thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.

Crystal Data for Compound 9. Crystals suitable for X-ray analysis were obtained by slow evaporation of toluene from the reaction mixture described above. Crystallographic data are summarized in Table VII. Single crystals are (at 20 °C) monoclinic, space group $P2_1/n$, with a = 19.928 (4) Å, b = 12.198 (2) Å, c = 26.345 (5) Å, β = 111.09 (1)°, V = 5975 (2) Å^3, and Z = 4 (D_{calcd} = 1.54 g cm^{-3}; μ_a(Mo Kα) = 2.55 mm^{-1}). A total of 9541 independent reflections having 2θ(Mo Kα) < 48.3° (the equivalent of 0.7 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation. The structure was solved by use of "direct methods" techniques with a Nicolet SHELXTL software package as modified at Crystalytics Co. The resulting structural parameters were refined to convergence (R_1 (unweighted, based on F) = 0.039 for 6002 independent absorption-corrected reflections having 2θ(Mo Kα) < 48.3° and $I > 3\sigma(I)$) with use of counterweighted cascade block-diagonal least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Hydrogen atom H_o was located from a difference Fourier map and refined as an independent isotropic atom. The methyl groups were included in the refinement as idealized sp^3-hybridized rigid rotors and gave final values for the SiCH angles that ranged from 96 to 121°. The remaining hydrogen atoms were fixed at idealized sp^3-hybridized positions with a C-H bond length of 0.96 Å.

Acknowledgment. We thank Dr. Yukio Kinoshita for the structural analysis of **6**, Dr. Cynthia Day of Crystalytics Co. for the structural analysis of **9**, and the Office of Naval Research for financial support.

Supplementary Material Available: Detailed information concerning the crystallographic analysis of **6** and **9**, which includes listings of anisotropic temperature factors and positional parameters of hydrogen atoms (14 pages); listings of observed and calculated structure factors (104 pages). Ordering information is given on any current masthead page.

Structure and Reactivity of a Titanocene η^2-Thioformaldehyde Trimethylphosphine Complex

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Received January 17, 1990

Bis(η^5-cyclopentadienyl)titanium titanocene η^2-thioformaldehyde trimethylphosphine (**3**) was prepared from titanocene methylidene trimethylphosphine and either sulfur-containing compounds (e.g., alkene sulfides, triphenylphosphine sulfide) or elemental sulfur. The product **3** crystallized in the orthorhombic system, in space group *Pnma* (No. 62), with a = 13.719 (3) Å, b = 12.384 (1) Å, c = 8.671 (1) Å, V = 1473.2 (6) Å^3; Z = 4. The reaction with *trans*-styrene sulfide-d_1 produced an equimolar mixture of *trans*- and *cis*-styrene-d_1 as byproducts, suggesting a stepwise reaction. The formation of a six-membered ring from titanocene methylidene trimethylphosphine and trimethylene sulfide also supports the stepwise mechanism. A biradical mechanism is preferred in view of the biradical mechanism observed in the analogous reaction with styrene oxide. The complex **3** reacted with methyl iodide to produce the cationic titanocene η^2-thiomethoxymethyl trimethylphosphine complex **5a**, which crystallized with acetonitrile in the orthorhombic system, space group *Pbca* (No. 61) with a = 14.839 (2) Å, b = 15.184 (14) Å, c = 18.461 (3) Å, V = 4159.5 (14)Å^3, Z = 8. Complexes **5b,c** having a less coordinating anion such as BF_4 or BPh_4 were obtained, and complex **5c** was converted to a trimethylphosphine-free complex by equilibration with copper(I) chloride. This cationic species (**7c**) does not catalyze the polymerization of ethylene or methyl vinyl ether in dichloromethane.

Titanocene metallacycles[1] react with a wide variety of organic and inorganic reagents. Methylene transfer to organic carbonyls, including enolizable carbonyls, is one of the most general reactions of these complexes.[2,3] Other important reactions include ring-opening polymerization of cyclic olefins,[4] complexation with metal halides,[5] and olefin metathesis.[6] All these reactions occur through a reactive intermediate that exhibits behavior consistent with that of a transition-metal methylene complex.[7] The titanocene methylidene trimethylphosphine complex, which is derived from titanocene metallacyclobutanes, reacts in a similar fashion.[8]

This family of compounds also provides a new route to thioformaldehyde complexes. Thioaldehydes are known to be stabilized through coordination to transition metals.[9] Although several thioaldehyde complexes of late transition metals have been reported, a zirconium complex is the only reported early-transition-metal analogue.[9a,b] The reaction of the titanocene methylidene trimethylphosphine complex with either organic sulfur compounds or elemental sulfur

† Contribution No. 7893.

(1) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariga, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358-7361.

(2) (a) Clawson, L. E.; Buchwald, S. L.; Grubbs, R. H. *Tetrahedron Lett.* **1984**, *50*, 5733. (b) Brown-Wensley, K. A. Ph.D. Thesis, California Institute of Technology, Pasadena, California, 1981. (c) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270-3272. (d) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2316-2323. (e) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 855-856. (f) For review, see: Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L. F.; Clawson, L. E.; Ho, S.; Meinhart, J. D.; Stille, J. R.; Straus, D. A.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733-1744.

(3) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664-1665.

(4) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733-742. For reviews, see: (b) Calderon, N. *J. Macromol. Sci.-Rev. Macromol Chem.* **1972**, *C7*(1), 105-159. (c) Katz, J. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219-226.

(5) (a) Mackenzie, P. B.; Ott, K. C.; Grubbs, R. H. *Pure Appl. Chem.* **1984**, *56*, 59-61. (b) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402-6404. (c) Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1319-1327. (d) Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8-14.

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Table I. Selected Bond Distances and Angles for Complex 3

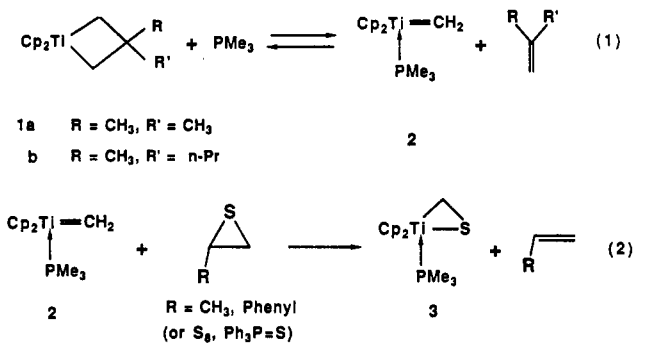
	Distance, Å		
Ti-S	2.452 (1)	S-C1	1.744 (3)
Ti-P	2.601 (1)	P-C2	1.824 (5)
Ti-C1	2.245 (3)	P-C3	1.813 (4)
Ti-CP_a	2.097	C1-$H1_a$	0.90 (3)
	Angle, deg		
CP_a-Ti-S	115.6	C1-S-Ti	62.0 (1)
CP_a-Ti-P	102.3	S-C1-Ti	74.7 (1)
CP_a-Ti-C1	104.2	$H1_a$-C1-Ti	118.2 (19)
CP_b-Ti-CP_a	127.4	$H1_a$-C1-S	115.2 (19)
S-Ti-P	74.1 (0)	$H1_a$-C1-$H1_a$	111.1 (27)
C1-Ti-S	43.3 (1)		

produces the corresponding thioformaldehyde complex in good yield.

