Synthesis and Characterization of Thioaldehyde Hydride Derivatives of Permethyltantalocene. Investigations of Their Equilibration with Thiolates and the Stereochemistry of Alkyl Migrations from Sulfur to Tantalum†

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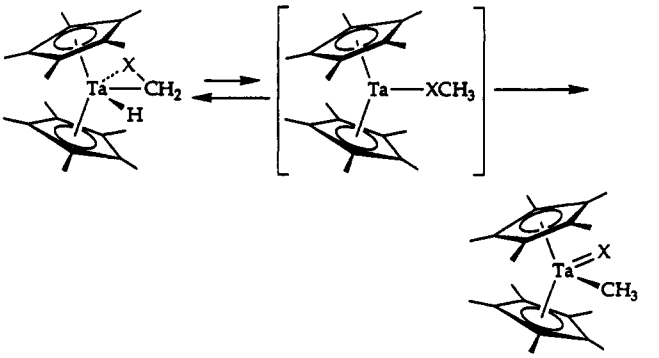
Permethyltantalocene thioaldehyde hydride complexes, $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHR)H$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = H, C_6H_5, $CH_2C_6H_5$, CH_2CMe_3), have been prepared by treating precursors to $[Cp^*_2Ta\text{—}R']$ (e.g. $Cp^*_2Ta(=C=CH_2)H$ for R′ = CH=CH_2) with the appropriate thiol RCH_2SH. Oxidative addition of the S—H bond leads to the unstable Ta(V) derivatives $Cp^*_2Ta(R')(H)(SCH_2R)$. Reductive elimination of R′H is facile, forming $[Cp^*_2Ta\text{—}SCH_2R]$, which subsequently undergoes β-H elimination to yield the thioaldehyde hydrides $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHR)H$. The results of an X-ray structure determination for $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$ are summarized. These permethyltantalocene thioaldehyde hydride complexes are shown to be in rapid equilibrium with the corresponding 16-electron thiolate species $[Cp^*_2Ta\text{—}SCH_2R]$ through a β-H migratory insertion/elimination process. When they are heated, the permethyltantalocene thioaldehyde hydride complexes undergo rearrangement to the thermodynamically favored tautomer, the permethyltantalocene sulfido alkyl $Cp^*_2Ta(=S)CH_2R$. An inverse kinetic deuterium isotope effect observed for $Cp^*_2Ta(\eta^2\text{-}S\text{—}CY_2)Y$ (Y = H, D) (k_H/k_D = 0.72 (3) at 138 °C) is indicative of a stepwise process involving fast preequilibrium of $Cp^*_2Ta(\eta^2\text{-}S\text{—}CY_2)Y$ with $[Cp^*_2Ta\text{—}SCY_3]$ and rate-determining α-CY_3 elimination to $Cp^*_2Ta(=S)CY_3$. Derivatives of the permethyltantalocene phenylthioacetaldehyde hydride have been prepared from the *erythro*- and *threo*-phenethyl-d_2 mercaptan, $C_6H_5CHDCHDSH$, to elucidate the mechanism of alkyl transfer. The migration has been found to proceed with ≥85% retention of stereochemistry at carbon for the migrating phenethyl-d_2 group. The sulfido methyl complex $Cp^*_2Ta(=S)CH_3$ is hydrogenated under forcing conditions to yield methane and $Cp^*_2Ta(=S)H$, but this product resists final hydrogenation to $Cp^*_2TaH_3$ and H_2S.

Introduction

Hydrodesulfurization (HDS) of organosulfur compounds from crude fossil fuels is an important commercial process that is practiced on an enormous scale.[2] The heterogeneous commercial HDS processes utilize a catalyst that consists of a mixture of cobalt and molybdenum sulfides supported on γ-alumina, with organosulfur compounds ultimately being converted to hydrocarbons and hydrogen sulfide at temperatures of 600–750 K and at pressures of 10–100 atm. At present, however, most features of the mechanism are poorly understood. Thiophene is representative of a common sulfur-containing functional group in fossil fuels. Hence, HDS of thiophene has received much attention in studies of heterogeneous catalytic reactions as well as in model studies with organotransition-metal complexes.[3] Whereas most thiophene complexes resist reactions which effect C–S bond cleavage, C–S cleavage has been shown to occur following two-electron reduction of Ir(III) thiophene complexes[4] and by reaction of thiophene with a coordinatively unsaturated Rh(I) derivative.[5] Rauchfuss and co-workers have also observed tetramethylthiophene desulfurization upon thermolysis of $Cp^*Rh\{(\eta^4\text{:}\eta^1\text{-}C_4Me_4S)Fe(CO)_4\}$.[6]

Carbon–sulfur bond cleavage has also been reported for compounds other than thiophenes. Grubbs, Park, et al. have reported abstraction of sulfur from olefin sulfides by the titanium methylene unit of $Cp_2Ti(=CH_2)PMe_3$ (Cp = $\eta^5\text{-}C_5H_5$), affording olefin and $Cp_2Ti(\eta^2\text{-}S\text{—}CH_2)PMe_3$, and the insertion of $[Ti=CH_2]$ into a carbon–sulfur bond of trimethylene sulfide to yield a titanathiacyclohexane product.[7] Rakowski DuBois has reported reversible addition of olefins to the bridging sulfide ligands of $CpMo(\mu_2\text{-}S)_2(\mu_2\text{-}S_2CH_2)MoCp$,[8] insertion of olefins into S—H bonds for cyclopentadienylmolybdenum dimers, and hydrogenolysis of sulfur–carbon bonds with these systems.[9]

Scheme I[a]



[a] X = O, S, NCH_3.

† Contribution No. 8511.

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(2) For general reviews, see: (a) Mitchell, P. C. H. In *Catalysis*; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1, p 223. (b) Mitchell, P. C. H. In *Catalysis*; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 4, p 203. (c) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979. (d) Weisser, O.; Landa, S. *Sulphide Catalysts, Their Properties and Applications*; Pergamon Press: Oxford, U.K., 1973. (e) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 382.

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Permethyltantalocene derivatives have proven to be amenable for studying a variety of fundamental organometallic transformations.[10] α and β migratory elimination and insertion reactions of alkoxide, thiolate, and amide derivatives have been observed. For example, it has been shown that reactions of [$Cp^*_2Ta^{III}$—R] sources (e.g. $Cp^*_2Ta(=CH_2)H$ in equilibrium with [Cp^*_2Ta—CH_3]) with methanol, dimethylamine, or methanethiol produce $Cp^*_2Ta(\eta^2\text{-X—}CH_2)H$ (X = O, S, NCH_3) with loss of RH.[10b] Rearrangement to the thermodynamically more stable tautomer $Cp^*_2Ta(=X)CH_3$ occurs at elevated temperatures (Scheme I), presumably via β-H migratory insertion to a [Cp^*_2Ta—XCH_3] intermediate followed by an α-alkyl migration.

α-Methyl migration for the thiolate intermediate (eq 1) represents a process for carbon–sulfur bond cleavage that is fundamentally different from those reported earlier.

$$L_nM\text{—}SR \xrightarrow{\alpha\text{-R migration}} L_nM(=S)R \qquad (1)$$

When this step is coupled with ones that effect hydrogenolysis of the L_nM—R bond to alkane and the L_nM=S bond to H_2S and subsequent (re)addition of RSH, a catalytic cycle for hydrodesulfurization of mercaptans may be envisioned. We report herein the synthesis of several thioaldehyde hydride derivatives of permethyltantalocene, $Cp^*_2Ta(\eta^2\text{-S—}CHR)H$, including the structure of $Cp^*_2Ta(\eta^2\text{-S—}CHCH_2C_6H_5)H$. Their rearrangement to the corresponding sulfido alkyls has been examined, and aspects of the chemistry of these new compounds have been explored. We also report on our studies of the stereochemistry for the rearrangement of [Cp^*_2Ta—$SCHDCHDC_6H_5$] to $Cp^*_2Ta(=S)CHDCHDC_6H_5$.

