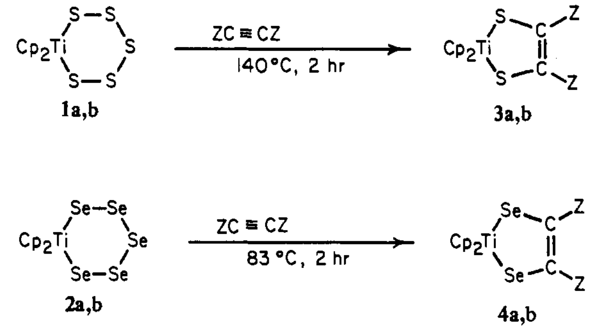
The pentachalcogenides $(C_5H_4R)_2TiE_5$ (R = H, CH_3; E = S, Se) react with acetylenes, $ZC{\equiv}CZ$ (Z = CO_2CH_3, CF_3) to give the alkene dichalcogenide compounds, $(C_5H_4R)_2TiE_2C_2Z_2$, which were isolated as dark green crystalline solids. The dithiolene syntheses proceed in ca. 40% yield at 140 °C while the corresponding diselenene synthesis was quantitative at 80 °C. The new compounds were characterized by ^1H, ^{13}C, ^{19}F, and ^{77}Se NMR, IR, mass spectrometry, and electrochemistry. $(C_5H_4CH_3)_2TiS_2C_2(CO_2CH_3)_2$ crystallizes in the triclinic space group $P\bar{1}$-C_i^1 (No. 2) with one molecule per unit cell of dimensions $a = 9.312$ (2) Å, $b = 9.886$ (2) Å, $c = 11.225$ (3) Å, $\alpha = 109.35$ (2)°, $\beta = 88.25$ (2)°, and $\gamma = 105.78$ (2)°. Empirically weighted full-matrix least-squares refinement employing isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others converged to R_1(based on f) = 0.032 and R_2 = 0.039 for 4098 independent reflections having $2\theta_{\mathrm{Mo}\,K\alpha} \leq 58.7°$ and $I > 3\sigma(I)$. The structure analysis revealed a conventional bis(methylcyclopentadienyl)titanium moiety chelated by the sulfur atoms of the dithiolene. The conversion of $(C_5H_5)_2TiSe_5$ to its alkene diselenide derivative was characterized as a function of reactant concentrations and temperature. In refluxing 1,2-dichloroethane solution, this reaction was found to be first order with respect to both acetylene and pentaselenide concentrations, the second-order rate constant being 1.58×10^{-3} M^{-1} s^{-1} at 83.5 °C. The compounds $(C_5H_4R)_2TiE_2C_2Z_2$ were found to react with a variety of dichloro compounds, L_nMCl_2, to give the ligand-exchange products $L_nME_2C_2Z_2$ (Z = CO_2CH_3) and $(C_5H_4R)_2TiCl_2$. In this way the following new compounds were prepared: $Ni(Se_2C_2Z_2)(Ph_2PCH_2CH_2CH_2PPh_2)$, $Pt(E_2C_2Z_2)(PPh_3)_2$ (E = S, Se), $Pt_2(Se_2C_2Z_2)_2(Ph_2PC_2PPh_2)_2$, $(AsPh_4)[Rh(Se_2C_2Z_2)(CO)_2]$, and $SCSe_2C_2Z_2$. Alcoholysis of $(C_5H_5)_2TiSe_2C_2(CO_2CH_3)_2$ in basic methanol gave solutions of $Na_2Se_2C_2(CO_2CH_3)_2$, which was derivatized with CH_3I (2 equiv) and *cis*-$PtCl_2(PPh_3)_2$.

Introduction

Transition-metal complexes containing polysulfido chelates have been recognized since the report of the $(NH_4)_2PtS_{15}$ structure in 1967.[1] This compound, whose synthesis was first described in 1903,[2] is composed of octahedral platinum(IV) coordinated to three bidentate S_5^{2-} chelates. In recent years several other examples of penta- and tetrasulfido metal chelates have been prepared although generally not by design. Those characterized crystallographically include $(C_5H_5)_2MS_5$ (M = Ti,[3,4] V[4]), $(C_5H_5)_2MS_4$ (M = Mo,[5a] W[5b]), $(Ph_4P)_2Fe_2(\mu\text{-}S)_2(S_5)_2$,[6a] $(Ph_4P)_2Mo(S)_2(\mu\text{-}S)_2FeS_5$,[6b] $(Et_4N)_2MoS(S_4)_2$,[7a] $Mo_2(\mu\text{-}S)_2(S)_2(S_2)(S_4)$,[7b] $(C_5H_5)Co(S_5)PMe_3$,[8] NH_4CuS_4,[9] $Os_2(Et_2NCS_2)_3(Et_2NCS_3)(\mu\text{-}S_5)$,[10] and $(NH_4)_2PdS_{11}$.[11]

Scheme I[a]



[a] Cp = η^5-C_5H_4R (R = H or CH_3).

Of the polysulfido chelates, the reactivity of only $(C_5H_5)_2TiS_5$ and $(NH_4)_2PtS_{15}$ have been examined. For the titanium complex two reactivity patterns have been elucidated: transfer of an S_5 unit to nonmetal halides and sulfur abstraction concomitant with rearrangement. Illustrative of the first of these is the synthesis of *cyclo*-S_7 from $(C_5H_5)_2TiS_5$ and S_2Cl_2 (eq 1),[12] a process that exploits the halophilicity of the

$$(C_5H_5)_2TiS_5 + S_2Cl_2 \rightarrow (C_5H_5)_2TiCl_2 + S_7 \qquad (1)$$

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[1] Jones, P. E.; Katz, L. *J. Chem. Soc., Chem. Commun.* **1967**, 842. For the structure of the related potassium salt, K_2PtS_{15}, see: Spangenberg, M.; Bronger, W. *Z. Naturforsch., B. Anorg. Chem., Org. Chem.* **1978**, *33B*, 482.

[2] Hofmann, K. A.; Höchtlen, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3090.

[3] Epstein, E. F.; Bernal, I. *J. Organomet. Chem.* **1971**, *26*, 229.

[4] Müller, K. G.; Petersen, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91.

[5] (a) Block, H. D.; Allman, R. *Cryst. Struct. Commun.* **1975**, *4*, 53. (b) Davis, B. R.; Bernal, I.; Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 921.

[6] (a) Coucouvanis, D.; Swenson, D.; Stremple, D.; Baenziger, N. C. *J. Am. Chem. Soc.* **1979**, *101*, 3392. (b) Coucouvanis, D.; Baenziger, N. C.; Simhon, E. D.; Stremple, P.; Swenson, D.; Kostikas, A.; Simopoulos, A.; Petrouleas, V.; Papaefthymiou, V. *Ibid.* **1980**, *102*, 1730.

[7] (a) Simhon, E. D.; Baenziger, N. C.; Kanatizidis, M.; Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 1218. (b) Clegg, W.; Christou, G.; Garner, C. D.; Sheldrick, G. M. *Inorg. Chem.* **1981**, *20*, 1562.

[8] Burschka, C.; Leonard, K.; Werner, H. *Z. Anorg. Allg. Chem.* **1980**, *464*, 30.

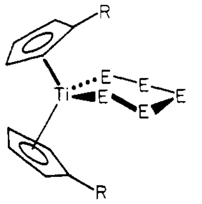
[9] Burschka, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1511.

[10] Maheu, L. J.; Pignolet, L. H. *J. Am. Chem. Soc.* **1980**, *102*, 6346.

[11] Haradem, P. S.; Cronin, J. L.; Krause, R. A.; Katz, L. *Inorg. Chim. Acta* **1977**, *25*, 173.

0020-1669/82/1321-3947$01.25/0

$(C_5H_5)_2Ti^{IV}$ moiety.[13] We have recently demonstrated that sulfur abstraction involving the reactions of $(C_5H_4R)_2TiS_5$ with tertiary phosphines gives $[(C_5H_4R)_2Ti]_2S_x$, $x = 4, 6$.[14] Similar sulfur abstractions occur in the reactions of $Pt(S_5)_3^{2-}$ with sulfite and phosphines to afford the platinum(II) complexes $Pt(S_5)_2^{2-}$ and $PtS_4(PPh_3)_2$, respectively.[15] The dicyclopentadienyltitanium pentasulfides, **1**, are particularly suitable substrates for characterizing the reactivity of a polychalcogenide chelate. They are kinetically and aerobically stable and can easily be synthesized with use of readily available materials.[16] A similar situation exists for the corresponding pentaselenides, $(C_5H_4R)_2TiSe_5$ (**2a**,**b**).