The reaction of metal carbenes with organic sulfides or elemental sulfur to make thioformaldehyde complexes serves as a model for the heterogeneous hydrodesulfurization (HDS) reaction[10] and the poisoning of catalysts during the Fischer–Tropsch reaction.[11]

Results and Discussion

The complex $Cp_2Ti(\eta^2\text{-}CH_2S)\cdot PMe_3$ (**3**) was prepared from the compound $Cp_2Ti{=}CH_2\cdot PMe_3$ (**2**), a well-characterized titanocene methylidene compound, and various sulfur-containing compounds including elemental sulfur (eqs 1 and 2). Reaction of **2** with propene sulfide gave



3 in the highest yield (83% by NMR, 70% isolated based on **2**). Easily polymerized styrene sulfide and crude cyclohexene sulfide (purity was 85%) gave **3** in lower yields (42% and 65%, respectively). Elemental sulfur and triphenylphosphine sulfide gave the same product, **3**, in a similar yield (41% and 35%, respectively) as well as several unidentified paramagnetic species. In all the above reactions, complex **3** was the only organometallic compound observed when the reaction was followed by ^1H NMR spectroscopy.

Table II. Selected Bond Distances and Angles for Complex 5a

	Distance, Å		
Ti-S	2.555 (1)	S-CS2	1.803 (7)
Ti-CS_1	2.215 (5)	I-Ti	5.027 (1)
Ti-P	2.581 (1)	I-S	4.075 (1)
Ti-Cp_a	2.065	N-Ti	5.132 (7)
Ti-Cp_b	2.078	N-S	5.372 (7)
S-CS1	1.751 (5)		
	Angle, deg		
Cp_a-Ti-Cp_b	130.7	Ti-CS1-S	79.3 (2)
Cp_a-Ti-P	102.3	Ti-S-CS1	58.4 (2)
Cp_b-Ti-P	102.4	CS1-S-CS2	105.4 (3)
Cp_a-Ti-S	107.3	Ti-S-CS2	119.0 (2)
Cp_b-Ti-S	99.6	HCS1CS1-HCS2	104.9 (35)
Cp_a-Ti-CS1	115.8 (1)	S-CS1-HCS1	115.7 (23)
Cp_b-Ti-CS1	112.1 (1)	S-CS1-HCS2	116.0 (26)
P-Ti-CS1	73.0 (1)	Ti-CS1-HCS1	122.9 (23)
S-Ti-CS1	42.3 (1)	Ti-CS1-HCS2	117.0 (26)
S-Ti-P	115.2 (4)	C5-C4-N	177.0 (8)

Table III. Crystal and Intensity Collection Data for Complex 3

formula: $C_{14}H_{21}SPTi$
formula wt: 300.25
crystal color: red
a = 13.719 (3) Å
b = 12.384 (1) Å
c = 8.671 (1) Å
V = 1473.2 (6) Å^3
Z = 4
λ = 0.7107 Å
T = 21 °C
graphite monochromator
space group: *Pnma*
absences: $hk0$, h odd; $0kl$, $k + l$ odd
crystal size: 0.48 × 0.41 × 0.56 mm
μ = 8.22 cm^{-1} (μr_{max} = 0.35)
CAD-4 diffractometer
θ–2θ scan
2θ range: 2–50°
octants coll: h, k, $\pm l$
no. of reflns measd: 2969
no. of indep reflns: 1354
no. with $F_o^2 > 0$: 1319
no. with $F_o^2 > 3\sigma(F_o^2)$: 1200
GOF for merging data: 0.991 (R factor for 1153 reflns with 2 obsns = 0.020)
final R index: 0.0311
final GOF: 2.75

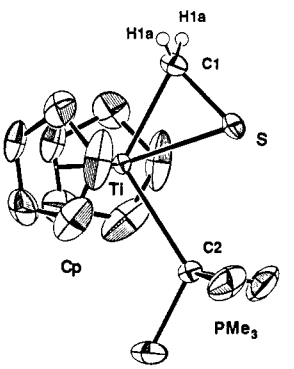


Figure 1. ORTEP diagram of complex **3**. The ellipsoids are drawn at 50% probability level except for the hydrogen atoms. The hydrogen atoms of the cyclopentadienyl and PMe_3 ligands are omitted for clarity.

(6) (a) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1978**, *101*, 5074–5075. (b) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37–51. (c) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876–6878. (d) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491–7496. (e) Straus, D. A.; Grubbs, R. H. *J. Mol. Catal.* **1985**, *28*, 9–25.

(7) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880–4890.

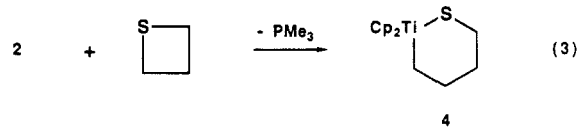
(8) Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583–589.

(9) (a) Buchwald, S. L.; Nielson, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171–3175. (b) Buchwald, S. L.; Nielson, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590–1591. (c) Buhro, W. E.; Etter, M. C.; Georgiou, S.; Gladysz, J. A.; McCormick, F. B. *Organometallics* **1987**, *6*, 1150–1156. (d) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1987**, *6*, 1717–1727. (e) Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 310–311. (f) Hofman, L.; Werner, H. *Chem. Ber.* **1985**, *118*, 4229. (f) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939–5940.

(10) For homogeneous model of HDS, see: (a) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897–1903. (b) Sanchez-Delgado, R. A.; Tiripicchio, A.; Tiripicchio, C. M. *J. Organomet. Chem.* **1986**, *316*, C35–38.

(11) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; pp 653–659.

Trimethylene sulfide, which has less ring strain than alkene sulfide, reacted with **2** to yield a different product (**4**), (eq 3), while tetrahydrothiophene and thiophene are inert toward **2**.

