Synthesis of Alkyltantalocene Oxide, Sulfide, and Imide Derivatives: Stereospecific Heteroatom and -group Transfers from Oxiranes, Thiiranes, and Aziridines to Methyltantalocene

Grant Proulx and Robert G. Bergman*

Department of Chemistry, University of California, Berkeley, California 94720-1460

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Irradiation of $Cp_2Ta(C_2H_4)(CH_3)$ or thermolysis of $Cp_2Ta(PMe_3)(CH_3)$ cleanly generates an intermediate that behaves as $Cp_2Ta(CH_3)$. This species efficiently abstracts heteroatoms and -groups from oxiranes, thiiranes, and aziridines resulting in the formation of $Cp_2Ta({=}X)(CH_3)$ (X = O, S, and NR) and the corresponding alkene. The sulfido product, $Cp_2Ta({=}S)(CH_3)$, retains a dual reactivity toward thiiranes. It undergoes further thermal sulfur atom abstraction from thiirane to give $Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$ and, in a competing photochemical pathway, the sulfido thiolate complex $Cp_2Ta({=}S)(SCH_3)$. Our results constitute a rare example of nitrene group transfer from an aziridine to a metal center (and the first one that has been demonstrated to be stereospecific) and the first formation of a soluble thiolate from a metal−alkyl sulfide species. The persulfido complex can be reconverted to $Cp_2Ta({=}S)(CH_3)$ by treatment with phosphines (phosphine sulfides are also generated in this process). All the heteroatom and -group transfer reactions are completely stereospecific at carbon. Mechanistic studies of the nitrene group transfer have revealed an early transition state with only minor charge buildup on the nitrogen center and very little dependence on substituents bound to the carbons of the heterocycle. Competition studies have shown that there is very little selectivity exhibited by $Cp_2Ta(CH_3)$ toward aziridines having different substituents (R) bound to the nitrogen unless the R-groups are extremely sterically demanding. An X-ray crystal structure determination of $Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$ has been carried out.

Because of their high oxygen, sulfur, and nitrene group affinities, low-valent early transition metal complexes such as group V, d^2 species are ideal candidates for heteroatom abstraction processes.[1] Such processes are important in a wide range of homogeneous and heterogeneous transformations.[2−10] Sterically demanding cyclopentadienyl ligands such as $Cp^{t\text{-Bu}}$ ($Cp^{t\text{-Bu}} = \eta^5\text{-}t\text{-BuC}_5H_4$)[11] and Cp* (Cp* = $\eta^5\text{-}C_5Me_5$)[12−16] stabilize these complexes, but they also hinder some of their further reactions.[11,17] With this in mind, we have investigated the thermal and photochemical reactions of the simple alkyltantalocene complexes $Cp_2Ta(CH_3)(C_2H_4)$ (**1a**) (Cp = $\eta^5\text{-}C_5H_5$) and $Cp_2Ta(CH_3)(PMe_3)$[18] (**1b**) (Scheme 1).

We have previously communicated some of the photochemical reactions which **1a** was found to undergo.[19] These transformations proceeded through the unsaturated intermediate "$Cp_2Ta(CH_3)$" and provided a number of novel products; however, it proved extremely difficult to perform even qualitative rate measurement data on these photochemical systems. This led us to investigate a thermal method for generation of the proposed reactive intermediate, "$Cp_2Ta(CH_3)$". We now report the full details of our previous photochemical work and extend it to include the thermal reactions of **1b** along with a general discussion of the kinetics involved in these heteroatom transfer processes. This work has allowed us to gain significant insight into the transition states of these heteroatom transfers. Although much work has been done on the transfer of oxygen and sulfur atoms to transition metal centers, there has been no systematic study of the transfer of nitrene groups from aziridines to metal centers, in part due to the small number of

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[17] For example, desulfurization of the more hindered $(t\text{-BuCp})_2Ta(S_2)(H)$ with PR_3 requires several hours in refluxing toluene whereas we observed the parent $Cp_2Ta(S_2)(CH_3)$ to undergo desulfurization at 45 °C over several hours. See ref 14.

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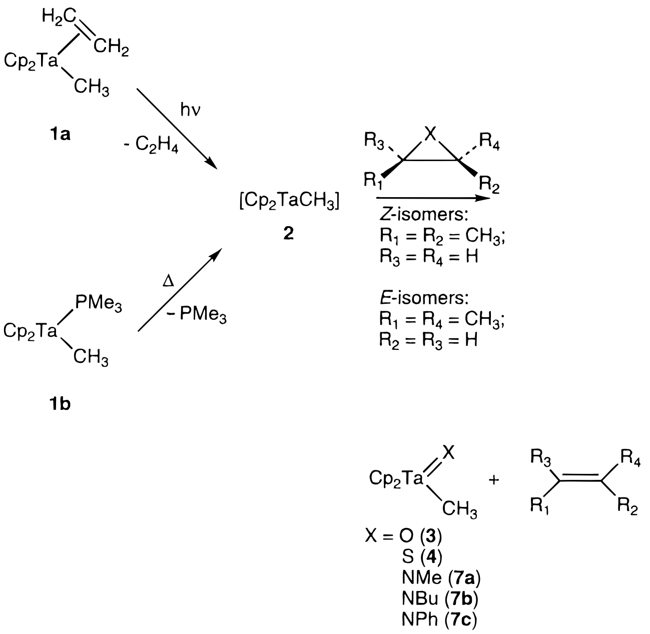
Scheme 1



systems that undergo this transformation.[20,21] Aziridines provide a unique "handle" with which to probe group transfer reactions: a structurally modifiable group substituted directly on the atom being transferred. This has allowed us to systematically vary the electronic and steric properties of the atom at which the highest degree of bonding change is occurring.

Results

Sulfur and Oxygen-Transfer Reactions. The 16-electron intermediate "$Cp_2Ta(CH_3)$" (**2**)[22-24] was first generated and studied by the thermal decomposition of $Cp_2Ta({=}CH_2)(CH_3)$; however, this pathway has a major drawback in that it always leads to 1 equiv of $Cp_2Ta(C_2H_4)(CH_3)$ (**1a**) along with the desired intermediate. This second-order decomposition was thermal and occurred mainly at higher temperatures and at high concentrations of starting material. As a result, slight variations in the concentration of starting material drastically change the amount of "$Cp_2Ta(CH_3)$" produced in solution.

In search of a method for access to **2** at reduced temperatures, we first irradiated a solution of $Cp_2Ta(C_2H_4)(CH_3)$ (**1a**). Photolysis of a C_6D_6 solution of $Cp_2Ta(C_2H_4)(CH_3)$ (**1a**) in the presence of 1 equiv of *cis*-2,3-dimethyloxirane at 5 °C leads to the prompt evolution of free ethylene and (*Z*)-2-butene along with the previously characterized oxo species, $Cp_2Ta({=}O)(CH_3)$ (**3**),[25,26] in quantitative yield (^1H NMR).[27] Photolysis of the *trans*-oxide in the presence of **1** gives (*E*)-2-butene and **3**. Less than 5% of the opposite alkene stereoisomer is formed in each case. A parallel reaction occurs upon thermolysis (45 °C) of a solution of $Cp_2Ta(PMe_3)(CH_3)$ (**1b**) under similar conditions. However, upon generation of the $Cp_2Ta({=}O)(CH_3)$ (**3**) at elevated temperatures, a white flocculent powder precipitates from solution. This is apparently the polymeric form of the tantalum oxide, $-[-(Cp_2(CH_3)Ta)-O-]_n-$, which is insoluble in common organic solvents. This insolubility has made it difficult to determine the exact structure and extent of polymerization of this species by crystallization or other methods.