1a, R = H, E = S
b, R = CH_3, E = S
2a, R = H, E = S
b, R = CH_3, E = Se

In the present report we describe the conversion of the titanium pentachalcogenides to the corresponding alkene dichalcogenide chelates via reactions with activated acetylenes[17] (Scheme I). While our acetylene addition process is unusual, it is not without precedent since the original dithiolene synthesis involved the reaction of diphenylacetylene with nonstoichiometric nickel sulfide NiS_x ($x > 1$).[18] Furthermore, the addition of acetylenes to organometallic sulfides has been the subject of more recent reports.[14,19,20] We have found that the addition of acetylenes to the organotitanium pentaselenides gives the corresponding 1,2-alkene diselenides (diselenenes). The previous entry into this class of ligands involved the reaction of refluxing selenium metal (bp 688 °C) with hexafluorobutyne.[21] The present results are particularly novel since once synthesized, the titanium diselenenes and dithiolenes can be used as reagents for the preparation of other organic, inorganic, and organometallic alkene dichalcogenide compounds.

Experimental Section

Materials and Methods. All preparative reactions were performed under an atmosphere of purified nitrogen, and unless otherwise noted, workups were done aerobically in an efficient hood. Tetrahydrofuran (THF), toluene, and hexanes were obtained as reagent grade solvents and were redistilled from sodium benzophenone ketyl. CH_2Cl_2 and 1,2-$C_2H_4Cl_2$ were obtained as reagent grade solvents and were redistilled from P_2O_5. Benzene, xylene (a mixture of isomers), carbon disulfide, and acetone were reagent grade and were stored over 4A molecular sieves. $(C_5H_5)_2TiCl_2$ was purchased from Pressure Chemical Co., and $(CH_3C_5H_4)_2TiCl_2$ was synthesized according to conventional methods. Dimethyl acetylenedicarboxylate (DMAD) was purchased from Aldrich and redistilled, the fraction boiling at 48.5–49.5 °C (0.3 mmHg) being retained. $(C_5H_5)_2TiS_5$ and $(C_5H_5)_2TiSe_5$ were prepared according to the published procedures. Hexafluoro-2-butyne was prepared from 2,2,3,3-tetrachlorohexafluorobutane and was a gift from Mr. Gene Janulis of this department. Thin-layer chromatography (analytical scale) was performed on Eastman 13181 silica gel plates; flash chromatography[22] (preparative scale) was performed with 2 × 20 cm columns packed with Woehm 32–63 silica gel.

The following instruments were used in this work: IR, Perkin-Elmer 599B; UV–vis, Varian Cary 219; ^1H and ^{19}F NMR, Varian EM-390 (with internal frequency lock); variable-temperature ^1H NMR, Varian EM-390 fitted with a Varian 3940 accessory (CH_3OH temperature calibration); ^{13}C and ^{77}Se NMR, Varian XL-100 (internal ^2H frequency lock, temperature calibration with a thermometer). Electron impact (EI) and field desorption (FD) mass spectra were measured as a service on Varian CH-5 and 731 spectrometers at the Mass Spectrometry Laboratory.

All new compounds were isolated as crystalline solids that gave satisfactory analyses (supplementary material). This data was obtained by the University of Illinois Microanalytical Laboratory.

$(CH_3C_5H_4)_2TiS_5$ (1b). Fisher Chemical dark ammonium sulfide solution was saturated with sulfur by stirring with excess sulfur overnight. A 20-mL quantity of this ammonium polysulfide reagent was added to a stirred solution of $(CH_3C_5H_4)_2TiCl_2$, 2.20 g (7.27 mmol), in 200 mL of acetone. After 2 h the red crystalline product was collected by filtration and purified by Soxhlet extraction with 600 mL of carbon disulfide. The red extract was concentrated to 100 mL, cooled to 0 °C, and filtered. The yield of the dark red crystalline product was 2.26 g (85%). Anal. C, H, Ti.

$(CH_3C_5H_4)_2TiSe_5$ (2b). An 11.0-mL quantity of a 1 M solution of $LiBHEt_3$ in THF (Aldrich "Super Hydride") was syringed directly onto Se powder, 2.02 g (25.6 mmol), with stirring. The resultant dark brown solution was then refluxed for 15 min. A solution of $(CH_3C_5H_4)_2TiCl_2$, 1.41 g (5.09 mmol) in 100 mL of THF, was added to the hot Li_2Se_x solution, causing a color change to purple. The reaction mixture was refluxed an additional 30 min and filtered hot. The residue was extracted with CH_2Cl_2 unti the filtrate was colorless. The combined filtrates were concentrated to 25 mL, cooled to 0 °C, and filtered. The dark purple crystals were rinsed with H_2O until the washings were colorless, followed by 50 mL of methanol and 10 mL of CH_2Cl_2. The yield of the analytically pure product was 2.58 g (85%). Anal. C, H, Ti.

$(C_5H_4R)_2TiS_2C_2(CO_2CH_3)_2$ (3a,b). In a representative procedure, a solution of **1a**, 0.338 g (1.00 mmol), and DMAD, 360 μL (2.94 mmol), in 10 mL of xylenes was refluxed for 2.5 h. The resultant dark green solution was evaporated to an oil, which was dissolved in a small amount of CH_2Cl_2, chromatographed on a 2.5 × 50 cm column of SX-4 Bio-Beads (Bio-Rad Laboratories), and eluted with CH_2Cl_2. The green band was collected, diluted with hexanes, and concentrated in vacuo to crystallize the product. After cooling at −20 °C, the dark green microcrystals were collected by filtration; the yield was 0.160 g (41%). Anal. C, H, S, Ti.

$(C_5H_4R)_2TiSe_2C_2(CO_2CH_3)_2$ (4a,b). In a representative procedure, a solution of **2a**, 0.114 g (0.238 mmol), and DMAD, 120 μL (0.98 mmol), in 10 mL of xylenes was refluxed for 0.5 h. The cooled solution was filtered to remove some gray selenium metal (0.025 g, 0.32 mmol), which was washed with CH_2Cl_2. The filtrate was evaporated to an oil and worked up in the manner outlined for **3a**. The yield of dark green crystals was 0.085 g (90%). Anal. C, H, Se, Ti.

$(C_5H_5)_2TiSe_2C_2(CF_3)_2$ (5a). A Carius tube was charged with **2a**, 0.508 g (0.887 mmol), and 15 mL of xylenes and attached to a vacuum line. Hexafluoro-2-butyne, 0.25 mL (3.2 mmol), was condensed into the reaction tube, which was then sealed and annealed. The sealed tube was heated at 150–160 °C for 2 h. The dark green solution was removed from the Carius tube and filtered. The yield of gray selenium was 0.166 g (2.10 mmol). The filtrate was evaporated to dryness and extracted with 10 mL of CH_2Cl_2, which was then filtered to remove unreacted **2a**. The CH_2Cl_2 solution was diluted with hexanes, concentrated to incipient crystallization, and cooled to −20 °C. Filtration

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(12) Schmidt, M.; Block, B.; Block, H. D.; Köpf, H.; Wilhelm, E. *Angew. Chem., Int. Ed. Engl.* **1971**, *7*, 632.

(13) The S_5 transfer reaction of **1a** and reactive nonmetal halides appears to be a general one. For a recent application, see: Roesky, H. S.; Zamankhan, H.; Bats, J. W.; Fuess, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 125.

(14) (a) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620. (b) Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223.

(15) (a) Wickenden, A. E.; Krause, R. A. *Inorg. Chem.* **1969**, *8*, 779. (b) Kreutzer, B.; Kreutzer, P.; Beck, W. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1979**, *27B*, 461. (c) Schmidt, M.; Hoffman, G. G. *Z. Anorg. Allg. Chem.* **1979**, *452*, 112.

(16) Köpf, H.; Block, B.; Schmidt, M. *Chem. Ber.* **1968**, *101*, 272.

(17) Aspects of this work were presented at the 117th National Meeting of the American Chemical Society, Houston, March 1979, and the 1981 Central and Great Lakes Regional Meeting of the American Chemical Society, Dayton, Ohio, May 1981.

(18) Schrauzer, G. N.; Mayweg, V. *J. Am. Chem. Soc.* **1962**, *84*, 3221.

(19) Rakowski Dubois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmeier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

(20) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1979**, *182*, C39.