Results and Discussion

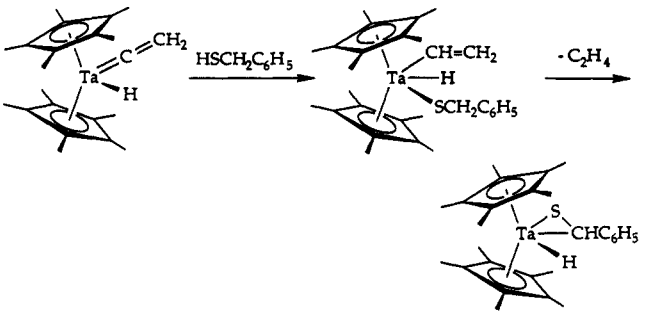
Thioaldehyde Hydride Derivatives of Permethyltantalocene. The complexes $Cp^*_2Ta(=CH_2)H$, $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$, etc. are precursors to [Cp^*_2Ta—R] (R = alkyl, aryl) and thus are useful starting materials for the synthesis of a number of permethyltantalocene derivatives. The benzyne hydride derivative $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$ was used for most of the studies reported here. Treatment with thiols leads to the new permethyltantalocene thioaldehyde hydride complexes with release of benzene (eq 2). Al-

$$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H + RCH_2SH \rightarrow Cp^*_2Ta(\eta^2\text{-S—}CHR)H + C_6H_6 \qquad (2)$$

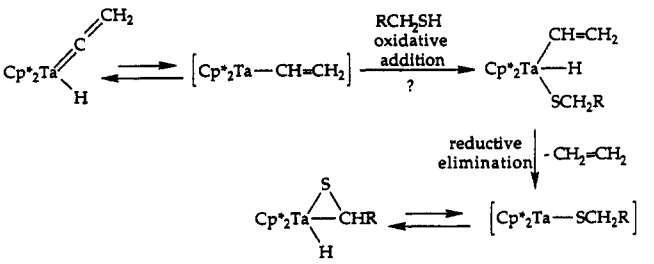
$$R = H,\ C_6H_5,\ CH_2C_6H_5,\ CH_2C(CH_3)_3$$

though generation of $Cp^*_2Ta(\eta^2\text{-X—}CR_2)H$ (X = O, NR) was found to be successful only with methanol[11] or dimethylamine,[10b,12] the reactions appear to be quite general

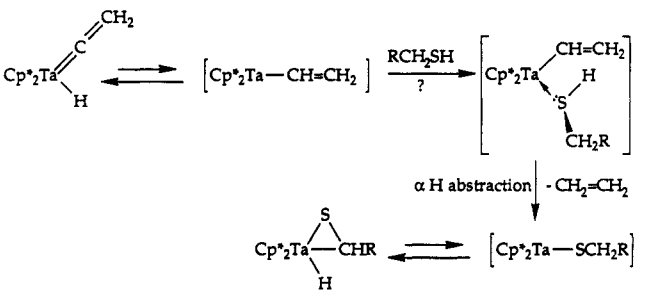
Scheme II



Scheme III



Scheme IV



and to proceed very cleanly for a variety of primary thiols (X = S).[13] Reactions carried out in NMR tubes appear to proceed quantitatively, although isolated yields are often lower due to high solubilities of the complexes.

Interestingly, reaction of permethyltantalocene vinylidene hydride with benzyl mercaptan proceeds cleanly to afford an initial product (^{1}H NMR), which eliminates ethylene to produce the expected thioaldehyde hydride upon mild heating. This intermediate may be isolated by carrying out the reaction in cold petroleum ether. ^{1}H NMR studies are consistent with a vinyl–thiolate–hydride structure, $Cp^*_2Ta(CHCH_2)(SCH_2C_6H_5)H$ (Scheme II). The kinetics of the ethylene loss are first order (^{1}H NMR) with $k = [3.7\ (4)] \times 10^{-5}\ s^{-1}$ and $\Delta G^* = 24.3\ (1)$ kcal/mol at 35 °C (assuming Eyring behavior).

Isolation of a $Cp^*_2Ta(CHCH_2)(SCH_2C_6H_5)H$ intermediate would support a mechanism where the RS—H bond of the incoming thiol oxidatively adds to the [Cp^*_2Ta—$CH{=}CH_2$] center. Reductive elimination of ethylene generates a Ta(III) thiolate intermediate, which eliminates β-H to the thioaldehyde hydride complex (Scheme III). On the other hand, the NMR data are also consistent with a thiol adduct of the vinyl derivative as the intermediate that was isolated. Hence, another mechanism for the

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(12) St. Clair, M. A. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1989. $HN(CH_3)(CH_2C_6H_5)$ was also shown to react with $Cp^*_2Ta(=CH_2)H$ at 130 °C over a period of days to give, among other products, $Cp^*_2Ta(\eta^2\text{-}CH_2{=}NCH_2C_6H_5)H$. Reactions with other amines resulted in metalation of the $\eta^5\text{-}C_5Me_5$ ligands and/or decomposition to unidentified products.

(13) No reaction occurs between thiophene and $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$, however.

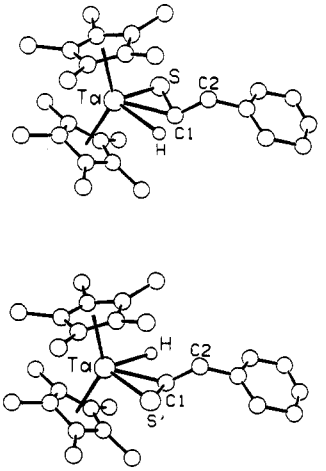
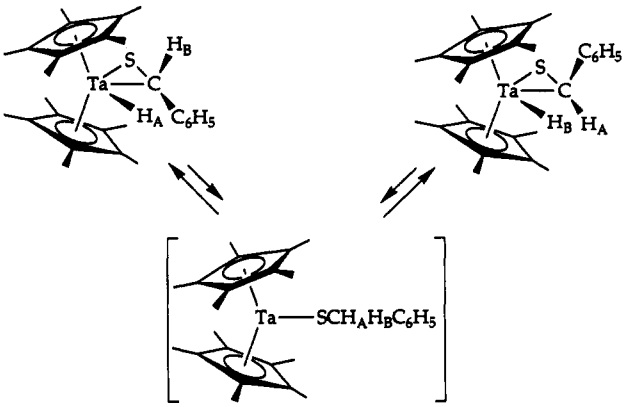


Figure 1. The two conformations for $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$ that are related by the approximate interchange of the sulfur and the hydrogen positions in the wedge. The major component at each site has a population of 0.68 (1).

formation of the η^2-thioaldehyde complex must also be considered: coordination of the thiol through the sulfur, followed by ethylene loss via an α-H abstraction to give the Ta(III) thiolate, which eliminates β-H to give the product (Scheme IV).[14]

Although NMR data for $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHR)H$ (R = H, C_6H_5, $CH_2C_6H_5$, CH_2CMe_3) (Table I) are consistent with η^2 coordination of the thioaldehyde unit to tantalum, they do not conclusively rule out a tantalathiacyclobutane type structure, $Cp^*_2TaSCH_2CHR'(H)$, for those complexes where γ-metalation rather than β-H elimination for $[Cp^*_2Ta\text{—}SCH_2CH_2R']$ is possible, i.e. for R′ = C_6H_5, CMe_3. In order to resolve this ambiguity, an X-ray structure determination for $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$ was undertaken. The details of the crystallography have been published elsewhere.[15] Drawings of the complex are shown in Figure 1. While several thioaldehyde–transition-metal complexes have been reported,[16] examples involving transition metals from groups 4 and 5 are rare. To our knowledge, no tantalum complexes have been reported; the only other examples from these groups are the zirconium complexes $Cp_2Zr(\eta^2\text{-}S\text{—}CHR)(PMe_3)$ (R = CH_3, C_6H_5), reported by Buchwald and co-workers,[17] and the titanium complex $Cp_2Ti(\eta^2\text{-}S\text{—}CH_2)(PMe_3)$, recently reported by Grubbs and co-workers.[7] The $[Cp^*_2Ta]$ geometry for $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$ is unexceptional. The hydrogen atom and the thioaldehyde ligand are contained in the wedge between the rings; however, unlike the titanocene or zirconocene thioaldehyde adducts, which have sulfur centrally located, the sulfur atom for $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$ is in the anti (lateral) position with the methine carbon next to the hydride ligand in the syn (central) position of the $[Cp^*_2Ta]$ wedge. This structure is the one that is anticipated to result from β-H elimination for $[Cp_2Ta\text{—}SCH_2CH_2C_6H_5]$. Disorder results from the superposition of two enantiomers. The two conformations are related by the approximate interchange of the sulfur and the hydrogen positions in the wedge. The major component at each site has a population of 0.68 (1). The centrosymmetric space group produces a racemic crystal.