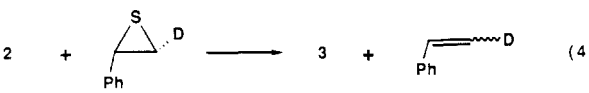


4

Alkene sulfides and triphenylphosphine sulfide have been used to make the thioaldehyde ligand from late-transition-metal methylidenes.[9] Utilization of elemental sulfur for this type of transformation has a precedent only in the case of a rhodium vinylidene complex.[12] Recently a different route to early-transition-metal η^2-thioaldehyde complexes from dimethylzirconocene and thiols has been reported.[9a,b]

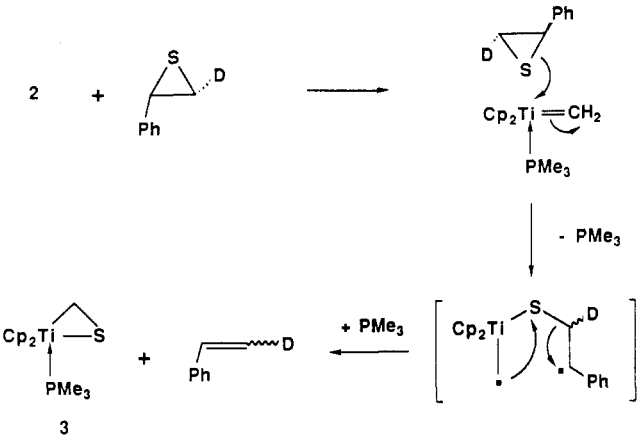
Crystal Structure of 3. Complex **3** was studied by single-crystal X-ray diffraction. Selected bond lengths and angles are listed in Table I. The crystal and intensity collection data are shown in Table III. An ORTEP diagram is shown in Figure 1. The molecule lies in a mirror plane, with the Ti, S, P, C1, and C2 atoms in this plane. The mirror relates the two Cp rings and two of the phosphine methyl groups plus the hydrogen atoms on C1. The Cp ring is coordinated normally to the titanium atom, with Ti–C distances averaging 2.393 (12) Å. The CH_2S group is bonded to titanium at both S and C. The H1a–C1–H1a′ plane nearly bisects the Ti–C1–S angle; in particular, the hydrogen atoms are not in the plane through C1 and S perpendicular to the mirror plane. The trimethylphosphine ligand has normal distances and angles. The C1–S bond distance of 1.744 (3) Å reflects the intermediate bonding character between a single and double bond.[13] This carbon–sulfur distance in **3** more resembles that of the rhenium thioformaldehyde (1.742 (9) Å)[9c] complex than that of the zirconium thioacetaldehyde complex (1.785 (11) Å)[9b] or of thioformaldehyde complexed to osmium clusters (1.77 (2), 1.82 (3) Å).[9d] The increased stability of Ti(II) relative to Zr(II) accounts for the shorter C1–S bond, the long Ti–S bond length (2.452 (1) Å),[14] and the high ^1H–^{13}C coupling constant of the thioformaldehyde group (157 Hz).

Mechanism for the Formation of 3. Although styrene sulfide did not produce the highest yields of **3**, it was used to study the mechanism since labeled analogues were more convenient to prepare. Stereospecific conversion of *trans*-styrene oxide-d_1 to *trans*-styrene sulfide-d_1 was achieved through the use of triphenylphosphine sulfide.[15] When the complex **2** was allowed to react with excess *trans*-styrene sulfide-d_1 at room temperature, *trans*-styrene-d_1, *cis*-styrene-d_1, **3**, and polystyrene sulfide were observed by ^1H NMR spectroscopy (eq 4).



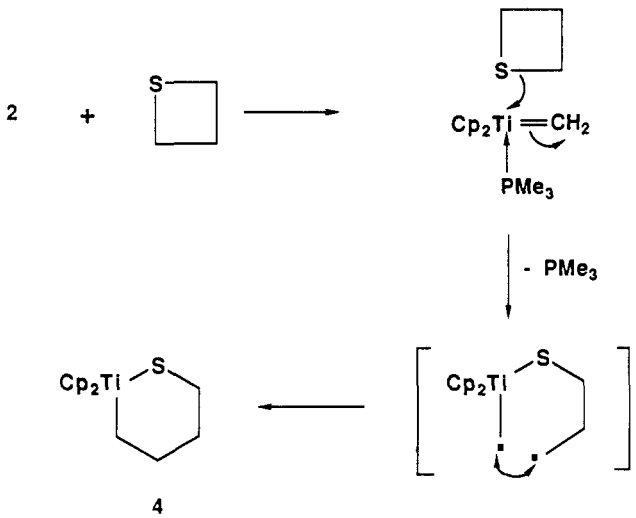
The ratio of *trans*-styrene-d_1 and *cis*-styrene-d_1 was 0.48; 0.52 as analyzed by ^2H NMR. No styrene sulfide-d_1 was observed after the reaction, even if it was rapidly quenched, because the polymerization of styrene sulfide was fast under the above reaction conditions. The formation of an equimolar mixture of *trans*- and *cis*-styrene-d_1 requires a stepwise reaction mechanism.

Scheme I. Stepwise Mechanism for the Reaction of 2 with Styrene Sulfide Required To Explain the Equimolar Mixture of *trans*- and *cis*-Styrene-d_1 as Byproducts[a]



[a] A biradical mechanism is preferred in view of the analogous reaction of styrene oxide.

Scheme II. Biradical Mechanism for the Reaction of 2 with Trimethylene Sulfide[a]



4

[a] The formation of a cyclopropane ring is unfavorable.

A six-membered ring is formed from the reaction between complex **2** and trimethylene sulfide. This observation is consistent with a stepwise mechanism. In this case, the formation of thioformaldehyde complex **2** from the intermediate would produce cyclopropane. Consequently, ring closure becomes the dominate pathway (Schemes I and II). The reaction of styrene oxide with **2** also yields an oxametallacyclopentane. In this case, the instability of the corresponding formaldehyde complex disfavors elimination of olefin from the intermediate, and ring closure becomes the dominate pathway.

This stepwise mechanism can be thought of as the general mechanism for the reaction of **2** with alkene sulfide and other reducible organic functional groups. An analogous reaction with styrene oxide is known to proceed by a similar stepwise mechanism.[16] In this case, a small

(12) Werner, H.; Wolf, J.; Zolk, R.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 981–982.

(13) Typical C=S and C—S bond distances are 1.70 and 1.82 Å, respectively. Sutton, L. E., Ed. *Tables of Interatomic Distances and configuration in Molecules and Ions*; Chemical Society: London, Supplement 1956–1959, 1965.

(14) Typical Ti–S bond distance is 2.40 Å; see: (a) Carrondo, M. A. A. F. d. C. T.; Jeffrey, G. A. *Acta Crystallogr., Sect. C* **1983**, *C39*, 42–44. (b) Kutoglu, V. A. *Z. Anorg. Allg. Chem.* **1972**, *390*, 195–209.

(15) Chan, T. H.; Finkenbine, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 2880–2882.