(21) Davison, A.; Shawl, E. T. *Inorg. Chem.* **1970**, *9*, 1820.

(22) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

afforded 0.342 g (78%) of dark green microcrystals. Anal. C, H, Se, Ti.

$Pt(Se_2C_2(CO_2CH_3)_2)(PPh_3)_2$. A solution of *cis*-$PtCl_2(PPh_3)_2$, 0.050 g (0.063 mmol), and **4a**, 0.031 g (0.063 mmol), in 5 mL of CH_2Cl_2 was stirred for 3 h at room temperature. During this time the color of the solution changed from green to brown. The solution was evaporated to dryness, dissolved in a minimum quantity of CH_2Cl_2, and subjected to flash chromatography with CH_2Cl_2 as the eluant. The yellow band was collected, diluted with methanol, and concentrated to induce crystallization. Filtration afforded 0.055 g (86%) of lemon yellow crystals. Anal. C, H, P, Se.

$Pt_2(Se_2C_2(CO_2CH_3)_2)_2(Ph_2PC{\equiv}CPPh_2)_2$. A solution of $Pt_2Cl_4(Ph_2PC{\equiv}CPPh_2)_2$,[23] 0.201 g (0.152 mmol), and **4a**, 0.146 g (0.305 mmol), in 5 mL of CH_2Cl_2 was stirred at room temperature for 5 min. The reaction was then worked up in the manner used for $Pt(Se_2C_2(CO_2CH_3)_2)(PPh_3)_2$. Filtration afforded 0.242 g (89%) of orange crystals. Anal. C, H, P, Se.

$Ni(Se_2C_2(CO_2CH_3)_2)(Ph_2PCH_2CH_2CH_2PPh_2)$. A solution of $NiCl_2(dppp){\cdot}CH_2Cl_2$, 0.394 g (0.629 mmol), and **4a**, 0.301 g (0.630 mmol), was stirred for 5 min at room temperature. The reaction was then worked up in the manner used for $Pt(Se_2C_2(CO_2CH_3)_2)(PPh_3)_2$ except that the product was crystallized by the addition of Et_2O to the CH_2Cl_2 solution. Filtration afforded 0.448 g (93%) of fibrous tan crystals. Anal. C, H, P, Se.

$Pt(S_2C_2(CO_2CH_3)_2)(PPh_3)$. A solution of *cis*-$PtCl_2(PPh_3)_2$, 0.171 g (0.216 mmol), and **3b**, 0.089 g (0.216 mmol), in 15 mL of benzene was refluxed for 2 h. The resultant brown solution was evaporated to dryness, dissolved in a small quantity of CH_2Cl_2, and flash-chromatographed. The yellow product was eluted off the column with CH_2Cl_2 followed by acetone. The combined eluents were evaporated to dryness, extracted with CH_2Cl_2, diluted with methanol, and concentrated to induce crystallization. Filtration afforded 0.195 g (98%) of lemon yellow crystals. Anal. C, H, P, S.

$(AsPh_4)[Rh(Se_2C_2(CO_2CH_3)_2)(CO)_2]$. $(AsPh_4)[RhCl_2(CO)_2]$,[24] 0.107 g (0.174 mmol), and **4a**, 0.083 g (0.174 mmol), were dissolved in 5 mL of THF. Within 1 min the color of the solution had changed from dark green to yellow and a solution IR spectra indicated that the reaction was complete: ν_{CO} = 2002, 1922 cm^{-1} (cf. for $(AsPh_4)[RhCl_2(CO)_2]$, ν_{CO} = 2060, 1975 cm^{-1}). In a different experiment, $(AsPh_4)[RhCl_2(CO)_2]$, 0.030 g (0.050 mmol), and **4a**, 0.035 g (0.073 mmol), were loaded into an ^1H NMR tube, which was then attached to a vacuum line. $CDCl_3$ was distilled into the tube, which was then sealed. The ^1H NMR spectrum of the solution was recorded within 15 min (Figure 5).

Chelate Transfer to Thiophosgene. A solution of **4a**, 0.206 g (0.431 mmol), in 10 mL of THF was heated to reflux, and thiophosgene, 0.100 mL (1.31 mmol), was added in one aliquot. After 1 h, the solution was stripped to dryness in vacuo to remove unreacted thiophosgene. The solid was dissolved in the minimum of CH_2Cl_2 and flash-chromatographed, with CH_2Cl_2 as the eluant. The yellow band was collected, diluted with methanol, and concentrated to incipient crystallization. The yield of orange, crystalline product was 0.115 g (75%); mp 123.0–124.7 °C.

$NaOCH_3$ Cleavage of the Alkene Dichalcogenide from 4a. (1) $NaOCH_3$, 0.0238 g (0.441 mmol), was added to a slurry of **4a**, 0.101 g (0.212 mmol), in 10 mL of methanol. A rapid reaction ensued, affording a purple solution assumed to contain $Na_2Se_2C_2(CO_2CH_3)_2$. *cis*-$PtCl_2(PPh_3)_2$, 0.166 g (0.211 mmol), was added as a solid to this solution, affording after 10 min a yellow slurry. The slurry was then concentrated to 1 mL and filtered, and the residue was washed with methanol. The solid was extracted with CH_2Cl_2, and the extract was diluted with methanol and concentrated to induce crystallization. The yield of lemon yellow crystals was 0.200 g (93%).

(2) CH_3I, 0.052 mL (0.82 mmol), was added to a methanolic solution of $Na_2Se_2C_2(CO_2CH_3)_2$ prepared from **4a**, 0.201 g (0.420 mmol), and $NaOCH_3$, 0.044 (0.82 mmol), as described above. After 15 min of stirring at room temperature, the solution was evaporated to dryness, dissolved in the minimum of CH_2Cl_2, and flash-chromatographed, with CH_2Cl_2 as the eluant. A yellow, fast-moving band was collected, diluted with hexanes (5 mL), and concentrated to 1 mL. After sitting at room temperature for 12 h, the solution was filtered, affording 0.0956 g (71%) of large, off-white prisms, mp 87.5–88.0 °C. Anal. C, H, Se.

Kinetic Studies of the Reaction of $(C_5H_5)_2TiSe_5$ and Dimethyl Acetylenedicarboxylate. All kinetic runs were performed in a 50-mL three-necked round-bottom flask equipped with a reflux condenser and two stoppers. In a typical procedure, a solution of **2a**, 0.101 g (0.176 mmol), in 10.00 mL of 1,2-dichloroethane was refluxed for 0.5 h. DMAD, 0.500 mL (4.07 mmol), was added to the refluxing $C_2H_4Cl_2$ solution with a syringe. The progress of the reaction was monitored by removing 50.0-μL aliquots from the reaction, diluting them to 5.00 mL, and recording the visible spectrum (350–720 nm). The reaction was monitored until it was at least 75% complete. The cooled solution was filtered to yield 0.033 g (0.42 mmol) of gray selenium. The filtrate was evaporated to dryness in high vacuum (to remove residual DMAD), and its ^1H NMR spectrum confirmed the identity and purity of the diselenene product (**4a**). This residue was then dissolved in CH_2Cl_2, and the solution was diluted with hexanes and concentrated in vacuo to afford 0.065 mg (77%) of dark green crystalline product.

Under pseudo-first-order conditions, $\ln (A_\infty - A_t) = -k_{obsd}t + \ln (A_\infty - A_0)$. The rate constant, k_{obsd}, was calculated by linear least-squares regression analysis for plots of $\ln (A_\infty - A_t)$ vs. t that included iterative fitting of A_∞. The absorbance at λ = 554 nm was used for all calculations. The average correlation coefficient was 0.998. The calculated second-order rate constant, $k = k_{obsd}/[DMAD]$, is the average of five runs. For the determination of activation parameters, rates were measured by similar procedures at 60.1, 70.1, and 83.5 °C. For the two lower temperature measurements, the 1,2-dichloroethane solution was saturated with **2a** at that temperature.

To determine whether solvent significantly affected the rate, we carried out the above procedure with benzene as the solvent. The average rate constant of two runs with [DMAD] = 0.388 M was 1.06×10^{-3} M^{-1} s^{-1}. To determine whether a radical scavenger affected the rate, we carried out the above reaction in the presence of galvinoxyl (2.0% of the concentration of **2a**). The rate of this reaction was not inhibited; the rate constant with [DMAD] = 0.388 M was found to be 1.51×10^{-3} M^{-1} s^{-1}.