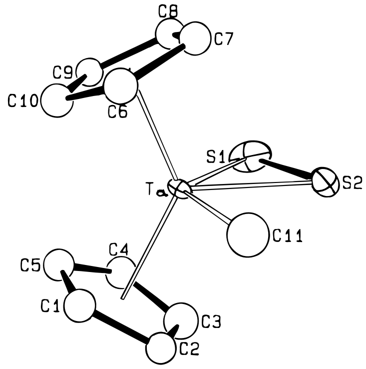


Figure 1. ORTEP diagram of $Cp_2(CH_3)Ta(\eta^2\text{-}S_2)$ (**5**).

In a similar fashion, photolysis of **1a** in the presence of 1 equiv of *cis*- or *trans*-2,3-dimethylthiirane gives $Cp_2Ta({=}S)(CH_3)$ (**4**) (81% isolated) along with the corresponding stereopure (>95%) alkenes (Scheme 1). The sulfido product has only two resonances in each of the ^1H (δ 5.44 and 0.74 ppm) and $^{13}C\ \{^1H\}$ NMR (δ 109.3 and 12.4 ppm) spectra attributable to the Cp and $Ta-CH_3$ groups, respectively. Mass spectral and combustion analysis also support our assignment of this structure. Several attempts at solving the structure of **4** by single-crystal X-ray diffraction analysis were made; however, there appeared to be long-range disorder between the sulfido and methyl groups of the tantalum which made the final solution difficult.[28] Compound **4** can be generated independently in high yield (^1H NMR) by photolysis of **1a** in the presence of stoichiometric amounts of $S{=}PMe_3$. Thermal reactions of **1b** also yield **4** along with the stereopure (>95%) alkenes in essentially quantitative yields (^1H NMR).

When 2 equiv of thiirane is treated with **1b**, the phosphine sulfide, $Me_3P{=}S$, is produced along with olefin and **4**. However, when a solution of pure **4** and a second 1 equiv of thiirane are allowed to react at 45 °C in the dark for 2 days, a new product $Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$ (**5**) begins to form along with a second 1 equiv of olefin. Compound **5** also has only two resonances in the ^1H (δ 4.89 and 0.89 ppm) and $^{13}C\ \{^1H\}$ (δ 104.7 and 5.1 ppm) NMR spectra, which are characteristic of Cp and $Ta-CH_3$ groups. The new product was isolated in 88% yield and showed an infrared absorbance at 536 cm^{-1} characteristic of a sulfur−sulfur bond.[29] The presence of a disulfur-containing product was also supported by combustion analysis and by the observation of a parent ion in the mass spectrum (FAB) of this product at m/z 390 (M^+).

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Table 1. Crystallographic Data for Compound 5

Crystal Parameters[a,b]	
formula	$TaS_2C_{11}H_{13}$
fw	390.3
cryst syst	monoclinic
space group	$P2_1/n$
Z	4
a, Å	7.4232(17)
b, Å	13.151(4)
c, Å	11.411(5)
β, deg	91.07(3)
V, Å^3	1113.8(10)
d_{calc}, g cm^{-3}	2.33
cryst dimens, mm	0.25 × 0.38 × 0.50
T, °C	−105
Measurement of Intensity Data	
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
monochromator	graphite
scan type	$\theta - 2\theta$
scan rate, deg/min	5.49
2θ range, deg	3−45
data collcd	$+h, +k, \pm l$
no. of data collcd	1655
no. of unique data	1450
unique data with $F^2 > 3\sigma(F^2)$	1311
no. of variables	72
μ_{calc}, cm^{-1}	100.7
R	0.037
R_w	0.050
GOF	2.60

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 28 and 30°. [b] In this table the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) of the reported value.

Table 2. Positional Parameters and B(eq) Values for $Cp_2Ta(CH_3)(\eta$-$S_2)$ (5)

atom	x	y	z	B^a (Å^2)
Ta	0.02734(1)	0.20176(1)	0.24551(1)	0.995(9)
S1	0.3604(4)	0.2139(3)	0.2865(4)	3.30(8)
S2	0.2827(5)	0.1414(3)	0.1354(3)	3.25(7)
C1	−0.198(2)	0.3297(9)	0.216(1)	1.9(2)*
C2	−0.080(1)	0.3399(9)	0.117(1)	1.8(2)*
C3	0.091(2)	0.369(1)	0.166(1)	2.8(3)*
C4	0.076(2)	0.381(1)	0.290(1)	2.4(2)*
C5	−0.107(2)	0.3585(9)	0.316(1)	2.0(2)*
C6	−0.190(2)	0.0766(9)	0.306(1)	2.0(2)*
C7	−0.014(1)	0.0262(9)	0.312(1)	1.9(2)*
C8	0.089(2)	0.0747(9)	0.397(1)	1.9(2)*
C9	−0.018(1)	0.1562(9)	0.447(1)	1.6(2)*
C10	−0.188(2)	0.1508(9)	0.392(1)	1.9(2)*
C11	−0.099(2)	0.132(1)	0.080(1)	3.0(3)*

[a] Starred B values are for atoms that were included with isotropic thermal parameters. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3))$, where a−c are real cell parameters and $\beta(i,j)$ values are anisotropic β's.

Table 3. Intramolecular Distances and Angles for $Cp_2(CH_3)Ta(\eta^2$-$S_2)$ (5)

atom 1	atom 2	dist (Å)
Ta	S1	2.512(3)
Ta	S2	2.427(3)
Ta	C11	2.292(14)
Ta	Cp1	2.108
Ta	Cp2	2.109
S1	S2	2.044(6)
Ta	C1	2.393(12)
Ta	C2	2.456(12)
Ta	C3	2.431(14)
Ta	C4	2.432(14)
Ta	C5	2.431(12)
Ta	C6	2.417(11)
Ta	C7	2.452(12)
Ta	C8	2.444(12)
Ta	C9	2.409(12)
Ta	C10	2.425(11)
C1	C2	1.446(17)
C1	C5	1.369(17)
C2	C3	1.431(18)
C3	C4	1.419(18)
C4	C5	1.426(17)
C6	C7	1.468(17)
C6	C10	1.379(17)
C7	C8	1.379(17)
C8	C9	1.458(16)
C9	C10	1.402(17)

atom 1	atom 2	atom 3	angle (deg)
Cp1	Ta	S1	101.86
Cp2	Ta	S1	104.10
Cp1	Ta	S2	116.12
Cp2	Ta	S2	113.71
Cp1	Ta	C11	100.27
Cp2	Ta	C11	99.54
Cp1	Ta	Cp2	129.43
S1	Ta	S2	48.84(14)
S2	Ta	C11	75.7(3)
S1	Ta	C11	124.5(3)
C2	C1	C5	108.9(11)
C1	C2	C3	105.5(12)
C2	C3	C4	109.3(11)
C3	C4	C5	106.2(11)
C1	C5	C4	109.9(10)
C7	C6	C10	106.7(11)
C6	C7	C8	107.8(10)
C7	C8	C9	108.4(10)
C8	C9	C10	106.1(11)
C6	C10	C9	110.8(11)

Because of the rarity of (alkyl)(persulfido)metal complex, an X-ray crystallographic analysis of **5** was performed. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The bonding and molecular geometry of **5** are shown in an ORTEP diagram in Figure 1. The crystallographic data and parameters for **5** are given in Table 1 with positional parameters in Table 2 and selected bond distances and angles in Table 3. The analysis confirmed the (alkyl)(persulfido)metal structure. It was found that the *endo* Ta−S bond (2.512(3) Å) was slightly longer than the *exo* (2.427(3) Å) in accord with the similar $Cp_2Nb(\eta^2$-$S_2)(CH_3)$structure.[30] The S−S bond length (2.044(6) Å) was consistent with a full single bond (the S−S bond length in S_8 is ~2.05 Å[31]).