Scheme V



The thioaldehyde hydride complexes $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHR)H$ appear to be in rapid equilibrium with the Ta(III), 16-electron thiolate complexes $[Cp^*_2Ta\text{—}SCH_2R]$ (eq 3).

$$Cp^*_2Ta(\eta^2\text{-}S\text{—}CHR)H \rightleftarrows [Cp^*_2Ta\text{—}SCH_2R] \quad (3)$$

Although these 16-electron complexes are in such low concentration as to preclude direct detection or isolation, evidence supporting their presence comes from (1) their trapping by the addition of suitable donor ligand (L = CO, $CNCH_3$) to give $Cp^*_2Ta(L)(SCH_2R)$,[18] (2) the observation of an inverse kinetic deuterium isotope effect for the conversion of $Cp^*_2Ta(\eta^2\text{-}S\text{—}CH_2)H$ to $Cp^*_2Ta(S)CH_3$ (vide infra), and (3) dynamic NMR experiments. Magnetization transfer experiments for exchange of $Cp^*_2Ta(\eta^2\text{-}S\text{—}CH_2)H$ with $Cp^*_2Ta(\eta^2\text{-}S\text{—}CH_2)H$ indicate a barrier for β-H migratory insertion of 21.3 (2) kcal mol^{-1} at 100 °C, indistinguishable from the value obtained for $Cp^*_2Ta(\eta^2\text{-}CH_2\text{=}CH_2)H$ ($\Delta G^\ddagger$ = 21.3 (1) kcal mol^{-1}).[19] For $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$ exchange of hydride and methine hydrogens also renders the η^5-C_5Me_5 ligands equivalent, as shown in Scheme V. The forward rate constant of this equilibrium for $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$ has not been determined quantitatively; however, magnetization transfer is observed at approximately 65 °C, establishing an approximate activation barrier for β-hydrogen migration of 19 kcal mol^{-1}.[20]

$Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$ and $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2CMe_3)H$ react with excess thiol to produce what appears by ^{1}H NMR spectroscopy[21] to be the permethyltantalocene dithiolate hydride complexes $Cp^*_2Ta(SR)_2H$ (R = $CH_2CH_2C_6H_5$, $CH_2CH_2CMe_3$). Curiously, $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHC_6H_5)H$ is unreactive toward excess benzyl mercaptan.

(14) There still remains the possibility that $Cp^*_2Ta(CHCH_2)(SCH_2C_6H_5)H$ first reductively eliminates the S–H bond to generate the thiol adduct, which subsequently undergoes α-H abstraction as shown in Scheme IV.

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(18) Neither the carbonyl nor the isocyanide complexes have been isolated. These compounds are obtained over a period of several hours by charging an NMR tube with roughly equal molar amounts of methyl isocyanide and the appropriate thioaldehyde hydride derivative in benzene-d_6 or by treating a benzene solution with 1 atm of carbon monoxide in a sealed NMR tube.

(19) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134.

(20) This activation barrier is almost identical with that for $Cp^*_2Ta(\eta^2\text{-}OCH_2)H$.[10]

(21) ^{1}H NMR (benzene-d_6): $Cp^*_2Ta(SCH_2CH_2C_6H_5)_2H$, δ 1.83 (s, 30 H), 3.05–3.30 (m, 8 H), 7.0–7.2 (m, 20 H), Ta–H not located; $Cp^*_2Ta(SCH_2CH_2CMe_3)_2H$, δ 1.92 (s, 30 H), 1.01 (s, 9 H), 1.05 (s, 9 H), methylene hydrogens not sufficiently well resolved to assign, Ta–H not located.

Table I. Summary of ^1H and ^{13}C NMR Data[a]

compd	assignt	δ (ppm)	J (Hz)
$Cp^*_2Ta(\eta^2\text{-}S\text{—}CH_2)H$	$\eta^5\text{-}C_5(CH_3)_5$	1.72 s	
	$S{=}CH_2$	1.70 d	$^3J_{HH} = 3$
	$Ta\text{—}H$	0.39 br t	
	$\eta^5\text{-}C_5(CH_3)_5$	11.9 q	$^1J_{CH} = 126$
	$\eta^5\text{-}C_5(CH_3)_5$	106.6 s	
	$S{=}CH_2$	40.2 dt	$^1J_{CH} = 155$, $^2J_{CH} = 10$
$Cp^*_2Ta(\eta^2\text{-}S\text{—}CHC_6H_5)H$	$\eta^5\text{-}C_5(CH_3)_5$	1.55 s	
		1.71 s	
	CHC_6H_5	7.76 d	$^3J_{HH} = 8$
		7.27 t	$^3J_{HH} = 8$
		7.01 m	
	SCH	*b*	
	$Ta\text{—}H$	*b*	
	$\eta^5\text{-}C_5(CH_3)_5$	11.4, 11.7	
	$\eta^5\text{-}C_5(CH_3)_5$	108.1, 108.3	
	CHC_6H_5	58.2	
	CHC_6H_5[c]	123.1	
		127.1	
		129.2	
		151.4	
$Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2C_6H_5)H$	$\eta^5\text{-}C_5(CH_3)_5$	1.64 s, 1.80 s	
	$S{=}CH_aCH_bH_cC_6H_5$	2.2 m	$J_{ab} = 10.8$
	$S{=}CH_aCH_bH_cC_6H_5$	3.0 dd	$J_{bc} = 14.2$
	$S{=}CH_aCH_bH_cC_6H_5$	3.8 dd	$J_{ac} = 3.1$
	$Ta\text{-}H_d$	1 br s	$J_{ad} = 1.2$
	$CHCH_2C_6H_5$	6.9–7.8 m	
	$\eta^5\text{-}C_5(CH_3)_5$[d]	11.4, 12.2	
	$\eta^5\text{-}C_5(CH_3)_5$	107.3, 108.5	
	$S{=}CH$	48.4	
	$CH_2C_6H_5$	60.7	
	CHC_6H_5	125.5	
		128.9	
		b	
$Cp^*_2Ta(\eta^2\text{-}S\text{—}CHCH_2CMe_3)H$	$\eta^5\text{-}C_5(CH_3)_5$	1.70 s, 1.78 s	
	$CH_aCH_bH_cC(CH_3)_3$	1.33 s	
	$CH_aCH_bH_cC(CH_3)_3$	1.93 m	$J_{ab} = 11.6$
	$CH_aCH_bH_cC(CH_3)_3$	1.55 dd	$J_{bc} = 13.7$
	$CH_aCH_bH_cC(CH_3)_3$	2.45 dd	$J_{ac} = 1.8$
	$Ta\text{—}H_d$	0.64 br	
	$\eta^5\text{-}C_5(CH_3)_5$	11.3, 12.1	
	$\eta^5\text{-}C_5(CH_3)_5$	106.8, 107.9	
	$S{=}CH$	51.8	
	$CH_2C(CH_3)_3$	56.6	
	$CH_2C(CH_3)_3$	30.3	
$Cp^*_2Ta(CH{=}CH_2)(SCH_2C_6H_5)H$[d]	$\eta^5\text{-}C_5(CH_3)_5$	1.76 s	
	$CH_a{=}CH_bH_c$	6.80 m	$J_{ab} = 12.4$
	$CH_a{=}CH_bH_c$	6.38 m	$J_{ac} = 18.0$
	$CH_a{=}CH_bH_c$	6.14 dd	$J_{bc} = 3.2$
	$CH_2C_6H_5$	3.99 s	
	$CH_2C_6H_5$	7.12–7.69 m	
	$Ta\text{—}H_d$	7.95 d	$J_{ad} = 9.1$
	$\eta^5\text{-}C_5(CH_3)_5$	11.6 q	$^1J_{CH} = 127$
	$\eta^5\text{-}C_5(CH_3)_5$	109.0 s	
	$CH_2C_6H_5$	49.1 t	$^1J_{CH} = 138$
	$CH_2C_6H_5$	108.0	
		149.8	
		b	
	$CHCH_2$	179.1 d	$^1J_{CH} = 123$
	$CHCH_2$	117.9 t	$^1J_{CH} = 152$
$Cp^*_2Ta(=S)H$	$\eta^5\text{-}C_5(CH_3)_5$	1.97 s	
	$Ta\text{—}H$	8.05 s	
	$\eta^5\text{-}C_5(CH_3)_5$	13.1 q	$^1J_{CH} = 127$
	$\eta^5\text{-}C_5(CH_3)_5$	114.6 s	
$Cp^*_2Ta(=S)CH_3$	$\eta^5\text{-}C_5(CH_3)_5$	1.81 s	
	CH_3	−0.02 s	
	$\eta^5\text{-}C_5(CH_3)_5$	12.7 q	$^1J_{CH} = 126$
	$\eta^5\text{-}C_5(CH_3)_5$	116 s	
	CH_3	24.6 q	$^1J_{CH} = 124$
$Cp^*_2Ta(=S)C_6H_5$	$\eta^5\text{-}C_5(CH_3)_5$	1.77 s	
	C_6H_5	6.52–7.71 m	
$Cp^*_2Ta(=S)CH_2C_6H_5$	$\eta^5\text{-}C_5(CH_3)_5$	1.77 s	
	C_6H_5	7.43 d	$^3J_{HH} = 7.5$
		7.21 t	$^3J_{HH} = 7.5$