(16) Park, J. W. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1989.

substituent effect on the rates of the reactions implied a biradical mechanism involving initial electron transfer to the coordinated oxide to form the ring-opened benzyl radical. A mechanism involing initial electron transfer was also proposed for the reaction of **2** with benzyl chloride.[17] A biradical mechanism for the reaction of **2** with alkene sulfide is preferred in view of the similarity of these related reactions.

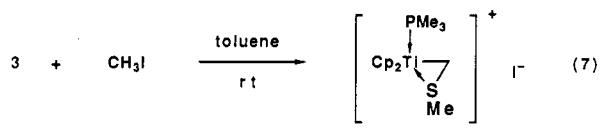
Reactivity of 3. The complex **3** did not show clean insertion products with various triple (CC and CN) and double (C=C, C=O, C=S) bonds. Of the many proton sources tested (e.g., HCl, CF_3CO_2H, H_2O, CH_3OH), trifluoroacetic acid gave the best yield of the protolysis products, $Cp_2Ti(O_2CCF_3)_2$, PMe_3, and CH_3SH (eq 5). The

$$3 + 2CF_3CO_2H \xrightarrow{-PMe_3} Cp_2Ti(O_2CCF_3)_2 + CH_3SH \quad (5)$$

reaction of complex **3** with dihydrogen yielded $Cp_2Ti(SMe)_2$ and an air-sensitive unidentified compound, that presumably resulted from disproportionation after hydrogenolysis (eq 6). Difficulty in regenerating complex **2** from the above products blocks a potential catalytic cycle for hydrodesulfurization.

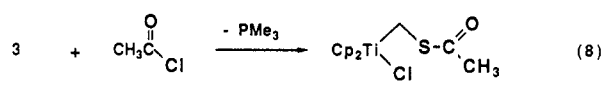
$$3 + H_2 \rightarrow Cp_2Ti(SCH_3)_2 \quad (6)$$

Complex **3** reacted with methyl iodide to produce the cationic titanocene η^2-thiomethoxymethyl trimethylphosphine complex **5a** with iodide as a counterion (eq 7).



5a

Late-transition-metal thioaldehyde complexes undergo similar reactions.[18] In contrast, the zirconocene thioaldehyde complex that is analogous to **3** reacted with methyl iodide to form the covalent adduct in which the iodide is directly bonded to zirconium.[9] Reaction of **3** with acetyl chloride gave a new product (**6**) together with Cp_2TiCl_2 as a minor product (eq 8). Complex 6 was



6

characterized by NMR and IR spectroscopy. A tentative structure was assigned based on the structure of **5a** (vide infra).

Crystal Structure of 5a. The structure of complex **5a** was determined by single-crystal X-ray diffraction. Selected bond lengths and angles are listed in Table II. Crystal and intensity collection data are shown in Table IV. An ORTEP diagram is shown in Figure 2. The titanium atom is bonded normally to the two Cp rings, with a ring centroid–Ti–ring centroid angle of 130.4° and Ti–C distances averaging 2.381 Å. Coordinated to the titanium in the wedge between the rings are a CH_2SCH_3 group and a trimethylphosphine. The CH_2SCH_3 group is bonded to the metal atom through both the methylene carbon, 2.215 (5) Å, and the sulfur, 2.555 (1) Å. The CS1–S bond distance of 1.751 (5) Å is slightly longer than that in the parent molecule, **3** (1.744 (3) Å). The titanium–sulfur

Table IV. Crystal and Intensity Collection Data for Complex 5a

formula: $C_{15}H_{24}SPTiI\cdot CH_3CN$
formula wt: 483.25
cryst color: yellow
a = 14.839 (2) Å
b = 15.184 (14) Å
c = 18.461 (3) Å
V = 4159.5 (14) Å^3
Z = 8
λ = 0.7107 Å
T = 21 °C
graphite monochromator
space group: *Pbca*
absences: 0*kl*, *k* odd; *h*0*l*, *l* odd; *hk*0, *h* odd
cryst size: 0.15 × 0.43 × 0.61 mm
μ = 20.98 cm^{-1} (μr_{max} = 0.80)
CAD-4 diffractometer
ω scan
2θ range: 2–50°
octants coll: h, k, ±l
no. of reflns measd: 8065
no. of indep reflns: 3650
no. with $F_o^2 > 0$: 3294
no. with $F_o^2 > 3\sigma(F_o^2)$: 2195
GOF for merging data: 0.947
final R index: 0.0598 (0.0326 for $F_o^2 > 3\sigma(F_o^2)$)
final GOF: 1.33

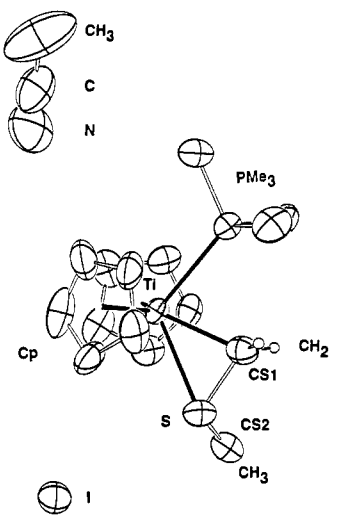


Figure 2. ORTEP diagram of complex **5a**. The ellipsoids are drawn at 50% probability level except for the hydrogen atoms. The hydrogen atoms of the cyclopentadienyl, terminal methyl, PMe_3 ligands, and acetonitrile are omitted for clarity.

distance, while longer than either that of complex **3** (2.452 (1) Å) or that of a typical Ti–S single bond (2.40 Å), is short enough to suggest considerable Ti–S bonding. The trimethylphosphine ligand is adjacent to the methylene carbon of the CH_2SCH_3 group and has normal distances and angles. The position of sulfur has changed from "inside" as in compound **3** to "outside". This type of conformational change is well-known in $Cp_2M(X)(\eta^2\text{-A–B})$ compounds (both the A and the B group interact with the metal atom).[19] The titanium and these three coordinated

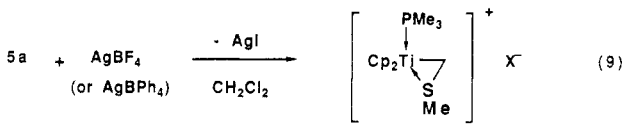
(17) Buchwald, S. L.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 1766–1768.

(18) (a) Werner, H.; Kolb, O.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1985**, *118*, 873–879. (b) Werner, H.; Paul, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 316–317.