Complex **5** appears to be quite thermally stable in the absence of reducing agents. However, it is possible to regenerate the terminal alkyl sulfide species, **4**, along with phosphine sulfide $R_3P{=}S$, by addition of phosphines to a solution of **5**. Our ability to reversibly interconvert the sulfido and persulfido complexes suggests that a tantalum-catalyzed thiirane desulfurization process might be possible using this system. However, when 10 mol % of **4** was added to a solution of PPh_3 and thiirane, there was only an approximate 20% increase in the rate of sulfur transfer at 45 °C compared with the uncatalyzed mixture. Both this weakly catalytic and the corresponding stoichiometric desulfurization reactions gave stereopure alkenes.

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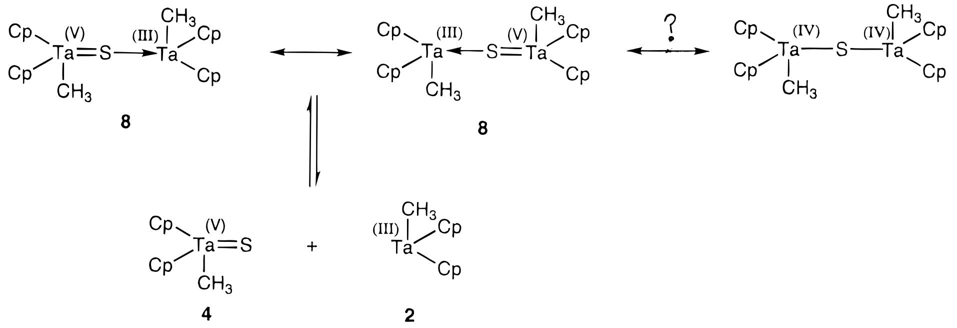
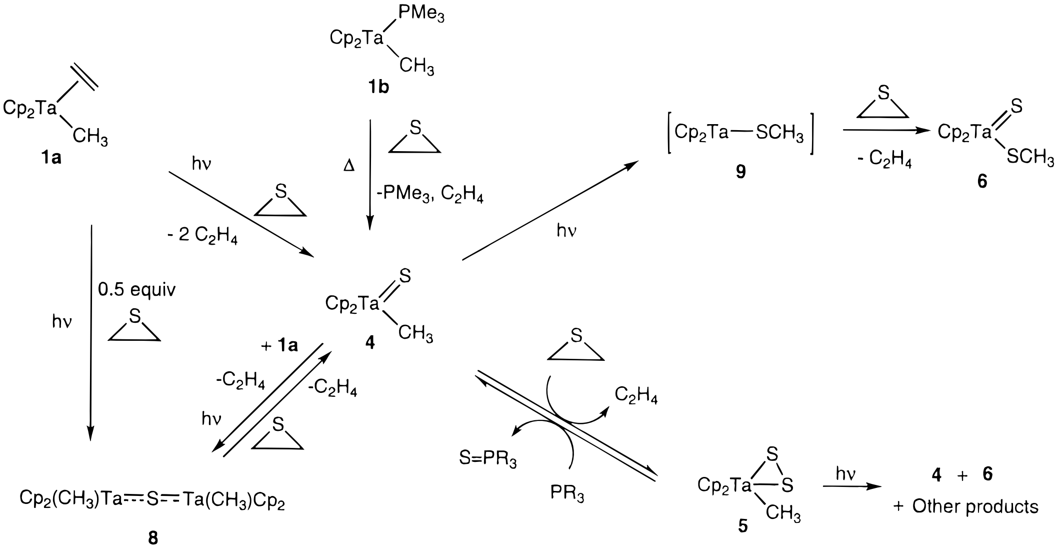


Figure 2. Resonance structures for $Cp_2(CH_3)Ta(\mu\text{-}S)Ta(CH_3)Cp_2$ (**8**) and equilibration of **8** with $Cp_2(CH_3)Ta({=}S)$ (**4**) and $Cp_2Ta(CH_3)$ (**2**).

Scheme 2



In marked contrast to the thermal chemistry of **4**, photolysis of the sulfido complex at 5 °C in the presence of a second 1 equiv of *cis*- or *trans*-2,3-dimethylthiirane forms a product different from **5** along with the stereopure alkenes (Scheme 2). Although this product was also found by mass spectral analysis to contain two sulfur atoms by yielding an ion with m/z at 390 (FAB), the ^1H NMR spectrum of this new product was markedly different. The resonances for the methyl group no longer appeared in the δ 0−1 ppm range that is normal for a $Ta{-}CH_3$ group, but instead a single sharp resonance appeared at δ 2.72 ppm consistent with a thiolate species. All spectral and analytical data are consistent with assignment of the identity of this material as $Cp_2Ta({=}S)(SCH_3)$ (**6**).

It is also possible to generate **6** in low yield by irradiation of a solution of **5** (^1H NMR). However, only a very small conversion of **5** to **6** is observed, and a number of other unknown products are formed as well.

In contrast to the above results, when 2 equiv of **1a** is irradiated with 1 equiv of $S{=}PMe_3$ or thiirane (Scheme 2), the diamagnetic bridging sulfido species $Cp_2(CH_3)Ta(\mu\text{-}S)Ta(CH_3)Cp_2$ (**8**) is formed along with phosphine or stereopure olefin, respectively. This complex can be obtained similarly by the photolysis of **1a** in the presence of 1 equiv of **4** and can be isolated as intensely colored blue crystals from benzene−pentane recrystallization in 93% yield. The structure of this complex can be understood in terms of the two similar Ta(III)/Ta(V) resonance structures shown in Figure 2. In each, the tantalum sulfide **4** acts as a donor to an unsaturated "$Cp_2Ta(CH_3)$" fragment. Consistent with this possibility, it was found that **8** appears to be in equilibrium with a mixture of **4** and the proposed "$Cp_2Ta(CH_3)$" species since treatment of a solution of **8** with a second 1 equiv of thiirane or phosphine sulfide forms 2 equiv of **4** and 1 equiv of olefin or phosphine in essentially quantitative yield at ambient temperatures (^1H NMR). However, we cannot rule out a contribution of the third (Ta(IV)/Ta(IV)) resonance form shown in Figure 2 to the overall structure of this complex.