Synthesis of $(C_5H_5)_2TiSe_2C_2(CO_2CH_3)_2$ in the Presence of 1b. A solution of **1b**, 0.060 g (0.164 mmol), **2a**, 0.103 g (0.179 mmol), and DMAD, 0.500 mL (4.07 mmol), in 10 mL of 1,2-dichloroethane was refluxed for 0.5 h. The cooled solution was filtered to yield 0.030 g (0.38 mmol) of Se. The filtrate was evaporated to dryness and dissolved in the minimum of methylene chloride (400 mL). A 20-mL quantity of this solution was evaporated to dryness and examined by 360-MHz ^1H NMR.

Variable-Temperature NMR Studies of $(C_5H_5)_2Ti(E_2C_2(CO_2CH_3)_2)$. Typically, temperatures were allowed to stabilize for 30 min before each spectrum was recorded. The width at half-height of the methyl (ester) resonance was used to check on the tuning of the instrument. Spectra were initially recorded at the slow-exchange limit and subsequently at the coalescence temperatures (T_c). Temperature calibration was performed immediately following this procedure. With this data and use of the formulas

$$k_c = 2^{-1/2}\pi\Delta\nu \qquad \Delta G^{*} = -RT_c \ln (hk_c/k_BT_c)$$

$\Delta G^{*}{}_c$ was calculated. For comparison to previous studies on similar compounds, the VT NMR of $Cp_2Ti(S_2C_7H_6)$ was also studied ($S_2C_7H_6$ is 3,4-dimercaptotoluene).

Electrochemistry. Electrochemical experiments were performed with Princeton Applied Research equipment, which included a Model 173 potentiostat–galvanostat, Model 176 current-to-voltage converter, and a signal generator built by the SOCS electronics service. Voltammograms were recorded at scan rates from 5 to 200 mV/s on an X-Y recorder. The electrochemical cell employed the standard three-electrode configuration: the working electrode, a Pt disk 1.4 mm in diameter sealed in a glass tube of 7.2-mm o.d., a Pt-wire auxiliary electrode, and the reference electrode. The last consisted of a Ag wire immersed in an acetonitrile solution that was 0.01 M in $AgNO_3$ and 0.1 M in supporting electrolyte and was isolated from the sample solution by a soft-glass–Pyrex cracked frit. All potentials were measured at ambient temperature vs. the Ag/0.01 M Ag^+ couple. Acetonitrile (Aldrich Gold Label) was distilled from CaH_2 under N_2. Solutions were $\sim 10^{-3}$ M in sample and 0.1 M in tetra-*n*-butylammonium tetrafluoroborate. Under these experimental conditions, $E_{1/2}$ for ferrocene was found to be +0.085 V, the cathodic and anodic peak separation was 0.075 V, and i_a/i_c was 1.0 at 0.20 V/s.

X-ray Crystallography. The structure of $(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_3)_2$ was determined by single-crystal X-ray diffraction by Dr.

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(23) Carty, A. M.; Efraty, A. *Can. J. Chem.* **1969**, *47*, 2573.

(24) Vallarino, L. M. *Inorg. Chem.* **1965**, *4*, 161.

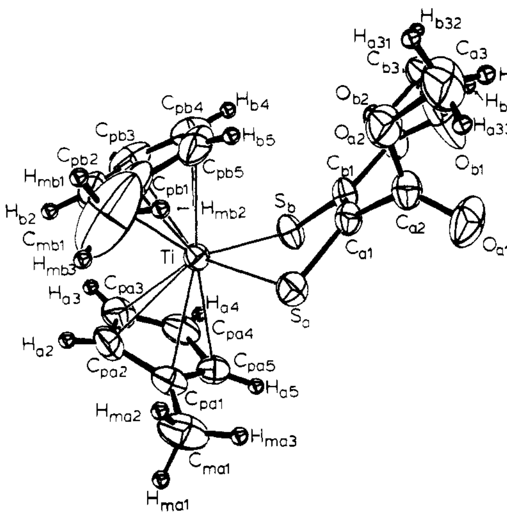

Figure 1. ORTEP drawing of the $(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_3)_2$ molecule with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are represented by arbitrarily small spheres.

C. S. Day of Crystallytics Co., Lincoln, NE. An ORTEP plot of the molecule is depicted in Figure 1, and atomic coordinates are listed in Table I. A full structure report is included in the supplementary material.

Results and Discussion

Synthesis and Characterization of Dicyclopentadienyltitanium 1,2-Alkene Dichalcogenides. This project started with the discovery that the red titanium pentasulfide **1a** reacted with dimethyl acetylenedicarboxylate (DMAD) to give the green dithiolene complex **3a** (Scheme I). The reaction is conveniently performed in refluxing xylenes solution where it was found that, after 2 h, **3a** could be isolated in ca. 40% yield. Also formed in this process was 2,3,4,5-tetrakis(carbomethoxy)thiophene, which arises from the further reaction of sulfur with DMAD. In a separate experiment it was confirmed that **3a** slowly undergoes further reaction with DMAD in refluxing xylenes to give intractable decomposition products (but not the thiophene), which accounts for the modest yield of **3a**.

The synthesis of the diselenene **4a** from **2a** and DMAD proceeds almost quantitatively and under considerably less vigorous conditions than required for the conversion of **1a** to **3a** (Scheme I). The formation of **4a** is accompanied by the precipitation of gray selenium, which, unlike sulfur, is unreactive toward DMAD. In order to obtain materials more suitable for spectroscopic measurements, we extended these reactions to include the methylcyclopentadienyl analogues **1b**–**4b**. Because of their enhanced solubilities, **1b** and **2b** could be synthesized more efficiently than could **1a** and **2a**.

Attempts were made to extend the acetylene addition reaction for the preparation of other diselenene complexes. **2a** did react efficiently with hexafluoro-2-butyne to give the bis(trifluoromethyl)diselenene complex $(C_5H_5)_2TiSe_2C_2(CF_3)_2$ (**5a**). However, with diphenylacetylene in refluxing mesitylene, **2a** afforded a complex mixture from which we could isolate only a small amount of material which possessed the chartreuse color characteristic of the dicyclopentadienyltitanium diselenenes.

The new 1,2-alkene dichalcogenide compounds exist as dark green crystalline solids that readily dissolve in most organic solvents to give air-stable green solutions. In keeping with the well-recognized oxophilic character of titanium(IV),[25] these compounds decompose significantly upon attempted silica gel or alumina chromatography although thin-layer chromatography is useful for their detection. It was found however that these compounds could be effectively purified with use of gel permeation chromatography. This methodology proved particularly important for the dithiolenes as their formation from **1a** or **1b** was complicated by competing side reactions.

Table I. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $(\eta^5\text{-}C_5H_4(CH_3))_2TiS_2C_6O_4H_6$ [a]

atom type[b]	x	y	z
Ti	0.183 69 (3)	−0.051 18 (3)	0.266 55 (3)
S_a	0.226 68 (6)	0.075 37 (5)	0.109 84 (4)
S_b	0.062 80 (6)	0.140 20 (k)	0.368 00 (5)
O_{a1}	0.317 22 (20)	0.426 96 (22)	0.105 30 (20)
O_{a2}	0.498 06 (18)	0.407 10 (19)	0.218 36 (18)
O_{b1}	0.290 28 (35)	0.545 99 (20)	0.389 05 (23)
O_{b2}	0.161 67 (19)	0.454 23 (16)	0.525 84 (14)
C_{a1}	0.257 64 (21)	0.253 64 (20)	0.217 94 (18)
C_{a2}	0.357 94 (23)	0.373 97 (22)	0.175 14 (20)
C_{a3}	0.603 60 (36)	0.526 93 (41)	0.187 99 (46)
C_{b1}	0.190 97 (22)	0.283 39 (20)	0.330 08 (19)
C_{b2}	0.220 86 (26)	0.440 20 (22)	0.415 80 (22)
C_{b3}	0.184 04 (35)	0.604 07 (28)	0.612 74 (27)
C_{pa1}	0.048 79 (24)	−0.253 51 (22)	0.083 86 (20)
C_{pa2}	0.104 73 (28)	−0.312 81 (22)	0.164 63 (25)
C_{pa3}	0.036 27 (28)	−0.277 76 (24)	0.279 74 (24)
C_{pa4}	−0.060 96 (25)	−0.196 12 (25)	0.271 42 (23)
C_{pa5}	−0.053 82 (22)	−0.180 82 (23)	0.151 15 (21)
C_{ma1}	0.082 03 (40)	−0.273 41 (35)	−0.051 58 (25)
C_{pb1}	0.441 38 (25)	−0.050 34 (36)	0.269 44 (28)
C_{pb2}	0.368 01 (26)	−0.133 87 (28)	0.342 74 (28)
C_{pb3}	0.315 62 (30)	−0.040 18 (36)	0.446 47 (26)
C_{pb4}	0.360 69 (35)	0.101 99 (35)	0.441 11 (33)
C_{pb5}	0.435 97 (27)	0.097 47 (32)	0.334 77 (38)
C_{mb1}	0.514 57 (71)	−0.109 54 (112)	0.149 13 (67)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled in agreement with Figure 1.