Table I (Continued)

compd	assignt	δ (ppm)	J (Hz)
$Cp^*_2Ta(=S)CH_2C_6H_5$	C_6H_5	6.94 t	$^3J_{HH}$ = 7.5
	CH_2	*b*	
$Cp^*_2Ta(=S)CH_2CH_2C_6H_5$	η^5-$C_5(CH_3)_5$	1.83 s	
	$CH_2CH_2C_6H_5$	0.79 m	AA'XX' pattern
	$CH_2CH_2C_6H_5$	2.92 m	AA'XX' pattern
	$CH_2CH_2C_6H_5$	6.8–7.8 m	
$Cp^*_2Ta(=S)CH_2CH_2CMe_3$	η^5-$C_5(CH_3)_5$	1.85 s	
	$CH_2CH_2C(CH_3)_3$	0.45	AA'XX' pattern
	$CH_2CH_2C(CH_3)_3$	*b*	
	$CH_2CH_2C(CH_3)_3$	1.02 s	
$Cp^*_2Ta(SCH_2CH_2C_6H_5)(CNCH_3)$	η^5-$C_5(CH_3)_5$	1.79 s	
	$CH_2CH_2C_6H_5$	2.93 dd	
	$CH_2CH_2C_6H_5$	3.19 dd	
	$CH_2CH_2C_6H_5$	*e*	
	Ta—$CNCH_3$	3.10 s	

[a] NMR spectra (500 MHz) in benzene-d_6 at ambient temperature unless noted. Chemical shifts are reported in ppm (δ) from tetramethylsilane added as an internal reference or to residual proton in deuterated solvent. [b] Resonance(s) not located. [c] Resonance for one carbon (likely C_{ipso}) not found. [d] Spectrum obtained in toluene-d_8. [e] Resonances not well enough resolved to make definite assignments.

Rearrangement of Thioaldehyde Hydride Derivatives to Sulfido Alkyls. When they are heated to ca. 100 °C, the permethyltantalocene thioaldehyde hydride complexes undergo an α-alkyl migration to the sulfido alkyl derivatives of permethyltantalocene (eq 4). Permethyltantalocene sulfido alkyls or aryls may also be prepared by direct transfer of sulfur from olefin sulfides to a $[Cp^*_2Ta—R]$ precursor. On the basis of similar chemistry with ethylene oxide,[22] $[Cp^*_2Ta—R]$ sources have been treated with ethylene sulfide (eqs 5 and 6) to produce the tantalum sulfido alkyl products (^{1}H NMR).[23]

$$Cp^*_2Ta(\eta^2\text{-S—CHR)H} \rightarrow Cp^*_2Ta(=S)CH_2R \quad (4)$$

$$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H + \overbrace{SCH_2CH_2} \rightarrow Cp^*_2Ta(=S)C_6H_5 + C_2H_4 \quad (5)$$

$$Cp^*_2Ta(\eta^2\text{-}CH_2CHC_6H_5)H + \overbrace{SCH_2CH_2} \rightarrow Cp^*_2Ta(=S)CH_2CH_2C_6H_5 + C_2H_4 \quad (6)$$

A stepwise conversion of thioaldehyde hydrides to sulfido alkyls, as shown in Scheme I, is implicated by the substantial *inverse* deuterium kinetic isotope effect (KIE; k_H/k_D = 0.72 (3)) for $Cp^*_2Ta(\eta^2\text{-S—}CH_2)H$ vs $Cp^*_2Ta(\eta^2\text{-S—}CD_2)D$ at 138 °C.[24] The effect is to shift the preequilibrium in eq 7 toward the reactive thiolate intermediate for $Cp^*_2Ta(\eta^2\text{-S—}CD_2)D$, and since only a relatively small secondary isotope effect is expected for the rate-limiting sulfur–carbon bond cleavage, a net inverse KIE obtains for the overall reaction. The first-order rate constant k_{obs} ($=k_1k_2/k_{-1}$, assuming the rapid preequilibrium mechanism of eq 7) of [2.07 (3)] × 10^{-4} s^{-1} at 138 °C corresponds to an activation free energy of 31.8 (1) kcal mol^{-1}, approximately 3 kcal mol^{-1} less than the barrier for conversion of the formaldehyde hydride derivative $Cp^*_2Ta(\eta^2\text{-O—}CH_2)H$ to the oxo methyl product $Cp^*_2Ta(=O)CH_3$.[23] A weaker S—CH_3 vs O—CH_3 bond dissociation energy undoubtedly contributes to greater facility of the α migratory process involving sulfur.

$$Cp^*_2Ta(\eta^2\text{-S=}CH_2)H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cp^*_2Ta—SCH_3] \xrightarrow[\text{slow}]{k_2} Cp^*_2Ta(=S)CH_3 \quad (7)$$

Stereochemistry at Carbon for the α-Alkyl Migration. In order to further probe the mechanistic features of this new sulfur–carbon bond-cleaving process, the stereochemistry at carbon for the α-alkyl migration has been examined. The use of ^{1}H NMR spectroscopy to investigate the stereochemistry for alkyl migrations occurring at metal centers has been previously described.[25] The specific removal of H–H couplings by double deuteration affords an isolated AX spin system (e.g. L_nM—CHDCHDCMe$_3$) and two possible isomers, threo and erythro. The observed $^3J_{HH}$ coupling is the weighted average of the couplings of one trans and two gauche conformers. Typical erythro couplings for L_nM—CHDCHDCMe$_3$ are generally greater than 9 Hz, whereas for the threo isomer couplings are usually less than 6 Hz. As the size of the two groups at either end of the dideuterioethylene linker is reduced, the $^3J_{HH}$ values for the erythro and threo isomers generally approach each other. Thus, diastereotopically labeled neohexanethiols (i.e. HSCHDCHDCMe$_3$) were considered for use as NMR probes of stereochemistry in this α migration.

Unfortunately, although the derivatives derived from neohexyl mercaptan can be prepared, the reaction of neohexyl mercaptan with the permethyltantalocene starting materials is not as clean as with other thiols. A variety of reaction conditions were examined (diluting the reactants, using different $[Cp^*_2Ta—R]$ sources, lowering reaction temperatures, etc.); however, contamination with a small amount of the permethyltantalocene dithiolate hydride complex $Cp^*_2Ta(SCH_2CH_2CMe_3)_2H$ was consistently observed. Since this impurity obscures the relevant ^{1}H NMR signals for the alkyl sulfide product, analogous derivatives derived from phenethyl mercaptan, HSCHDCHDC$_6$H$_5$, were chosen as the diastereomeric probes, since $HSCH_2CH_2C_6H_5$ reacts very cleanly with the $[Cp^*_2Ta—R]$ sources. A drawback, which ultimately limits the utility of this thiol, is the smaller size of phenyl vs *tert*-butyl and hence the smaller difference in $^3J_{HH}$ for threo vs erythro

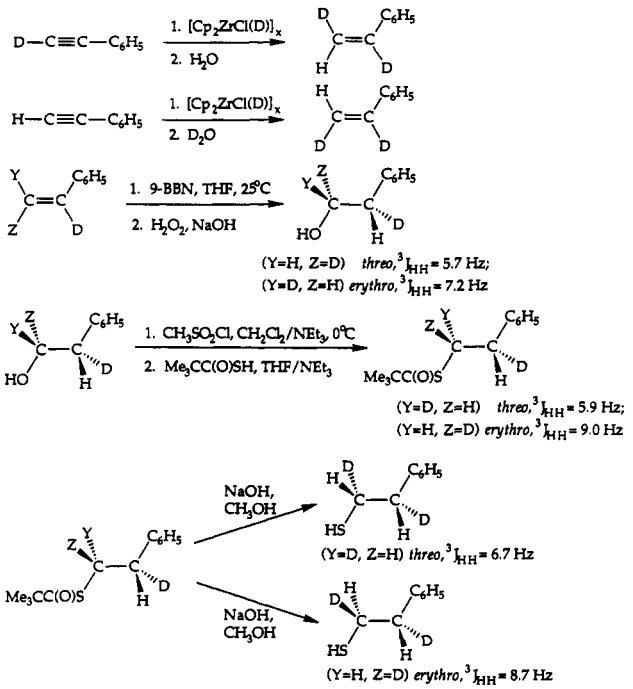
(22) Whinnery, L. L.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 7575.