Nitrene Group Transfer from Aziridines. We have communicated previously that complex **1a** reacts photochemically with aziridines,[19] and we have now extended this to the thermolysis of **1b**. Upon irradiation of a C_6D_6 solution of *N*-methylaziridine with **1a** or heating a solution with **1b** to 45 °C, prompt formation of ethylene is observed along with >95% (^1H NMR) of a new product which has ^1H and $^{13}C\{^1H\}$ NMR spectra consistent with its assignment as the imido complex $Cp_2Ta({=}NCH_3)(CH_3)$ (**7a**) (Scheme 1). Two singlet methyl resonances in the ^1H NMR at δ 3.86 ($N{-}CH_3$) and 0.88 ($Ta{-}CH_3$) ppm along with a sharp singlet at δ 5.51 ppm attributable to the equivalent Cp rings are observed in the ^1H NMR spectrum of **7a**. This imido complex, along with all other tantalum−imido species described herein, are glassy oils at room temperature. If one is careful to grow crystals at −80 °C and allow them to warm slowly, they appear to have melting points in the range of −50 to −20 °C depending on the size of the imido group. Reactions similar to the **1** and *N*-methylaziridine transformation were observed using

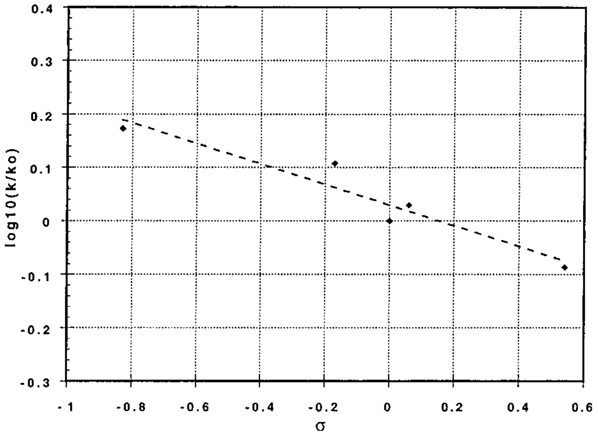


Figure 3. Hammett plot for relative rates of nitrene group transfer to $Cp_2Ta(CH_3)$ from para-substituted *N*-phenylaziridines.

N-(*n*-butyl)- and *N*-phenylaziridine, leading to ethylene and $Cp_2Ta(=NR)(CH_3)$ (R = *n*-Bu (**7b**), Ph (**7c**)). Somewhat to our surprise, however, after irradiation of a benzene or THF solution of **1a** and *N*-(*tert*-butyl)aziridine for several hours in a quartz vessel, no significant reaction had occurred. This apparent steric effect at the transferring group was interesting because increasing the steric bulk of substituents attached to the carbon atoms in the thiirane and oxirane rings did not significantly retard the transfer of S and O atoms to Ta.

Importantly, irradiating a solution of **1a** or heating a solution of **1b** in the presence of *cis*- or *trans*-2,3-dimethyl-*N*-methylaziridine (Scheme 1) leads to the imido complex **7a** along with >95% of the (*Z*)- or (*E*)-2-butene, respectively (^1H NMR). No intermediates (such as aziridine adducts) could be observed by ^1H NMR spectroscopy at any point during these reactions.

Substituent Effect Studies. In order to examine the extent of charge development in the transition state, we next decided to examine the relative rates of nitrene-group transfer from *N*-arylaziridines that carry electron-withdrawing and -donating substituents on the aromatic ring. However, we were somewhat limited in the types of groups we could use due to the reactivity of the "Cp_2TaCH_3" fragment. The fragment was found to react directly with a number of common substituents including nitro, nitroso, cyano, cyanate, primary and secondary amino, alcohol, acid, ester, ketone, and olefinic groups. We found however, the the *para*-CH_3, NMe_2, F, and CF_3 groups were suitable for such experiments and did not react directly with the Ta fragment. The competition studies were performed by allowing a C_6D_6 solution of **1b** to react with an excess of *N*-phenylaziridine and each of the para-substituted *N*-phenylaziridines. The disappearance of starting material and the appearance of products were monitored by ^1H NMR, and the relative rates of formation of the different imido complexes were obtained. The data were then used to construct the Hammett plot shown in Figure 3. Somewhat to our surprise, the ρ value obtained was quite small (−0.2) though it demonstrated the expected polarity.[32,33]

When similar competition studies were performed between the *N*-phenyl- and the *N*-methyl- or *N*-(*n*-butyl)-substituted aziridines, the *N*-phenylaziridine was found to transfer nitrogen approximately three times faster than the corresponding alkyl-substituted aziridines.

We have also carried out some relative rate measurements using *N*-methylaziridines in which the ring carbons were substituted with either methyl groups or a phenyl group. These qualitative measurements showed (as with the thiirane and oxirane reactions) that there was no significant increase in the rate of nitrogen group transfer relative to the unsubstituted *N*-methylaziridine. The only dramatic change encountered was with the *N*-(*tert*-butyl) group; this bulky group shut down the nitrene-group transfer entirely.

Mechanistic Discussion. It appears in this system that both the ethylene complex **1a** and the phosphine complex **1b** allow easy access to an intermediate which behaves like $Cp_2Ta(CH_3)$. To our surprise, there was no evidence for an equilibrium between $Cp_2Ta(CH_3)$ and the hydrido−methylidene species $Cp_2Ta(=CH_2)(H)$ to any significant extent, in contrast to the bulkier Cp* system in which there is facile α-migratory insertion from $Cp^*_2Ta(=CH_2)(H)$[14] to generate "$Cp^*_2Ta(CH_3)$". In the Cp* case, the hydrido−methylidene species is actually the isolable isomer of the product. The absence of this interconversion allowed us to focus on the intermolecular chemistry of the unsaturated center. However, the mechanism of oxygen and sulfur atom abstraction from oxiranes and thiiranes in this system appears to be similar to the pathway taken in more sterically encumbered systems.[14] The heteroatom transfers take place with high stereoselectivity at the three-ring carbon atoms, and no intermediates or metallacycles are visible by normal spectroscopic methods. It is likely that the mechanisms proceed via a concerted three-center transition state analogous to those proposed by Bercaw in his elegant oxygen atom transfer studies. As in Bercaw's system, though, we are unable to rigorously rule out an extremely fast biradical or zwitterionic pathway (one in which M−X bond cleavage is substantially faster than rotation about the carbon−carbon bond).

Ta=S to Ta(η-S_2) Transformation. The rich reactivity of this system shows other contrasts with data on related reactions in the literature. One example is the unusual sulfur atom transfer from thiirane to **4** to form persulfide **5**. This type of transformation may be important in the heterogeneous hydrodesulfurization of alkanes and may possibly be a so far unrecognized route for the homogeneous desulfurizations of other organics. Early metal persulfides and peroxides[11,13,30,34−36] are not typically formed by heteroatom transfer from an organic, presumably due to the relative thermodynamic instability of the peroxide or persulfide with respect to the terminal oxide or sulfide.