The dithiolenes prepared in this work appear to be strictly similar to related derivatives such as $(C_5H_5)_2TiS_2C_2(CN)_2$, which has been prepared from $(C_5H_5)_2TiCl_2$ via conventional metathetical reactions.[26] The solid-state structure found for **3b** (Figure 1) by X-ray diffraction is comparable to that found for related compounds.[27] The dithiolene chelate ring is tilted by 44° (with the S_aTiS_b and $S_aC_{a1}C_{a2}C_{b1}C_{b2}S_b$ planes) about the S···S vector; this distortion is due to π donation from the formally dianionic dithiolene to an empty a_1 orbital of the 16e titanium(IV) center.[28] Essential structural parameters for **3b** are collected in Table II. The spectroscopic similarities (Tables III–V) between the crystallographically characterized **3b** and **3a**, **4a**, and **5a** confirm that all of these compounds possess structures very similar to that depicted in Figure 1.

The ^{77}Se NMR spectrum of **4a** was measured at 19 MHz. One absorption was observed, its chemical shift being 1001 ppm downfield of that for neat $(CH_3)_2Se$. This is one of the lowest field chemical shifts reported for any organic derivative of divalent selenium.[29] The extreme downfield shift is consistent with the π acidity of the $(C_5H_4R)_2Ti^{IV}$ moiety and the delocalized nature of the diselenene chelate. For comparison, ^{77}Se chemical shifts for diselenocarbamate complexes fall in the range of 343–717 ppm downfield of $(CH_3)_2Se$.[30]

The NMR properties of the new compounds were subjected to scrutiny because of the relevance of this data to the π interaction between the alkene dichalcogenide ligands and the

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(25) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

(26) Locke, J.; McCleverty, J. A. *Inorg. Chem.* **1966**, *5*, 1157.

(27) Villa, A. C.; Manfredolti, A. G.; Guastini, C. *Acta Crystallogr., Sect. B* **1976**, *B32*, 909 and references therein.

(28) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(29) Rodger, C.; Sheppard, N.; McFarlane, C.; McFarlane, W. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; p 383.

(30) Pan, W.-H.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5783.

Table II. Polyhedral Edge Lengths, Bond Lengths, and Bond Angles Subtended at the Ti Atom in the Coordination Group of $(\eta^5\text{-}C_5H_4(CH_3))_2TiS_2C_6O_4H_6$[a]

type[b]	length, Å	type[b]	length, Å
Ti-S_a	2.442 (1)	Ti-S_b	2.407 (1)
Ti-C_{pa1}	2.420 (2)	Ti-C_{pb1}	2.399 (3)
Ti-C_{pa2}	2.365 (2)	Ti-C_{pb2}	2.380 (3)
Ti-C_{pa3}	2.336 (2)	Ti-C_{pb3}	2.352 (3)
Ti-C_{pa4}	2.348 (2)	Ti-C_{pb4}	2.392 (3)
Ti-C_{pa5}	2.397 (2)	Ti-C_{pb5}	2.398 (3)
Ti-C_{ga}[c]	2.052	Ti-C_{gb}	2.072
$S_a\cdots S_b$	3.189 (1)		
$S_a\cdots C_{gb}$[c]	3.615	$S_b\cdots C_{ga}$[c]	3.568
$S_a\cdots C_{gb}$[c]	3.678	$S_b\cdots C_{gb}$[c]	3.654
$C_{ga}\cdots C_{gb}$[c]	3.773		

type[b]	angle, deg	type[b]	angle, deg
S_aTiS_b	82.23 (2)	$C_{ga}TiC_{gb}$[c]	132.43
S_aTiC_{ga}[c]	106.80	S_bTiC_{ga}[c]	105.99
S_aTiC_{gb}[c]	108.86	S_bTiC_{gb}[c]	109.09

[a] The numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled in agreement with Figure 1. [c] The symbols C_{ga} and C_{gb} are used to denote the center of gravity for the A and B cyclopentadienyl rings, respectively.

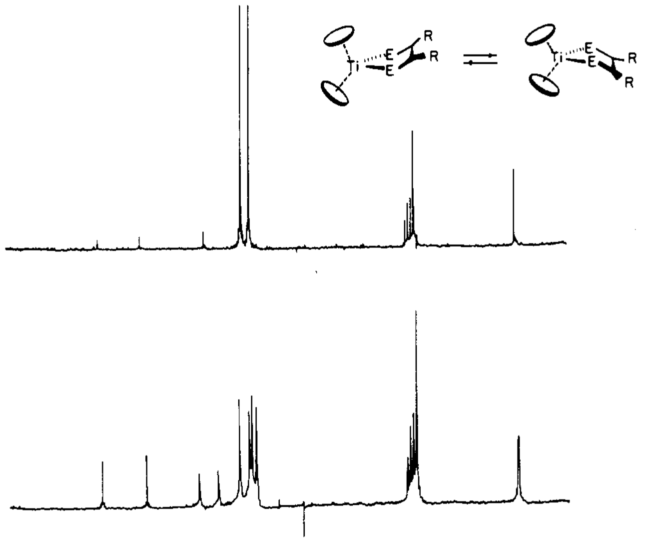

Figure 2. ^{13}C NMR spectra (25.2 MHz) of $(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_3)_2$ at 20 (top) and -90 °C (bottom).

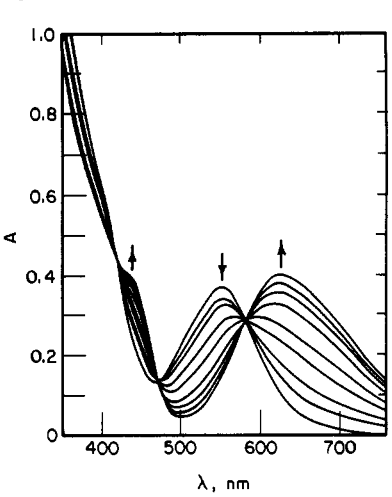

Figure 3. Electronic absorption spectra recorded at various stages of the $(C_5H_5)_2TiSe_5$ + DMAD reaction: $[(C_5H_5)_2TiSe_5]_i = 1.71 \times 10^{-2}$ M; $[DMAD]_i = 8.36 \times 10^{-2}$ M. The solvent was $1,2\text{-}C_2H_4Cl_2$.

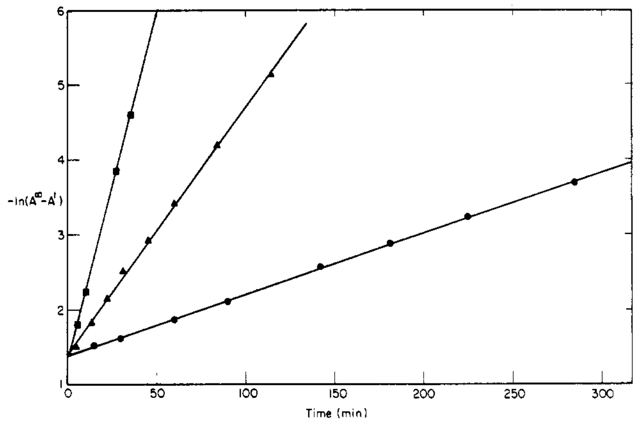

Figure 4. First-order plots of $-\ln(A_\infty(554) - A_t(554))$ vs. time for various initial DMAD concentrations: (●) $[(C_5H_5)_2TiSe_5]_i = 1.71 \times 10^{-2}$ M, $[DMAD]_i = 8.36 \times 10^{-2}$ M; (▲) $[(C_5H_5)_2TiSe_5]_i = 1.68 \times 10^{-2}$ M, $[DMAD]_i = 3.87 \times 10^{-1}$ M; (■) $[(C_5H_5)_2TiSe_5]_i = 1.60 \times 10^{-2}$ M, $[DMAD]_i = 9.04 \times 10^{-1}$ M. Reactions were performed in refluxing $1,2\text{-}C_2H_4Cl_2$.

titanium center. Variable-temperature ^1H NMR studies provided activation energies for the degenerate ring inversion process[31] (Table V). The ^{13}C NMR spectra of **3b** at two different temperatures are depicted in Figure 2. The activation energy for these ring inversion reactions is related to the energy difference between the C_2 (π bonding) and C_{2v} (no net π bonding) conformers. It was therefore surprising to find that activation energies measured indicate that the π bonding is largely insensitive both to the nature of the chalcogenide (S or Se) and to the organic substituents (toluenedithiolate vs. bis(carboxymethyl)ethylenedithiolate).