(23) Although permethyltantalocene styrene hydride reacts with ethylene sulfide cleanly to afford $Cp^*_2Ta(=S)(CH_2CH_2C_6H_5)$, it does not exhibit analogous reactivity toward ethylene oxide or nitrous oxide. $Cp^*_2Ta(=O)(CH_2CH_2C_6H_5)$ may be prepared, however, via treatment of $Cp^*_2Ta(\eta^2\text{-}CH_2CHC_6H_5)H$ with iodosylbenzene.

(24) A inverse k_H/k_D = 0.46 (3) at 140 °C is observed in the closely related rearrangement of $Cp^*_2Ta(\eta^2\text{-O=}CH_2)H$ to $Cp^*_2Ta(=O)CH_3$: van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

(25) (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (b) Whitesides, G. M.; Boschetto, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 1529. (c) Whitesides, G. M.; Boschetto, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 4313.

Scheme VI



isomers (vide infra). Moreover, initial attempts to prepare pure erythro-d_2- and threo-d_2-labeled derivatives for phenethyl mercaptan using hydrozirconation routes[26] revealed an unexpected and interfering isotope scrambling process accompanying hydrozirconation of styrene.[27] Thus, another route to the diastereomeric thiols has been developed. The synthetic strategy is outlined in Scheme VI.

cis- and *trans*-styrene-d_2 are cleanly prepared by deuteriozirconation of phenylacetylene or deuteriophenylacetylene, followed by hydrolysis with D_2O or H_2O. Hydroboration/oxidation with H_2O_2 is used to convert the olefin to the *erythro*- or *threo*-phenethyl alcohol. 9-Borabicyclo[3.3.1]nonane (9-BBN) was chosen as the hydroborating reagent, since it adds to hindered alkenes with much greater selectivity than is observed with other hydroborating reagents. The alcohol is treated with methanesulfonyl chloride to produce the mesylate derivative, which is then converted to the thiopivalate with thiopivalic acid. This step is expected to proceed with inversion of stereochemistry at the phenethyl β-carbon (vide infra). Finally, the thiopivalate is cleaved in the presence of base to yield the labeled phenethyl mercaptan. In isolating the thiol, it is important to neutralize the reaction mixture at this point before exposure to air, since thiols are readily oxidized to disulfides in the presence of base. The $^3J_{HH}$ values for the erythro and threo intermediates and product mercaptans are shown. Although ^{1}H NMR spectra for the dideuteriated phenethyl alcohol, thiopivalate, and mercaptan intermediates appear to indicate a single isomer in each case, the similarity of the $^3J_{HH}$ values for the erythro and threo isomers makes quantitative determination of the isomeric purity by ^{1}H NMR spectroscopy unreliable, particularly since the ^{1}H chemical shifts also are very nearly the same (vide infra).

$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$ was treated with each of the diastereotopic thiols to produce the corresponding permethyltantalocene thioaldehyde hydride complexes Cp^*_2Ta-

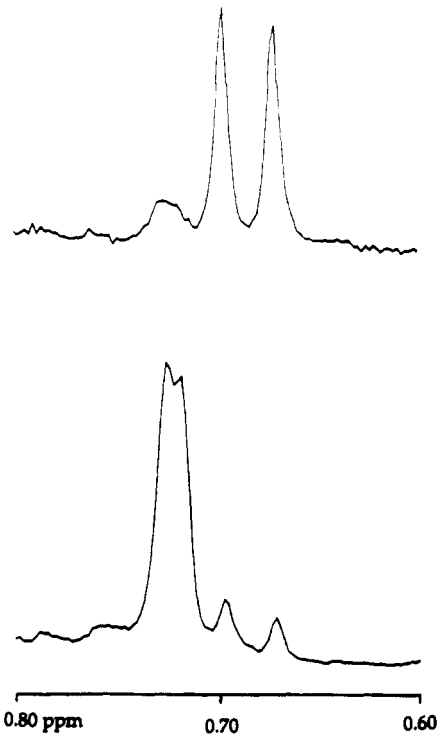


Figure 2. ^{1}H NMR spectra (500 MHz) of the α-methylene regions for $Cp^*_2Ta(=S)CHDCHDC_6H_5$ products obtained from Cp^*_2Ta(*erythro*-S-$CYCHDC_6H_5$)(Z) (top) and Cp^*_2Ta(*threo*-S-$CYCHDC_6H_5$)(Z) (bottom) (Y, Z = H, D or D, H).

(*threo*-S—$CYCHDC_6H_5$)(Z) and Cp^*_2Ta(*erythro*-S—$CYCHDC_6H_5$)(Z) (Y, Z = H, D or D, H).[28] Their rearrangements to the sulfido alkyl species were followed by ^{1}H NMR spectroscopy. As shown in Figure 2, the ^{1}H NMR resonances for the α-methylene proton of the product phenethyl permethyltantalocene sulfides, $Cp^*_2Ta(=S)$(*threo*-$CHDCHDC_6H_5$) ($^3J_{HH}$ = 3.4 Hz) and $Cp^*_2Ta(=S)$(*erythro*-$CHDCHDC_6H_5$) ($^3J_{HH}$ = 12.7 Hz) reveal ca. 15% of the other diastereomer present following alkyl migration (eqs 8 and 9). Whereas it may be safely con-

$$Cp^*_2Ta(\textit{threo}\text{-S—}CYCHDC_6H_5)(Z) \rightarrow Cp^*_2Ta(=S)(\textit{threo}\text{-}CHDCHDC_6H_5) + Cp^*_2Ta(=S)(\textit{erythro}\text{-}CHDCHDC_6H_5) \quad (8)$$

(~85% / ~15%)

$$Cp^*_2Ta(\text{erythro-S—}CYCHDC_6H_5)(Z) \rightarrow Cp^*_2Ta(=S)(\textit{erythro}\text{-}CHDCHDC_6H_5) + Cp^*_2Ta(=S)(\textit{threo}\text{-}CHDCHDC_6H_5) \quad (9)$$

(~85% / ~15%)

Y, Z = H, D or D, H

cluded that the migration proceeds predominantly with retention of stereochemistry at carbon, it is unclear whether the ~15% of the opposite stereoisomer arises from (1) contamination with the opposite diastereomer in the starting thioaldehyde hydride, (2) partial loss of stereochemistry during the synthesis of the thioaldehyde hydrides Cp^*_2Ta(*threo*-S—$CYCHDC_6H_5$)(Z) and Cp^*_2Ta(*erythro*-S—$CYCHDC_6H_5$)(Z) (Y, Z = H, D or D, H) or prior to their rearrangement to the alkyl sulfides, or (3) migration occurring with partial loss/inversion of stereochemistry at the α-methylene carbon.

In order to establish whether the label loss occurs before migration, Cp^*_2Ta(*threo*-S—$CYCHDC_6H_5$)(Z) and

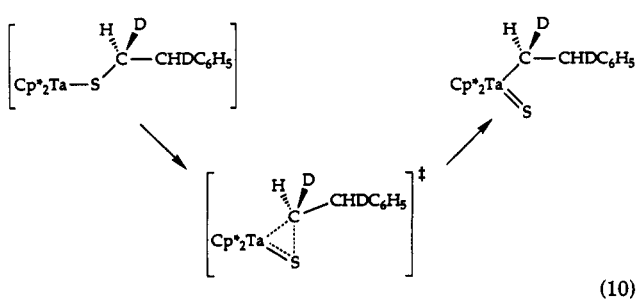
(26) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333.

(27) Nelson, J. E.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 2484.

(28) The threo and erythro designations refer to the thiolate precursors [Cp^*_2Ta-threo-$CHDCHDC_6H_5$] and [Cp^*_2Ta-threo-$CHDCHDC_6H_5$].