In understanding the mechanism of the Ta=S to Ta(η^2-S_2) reaction, it is important that we see no intermediates (e.g. five-membered heterocycles or thiirane adducts) when the reactions are closely monitored by ^1H NMR. Also, since we see stereoretention at carbon,

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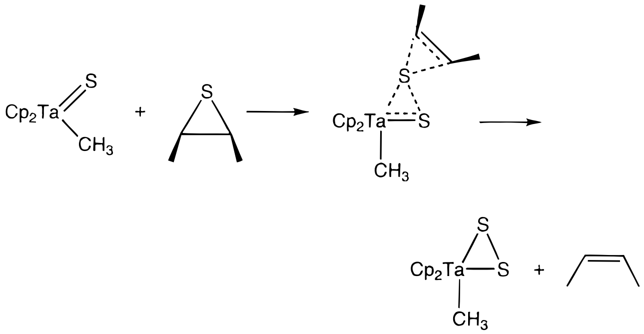
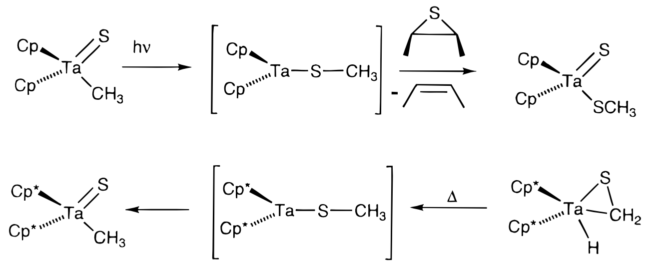
Scheme 3



Scheme 4



as we observe in the atom- and group-transfer reactions to $Cp_2Ta(CH_3)$, we believe that the transition state for the second sulfur atom transfer involves the simultaneous formation of a sulfur−sulfur and sulfur−tantalum bond with cleavage of the sulfur carbon bonds (Scheme 3).

Photochemical Conversion of $Cp_2(CH_3)Ta{=}S$ (4) to $Cp_2(CH_3S)Ta{=}S$ (6). The photochemistry of tantalum sulfide **4** with thiiranes differs dramatically from its thermal behavior, leading to sulfido thiolate **6** and alkenes. We believe that this occurs by transfer of a second sulfur atom (to make **6**) following photochemically induced migration of the methyl group to the sulfide ligand of **4**. The sulfur-transfer step is likely also concerted because there is again no mixing of olefin isomers. We believe that the intermediate in this reaction (intermediate **9**, Scheme 2) is very similar to **2**, proposed in the transfer reactions discussed above, except that there is an $-S-CH_3$ group in place of $-CH_3$. Control experiments demonstrate that it was only possible to generate **6** in low yield by irradiation of a solution of persulfido complex **5**. Therefore, we do not believe that **5** is a significant intermediate in the low-temperature photolytic formation of **6** from **4**.

Sulfide Insertion vs α-CH_3 Elimination. The conversion of **4** to **6** involves a photochemical insertion of a sulfide ligand into a methyl−tantalum bond. In contrast, in Bercaw's recent work on the η^2-thioaldehyde−hydride derivatives of permethyltantalocene (Scheme 4)[12] it was noted that there was a thermal migration of a methyl *from* the sulfur to the tantalum. Comparing these two similar systems has helped us gain insight into the accessibility and stability of these fragments.

It has been noted that between the terminal (alkyl)(sulfido)tantalum complex and the thiolate species, the thermodynamically more stable isomer is the sulfide.[23] Consistent with this, our results show that access to the thiolate from the terminal sulfide requires ultraviolet irradiation. The thermal insertion of the methylidene carbon of $Cp^*_2Ta(CH_2)(CH_3)$ into the Ta−CH_3 bond was shown to be about 10^{10} times slower than the corresponding insertion of a methylidene into the Ta−H bond.[23] On the basis of our results, it appears that the often overlooked photochemistry of these metal systems can overcome at least some of the seemingly insurmountable thermal barriers often observed.

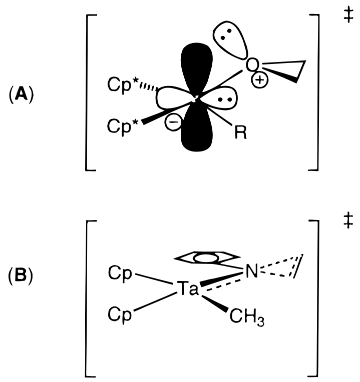


Figure 4. (A) Proposed transition state for oxygen transfer to $Cp^*_2Ta(R)$ from oxiranes. (B) Proposed transition state of nitrene-group transfer to $Cp_2Ta(CH_3)$ from aziridines.

Mechanism of Nitrene Group Transfer. Due to the small number of nitrene group transfers from aziridines to metals reported in the literature, one important goal of the work described in this paper was to investigate the possibility of using the reactive fragment "Cp_2TaCH_3" to accept a nitrene fragment, in analogy to its abstraction of oxygen and sulfur atoms. As we hoped, the transfer of a nitrene group from aziridines proceeds similarly to the oxygen or sulfur transfers from oxiranes or thiiranes. In contrast to the O- and S-transfer reactions, however, steric effects can be used to shut down the nitrogen-group transfer completely by taking advantage of the ability to modify the N-bound substituents on the aziridine precursors.

The transition state shown in Figure 4 for the concerted transfer of an oxygen atom from an oxirane to a Cp^*_2TaR center has been proposed by Bercaw.[14] The Cp^*_2TaR case proceeds with retention of cis or trans geometry, supporting a concerted mechanism, in which the Ta═O bond forms simultaneously with breakage of the two C−O bonds of the epoxide. The transition state was proposed[14] to contain a positive formal charge on the oxygen atom and a negative charge on the metal center. This is in direct contrast to Bercaw's proposed nonpolar transition state for olefin loss from oxametallacyclobutanes ($Cp^*_2(CH_3)Ta(\eta^2\text{-}CH_2CHRO)$) in this series.

We also observed retention of cis or trans geometry in the O-, S-, and RN-transfer reactions. In O- and S-transfer systems, it is difficult to test the hypothesis of a large charge buildup on the atom to be transferred,[14] but in the nitrogen-transfer study it was possible to explore this idea by variation of the groups directly bound to the nitrogen atom. If the transition state contains significant positive charge buildup at nitrogen, electron-donating groups should stabilize the transition state and speed up the reaction significantly.

The substituent effect studies were performed by allowing "$Cp_2Ta(CH_3)$" to compete for *N*-arylaziridines carrying electron-withdrawing and -donating groups in the para-position of the nitrogen-bound phenyl rings. A plot of relative rate constants vs Hammett σ values gave a small ρ value of −0.2. This suggests that the transition state has positive charge buildup on nitrogen, but the modest magnitude of the effect points toward an early transition state. We cannot say rigorously whether the same holds true for the sulfur and oxygen atom transfers, although it is likely to be the case.

A serious question remains as to what the orbital character around the nitrogen center in the transition state may be: i.e., whether it is sp^3 (bent at the nitrogen with respect to the carbon ring and metal center) or sp^2 (with significant π-orbital character about the nitrogen center). We attempted to probe this question by performing competition experiments between aziridines carrying nitrogen groups with different π-character.[37] For example, in competition studies performed using mixtures of *N*-aryl (sp^2-hybridized nitrogen) and *N*-methyl- or *N*-(*n*-butyl)-substituted (sp^3-hybridized nitrogen) aziridines,[38] and *N*-arylaziridines were found to transfer nitrogen approximately three times faster than the corresponding alkyl systems. Although this increase is not a dramatic change, it supports the idea that increased π-character at the nitrogen lone pair helps lower the barrier for transfer of the nitrogen group.