(19) (a) Rodulfo de Gil, E.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3751–3756. (b) Sepelak, D. J.; Pierpont, C. G.; Barefield, E. K.; Budz, J. T.; Poffenberger, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 6178–6185. (c) Karsch, H. H.; Deubelly, B.; Hofmann, J.; Pieper, U.; Müller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654–3656. (d) Erker, G.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251–2257. (e) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440–4451. (f) Hofmann, P.; Stauffert, P.; Shore, N. E. *Chem. Ber.* **1982**, *115*, 2153–2174. (g) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W., Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220.

atoms lie in the same plane within ±0.04 Å. The methyl carbon of the CH_2SCH_3 group is 1.52 Å from this plane. The charge balancing iodide ion interacts with neither the titanium nor the sulfur atom. The Ti–I and S–I distances (5.027 (1) and 4.075 (1) Å) are greater than the sums of the van der Waals radii. Likewise, the acetonitrile, the solvent of recrystallization, does not show any significant interaction with other atoms of the complex.

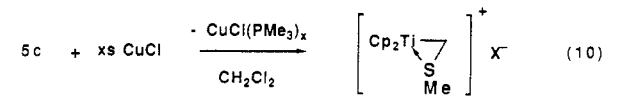
Preparation and Reactivity of 5b,c. Silver salts were used to metathesize the iodide anion with the less coordinating BF_4 and BPh_4 anions (eq 9) in **5a**. After isolation



(9)

5b X = BF_4

5c X = BPh_4



(10)

7c

of the complex **5c**, copper(I) chloride[20] was added to make a phosphine-free complex (**7c**) in dichloromethane (eq 10). Free $CuCl(PMe_3)_x$, which was synthesized and identified independently, was observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra, and a phosphine-free organometallic product was confirmed by the loss of ^{31}P coupling in ^1H NMR of the titanocene complex. Line broadening of the Cp, the methylene, and the methyl peaks was observed in ^1H NMR when excess acetonitrile-d_3 was added. This phenomenon, demonstrating an equilibrium between the solvent-free and the solvent-bound cationic titanium complex, confirmed the presence of a vacant coordination site resulting from the loss of trimethylphosphine. It has been shown that titanocene methyl cations with a labile two-electron-donor ligand catalyze the polymerization of ethylene in noncoordinating solvents.[21a] This type of behavior was observed with the analogous zirconium[22a,b] and chromium[22c] methyl cations. However, the complex **7c** does not catalyze the polymerization of ethylene or methyl vinyl ether and decomposes above room temperature. There are two possible reasons for this lack of activity: (1) the intramolecular sulfide ligand is expected to bind strongly to the more electron-deficient titanium in complex **7c**; (2) the residual π-bonding character of the CH_2SCH_3 ligand will inhibit the insertion of ethylene into the Ti–CH_2SCH_3 bond.

Experimental Section

General Procedures. All manipulation of air- and/or moisture-sensitive compounds was carried out with use of standard Schlenk or vacuum-line techniques. Argon was purified by passage through columns of BASF RS-11 catalyst (Chemalog) and Linde 4-Å molecular sieves. Solids were transferred and stored in a N_2-filled Vacuum Atmosphere glovebox equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and Dri-Cold Freezer.

Toluene, benzene, and diethyl ether were stirred over CaH_2 and then transferred from a purple sodium/benzophenone ketyl. Pentane was stirred over concentrated H_2SO_4, washed with H_2O, dried over CaH_2, and then transferred from a purple sodium/benzophenone ketyl. Dichloromethane and acetonitrile were dried over P_2O_5 or CaH_2 and degassed by evacuation using freeze–pump–thaw cycles. Dried degassed solvents were vacuum-transferred into dry glass vessels equipped with Teflon valve closures and stored under argon. Benzene-d_6 and toluene-d_8 (Cambridge Isotope) were dried over and vacuum-transferred from purple sodium/benzophenone ketyl. Dichloromethane-d_2 and acetonitrile-d_3 (Cambridge Isotope) were dried over CaH_2 and degassed by several freeze–pump–thaw cycles. Propene sulfide, cyclohexene sulfide (85%), trimethylene sulfide, methyl iodide, triphenylphosphine sulfide, trifluoroacetic acid, silver tetrafluoroborate, copper(I) chloride (Aldrich), hydrogen (H_2), and deuterium (D_2, Matheson) were used as purchased. β,β-Dimethyltitanacyclobutane (1), $Cp_2Ti{=}CH_2{\cdot}PMe_3$ (**2**),[8] $AgBPh_4$,[23] and styrene sulfide[15] were prepared by using known methods.

NMR spectra were recorded on Varian EM-390 (90 MHz, ^1H), a JEOL FX-90Q or a JEOL GX-400 spectrometers. Chemical shifts are reported in δ, referenced to residual solvent signals. $^{31}P\{^1H\}$ NMR data are referenced externally to 85% H_3PO_4 (downfield positive). $^{19}F\{^1H\}$ NMR data are referenced externally to CCl_3F (downfield positive). IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Elemental analyses (C, H, N, S) were performed by either California Institute of Technology Analytical Services or SPANG Microanalytical Laboratory.

Preparation of 3. Propene sulfide (248 μL, 3.16 mmol) was added to compound **2** (825 mg, 3.08 mmol) in toluene (27 mL) at 0 °C. The solution was evaporated to dryness after 5 min at room temperature. (^1H NMR analysis with the internal standard showed that the yield was 83% based on the amount of **2**.) Diethyl ether (13 mL) was added to wash the residue. The precipitate was filtered and washed with cold (−78 °C) diethyl ether (5 mL). Drying in vacuo produced a yellow powder (678 mg, 2.26 mmol, 74%). For recrystallization, the powder was dissolved at room temperature in dichloromethane (7 mL), and pentane (28 mL) was layered on top of the solution. At −50 °C, the solution produced large needle-type crystals (550 mg, 71%) suitable for single-crystal X-ray crystallography and elemental analysis: ^1H NMR (C_6D_6) δ 4.93 (s, 10 H, Cp), 2.72 (s, 2 H, CH_2), 1.01 (d, 9 H, J_{CH} = 6.3 Hz, PMe_3); ^{13}C NMR (C_6D_6) δ 102.9 (dm, J_{CH} = 172 Hz, Cp), 43.3 (t, J_{CH} = 157 Hz, CH_2), 17.3 (dq, J_{CH} = 129 Hz, J_{PC} = 16 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 10.8 (s). Anal. Calcd for $C_{14}H_{21}PSTi$: C, 56.00; H, 7.05; S, 10.68. Found: C, 55.87; H, 7.17; S, 10.58.

Reaction of compound **2** with cyclohexene sulfide, styrene sulfide, elemental sulfur, and triphenylphosphine sulfide gave the same product **3** in poorer yields (65, 42, 41, and 35%, respectively). The reaction with triphenylphosphine sulfide produced a green solution suggesting the formation of Ti(III) species.