$Cp^*_2Ta(erythro\text{-}S\text{—}CYCHDC_6H_5)(Z)$ (Y, Z = H, D or D, H) were treated with methyl isocyanide to produce *erythro*- and *threo*-$Cp^*_2Ta(SCHDCHDC_6H_5)(CNMe)$. Surprisingly, these diastereomeric complexes, unlike the permethyltantalocene sulfido alkyls, do not have sufficiently different chemical shifts or $^3J_{HH}$ values to cleanly resolve mixtures of erythro and threo isomers. Thus, we were unable to assess whether or not as much as 15% of the other diastereomer is present as a contaminant prior to phenethyl migration from sulfur to tantalum. This result led us to examine the purity of the starting *erythro*- and *threo*-phenethyl mercaptans. Although initially we had no reason, on the basis of their ^1H NMR spectra, to suspect the purity of the erythro and threo isomers, we subsequently established that a sample prepared from a 70:30 mixture of *erythro*- and *threo*-phenethyl mercaptans showed only *one set* of doublets for $HSCHDCHDC_6H_5$. Even using $^1H\{^2H\}$ NMR techniques, the sample of the mixture exhibited an averaged $^3J_{HH}$ coupling rather than two distinct sets of doublets for the two diastereomers. The $^{13}C\{^1H\}$ NMR spectra for the thiols also were examined to determine whether a difference in chemical shifts could be seen for the diastereomers. Unfortunately, again the patterns showed identical methylene carbon chemical shifts within the resolution of the instrument. We therefore conclude that as much as 15% of the other diastereomer may have been introduced as impure mercaptan in the synthesis of $Cp^*_2Ta(threo\text{-}S\text{—}CYCHDC_6H_5)(Z)$ and $Cp^*_2Ta(erythro\text{-}S\text{—}CYCHDC_6H_5)(Z)$ (Y, Z = H, D or D, H).

In retrospect, it is apparent that, with the exception of the sulfido alkyl derivative, the H–H coupling constants and chemical shifts for the threo and erythro isomers are too similar to allow quantitative assessment of the amount of one diastereomer in the other. Only for the very large $[Cp^*_2(=S)Ta]$ moiety is the trans conformer of $X\text{—}CHDCHDC_6H_5$ (X = HO, $Me_3C(O)S$, HS, $[Cp^*_2(=S)Ta]$) sufficiently favored over the two gauche conformers to give rise to substantially different average $^3J_{HH}$'s, and only after migration from sulfur to tantalum was effected would it become apparent that a mixture of isomers was present. We are forced to the rather unsatisfactory conclusion that phenethyl migration proceeds with ≥85% retention of stereochemistry at the migrating carbon. The degree of retention is likely greater; however, since we are unable to adequately determine the purity of the precursor to ascertain whether or not the ca. 15% other diastereomer is present, we cannot be sure. Nonetheless, the results of this stereochemical study are in accord with a concerted C—S bond cleavage in the alkyl migration with retention via the expected three-center transition state shown in eq 10.

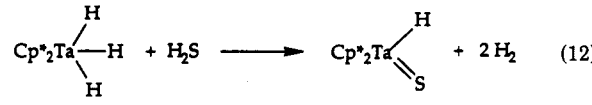


(10)

Reactivity of the Permethyltantalocene Sulfide Hydride and Alkyl Derivatives toward Dihydrogen. Permethyltantalocene sulfide hydride shows no reactivity toward H_2 (1–4 atm), even at temperatures as high as ca. 200 °C (eq 11). This finding is not surprising in view of

$$Cp^*_2Ta(=S)H + H_2 \rightarrow \text{no reaction} \qquad (11)$$

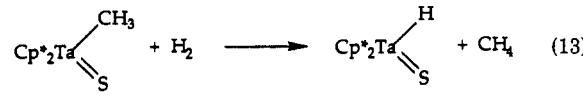
the oxophilic, and likely sulfophilic, character of early-transition-metal complexes. Indeed, $Cp^*_2TaH_3$ reacts with H_2S at room temperature to give H_2 and the permethyltantalocene sulfide hydride complex (eq 12). Hence, a



(12)

reaction sequence involving $Cp^*_2TaH_3$, $Cp^*_2Ta(\eta^2\text{-}S\text{—}CHR)H$, $Cp^*_2Ta(=S)CH_2R$, and $Cp^*_2Ta(=S)H$ to effect hydrodesulfurization in a catalytic manner is doubtful, since removal of sulfur with H_2 as H_2S is excessively endothermic.

One observation is particularly encouraging, however: $Cp^*_2Ta(=S)CH_3$ reacts with H_2 (≥4 atm), albeit slowly and only at elevated temperatures, to produce the permethyltantalocene sulfide hydride and methane (eq 13).[29] A true catalytic hydrodesulfurization of methanethiol has not been realized with this system, nonetheless.



(13)

Experimental Section

General Considerations. All manipulations of air-sensitive compounds were performed by using high-vacuum-line or glovebox techniques.[30] Argon, hydrogen, and nitrogen gases were purified by passage over MnO on vermiculite and activated 4-Å molecular sieves. Solvents were dried over CaH_2, $LiAlH_4$, or Na/benzophenone and stored under vacuum over "titanocene"[31] or sodium benzophenone ketyl. Solvents for preparation and purification of organic compounds were reagent grade and were used as received unless otherwise noted. Benzene-d_6 was dried over activated 4-Å sieves and stored over titanocene. Hydrogen sulfide, methanethiol, $DSCD_3$, butanethiol, thiophenol, benzyl mercaptan, phenethyl mercaptan, ethylene sulfide, styrene, neohexyl alcohol, triphenylphosphine, Br_2, potassium thioacetate, phenylacetylene, *n*-butyllithium (1.6 M in hexanes), thiopivalic acid, methanesulfonyl chloride, and Cp_2ZrCl_2 are commercially available and were used without further purification. (*Caution*! H_2S is extremely toxic.) Triethylamine was dried over CaH_2 and distilled prior to use. Methyl isocyanide was prepared by literature methods[32] and vacuum-transferred and stored over molecular sieves prior to use. $LiAlH_4$ and $LiAlD_4$ (Aldrich, received as a gray powder) were dissolved in ether, the solutions were filtered, and the solvent was removed in vacuo to yield white ether-soluble powders. $Cp^*_2TaCl_2$ and $Cp^*_2TaH_3$ were prepared as previously reported.[33] $Cp^*_2Ta(=C=CH_2)H$ and $Cp^*_2Ta(=CH_2)H$ have been previously reported.[34] $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$ was prepared as described else-

(29) An alternate catalytic cycle incorporating the requisite features of hydrodesulfurization (i.e., RSH + H_2 → H_2S + RH), but involving persistent tantalum sulfido species, has been considered: (1) 1,2-addition of thiol to the $Cp^*_2Ta(=S)H$ complex, (2) reductive elimination of H_2S to yield the thiolate complex, (3) S—C bond cleavage for the thiolate complex, which is in equilibrium with the permethyltantalocene thioaldehyde hydride, and (4) hydrogenation of the sulfido alkyl to liberate alkane, thus regenerating the sulfido hydride to complete the catalytic cycle. Unfortunately, even under forcing conditions (180 °C, 4 atm of H_2) $Cp^*_2Ta(=S)H$ failed to promote conversion of CH_3SH to methane and hydrogen sulfide prior to its decomposition.

(30) Burger, B. J.; Bercaw, J. E. In *New Developments in the Synthesis, Manipulation, and Characterization of Organometallic Compounds*; Wayda, A., Darensbourg, M., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 79–98.

(31) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

(32) Ugi, I.; Fetzer, U.; Enolzer, U.; Knupfer, H.; Offermann, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 472.

(33) Gibson, V. C.; Bercaw, J. E.; Bruton, W. J.; Sanner, R. D. *Organometallics* **1986**, *5*, 986.

(34) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

where.[35] $[Cp_2ZrHCl]_x$ and $[Cp_2ZrDCl]_x$ were prepared according to the procedure described by Buchwald[36] with the following modifications: (1) $LiAlH_4$ and $LiAlD_4$ were *always* isolated from ether and redissolved before use and (2) the entire procedure was performed in a glovebox, thus eliminating cannula filtration and slow line filtration. ^1H NMR spectra were recorded with Varian EM-390 (90 MHz), JEOL FX90Q (89.56 MHz), JEOL GX400 (400 MHz), and Bruker WM500 (500.13 MHz) spectrometers. ^{13}C NMR spectra were recorded on a Bruker WM500 (125.767 MHz) spectrometer. ^2H NMR spectra were recorded on a Bruker WM500 (76.775 MHz) spectrometer. IR spectra were obtained on a Beckman 4240 spectrometer as Nujol mulls. Elemental analyses were performed by the analytical services at Caltech.

Procedures. Many of the reactions reported were initially monitored in septum-capped NMR tubes. Approximately 15 mg of $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$, or other source of [Cp*Ta—R], was dissolved in 0.4 mL of benzene-d_6, and the sample tube was capped with a rubber septum. Known amounts of the appropriate reagent were syringed into the tube through the septum, and the reaction was followed by NMR spectroscopy. For reactions that needed to be monitored longer than 2 days, starting material and solvent were added to a sealable tube in the glovebox. The reagents were syringed in against an Ar counterflow or condensed in from a calibrated gas bulb. The tube was sealed with a flame and the reaction monitored by NMR spectroscopy.