The electrochemistry of the titanium dithiolenes and diselenenes was characterized. The cyclic voltammograms for **3a**, **3b**, and **4a** were similar and were interpreted as consisting of a reversible one-electron reduction process at ~-1.20 V and an irreversible oxidation at ~+0.55 V (relative to Ag/0.01 M $AgNO_3$). A reasonable interpretation of this data is that the reduction is metal localized; the resulting $(C_5H_4R)_2TiE_2C_2R_2^-$ compounds would be isoelectronic with the known neutral vanadium(IV) analogues.[32] The 16e titanium unit apparently does not stabilize a ligand-based oxidation to the radical cation.

Kinetics and Mechanism. The kinetics of the conversion of **2a** and **4a** were determined spectrophotometrically as a function of DMAD and pentaselenide concentrations. The results of a typical experiment are shown in Figure 3 and illustrate the dramatic color change that characterizes this process. The rate of the reaction in refluxing 1,2-dichloroethane (bp 83.5 °C) was found to be first order in **2a** over the concentration range (1.94×10^{-3})-(1.71×10^{-2}) M and first-order in DMAD over the range (8.36×10^{-2})-(9.04×10^{-1}) M. The effect of [DMAD] on the observed rate is illustrated in Figure 4. From these data a second-order rate constant of $(1.58 \pm 0.22) \times 10^{-3}$ M^{-1} s^{-1} was deduced. Second-order rate constants determined at 60.1, 70.1, and 83.5 °C indicate activation parameters of -19 cal/(mol K) for $\Delta S^\ddagger$ and 19 kcal/mol for $\Delta H^\ddagger$. The reaction kinetics were not affected by the presence of 2% galvinoxyl. The second-order rate constant measured in refluxing benzene solution (bp 80.5 °C) was 1.06×10^{-3} M^{-1} s^{-1}, indicative that solvent effects are modest.

The observed kinetic behavior, in conjunction with other studies, suggests an associative mechanism for the acetylene

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(31) Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 134.

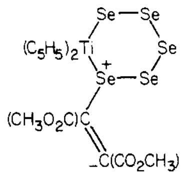
(32) Casey, A. T.; Thackeray, J. R. *Aust. J. Chem.* **1975**, *28*, 471.

Table III. NMR and IR Data for New Compounds

compd	^{1}H NMR^a (CDCl$_3$), ppm	IR, cm^{-1}	^{13}C, ^{19}F, ^{31}P, ^{77}Se NMR,^{a} ppm
$(CH_3C_5H_4)_2TiS_5$ (**1b**)	6.18 (2 H, m) 6.13 (2 H, m) 6.09 (2 H, m) 5.92 (2 H, m) 2.26 (3 H, s) 2.00 (3 H, s)	1039 (m), 1021 (m), 903 (m) 840 (sh), 834 (s)	
$(CH_3C_5H_4)_2TiSe_5$ (**2b**)	6.24 (2 H, m) 6.08 (2 H, m) 5.97 (2 H, m) 5.82 (2 H, m) 2.32 (3 H, s) 1.98 (3 H, s)	1024 (m), 1008 (m), 890 (m), 882 (m), 836 (m), 817 (s)	
$(C_5H_5)_2Ti(S_2C_2(CO_2CH_3)_2)$ (3a)	6.00 (10 H, s) 3.76 (6 H, s)	3120 (m), 1740 (s), 1685 (s), 1240 (s), 1015 (s), 825 (s)	
$(CH_3C_5H_4)_2Ti(S_2C_2(CO_2CH_3)_2)$ (**3b**)	5.93 (8 H, s) 3.80 (6 H, s) 2.05 (6 H, s)	3116 (w), 3095 (w), 1729 (s), 1695 (s), 1232 (s), 1010 (m), 826 (m), 803 (m)	^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 165.8, 150.9, 127.9, 114.8, 111.7, 52.8, 16.5
$(C_5H_5)_2Ti(Se_2C_2(CO_2CH_3)_2)$ (4a)	6.20 (10 H, s) 3.82 (6 H, s)	3120 (m), 1715 (s), 1685 (s), 1240 (s), 830 (s)	^{77}Se{^{1}H} NMR (CDCl$_3$): 1001 (s)
$(C_5H_5)_2Ti(Se_2C_2(CF_3)_2)$ (**5a**)	6.31 (s)^b	3125 (w), 1561 (s), 1231 (vs), 1160 (vs), 1122 (vs), 1025 (w), 1015 (w), 843 (m), 829 (s), 818 (s), 686 (s)	^{19}F NMR (acetone-d_6): −52.9 (s)
$Pt(Se_2C_2(CO_2CH_3)_2)(P(C_6H_5)_3)_2$	7.30 (30 H, m) 3.65 (6 H, s)	1722 (s), 1680 (m), 1544 (s), 1225 (s), 1090 (m), 735 (m), 718 (m), 696 (sh), 683 (m)	^{31}P{^{1}H} NMR (CDCl$_3$): 15.7 (s); $^1J_{PPt}$ = 2931 Hz, $^2J_{PSe}$ = 52 Hz
$Pt(S_2C_2(CO_2CH_3)_2)(P(C_6H_5)_3)_2$	7.22 (30 H, m) 3.60 (6 H, s)	1741 (vs), 1711 (s), 1694 (s), 1545 (s), 1491 (m), 1446 (s), 1238 (vs), 1190 (m), 1097 (m), 1081 (sh), 1021 (s), 741 (s), 685 (s)	^{31}P{^{1}H} NMR (CDCl$_3$): 17.7 (s); $^1J_{PPt}$ = 2877 Hz
$Ni(Se_2C_2(CO_2CH_3)_2)(P(C_6H_5)_2(CH_2)_3P(C_6H_5)_2)$	7.45 (20 H, m)^c 3.55 (6 H, s) 2.41 (6 H, m)	1730 (s), 1706 (s), 1560 (s), 1448 (s), 1231 (vs), 1102 (m), 975 (m), 833 (m), 741 (m), 692 (s)	^{31}P{^{1}H} NMR (33% CD$_2$Cl$_2$, 67% CH$_2$Cl$_2$): 48.5 (br)
$Pt_2(Se_2C_2(CO_2CH_3)_2)_2(Ph_2PC_2PPh_2)_2$	7.25 (40 H, m) 3.78 (12 H, s)	1730 (vs), 1559 (s), 1446 (s), 1233 (vs), 1098 (m), 1058 (m), 1016 (m), 831 (s), 738 (m), 685 (s)	
$(AsPh_4)[Rh(Se_2C_2(CO_2CH_3)_2)(CO)_2]$	7.70 (20 H, m) 3.65 (6 H, s)	2002 (s), 1922 (s)	
$(CH_3)_2Se_2C_2(CO_2CH_3)_2$	3.84 (6 H, s) 2.26 (6 H, s)	1730 (vs), 1711 (vs), 1556 (s), 1442 (s), 1430 (s), 1245 (vs), 1070 (m), 1008 (s), 978 (m), 921 (m), 892 (m), 761 (s), 719 (s)	
$(S)CSe_2C_2(CO_2CH_3)_2$	3.90 (s)	1746 (vs), 1718 (vs), 1557 (s), 1422 (s), 1235 (vs), 1055 (s), 1027 (m), 987 (m), 734 (m), 725 (m)	

^{a} Chemical shifts are quoted (upfield shifts being negative) relative to the following standards: Si(CH$_3$)$_4$ (^{1}H and ^{13}C), CFCl$_3$ (^{19}F), 85% H$_3$PO$_4$ (^{31}P), and neat (CH$_3$)$_2$Se (^{77}Se). ^{b} Acetone-d_6 solvent. ^{c} CD$_2$Cl$_2$ solvent.

addition reaction whereby the acetylene binds to the chalcogenide chelate ring in the rate-determining step. A reasonable mechanistic scenario for diselenene formation would involve a dipolar intermediate[33]



wherein the acetylene is attached to a titanium-bound selenium atom.