We also performed competition studies aimed at probing the nature of the bonding in the transition state at the carbon centers of the ring. By allowing the phosphine complex **1b** to react with mixtures of *C*-phenyl- or *C*-methylaziridines and the corresponding *C*-unsubstituted aziridines, we were able to test by competition whether these substituents stabilize the transition state for nitrene-group transfer. These measurements showed little competitive difference across the range of substituents tried: carbon-bound phenyl or methyl groups did not significantly increase the relative rate of nitrogen group transfer. This reflects a small overlap in the transition state between the alkyl or aromatic groups and the developing carbon π-system, a conclusion that is consistent with the postulate of an early transition state in which little electronic interaction has yet developed.

Conclusions

As illustrated in Scheme 1, we believe that the oxygen, sulfur, and nitrene group transfer reactions observed in the photochemical reaction of **1a** and the thermochemical reaction of **1b** reported here take place via the initial formation of "Cp_2TaCH_3" or a solvate of this species. This reactive Ta(III) intermediate then rapidly abstracts O, S, or NR from the three-membered rings. A variety of mechanisms have been suggested for the deoxygenation of epoxides to form metal−oxo species and for the reverse process, the epoxidation of olefins by metal−oxo complexes, and Bercaw and his colleagues have published a detailed analysis of epoxide deoxygenation by a tantalum system similar to the one reported here.[14] Analogous studies of nitrene group transfer have not been performed, presumably due to the lack of previously known complexes that undergo this reaction.[20] In both the nitrene transfer reactions and the sulfide/persulfide transformation, we believe the unusual reactivity of this system is due, in part, to the lack of sterically encumbering ligands on the tantalum.[17] This allows easier attack of the heteroring at Ta or Ta=S and (in the sulfur case) facilitates phosphine-mediated reconversion of the persulfido to the sulfido complex.

Mechanistic studies of our reactions have provided significant insight into the transition state for the nitrene group transfer. The overall mechanism involves concerted atom- or group-transfer from the ring to the metal center. Stereochemical data argue against mechanisms involving long-lived radical, carbocation, or carbanion intermediates. The almost negligible rate enhancements observed in studies with *para*-substituted phenyl rings show that there is very little effect even by strongly electron-donating groups. This seems to argue for a very early transition state and one which has relatively little positive charge buildup on the nitrogen atom. Similarly, the somewhat more pronounced (but still small) rate enhancement by aziridines with phenyl groups versus alkyl groups point toward a transition state with a significant amount of π-character involved.

Experimental Section

General Procedures. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere in a Vacuum Atmospheres HE-553-2 drybox equipped with a MO-40-2 Dri-train or using standard Schlenk techniques. Unless otherwise noted, all oxiranes, thiiranes, and aziridines were degassed by three freeze−pump−thaw cycles before vacuum transferring them. For descriptions of the NMR, IR, UV/vis, and mass spectral instruments as well as solvents and experimental techniques used, see a related paper from this group.[39] $Cp_2Ta(C_2H_4)(CH_3)$ (**1a**),[18] $Cp_2Ta(PMe_3)(CH_3)$ (**1b**),[18] *N*-(*n*-butyl)aziridine,[38] *N*-phenylaziridine,[40] *N*-(*p*-X-phenyl)aziridine,[41] *N*-(*tert*-butyl)aziridine,[38] *N*-methylaziridine,[38] and *cis*- and *trans*-*N*-methyl-2,3-dimethylaziridine[42] were all prepared by literature methods.

$Cp_2(CH_3)Ta(=O)$ (3). $Cp_2Ta(C_2H_4)(CH_3)$ (**1a**) (64.0 mg, 0.181 mmol) was dissolved in THF (4 mL) in a small quartz bomb, and the bomb was attached to a vacuum line and degassed by three freeze−pump−thaw cycles. Next, *cis*-2,3-dimethyloxirane (16.7 mg, 0.232 mmol) was vacuum transferred into the bomb kept frozen in liquid N_2. Once the transfer was complete, the bomb was placed in a photolysis apparatus cooled to −10 °C where it was irradiated for 1 h. The volatile materials were transferred away *in vacuo* at 0 °C, and the remaining off-white residue was kept cold and used for analysis. The product, **3**, was isolated as an off-white powder (60.1 mg; 97%). Upon warming of a THF-d_8 or C_6D_6 solution of **3** to room temperature, the ^1H NMR resonances broadened dramatically until a white powder began to precipitate, at which point the NMR resonances disappeared. The volatile materials in this reaction were identified by NMR and GC as *cis*-2,3-dimethyloxirane, *cis*-2-butene, and ethylene. NMR data for $Cp_2(CH_3)Ta(=O)$ (**3**): ^1H NMR (400 MHz, THF-d_8, 0 °C) δ 6.00 (s, 10H, C_5H_5) 0.74 (s, 3H, Ta−CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8, 0 °C) δ 111.6 (s (br), C_5H_5) 16.1 (s

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(37) Previous reports on the Cp^*_2Ta system have postulated a transition state for oxygen atom transfer having an sp^3-hybridized oxygen atom. This apparently allows for the best positioning of the doubly occupied $1a_1$ orbital of the Cp^*_2Ta fragment. See ref 17.

(38) Aziridines with alkyl substituents are known to have a high barrier with respect to inversion at the sp^3 nitrogen center, whereas aziridines with aryl substituents are known to have sp^2 character at nitrogen. For example, see: Bottini, A. T.; Roberts, J. D. *J. Am. Chem. Soc.* **1958**, *80*, 5203.

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(42) Bottini, A. T.; VanEtten, R. L. *J. Org. Chem.* **1965**, *30*, 2994.

(br), Ta−CH_3). MS (FAB) (*m*/*z*): 648, $[M_2]^+$, 342 $[M]^+$, 327 $[M - CH_3]^+$. Anal. Calcd for $C_{11}H_{13}OTa$: C, 38.61; H, 3.83. Found: C, 38.25; H, 3.55.

$Cp_2(CH_3)Ta({=}S)$ (4). This material was prepared by the following four methods.

Method a. A medium-sized bomb (40 mL) equipped with a stirbar was charged with $Cp_2Ta(C_2H_4)(CH_3)$ (**1a**) (254 mg, 0.717 mmol) dissolved in 20 mL of C_6H_6. The bomb was attached to a vacuum line and degassed, and thiirane (49.6 mg, 0.824 mmol) was vacuum transferred in. The bomb was then placed in a photolysis apparatus cooled to 0 °C where it was photolyzed for 1 h. Following this, the red-brown solution was concentrated *in vacuo* to ca. 15 mL and filtered through a 1 cm plug of silylated silica gel (Keiselgel 60). The filtrate was then concentrated further *in vacuo* to ca. 10 mL when microcrystals began to precipitate from solution. The product was then isolated by slow pentane vapor diffusion into the remaining benzene solution. The orange-red crystals of **4** which formed were obtained in 81% (208 mg) yield. Several attempts at single-crystal X-ray diffraction analysis were frustrated by apparent long-range disorder. NMR data for $Cp_2(CH_3)Ta({=}S)$ (**4**): ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 5.44 (s, 10H, C_5H_5), 0.74 (s, 3H, Ta−CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ 109.3 (s, C_5H_5), 12.4 (s, Ta−CH_3). IR (KBr): $\nu(Ta{=}S) = 430\ cm^{-1}$. IR (KBr): 3070 (w), 2949 (w), 2920 (m), 2850 (w), 1731 (s), 1657 (m), 1438 (s), 1387 (m), 1273 (w), 1192 (w), 1149 (m), 1022 (m), 837 (s), 667 (w), 474 (w), 430 (m) cm^{-1}. MS (FAB) (*m*/*z*): 358 $[M]^+$, 343 $[M - CH_3]^+$. Anal. Calcd for $C_{11}H_{13}STa$: C, 36.88; H, 3.66. Found: C, 37.22; H, 3.71.