Preparation of 4. A mixture of trimethylene sulfide (270 μL, 3.54 mmol) and the compound **2** (500 mg, 1.86 mmol) in toluene (10 mL) was stirred for 2 h at room temperature. (^1H NMR analysis with an internal standard showed that the yield was 75% based on **2**.) The product was dissolved in diethyl ether (30 mL). The solution was concentrated to 10 mL, and pentane (40 mL) was added to make a double-layered solution. The pentane/ether layer produced a red precipitate (188 mg, 0.706 mmol, 38%) at −50 °C; ^1H NMR (C_6D_6) δ 5.71 (s, 10 H, Cp), 3.31 (s, 2 H, CH_2), 2.06 (s, 2 H, CH_2), 1.35 (br, 2 H, CH_2), 0.91 (br, 2 H, CH_2); ^{13}C NMR (C_6D_6) δ 112.0 (dm, J_{CH} = 174 Hz, Cp), 64.7 (t, J_{CH} = 129 Hz, CH_2), 41.3 (t, J_{CH} = 136 Hz, CH_2), 34.9 (t, J_{CH} = 125 Hz, CH_2), 34.1 (t, J_{CH} = 125 Hz, CH_2). Anal. Calcd for $C_{14}H_{18}STi$: C, 63.16; H, 6.81. Found: C, 62.84; H, 6.82.

Crystal Structure Determination of 3. Compound **3** formed large prismatic crystals; a small chunk was cut from one with a

(20) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483–7491.

(21) (a) Taube, R.; Krukowka, L. *J. Organomet. Chem.* **1988**, *347*, C9–C11. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148–1154. (c) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556–2563. In cases b and c, the polymerization of alkenes was inhibited by the tightly bound nitrile or phosphine ligand.

(22) (a) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410–7411. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111–4113. (c) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902–5903.

(23) Wittig, V. G.; Raff, P. *Ann. Chem.* **1951**, *573*, 195–209.

razor blade and mounted in a capillary. Data collection details are given in Table I. The titanium atom was located from a Patterson map, and the remaining atoms were found by successive structure factor Fourier calculations. The centrosymmetric space group *Pnma* (rather than $Pna2_1$) was chosen on the basis of statistics and confirmed by the successful refinement. The refinement converged quickly. Hydrogen atoms were placed by calculation or difference maps and subsequently included in the single full-matrix refinement. The carbon-hydrogen distances range from 0.7 (0) to 1.00 (4) Å, but all are in acceptable locations.

Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference (*International Tables for X-ray Crystallography*, 71, p. 149; Kynoch: Birmingham 1974; Vol. IV, pp 71, 149); $R = \sum||F_o| - |F_c||/\sum F_o$, for only $F_o^2 > 0$, and goodness of fit = $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of data and p is the number of parameters refined. The function minimized in least squares was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned on the basis counting statistics plus an additional term, $0.014I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.014\langle I\rangle^2$. The absorption correction was done by Gaussian integration over an 8 × 8 × 8 grid. Transmission factors varied from 0.677 to 0.735. The secondary extinction parameter (Larson, E. C. *Acta Crystallogr.* **1967**, *23*, 664, eq 3) refined to 1.8×10^{-6}.

Preparation of *trans*-Styrene Sulfide-d_1. *trans*-Styrene oxide-d_1 was synthesized from phenylacetylene via hydrozirconation,[24] hydrolysis with D_2O, and epoxidation of the double bond with *m*-chloroperbenzoic acid.[25] Stereospecific conversion of styrene oxide to styrene sulfide was achieved through the use of triphenylphosphine sulfide. Trifluoroacetic acid (0.64 mL, 8.3 mmol) was added to a mixture of *trans*-styrene oxide-d_1 (1.00 g, 8.25 mmol) and triphenylphosphine sulfide (2.45 g, 8.32 mmol) in dry benzene (35 mL) at room temperature. After the solution was allowed to react for 2.5 h, it was stirred overnight with excess sodium bicarbonate. After filtration, the solvent was evaporated to dryness. The residue was dissolved in benzene (5 mL), and the mixture was filtered to remove triphenylphosphine oxide. The product, *trans*-styrene sulfide-d_1, was isolated by flash column chromatography (eluent, benzene; R_f value, 0.8; separation yield ≥30%): ^{1}H NMR (C_6D_6) δ 7.02 (m, 5 H, Ph), 3.42 (d, 1 H, J_{HH} = 5.4 Hz, α-CH), 2.28 (m, 0.14 H, β-CH), 2.16 (d, 1 H, J_{HH} = 5.4 Hz, β-CH). (The product contained 14% of hydrogen at the trans α-position of styrene sulfide.) The product polymerized overnight when stored neat at room temperature. Polymerization can be avoided through dilution with benzene and freezing at low temperature (−50 °C).

Reaction of 2 with *trans*-Styrene Sulfide-d_1. *trans*-Styrene sulfide-d_1 (10 μL, 0.082 mmol) was injected into a NMR tube containing a solution of complex **2** (10 mg, 0.037 mmol) in C_6D_6 (0.4 mL) at room temperature. A mixture of **3**, polystyrene sulfide, *trans*-styrene-d_1, and *cis*-styrene-d_1 was observed by ^{1}H NMR. (^{1}H NMR (C_6D_6, room temperature) of independently prepared polystyrene sulfide-d_1: δ 7.08 (br, 5 H, Ph), 3.64–3.55 (br, 1 H), 2.66 (br, 1 H).) The ratio of *trans*-styrene-d_1 and *cis*-styrene-d_1 was easily analyzed by 2H NMR. (^{2}H NMR (toluene-d_8, room temperature) δ 5.63 (cis isomer, 52%), 5.10 (trans isomer, 48%).) After the reaction mixture was prepared, NMR spectra were taken at various temperatures (−78 °C to room temperature). It was impossible to recover starting sulfide by rapid quenching of the reaction since polymerization of *trans*-styrene sulfide-d_1 and decomposition of **2** were the major pathways of the reaction at low temperature.

Reaction of 3a with Trifluoroacetic Acid. The red color of the C_6D_6 solution chaned to orange when the complex **3** (10 mg, 0.033 mmol) and trifluoroacetic acid (6 μL, 0.078 mmol) were allowed to react for 30 min at room temperature; ^{1}H NMR (C_6D_6, room temperature) δ 5.76 (br, $Cp_2Ti(O_2CCF_3)_2$), 1.51 (d, J_{HH} = 7.2 Hz, CH_3SH), 0.85 (br, PMe_3 and CH_3SH).