The final word on the regiochemistry of the acetylene addition must await the results of a labeling study; however, recent experiments indicate that it is the titanium-bound chalcogenides that bind the acetylene. Relevant to this issue is the compound $[(CH_3C_5H_4)_2Ti]_2S_4$, which is related to **1b** by replacement of its unique sulfur with a $(CH_3C_5H_4)_2Ti$ moiety. Since all of the sulfur atoms in this Ti_2S_4 ring are adjacent to titanium atoms, it is significant that it reacts very efficiently with DMAD (41 °C, 12 h) to give dithiolene **3b** in good yield.[14]

The distinct differences in reactivity of compounds **1** and **2** toward DMAD is illustrated by a competition experiment. An equimolar mixture of **1b** and **2a** was partially reacted with DMAD in refluxing 1,2-dichloroethane. A 360-MHz ^{1}H NMR analysis of the titanium-containing products of this experiment revealed the presence of unreacted **1b**, some **2a**, and **4a**. The sum of the concentrations of **4a** and **2a** was equal to the concentration of **1b**. Absolutely no evidence was found for any **3b**, which would result from the addition of DMAD to **1b**, or any **4b**, which would result from the capture of a reactive organoselenium intermediate by **1b**.

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(33) Winterfeldt, E. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 423.

Table IV. Mass Spectral Data[a]

compd	*m/e* (*I*/base)	assignt
$(C_5H_5)_2Ti(S_2C_2(CO_2CH_3)_2)$ (**3a**)	384 (41%)	M^+
	319 (13%)	$(C_5H_5)Ti(S_2C_2(CO_2CH_3)_2)^+$
	291 (18%)	$(C_5H_5)Ti(S_2C_2(CO_2CH_3)(OCH_3))^+$
	178 (100%)	$(C_5H_5)_2Ti^+$
	175 (55%)	$(C_5H_5)Ti(OCH_3)_2{}^+$
$(CH_3C_5H_4)_2Ti(S_2C_2(CO_2CH_3)_2)$ (**3b**)	412 (39%)	M^+
	333 (18%)	$(CH_3C_5H_4)Ti(S_2C_2(CO_2CH_3)_2)^+$
	305 (29%)	$(CH_3C_5H_4)Ti(S_2C_2(CO_2CH_3)(OCH_3))^+$
	206 (100%)	$(CH_3C_5H_4)_2Ti^+$
	189 (77%)	$(CH_3C_5H_4)Ti(OCH_3)_2{}^+$
$(C_5H_5)_2Ti(Se_2C_2(CO_2CH_3)_2)$ (**4a**)	480 (6%)	M^+
	338 (3%)	$(C_5H_5)_2TiSe_2{}^+$
	178 (100%)	$(C_5H_5)_2Ti^+$
	113 (10%)	$(C_5H_5)Ti^+$
$(C_5H_5)_2Ti(Se_2C_2(CF_3)_2)$ (**5a**)	500 (2%)	M^+
	197 (9%)	$(C_5H_5)_2TiF^+$
	178 (100%)	$(C_5H_5)_2Ti^+$
	113 (10%)	$(C_5H_5)Ti^+$
$Pt(Se_2C_2(CO_2CH_3)_2(P(C_6H_3)_2))$	1020[b]	M^+
$(CH_3)_2Se_2C_2(CO_2CH_3)_2$	332 (100%)	M^+
	317 (47%)	$(CH_3)Se_2C_2(CO_2CH_3)_2{}^+$
	190 (44%)	$(CH_3)_2Se_2{}^+$
	175 (39%)	$(CH_3)_2Se^+$
$(S)CSe_2C_2(CO_2CH_3)_2$	346 (61%)	M^+
	302 (17%)	$Se_2C_2(CO_2CH_3)_2{}^+$
	111 (70%)	$CH_3O_2CC_2(CO)^+$
	59 (100%)	CH_3CS^+

[a] Unless indicated otherwise, these data were obtained from the 70-eV electron impact mass spectra. [b] Field desorption mass spectrum.

Table V. Variable-Temperature ^1H NMR Data

compd	solvent	$\Delta\nu$, Hz	T_c, °C[a]	$\Delta G^\ddagger{}_c$, kcal/mol[b]
$(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ (**3a**)	CD_2Cl_2	27.6	−34	11.9
$(C_5H_5)_2TiSe_2C_2(CO_2CH_3)_2$ (**4a**)	CD_2Cl_2	25.0	−27	12.3
$(C_5H_5)_2TiS_2C_6H_3$-4-CH_3	CD_2Cl_2	53.2	−10	12.8[c]
$(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ (**3a**)	CS_2	54.2	−3	13.2

[a] T_c = coalescence temperature. [b] See the Experimental Section. [c] Reported, 11.5 kcal/mol.[32]

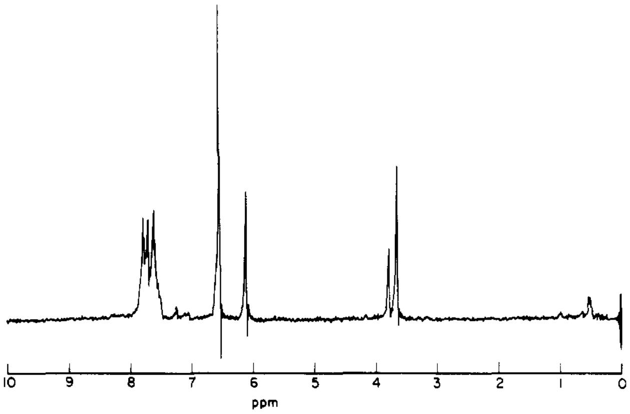
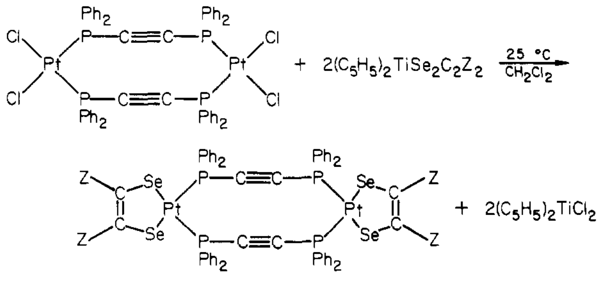


Figure 5. ^1H NMR spectrum (90 MHz) of a solution prepared by dissolving 3 equiv of $(C_5H_5)_2TiSe_2C_2(CO_2CH_3)_2$ (**4a**) and 2 equiv of $(Ph_4As)[RhCl_2(CO)_2]$ in $CDCl_3$. The assignments are as follows: 7.5–7.9 ppm (m, Ph_4As^+), 6.75 (s, $(C_5H_5)_2TiCl_2$), 6.12 (s, **4a**), 3.80 (s, **4a**), 3.67 (s, $[Rh(Se_2C_2(CO_2CH_3)_2)(CO)_2]^-$).

Transmetalation and Removal of the Diselenene Chelates. Our template synthesis of the diselenene chelates is notable since the previous route to this class of ligands employs extremely vigorous reaction conditions.[21] It was therefore of interest to find that the titanium-bound diselenene ligands could be easily transferred to other metals. Our approach exploits both the halophilicity of titanium(IV) and the thiophilicity of the later transition metals. For example, addition of $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$ to a dichloromethane solution containing an equimolar quantity of **4a** resulted in the complete bleaching of the latter's dark green color in minutes. Filtration of the solution through alumina or silica gel quantitatively removed the oxophilic[25] $(C_5H_5)_2TiCl_2$ moiety, affording solutions from which $Ni(Se_2C_2(CO_2CH_3)_2)(Ph_2PCH_2CH_2CH_2PPh_2)$ could be isolated in 93% yield. In a completely similar manner, $Pt(E_2C_2(CO_2CH_3)_2)(PPh_3)_2$ (E = S, Se) and $Pt_2(Se_2C_2(CO_2CH_3)_2)_2(Ph_2PC{\equiv}CPPh_2)_2$ were prepared from their chloro complexes. Interestingly, chelate transfer to the binuclear platinum complex (eq 2) was considerably more facile than the same reaction involving *cis*-$PtCl_2(PPh_3)_2$. Chelate transfer involving $(AsPh_4)[RhCl_2(CO)_2]$ and **4a** was characterized by ^1H NMR spectroscopy (Figure 5) where it was seen that the reaction is rapid and clean. The solution IR spectrum of the yellow reaction solution showed two terminal carbonyl bands consistent with the presence of $[Rh(Se_2C_2(CO_2CH_2)_2)(CO)_2]^-$, which is analogous to the known $[Rh(mnt)(CO)_2]^-$.[34]



(2)

While the titanium diselenenes do not react directly with conventional organic halides, we have found that **4a** does react readily with thiophosgene, $SCCl_2$. The overall process resembles the aforementioned transmetalation reaction, and the stable crystalline 3,4-bis(carboxymethyl)-2,5-diselena-1-thione[35] was isolated in high yield (eq 3). Interest in this class of organic heterocycles has increased in recent years because

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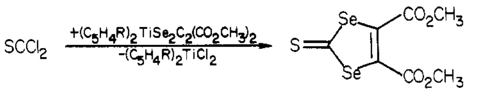
[34] Cheng, C.-H.; Spivack, B. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 3303.