$(CH_3)_3CCH_2CH_2Br$. Neohexyl alcohol (8.44 g, 0.083 mol) and $P(C_6H_5)_3$ (22 g, 1.1 equiv) were added to 100 mL of DMF under N_2. After the mixture was stirred until the solids were dissolved, Br_2 (4 mL) was added dropwise over 20 min until the orange color persisted. This solution was stirred for 2 h, and the neohexyl bromide was vacuum-distilled. The distillate was extracted into ether and washed with three 50-mL portions of water. The ether was removed in vacuo, yielding 5.80 g (43%) of neohexyl bromide. ^1H NMR (benzene-d_6, 25 °C): δ 0.61 (s, 3 H, CH_3), 1.61 (t, 2 H, CH_2), 3.02 (t, 2 H, CH_2).

$(CH_3)_3CCH_2CH_2SH$. Neohexyl bromide (8.3 g, 0.050 mol) and potassium thioacetate (5.7 g, 0.050 mol) were dissolved in 25 mL of absolute ethanol, and the solution was refluxed for 2 h under N_2. KOH (10 g) in 25 mL of H_2O was added, and the mixture was stirred for 1 h under N_2. After neutralization with glacial acetic acid, the product was extracted into ether and washed with three 50-mL portions of water. The ether was removed in vacuo, and the product was distilled and dried over calcium sulfate to yield 5.2 g (0.044 mol, 88%) of neohexanethiol. Anal. Calcd for $C_6H_{14}S$: C, 60.95; H, 11.93. Found: C, 61.33; H, 11.22. ^1H NMR (benzene-d_6, 25 °C): δ 0.68 (s, 3 H, CH_3), 1.32 (m, 2 H, CH_2), 2.15 (m, 2 H, CH_2), 1.07 (t, 1 H, SH).

$C_6H_5CH_2CH_2OH$. Styrene (2.0 mL, 17 mmol) was added via syringe against an Ar counterflow to a three-necked round-bottom flask. 9-Borabicyclo[3.3.1]nonane dimer (9-BBN; 2.1 g, 17 mmol, suspended in 40 mL of THF) was added over a 30-min period. The solution was stirred for 2 h. H_2O (2 mL) and NaOH (5.8 mL, 3 M) were added via syringe, followed by the slow addition of H_2O_2 (5.8 mL, 30%). The solution was stirred for 3 h and quenched with saturated NaCl solution. The water phase was extracted with 50:50 ethyl acetate/hexanes, and the combined organic phases were dried over $MgSO_4$. The solution was reduced in volume to 50 mL. (*Caution!* To avoid a potential explosion due to peroxides in the solution, 10 mL of DMF and 50 mL of methanol were added and the solution was stirred 12 h until a peroxide test was negative.) The solution was concentrated, and the alcohol was purified by column chromatography on silica gel, with 50:50 ethyl acetate/toluene as eluent, to yield 2 mL of $C_6H_5CH_2CH_2OH$ (^1H NMR).

$C_6H_5CH_2CH_2OSO_2CH_3$. $C_6H_5CH_2CH_2OH$ (2.0 mL, 17 mmol) was dissolved in 30 mL of dry CH_2Cl_2. Et_3N (4.0 mL, 1.3 equiv) was added via syringe against an Ar counterflow. The solution was cooled to 0 °C. CH_3SO_2Cl (2.0 mL, 1.5 equiv) was added dropwise via syringe against an Ar counterflow to the rapidly stirred solution over a 5-min period. The solution was quenched with 50 mL of H_2O and extracted with two 75-mL portions of 50:50 ethyl acetate/hexanes. The combined organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure to yield 2.0 mL of $C_6H_5CH_2CH_2OSO_2CH_3$. The product was not further purified.

$C_6H_5CH_2CH_2SC(O)C(CH_3)_3$. $C_6H_5CH_2CH_2OSO_2CH_3$ (2.0 mL) was dissolved in 15 mL of THF, and the solution was cooled to 0 °C. Et_3N (14.0 mL, 6 equiv) was added via syringe against an Ar counterflow. Thiopivalic acid (6.6 mL, 3 equiv) was added via syringe against an Ar counterflow. The solution was stirred 10 min at 0 °C, warmed to 50 °C, and stirred for 1 h. The solution was quenched with 100 mL of H_2O and extracted with three 75-mL portions of 50:50 ethyl acetate/hexanes. The combined organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel, with 5:95 ethyl acetate/hexanes as eluent, to yield 3.4 g of $C_6H_5CH_2CH_2SC(O)C(CH_3)_3$. ^1H NMR (benzene-d_6, 25 °C): δ 1.06 (s, 9 H, CMe_3), 2.66 (t, 2 H, CH_2), 2.97 (t, 2 H, CH_2), 7.00 (t, 2 H, phenyl), 7.07 (d, 2 H, phenyl).

$C_6H_5CH_2CH_2SH$. $C_6H_5CH_2CH_2SC(O)C(CH_3)_3$ (2.0 mL) was dissolved in 15 mL of degassed CH_3OH, and the solution was cooled to 0 °C. NaOH (10 mL, 50%) was added via syringe against an Ar counterflow. The solution was stirred for 5 h at 0 °C, warmed to room temperature, and stirred for 1 h until TLC showed the reaction to be complete. The solution was quenched with 100 mL of saturated NH_4Cl solution, and the product was extracted into 150 mL of 50:50 ethyl acetate/hexanes. The organic phase was washed with three 50-mL portions of H_2O and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The thiol was purified by column chromatography on silica gel, with 15:85 toluene/hexane as eluent, to yield 2.0 mL of $C_6H_5CH_2CH_2SH$ (^1H NMR).

***erythro*- and *threo*-$C_6H_5CHDCHDSH$.** These derivatives were prepared as described for $C_6H_5CH_2CH_2SH$ above, by starting from *cis*- and *trans*-styrene-d_2, prepared as described below.

$DC{\equiv}CC_6H_5$. Phenylacetylene (10.0 mL, 91 mmol) was dissolved in 70 mL of THF, and the solution was cooled to −78 °C. *n*-BuLi (60 mL, 1.6 M in hexanes) was added via syringe against an Ar counterflow. The solution was stirred at −78 °C for 1 h and at room temperature for 2 h. D_2O (2 mL) was added via syringe against an Ar counterflow to produce a yellow solution with much white precipitate. The solution was washed with three 50-mL portions of saturated NH_4Cl, and the water phases were extracted into diethyl ether. The combined organic phases were combined, dried over Na_2SO_4, and stripped to dryness to yield 9 mL of DC≡CPh. ^1H NMR spectroscopy showed ≥95% deuterium incorporation.

***cis*-Styrene-d_2.** $[Cp_2ZrDCl]_x$ (10.5 g, 40.5 mmol) was suspended in 50 mL of toluene. Phenylacetylene (5.0 mL, 1.1 equiv) was added via syringe against an Ar counterflow. The solution was stirred 2 h until all $[Cp_2ZrDCl]_x$ had dissolved, yielding a dark orange solution. The toluene was removed in vacuo, and the remaining orange residue was dissolved in 50 mL of diethyl ether. The solution was cooled to 0 °C, and 1.0 mL of degassed D_2O was slowly added via syringe against an Ar counterflow over 30 min. $[Cp_2ZrO]_x$ was filtered off, and the styrene was vacuum-distilled to yield 5.1 mL of *cis*-styrene-d_2. ^1H NMR spectroscopy showed ≥95% deuterium incorporation.

***trans*-Styrene-d_2.** $[Cp_2ZrDCl]_x$ (11 g, 41 mmol) was suspended in 60 mL of toluene. Deuteriophenylacetylene (5.0 mL, 1.1 equiv) was added via syringe against an Ar counterflow. The solution was stirred 3 h until all $[Cp_2ZrDCl]_x$ had dissolved, yielding a dark orange solution. The toluene was removed in vacuo, and the remaining orange goo was dissolved in 50 mL of diethyl ether. The solution was cooled to 0 °C, and 1.0 mL of degassed D_2O was slowly added via syringe against an Ar counterflow over 30 min. $[Cp_2ZrO]_x$ was filtered off, and the styrene was vacuum-distilled to yield 2.75 mL of *trans*-styrene-d_2. ^1H NMR spectroscopy showed ≥95% deuterium incorporation.