Reaction of 3 with H_2. An intense purple solution was obtained when **3** in C_6D_6 was allowed to react with hydrogen at room temperature. The color of the solution changed to red immediately after the solution was exposed to air. One of the products decomposed very rapidly in the presence of moist air, while another product was stable. The air-stable compound was identified as $Cp_2Ti(SMe)_2$[26] by ^{1}H NMR: ^{1}H NMR (C_6D_6) δ 5.70 (s, 10 H, Cp), 2.70 (s, 6 H, SMe). A single-crystal X-ray crystallographic study confirmed the structure. With the use of D_2, $Cp_2Ti(SCH_2D)_2$ was prepared and characterized by ^{1}H and ^{2}H NMR: ^{1}H NMR (C_6D_6) δ 5.70 (s, 10 H, Cp), 2.68 (t, J_{HH} = 2.3 Hz, 4 H, CH_2D); ^{2}H NMR (C_6H_6) δ 2.57 (br).

Reaction of 3 with Acetyl Chloride. Distilled acetyl chloride[27] (23.5 μL, 0.33 mmol) was added dropwise to the compound **3** (50 mg, 0.167 mmol) in toluene (3 mL) at room temperature. The solution was filtered and concentrated to 1 mL after stirring for an hour at room temperature. Pentane (4 mL) was layered on the top of the toluene solution. Storing the solution at −50 °C produced an orange powder and red crystals. The red crystals were identified as Cp_2TiCl_2 by comparison of its ^{1}H NMR spectrum to a standard. The orange powder was assumed to be **6** on the basis of the NMR and IR data: ^{1}H NMR (C_6D_6) δ 5.75 (s, 10 H, Cp), 2.80 (s, 2 H, CH_2), 2.03 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 196.7 (CO), 116.8 (Cp, J_{CH} = 176 Hz), 47.0 (CH_2, J_{CH} = 139 Hz), 29.5 (CH_3, J_{CH} = 129 Hz); IR (KBr pellet) 3107, 1670, 1443, 1351, 1126, 1017, 952, 826, 719, 631 cm^{-1}.

Preparation of 5a. Finely ground compound **3** (680 mg, 2.27 mmol) was stirred in toluene (35 mL) for 30 min to dissolve. The solution was allowed to react with excess methyl iodide (286 μL, 4.59 mmol) at room temperature. Additional methyl iodide (143 μL, 2.30 mmol) was added dropwise after 3 h. A yellow powder (825 mg, 1.87 mmol, 82%) was removed by filtration after the solution had stirred for another 3 h. Diethyl ether was layered on top of a solution of the powder dissolved in acetonitrile at −20 °C. Crystals suitable for single-crystal X-ray crystallography and elemental analysis were obtained after storing the solution at −25 °C for several days: ^{1}H NMR (CD_3CN, −20 °C) δ 5.59 (br, 10 H, Cp), 2.28 (s, 2 H, CH_2), 1.95 (s, 3 H, CH_3), 1.47 (d, 9 H, J_{PH} = 8 Hz, PMe_3); ^{13}C NMR (CD_3CN, −20 °C) δ 106.1 (dm, J_{CH} = 178 Hz, Cp), 41.7 (td, J_{CH} = 155 Hz, J_{PC} = 36 Hz, CH_2), 21.9 (q, J_{CH} = 140 Hz, CH_3), 17.3 (dq, J_{CH} = 130 Hz, J_{PC} = 23 Hz, PMe_3); ^{31}P{^{1}H} NMR (CD_3CN, room temperature) δ 18.85. Anal. Calcd for $C_{15}H_{24}IPSTi \cdot CH_3CN$: C, 42.25; H, 5.63; N, 2.90. Found: C, 42.40; H, 5.53; N, 3.04.

Crystal Structure Determination of 5a. A plae yellow crystal of **5a** was mounted in a greased capillary and centered on a CAD-4 diffractometer. Unit cell parameters and an orientation matrix were obtained by a least-squares calculation from the setting angles of 25 reflections with 39° < 2θ < 46°. Two equivalent data sets out to a 2θ of 50° were collected and corrected for absorption and decay. Lorentz and polarization factors were applied, and the two data sets were then merged to yield the final data set. Systematic absences in the diffraction data revealed the space group to be *Pbca*.

The iodide ion was located from a Patterson map, and positions of the other non-hydrogen atoms were obtained from successive structure factor Fourier calculations. The three acetonitrile hydrogen atoms, represented by six half-weight hydrogen atoms at calculated positions with isotropic B values 20% greater than that of the attached carbon, were not refined. The remaining 24 hydrogen atoms, located by calculation or from difference maps, were included in the least-squares calculations. The final full matrix contained 295 parameters: a scale factor, spatial and anisotropic thermal parameters for non-hydrogen atoms, and spatial and anisotropic thermal parameters for the refined hydrogen atoms. The hydrogen results were reasonable. A final difference Fourier showed maximum excursions of −0.75 and +0.90 e $Å^{-3}$ in the neighborhood of the iodide ion, with deviations of less than ±0.64 e $Å^{-3}$ elsewhere. The final R index was 0.0598

(24) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; pp 698–704.
(25) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, pp 135–139.
(26) (a) Köpf, H.; Block, B.; Schmidt, M. *Chem. Ber.* **1968**, *101*, 272–276. (b) Giddings, S. A. *Inorg. Chem.* **1967**, *6*, 849–850. (c) Chaudhari, M. A.; Stone, F. G. A. *J. Chem. Soc. A* **1966**, 838–841.
(27) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1966; p 59.

(0.0326 for $F_o^2 > 3\sigma(F_o^2)$) with a goodness of fit of 1.33.

Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference (*International Tables for X-ray Crystallography*; 71, p. 149; Kynoch: Birmingham, 1947; Vol. IV, pp 71, 149): $R = \sum||F_o| - |F_c||/\sum F_o$, for only $F_o^2 > 0$, and goodness of fit = $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of data and p is the number of parameters refined. The function minimized in least squares was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned on the basis of counting statistics plus an additional term, $0.014I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.014\langle I\rangle^2$. The absorption correction was done by Gaussian integration over an 8 × 8 × 8 grid. Transmission factors varied from 0.431 to 0.732.

Preparation of 5b. A mixture of **5a** (200 mg, 0.45 mmol) and $AgBF_4$ (88 mg, 0.45 mmol) in dichloromethane (25 mL) was allowed to react for 3 h at -20 °C. The resultant solution was filtered and evaporated to give a yellow powder (130 mg, 0.32 mmol, 72%): ^1H NMR (CD_2Cl_2, -10 °C) δ 5.57 (s, 5 H, Cp), 5.54 (s, 5 H, Cp), 2.20 (d, J_{CH} = 10 Hz, 1 H, CH_2), 2.03 (d, J_{CH} = 10 Hz, 1 H, CH_2), 1.99 (s, 3 H, CH_3), 1.51 (d, J_{PH} = 7.2 Hz, 9 H, PMe_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, -10 °C) δ 18.58; $^{19}F\{^1H\}$ NMR (CD_2Cl_2, -10 °C) δ -7.6. Anal. Calcd for $C_{15}H_{24}BF_4PSTi$: C, 44.81; H, 6.02. Found: C, 44.67; H, 5.84.