[35] Engler, E. M.; Patel, V. V.; Schumaker, R. R. *J. Chem. Soc., Chem. Commun.* **1977**, 835.



(3)

of their involvement in the synthesis of tetrathiafulvalenes and their selenium analogues.[36]

In closing this section it should be pointed out that other organosulfur derivatives of d^0 and d^{10} metals are known to function as ligand-transfer reagents. Abel's group in particular has made extensive use of tin(IV) mercaptides in this capacity.[37,38] The unique feature of our approach is that the organotitanium species function as *both* synthetic templates and transfer reagents. Since $(C_5H_4R)_2TiCl_2$ is both the precursor to pentachalcogenides **1** and **2** and the product of the chelate-transfer reactions, its role is formally catalytic (Scheme II).

Scheme II

$$\begin{aligned} &(C_5H_4R)_2TiCl_2 + E_5^{2-} \rightarrow (C_5H_4R)_2TiE_5 + 2Cl^- \\ &(C_5H_4R)_2TiE_5 + RC\equiv CR \rightarrow (C_5H_4R)_2TiE_2C_2R_2 + 3E \\ &(C_5H_4R)_2TiE_2C_2R_2 + L_nMCl_2 \rightarrow \\ &\qquad (C_5H_4R)_2TiCl_2 + L_nME_2C_2R_2 \\ \hline &L_nMCl_2 + E_2^{2-} + RC\equiv CR \rightarrow L_nME_2C_2R_2 + 2Cl^- \end{aligned}$$

We were able to exploit the high oxophilicity of our titanium(IV) dithio- and diselenochelates in an alternative method of transferring the template-synthesized diselenene moiety. Thus treatment of solutions of **4a** with sodium methoxide effected a rapid color change from deep green to dark purple. This color change is consistent with release of $Na_2Se_2C_2(CO_2CH_3)_2$ concomitant with the formation of a titanium methoxide complex (eq 4). Addition of methyl iodide or *cis*-$PtCl_2(PPh_3)_2$ discharges the purple color concomitant with the formation of the anticipated neutral derivatives (eq 5, 6) in excellent yields.

$$(C_5H_4R)_2TiSe_2C_2(CO_2CH_3)_2 + 2NaOCH_3 \rightarrow (C_5H_4R)_2Ti(OCH_3)_2 + Na_2Se_2C_2(CO_2CH_3)_2 \quad (4)$$

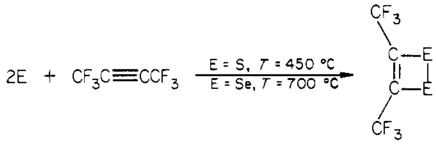
$$Na_2Se_2C_2(CO_2CH_3)_2 + 2CH_3I \rightarrow (CH_3Se)_2C_2(CO_2CH_3)_2 + 2NaI \quad (5)$$

$$Na_2Se_2C_2(CO_2CH_3)_2 + cis\text{-}PtCl_2(PPh_3)_2 \rightarrow Pt(Se_2C_2(CO_2CH_3)_2)(PPh_3)_2 + 2NaCl \quad (6)$$

Summary

The dicyclopentadienyltitanium pentachalcogenides have been found to react with activated acetylenes to form dicyclopentadienyltitanium 1,2-alkene dichalcogenides. The conditions required to effect the diselenene synthesis are dramatically milder than for the dithiolene synthesis. This reactivity involves the nucleophilic attack of a titanium-bound polychalcogenide on the acetylene as suggested by the following facts: (1) only activated, electrophilic acetylenes react in moderate to high yield, (2) the results of the kinetic studies indicate a nonradical bimolecular pathway, (3) $Cp_4Ti_2S_4$ (wherein all of the chalcogenides are equivalent) reacts efficiently with activated acetylenes to give the dithiolene,[14] and (4) $(C_5H_4R)_2TiSe_5$ reacts in a more efficient manner and under milder conditions than does $(C_5H_4R)_2TiS_5$. We attribute this reactivity difference to the greater nucleophilicity of the titanium polyselenide compared to the corresponding polysulfide. A similar situation is observed for compounds $[Ir(Ph_2PCH_2CH_2PPh_2)_2E_2]Cl$ (E = S, Se) where the diselenide is seen to be decisively more nucleophilic than the disulfido complex.[39] These findings are in accord with relative nucleophilicities of the organic chalcogenides,[40] RS^- and RSe^-, as well as their metal complexes.[41]

The dicyclopentadienyltitanium dithiolenes and diselenenes in this study were found to transfer their chelates to transition-metal and organic halides in high yield and under extremely mild conditions. In the case of the diselenenes, this reaction may be of some utility since the only route to such compounds requires vigorous conditions[21] (eq 7).



(7)

In an effort to extend these studies, we are presently examining the chemistry of the known vanadium pentachalcogenides, $(C_5H_4R)_2VE_5$ (E = S, Se).[4]

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Registry No. **1a**, 12116-82-4; **1b**, 78614-86-5; **2a**, 12307-22-1; **2b**, 78614-88-7; **3a**, 78961-80-5; **3b**, 82865-09-6; **4a**, 82865-10-9; **4b**, 82865-11-0; **5a**, 82865-12-1; $Pt(Se_2C_2(CO_2CH_3)_2)(PPh_3)_2$, 82865-13-2; $Pt_2(Se_2C_2(CO_2CH_3)_2)_2(Ph_2PC\equiv CPPh)_2$, 82865-14-3; $Ni(Se_2C_2(CO_2CH_3)_2(Ph_2PCH_2CH_2CH_2PPh_2)$, 82865-15-4; $Pt(S_2C_2(CO_2CH_3)_2)(PPh_3)_2$, 82865-16-5; $(AsPh_4)[Rh(Se_2C_2(CO_2CH_3)_2(CO)_2]$, 82865-18-7; $(CH_3C_5H_4)_2TiCl_2$, 1282-40-2; *cis*-$PtCl_2(PPh_3)_2$, 15604-36-1; $Pt_2Cl_4(Ph_2PC\equiv CPPh_2)_2$, 21108-38-3; $NiCl_2$(dppp), 15629-92-2; $(AsPh_4)[RhCl_2(CO)_2]$, 30193-19-2; DMAD, 762-42-5; $(CH_3)_2Se_2C_2(CO_2CH_3)_2$, 82849-75-0; $(S)CSe_2C_2(CO_2CH_3)_2$, 66251-93-2; $(C_5H_5)_2TiS_2C_6H_3$-4-CH_3, 12094-79-0; hexafluoro-2-butyne, 692-50-2.

Supplementary Material Available: A listing of analytical data on new compounds and a structural analysis report including a description of details of structure analysis and refinement and tables of bond distances, bond angles, intermolecular contacts, thermal parameters for all atoms, and structure factors (33 pages). Ordering information is given on any current masthead page.

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(36) Narita, M.; Pittman, C. U., Jr. *Synthesis* **1976**, 489.
(37) Abel, E. W.; Armitage, D. A. *Adv. Organomet. Chem.* **1967**, *5*, 1.
(38) For a recent example of this approach, see: Uson, R.; Vicente, J.; Oro, J. *Inorg. Chim. Acta* **1981**, *52*, 29.
(39) Hoots, J. E.; Rauchfuss, T. B., unpublished results.
(40) Pearson, R. G.; Sobel, H.; Songsted, J. *J. Am. Chem. Soc.* **1968**, *90*, 319.
(41) Root, M. J.; Deutsch, E. *Inorg. Chem.* **1981**, *20*, 4376.