Method b. A small bomb (15 mL) equipped with a stirbar was charged with $Cp_2Ta(PMe_3)(CH_3)$ (63.8 mg, 0.159 mmol) dissolved in C_6H_6 (10 mL). After degassing of the bomb, thiirane (18.0 mg, 0.299 mmol) was vacuum transferred in, and the bomb was heated to 45 °C for 12 h. The red-brown solution was concentrated *in vacuo* to remove any volatile materials. The residue was redissolved in C_6H_6 (8 mL), and the solution was filtered through a 1 cm plug of silylated silica gel (Keiselgel 60). The product was then isolated as described above. The orange-red crystals of **4** which formed were obtained in 76% (43.3 mg) yield and had spectroscopic properties identical to those listed above.

Method c. The persulfide species $Cp_2(CH_3)Ta(\eta^2\text{-}S_2)$ (**5**) (81.1 mg, 0.208 mmol) was dissolved in C_6H_6 (20 mL) in a 50 mL round-bottomed flask equipped with a stirbar. Next, degassed trimethylphosphine (60 mg, 0.30 mmol) was vacuum transferred in, and the stirred solution was heated to 45 °C for 2 d. The workup was identical to that given above. The product, **4**, was isolated in 73% (54.5 mg) yield and had spectroscopic properties identical to those listed above.

Method d. The bridging sulfide complex $Cp_2(CH_3)Ta(\mu\text{-}S)Ta(CH_3)Cp_2$ (**7**) (21.2 mg, 0.0310 mmol) was dissolved in C_6H_6 (5 mL) in a glass bomb (20 mL) equipped with a stirbar. After degassing of the solution, thiirane (7.8 mg, 0.13 mmol) was vacuum transferred in, and the bomb was heated to 45 °C for 1 d. After the solution had turned from deep blue to orange-red, the product was isolated as described above in 93% (20.6 mg) yield and had spectroscopic properties identical to those listed above.

$Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$ (5). A glass bomb (60 mL) was charged with $Cp_2(CH_3)Ta({=}S)$ (**4**) (71.0 mg, 0.198 mmol) dissolved in C_6H_6 (35 mL). After degassing of the bomb by three freeze−pump−thaw cycles, thiirane (32.4 mg, 0.539 mmol) was vacuum transferred in. The bomb was wrapped in foil and then warmed to 45 °C for 2 days. The solution was then concentrated to ca. 4 mL at which point crystals began to form, and this mixture was used in a benzene/pentane vapor diffusion crystallization at room temperature. The product (**5**) was isolated as orange crystals in 88% (67.8 mg) yield. NMR data for $Cp_2(CH_3)Ta(\eta^2\text{-}S_2)$ (**5**): ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 4.89 (s, 10H, C_5H_5), 0.89 (s, 3H, Ta−CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ 104.7 (s, C_5H_5), 5.1 (s, Ta−CH_3). IR (KBr): 2922 (s), 2850 (m), 1729 (s), 1660 (m), 1641 (m), 1435 (s), 1382 (s), 1263 (w), 1149 (m), 1018 (m), 825 (m), 536 (m) cm^{-1}. MS (FAB) (*m*/*z*): 390 $[M]^+$, 375 $[M - CH_3]^+$, 358 $[M - S]^+$, 343 $[M - S - CH_3]^+$, 326 $[M - S_2]^+$. Anal. Calcd for $C_{11}H_{13}S_2Ta$: C, 33.85; H, 3.36. Found: C, 33.72; H, 3.35.

$Cp_2Ta({=}S)(SCH_3)$ (6). A medium-sized quartz bomb (50 mL) was charged with $Cp_2Ta(C_2H_4)(CH_3)$ (88.4 mg, 0.250 mmol) dissolved in C_6H_6 (30 mL). The solution was degassed, and thiirane (82.5 mg, 1.37 mmol) was vacuum transferred in. The bomb was then placed into a photolysis apparatus (450 W medium-pressure Hanovia mercury lamp) maintained at 20 °C and irradiated while intermittently being monitored by ^1H NMR by removing aliquots, concentrating *in vacuo*, and redissolving in C_6D_6 (the solutions were not degassed again). After ca. 6 h of irradiation, the solution was concentrated to 15 mL *in vacuo* and filtered through a 1 cm plug of silylated silica gel (Kesielgel 60). The product (**6**) was then crystallized by pentane layering, and deep orange microcrystals were formed in 53% (51.7 mg) yield. NMR data for $Cp_2Ta({=}S)(SCH_3)$ (**6**): ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 5.62 (s, 10H, C_5H_5), 2.72 (s, 3H, Ta−SCH_3); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ 110.6 (s, C_5H_5), 29.8 (s, Ta−SCH_3). MS (FAB) (*m*/*z*): 390 $[M]^+$, 375 $[M - CH_3]^+$. Anal. Calcd for $C_{11}H_{13}S_2Ta$: C, 33.85; H, 3.36. Found: C, 33.62; H, 3.33.

$Cp_2Ta({=}NCH_3)(CH_3)$ (7a). A glass bomb was charged with $Cp_2Ta(C_2H_4)(CH_3)$ (141 mg, 0.399 mmol) and C_6H_6 (30 mL). After degassing of the solution, *N*-methylaziridine (32.9 mg, 0.576 mmol) was vacuum transferred into the bomb. The resulting yellow solution was placed in a photolysis apparatus (450 W medium-pressure Hanovia mercury lamp) maintained at 15 °C and irradiated for 1.5 h. The solution was then filtered through a 1 cm plug of silylated silica gel (Keiselgel 60) and concentrated *in vacuo* to a yellow-brown-glassy oil. This oil (**7a**) was isolated in 97% (137 mg) yield and showed >95% purity by ^1H NMR versus a Cp_2Fe internal standard. NMR data for $Cp_2(CH_3)Ta({=}NCH_3)$ (**7a**): ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 5.51 (s, 10H, C_5H_5), 3.86 (s, 3H, Ta=NCH_3), 0.88 (s, 3H, Ta−CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ 107.2 (s, C_5H_5), 50.3 (s, Ta=NCH_3), 5.5 (s, Ta−CH_3). MS (FAB) (*m*/*z*): 356 $[M + H]^+$, 341 $[M + H - CH_3]^+$, 326 $[M - NCH_3]^+$, 311 $[M - N - 2CH_3]^+$. HRMS (EI) $[M + H]^+$ (*m*/*z*): calcd for $C_{12}H_{17}NTa$, 356.0841; found, 356.0845. Mp: <−20 °C.