Preparation of 5c. A mixture of **5a** (200 mg, 0.45 mmol) and $AgBPh_4$ (200 mg, 0.46 mmol) in dichloromethane (20 mL) was stirred for 3 hours at room temperature. After the solution was filtered to separate the precipitated silver iodide and evaporated to dryness, the yellow residue was dissolved in dichloromethane (15 mL). Pentane (40 mL) was added to make a double-layered solution, which gave a yellow powder on storing at -78 °C. The product (165 mg, 0.26 mmol, 58%) was recovered by tiltration at -78 °C: ^1H NMR (CD_3CN, 0 °C) δ 7.3-6.8 (m, 20 H, Ph), 5.58 (s, 5 H, Cp), 5.56 (s, 5 H, Cp), 2.20 (CH_2), 1.92 (s, 3 H, CH_3), 1.46 (d, J_{PH} = 8 Hz, 9 H, PMe_3); $^{31}P\{^1H\}$ NMR (CD_3CN, 0 °C) δ 17.23. Anal. Calcd for $C_{39}H_{44}BPSTi\cdot CH_2Cl_2$: C, 66.78; H, 6.44. Found: C, 66.49; H, 6.36.

Reaction of 5c with CuCl. A mixture of **6c** (20 mg, 0.03 mmol) and CuCl (6 mg, 0.06 mmol) in dichloromethane-d_2 was allowed to react at -20 °C. The yellow-red solution obtained after an hour showed a new product (**7c**) together with $CuCl(PMe_3)_x$ in the ^1H NMR spectrum: ^1H NMR (CD_2Cl_2, -20 °C) δ 7.37-7.14 (m, 20 H, Ph), 6.37 (s, 10 H, Cp), 2.26 (s, 3 H, CH_3), 2.10 (s, 2 H, CH_2), 0.92 (d, J_{PH} = 7 Hz, free $CuCl(PMe_3)_x$); $^{31}P\{^1H\}$ NMR δ -42.87 (br, free $CuCl(PMe_3)_x$, which was characterized by control reactions between CuCl and PMe_3). Addition of excess acetonitrile-d_3 (19 μL) into the above sample broadened the Cp peak and merged the methylene and the methyl peaks into a broad peak in ^1H NMR: ^1H NMR (CD_2Cl_2/CD_3CN, -20 °C) δ 7.34-7.09 (m, 20 H, Ph), 6.28 (br s, 10 H, Cp), 2.19 (br s, CH_2, CH_3), 1.11 (d, J_{CH} = 8 Hz, PMe_3 complex). These peaks broaden reversibly at lower temperatures (-50 °C). In separate experiments an excess of either ethylene or methyl vinyl ether was injected into a solution of **7c** at -20 °C. No sign of polymerization was observed upon warming to room temperature. Above room temperature, only decomposition products of **7c** were detected.

Acknowledgment. We acknowledge the financial support of the National Science Foundation, the Department of Energy, the Exxon Educational Foundation, and the NSF for Grant CHE-8219039 to purchase the diffractometer.

Supplementary Material Available: Atomic numbering schemes and tables of complete bond distances and angles, final parameters, and anisotropic displacement parameters (9 pages); a table of structure factors (22 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of Reductive Elimination of Hydrocarbons from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ (X = Ph, Et, Cl, CO_2Me, SEt, $CHPhCH_2Ph$)

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The reaction of CO with $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ forms the corresponding CH_3X (X = CO_2Me, Ph, Et, $CHPhCH_2Ph$) and $Ru_3(CO)_{12}/Ru(CO)_5$; if β-hydrogens are present, alkenes and $H_4Ru_4(CO)_{12}$ are also products. The rate law (X = Ph, Cl, and Et) is of the following form: rate = $\{k_a k_c P_{CO}/(k_b + k_c P_{CO})\}[H_3Ru_3(CX)(CO)_9]$ (X = Ph, $k_a = (6.4 \pm 0.6) \times 10^{-6}$ s^{-1}, $k_b/k_c = 0.49 \pm 0.14$ atm, 100 °C; X = Cl, $k_a = (7.5 \pm 0.7) \times 10^{-5}$ s^{-1} and $k_b/k_c = 3.5 \pm 0.9$ atm, 100 °C; X = Et, $k_a = (7.6 \pm 2.5) \times 10^{-5}$ s^{-1}, $k_b/k_c = 14 \pm 7$ atm, 125 °C). For X = CO_2Me the rate law is zero order in P_{CO}. Activation parameters for the limiting rate constant k_a were determined (Ph, 35 atm, $\Delta H^\ddagger = 131 \pm 3$ kJ/mol, $\Delta S^\ddagger = 6 \pm 8$ J/(K mol); Cl, 35 atm, $\Delta H^\ddagger = 125 \pm 9$ kJ/mol, $\Delta S^\ddagger = 9 \pm 25$ J/(K mol); Et, 34 atm, $\Delta H^\ddagger = 140 \pm 19$ kJ/mol, $\Delta S^\ddagger = 22 \pm 49$ J/(K mol); CO_2Me, 1 atm, $\Delta H^\ddagger = 111.2 \pm 1.3$ kJ/mol, $\Delta S^\ddagger = -0.8 \pm 4$ J/(K mol)). For X = Ph, Cl, and Et inverse deuterium isotope effects were measured (Ph, 86% d, $k_H/k_D = 0.64 \pm 0.08$, 100 °C, 35 atm; Cl, 85% d, $k_H/k_D = 0.56 \pm 0.06$, 100 °C, 6.8 atm; Et, 80% d, $k_H/k_D = 0.46 \pm 0.03$, 100 °C, 35 atm), but $k_H/k_D = 1.01 \pm 0.03$ (95% d, 70 °C, 1 atm) for X = CO_2Me. The proposed mechanism involves a sequence of C-H reductive eliminations, each of which is preceded by reversible migration of hydrogen from Ru-H-Ru bridging to Ru-H-C bridging. The rate-determining step at high CO pressures is cleavage of the first Ru-H-C bond. For X = CO_2R or SEt anchimeric assistance of the reductive elimination, perhaps through a species containing a $(\mu_3\text{-H})Ru_2C$ interaction, is proposed.

Introduction

The reductive elimination of a C-H bond from a transition-metal center is one of the fundamental reactions of organometallic chemistry. This reaction is the final step in many catalytic processes, occurring in both homogeneous and heterogeneous catalytic systems. Numerous studies of the mechanism of this process have been conducted for monometallic complexes.[2-6] A variety of

(1) Alfred P. Sloan Fellow, 1987-89.

(2) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332.

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