$Cp^*_2Ta(CH_2{=}CHC_6H_5)H$.[37] $Cp^*_2TaH_3$ (0.75 g, 1.7 mmol) was dissolved in 3 mL of benzene in a glass bomb. Styrene (0.57 mL, 5 equiv) was added via syringe against an Ar counterflow. The bomb was placed in a 110 °C oil bath for 3 days. The solvent was removed in vacuo, and the residue was washed with pentane

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(37) $Cp^*_2Ta(CH_2{=}CHC(CH_3)_3)H$ could not be prepared by this method: Nelson, J.; Quan, R. Unpublished results.

to yield 0.62 g (1.1 mmol, 65%) of tan product. Anal. Calcd for $C_{28}H_{39}Ta$: C, 60.43; H, 7.06. Found: C, 60.26; H, 6.81. ^1H NMR (benzene-d_6, 25 °C): δ −1.25 (s, 1 H, Ta–H), 0.15 (d, 2 H, CH_2), 1.53 (s, 15 H, Cp*), 1.67 (s, 15 H, Cp*), 1.90 (t, 1 H, CH), 6.97 (t, 2 H, phenyl), 7.27 (t, 2 H, phenyl), 7.70 (d, 1 H, phenyl).

$Cp^*_2Ta(=S)H$. A solution of $Cp^*_2Ta(=C=CH_2)H$ (0.200 g, 0.42 mmol) was stirred in 10 mL of toluene under an atmosphere of H_2S for 2 h at room temperature, giving a rose pink solution. The solvent was removed in vacuo, the residue was extracted into 25 mL of pentane, and the extract was filtered. The filtrate was concentrated to ca. 10 mL and placed at −80 °C, giving pink needles that were isolated by filtration and washed with cold pentane. Yield of $Cp^*_2Ta(=S)H$: 0.120 g (0.25 mmol, 59%). Anal. Calcd for $C_{20}H_{31}STa$: C, 49.6; H, 6.4. Found: C, 49.6; H, 6.4.

$Cp^*_2Ta(\eta^2\text{-}S{-}CH_2)H$. CH_3SH (ca. 0.6 mmol) was added to a solution of $Cp^*_2Ta(=C=CH_2)H$ (0.190 g, 0.40 mmol) in 10 mL of pentane, and the mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo, the residue was extracted into 20 mL of pentane, and the extract was filtered, concentrated to ca. 5 mL, and placed at −80 °C. The white needles that formed were separated by filtration, washed with cold pentane, and dried in vacuo to yield 0.100 g (0.20 mmol, 50%) of $Cp^*_2Ta(\eta^2\text{-}S\text{-}CH_2)H$. The d_3 complex was prepared in a similar manner using CD_3SD. Anal. Calcd for $C_{21}H_{33}STa$: C, 50.7; H, 6.7. Found: C, 50.6; H, 6.6. IR (Nujol mull, cm^{-1}): 1780, ν(Ta—H).

$Cp^*_2Ta(\eta^2\text{-}S{-}CHC_6H_5)H$. $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$ (0.880 g, 1.67 mmol) was dissolved in 15 mL of toluene. While the solution was cold (−78 °C), $HSCH_2C_6H_5$ (200 μL, 1 equiv) was added via syringe. The solution was warmed to room temperature, stirred for 18 h, and filtered. The toluene was removed in vacuo. Petroleum ether was added and removed in vacuo for four cycles to remove any excess thiol. Isolation from pentane at −78 °C afforded 0.61 g (1.07 mmol, 64% yield) of pale tan solid. Anal. Calcd for $C_{27}H_{37}STa$: C, 56.44; H, 6.50. Found: C, 56.14; H, 6.24.

$Cp^*_2Ta(CHCH_2)(SCH_2C_6H_5)H$. $Cp^*_2Ta(=C=CH_2)H$ (0.560 g, 1.17 mmol) was dissolved in 15 mL of petroleum ether. While the solution was cold (0 °C), $HSCH_2C_6H_5$ (135 μL, 1 equiv) was added via syringe. The solution was stirred for 30 min at 0 °C, during which time the product precipitated. The reaction mixture was cooled to −78 °C and filtered to yield 0.26 g (0.43 mmol, 37% yield) of tan solid. Anal. Calcd for $C_{29}H_{41}STa$: C, 57.80; H, 6.86. Found: C, 56.60; H, 6.25.[38] IR (Nujol mull, cm^{-1}): 1950, ν(Ta—H).

$Cp^*_2Ta(\eta^2\text{-}S{-}CHCH_2C(CH_3)_3)H$. $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$ (0.525 g, 0.947 mmol) was dissolved in 15 mL of toluene. While the solution was cold, neohexyl mercaptan (100 μL, 1 equiv) was added via syringe against an Ar counterflow. The solution was stirred 12 h and filtered. The toluene was removed in vacuo. Petroleum ether was added and removed in vacuo for three cycles to remove any excess thiol. Isolation from pentane at −78 °C afforded 0.075 g (0.132 mmol, 15% yield) of light green solid. Anal. Calcd for $C_{26}H_{43}STa$: C, 54.92; H, 7.62. Found: C, 54.45; H, 6.33.

(38) The elemental analysis for this compound appears low, probably due to a significant amount of $Cp^*_2Ta(\eta^2\text{-}S{=}CHPh)H$ present.

$Cp^*_2Ta(\eta^2\text{-}S{-}CHCH_2C_6H_5)H$. $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$ (0.220 g, 0.417 mmol) was dissolved in 10 mL of toluene. While the solution was cold, phenethyl mercaptan (48 μL, 0.85 equiv) was syringed in against argon. The solution was warmed to room temperature, stirred 2 h, and filtered. Toluene was removed in vacuo. Petroleum ether was added and removed in vacuo for three cycles to remove any excess thiol. Isolation from pentane at −78 °C afforded 0.175 g (0.297 mmol, 87% yield) of solid. Anal. Calcd for $C_{28}H_{39}STa$: C, 57.13; H, 6.68. Found: C, 57.41; H, 6.55.

$Cp^*_2Ta(=S)CH_3$. A solution of $Cp^*_2Ta(\eta^2\text{-}S{-}CH_2)H$ (0.055 g, 0.11 mmol) in 20 mL of toluene was heated at 130 °C in a glass ampule for 5 days. The solvent was removed under reduced pressure, and the residue was washed with pentane to yield 0.50 g of pink flakes (91%). Anal. Calcd for $C_{21}H_{33}STa$: C, 50.6; H, 6.6. Found: C, 50.6; H, 6.6.

Preparation of Other Sulfido Alkyls. Method 1. A sample of permethyltantalocene thioaldehyde hydride (ca. 15 mg) was dissolved in benzene-d_6 in a sealed NMR tube. The sample was heated in an oil bath to 110 °C, and the reaction was monitored by ^1H NMR spectroscopy until the migration was complete.

Method 2. A sealable NMR tube was charged with ca. 15 mg of $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$ or $Cp^*_2Ta(\eta^2\text{-}CH{=}CH_2C_6H_5)H$ dissolved in benzene-d_6. Approximately 1.1 equiv of ethylene sulfide was condensed into the solution, and the NMR tube was sealed. The reaction was monitored by ^1H NMR spectroscopy.

Kinetics of the Conversion of $Cp^*_2Ta(CHCH_2)(SCH_2C_6H_5)H$ to $Cp^*_2Ta(\eta^2\text{-}SCHC_6H_5)H$. A sample of $Cp^*_2Ta(CHCH_2)(SCH_2C_6H_5)H$, dissolved in benzene-$d_6$ in a sealed NMR tube, was submerged in an oil bath at 35 °C. Approximately 10 spectra were taken over 3 half-lives. The rate of the reaction was determined by measuring the increases of Cp* resonances for the product relative to an internal standard (ferrocene) as a function of time. A first-order rate constant was obtained from a plot of ln $([Cp^*]_{t=\infty} - [Cp^*]_{t=t})$ versus time.

Kinetic Isotope Effect for Conversion of $Cp^*_2Ta(\eta^2\text{-}S{-}CH_2)H$ to $Cp^*_2Ta(=S)CH_3$. Two independent samples of $Cp^*_2Ta(\eta^2\text{-}S{-}CH_2)H$ and $Cp^*_2Ta(\eta^2\text{-}S{-}CD_2)D$, dissolved in benzene-$d_6$ in sealed NMR tubes, were heated side-by-side submerged in an oil bath at 138 °C. The rates of the reactions were determined by measuring the decreases in intensity of the Cp* resonances of the starting material, relative to an internal standard (ferrocene), as a function of time. The measured rate constants were $k_H = [2.07\ (3)] \times 10^{-4}\ s^{-1}$ and $k_D = [2.87\ (3)] \times 10^{-4}\ s^{-1}$, thus giving rise to an *inverse* primary kinetic isotope effect of $k_H/k_D = 0.72\ (3)$ at 138 °C.

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