$Cp_2Ta({=}NBu)(CH_3)$ (7b). $Cp_2Ta({=}NBu)(CH_3)$ (**7b**) can be isolated in a fashion identical to that reported for **7a** except that *N*-(*n*-butyl)aziridine is used in place of *N*-methylaziridine. Yield: 93%. NMR data for $Cp_2(CH_3)Ta({=}NBu)$ (**7b**): ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 5.53 (s, 10H, C_5H_5), 4.01 (m, 2H, Ta=NCH_2), 1.34 (m, 4H, Ta=$NCH_2(CH_2)_2CH_3$), 0.93 (m, 3H, Ta=$N(CH_2)_3CH_3$); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ 107.2 (s, C_5H_5), 62.3 (s, Ta=NCH_2), 35.9 (s, Ta=NCH_2CH_2), 20.7 (s, Ta=$N(CH_2)_2CH_2$), 14.2 (s, Ta=$N(CH_2)_3CH_3$). IR (hexane): 3107 (w), 3087 (w), 3059 (w), 2795 (m), 2633 (w), 1326 (w), 1287 (m), 1247 (w), 1022 (m), 1007 (m), 807 (s), 697 (m), 427 (w) cm^{-1}. MS (FAB) (*m*/*z*): 398 $[M + H]^+$, 354 $[M - Pr]^+$, 326 $[M - NBu]^+$. HRMS (EI) $[M + H]^+$ (*m*/*z*): calcd for $C_{15}H_{23}NTa$, 398.1310; found, 398.1310. Mp: <−20 °C.

$Cp_2Ta({=}NC_6H_5)(CH_3)$ (7c). $Cp_2Ta({=}NC_6H_5)(CH_3)$ (**7c**) was isolated in a fashion identical to that reported for **7a**. Yield: 88%. NMR data for $Cp_2Ta({=}NC_6H_5)(CH_3)$ (**7c**): ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 7.24 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_5), 6.70 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_5), 6.45 (d, 2H, $^3J_{HH}$ = 8Hz, *o*-C_6H_5), 5.42 (s, 10H, C_5H_5), 0.88 (s, 3H, Ta−CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ 161.2 (s, *i*-C_6H_5), 127.8 (s, *m*-C_6H_5), 119.1 (s, *p*-C_6H_5), 119.0 (s, *o*-C_6H_5), 107.0 (s, C_5H_5), 6.3 (s, Ta-CH_3). IR (hexane): 3069 (w), 2060 (w), 2931 (w), 2884 (w), 2854 (w), 1584 (m), 1489 (m), 1357 (s), 1163 (w), 821 (w), 797 (w), 768 (w), 814 (s), 793 (m), 751 (m), 689 (m), 674 (m), 429 (w), 417 (m) cm^{-1}. MS (FAB) (*m*/*z*): 417 $[M]^+$, 402 $[M - CH_3]^+$. HRMS (EI) $[M + H]^+$ (*m*/*z*): calcd for $C_{17}H_{19}NTa$, 418.0997; found, 418.1000. Mp: <−20 °C.

$Cp_2(CH_3)Ta(\mu\text{-}S)Ta(CH_3)Cp_2$ (8). A glass bomb (50 mL) was charged with $Cp_2Ta({=}S)(CH_3)$ (**4**) (62.1 mg, 0.173 mmol) and $Cp_2Ta(C_2H_4)(CH_3)$ (61.6 mg, 0.174 mmol) and C_6H_6 (40 mL). The bomb was then irradiated for 1 h at 20 °C. The solution was monitored every 20 min by removing aliquots for ^1H NMR analysis, and after the reaction appeared complete, the deep blue solution was filtered through a glass wool plug. The filtrate was concentrated *in vacuo* to ca. 10 mL. Deep blue feathery crystals of **7** were grown by layering pentane (25 mL) onto the remaining solution. These crystals were then washed with pentane (5 mL) and dried *in vacuo*. Dark violet **7** was isolated in 93% (110 mg) yield. NMR data for $Cp_2(CH_3)Ta(\mu\text{-}S)Ta(CH_3)Cp_2$ (**7**): ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 5.08 (s, 20H, C_5H_5), 0.60 (s, 6H, Ta$-$CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C) δ 100.0 (s, C_5H_5), -10.2 (s, Ta$-CH_3$). IR (KBr): 3101 (w), 3091 (w), 2950 (w), 2921 (m), 2852 (w), 1732 (s), 1633 (w), 1432 (m), 1265 (w), 1240 (w), 1192 (m), 1149 (m), 1014 (w), 839 (m), 827 (m), 667 (w), 603 (w), 435 (w) cm^{-1}. MS (FAB) (m/z): 684 $[M]^+$, 358 $[M - Cp_2Ta(CH_3)]^+$, 326 $[M - Cp_2(CH_3)Ta(S)]^+$. Anal. Calcd for $C_{22}H_{26}STa_2$: C, 38.61; H, 3.83. Found: C, 38.41; H, 3.72.

Attempted Catalytic Transfer of Sulfur from Thiirane to Phosphine. From a stock solution, two NMR tubes were charged with thiirane (12.1 mg, 0.201 mmol) and triphenylphosphine (51.8 mg, 0.197 mmol) in C_6D_6 (0.6 mL). One of the two NMR tubes was also charged with $Cp_2Ta(S)(CH_3)$ (7.0 mg, 0.020 mmol). Both tubes were then attached to cajon fittings, degassed by three freeze$-$pump$-$thaw cycles, and sealed. The tubes were wrapped in foil and heated to 45 °C. Every 30 min until completion the reactions monitored by ^1H and ^{31}P NMR. Throughout the reaction both tubes showed similar amounts of Ph_3P and $Ph_3P{=}S$ with the tube containing the $Cp_2Ta(S)(CH_3)$ never having more than 15$-$20% more $Ph_3P{=}S$ than the other tube.

X-ray Crystal Structure Determination of $Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$. Yellow crystals of $Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$ (**5**) shaped as blocks and points were obtained by slow crystallization from benzene/pentane vapor diffusion as described above in synthesis section. A fragment cut from one of these crystals was mounted on a glass fiber using Paratone N hydrocarbon oil. The crystal was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. It was cooled to -105 °C by a nitrogen flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. Automatic peak search and indexing procedures yielded a monoclinic cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The final cell parameters and specific data collection parameters for these data sets are given in Table 1.

The 1655 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No correction for crystal decomposition was necessary. An empirical correction based on the observed variation in the azimuthal scan data was applied. The choice of the group $P2_1/n$ was confirmed by the successful solution and refinement of the structure. Removal of 205 data affected by misorientation just prior to a recalculation of the orientation matrix during data collection left 1450 unique data in the final data set.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. To minimize the cost of the structure determination, only the sulfur and tantalum atoms were refined anisotropically. In the final cycles of least-squares, 139 data with abnormally large weighted difference values (possibly caused by multiple diffraction effects) were given zero weight.

The final residuals for 72 variables refined against the 1311 accepted data for which $F^2 > 3\sigma(F^2)$ were $R = 3.7\%$, $wR = 5.0\%$, and GOF = 2.60.

The quantity minimized by the least squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p-factor, used to reduce the weight of intense reflections, was set to 0.03 in the last cycles of refinement. The analytical forms of the scattering factor tables for the neutral atoms were used,[43] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

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Supporting Information Available: A table of least-squares planes for compound **5** (2 pages). Tables of anisotropic thermal parameters and root-mean-square amplitudes of anisotropic displacement in angstroms are already on file.[19] This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS. See any current masthead page for ordering information.

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[43] Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.