

Thermodynamic Scales for Sulfur Atom Transfer and Oxo-for-Sulfido Exchange Reactions

James P. Donahue[†]

Department of Chemistry, Tulane University, 6400 Freret Street, New Orleans, Louisiana 70118-5698

Received November 21, 2005

Contents

1. Introduction	4747
1.1. Homogeneous Catalysis	4747
1.2. Sulfur Atom Transfer Reactions in Biology	4748
1.3. Sulfur Atom Transfer in the Context of Petroleum Desulfurization	4748
1.4. Sulfur Vulcanization of Polyolefins	4749
2. Definitions and Scope	4749
3. Tables of Thermodynamic Data	4750
3.1. Thermodynamic Tables for Sulfur Atom Transfer	4750
3.2. Thermodynamic Data for Oxo-for-Sulfido Exchange Reactions	4751
3.3. Bond Dissociation Energies	4754
4. Compounds Prepared by Sulfur Atom Transfer Reactions	4755
5. Sulfur Atom Donors	4756
5.1. Allotropes of Sulfur	4757
5.2. Oxathiiranes, Dithiiranes, and Sulfines	4757
5.3. R ₃ ES Compounds (E = P, As, Sb)	4765
5.4. Bis(tri- <i>n</i> -butylstannyl)sulfide, ⁿ Bu ₃ SnSS ⁿ Bu ₃	4766
5.5. Phosphorus Sulfides, P ₄ S _n	4767
5.6. Sulfur Diimides	4768
5.7. Carbonyl Sulfide, COS	4768
5.8. Dibenzyl Trisulfide	4769
5.9. Hydrogen Sulfide, H ₂ S	4769
5.10. 5-Aryloxy-1,2,3,4-thiazoles	4770
6. Compounds Prepared by Oxo-for-Sulfido Exchange Reactions	4770
7. Oxo-for-Sulfido Exchange Reagents	4771
7.1. Lawesson's Reagent, 2,4-Bis-(<i>p</i> -methoxyphenyl)-1,3-dithiaphosphetane-2,4-disulfide	4771
7.2. Boron Trisulfide, B ₂ S ₃	4771
7.3. Hexamethyldisilathiane, Me ₃ SiSSiMe ₃	4774
7.4. COS, CS ₂ , and R ₂ NC(S)Cl	4775
8. Ligand-Centered Sulfur Atom Transfer Reactions	4776
9. Catalytic Sulfur Atom Transfer Systems	4778
10. Summary and Conclusions	4779
11. Abbreviations	4779
12. Acknowledgments	4780
13. References	4780



Jim Donahue was born in 1968 in Mishawaka, IN. He graduated in 1987 from Mishawaka Marian High School and then attended M.I.T. for his undergraduate studies, graduating in 1991 with a B.S. in chemistry. As a National Defense Science and Education Grant predoctoral fellow, he joined the research group of Professor Richard H. Holm of Harvard University. His doctoral work focused on small-molecule analogues of the active sites of molybdo- and tungstoenzymes. In 1998 he received his Ph.D. degree and moved to Texas A&M University in College Station to do a postdoctoral study with Professor F. A. Cotton with the support of an NIH postdoctoral fellowship. In 2004 he accepted a position in inorganic chemistry at Tulane University in New Orleans, where he is currently an assistant professor of chemistry.

of the fundamental reaction types of transition metal chemistry. This reaction type is ubiquitous in biology and also of tremendous significance in industrial homogeneous catalysis. Transition metal mediated oxo transfer reactions comprise by far the greatest number of these reactions and have been the subject of several comprehensive reviews.¹ Within the past decade, imido group (nitrene) transfer reactions, particularly in the context of olefin aziridination, have also been investigated systematically and surveyed in a recent paper.²

Of the heavier chalcogens, the atom transfer reactions of sulfur comprise a significant majority of the systems that have been studied thoroughly. The steady growth that the past 15 years has seen in the number of well-defined metal sulfido complexes and metal-mediated sulfur atom transfer reactions stems from the convergence of several distinct interests. Some of the attention directed toward the synthesis of metal sulfido compounds simply arises from an interest in better understanding their structures, properties, and intrinsic reactivities. To an extent, the relative paucity of such molecules can be attributed to previous lack of a systematic effort to prepare and study them.

1.1. Homogeneous Catalysis

One reason for the increased attention that has been given to sulfur atom transfer reactions is interest on the part of

1. Introduction

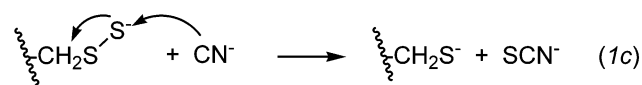
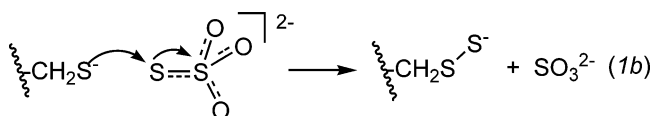
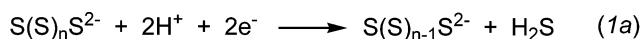
Inner sphere two-electron redox processes as represented by chalcogenido and imido transfer reactions constitute one

[†] Telephone (504) 862-3562; fax (504) 865-5596; e-mail donahue@tulane.edu.

organic chemists in developing synthetically useful organic transformations. In this regard, recent work by Adam on the direct sulfidation of olefins,³ allenes,^{3b,c} and isonitriles^{3c,4} with homogeneous molybdenum catalysts is particularly noteworthy. An incentive for such studies is the tremendously greater cost-effectiveness promised by direct sulfur atom transfer to organic substrates with S₈, which is by far the least expensive form of the element. It is also worthwhile to simply have available another option in the synthetic toolbox for organic chemists seeking to prepare valuable functional groups, such as the thiacyclopropane ring, under mild conditions. These kinds of metal-mediated sulfur atom transfer reactions are completely analogous to metal-catalyzed oxygen atom transfer reactions, which have long been known.⁵

1.2. Sulfur Atom Transfer Reactions in Biology

In biology, metal sulfido ligation is known to occur at the active site of the oxidized form of molybdoenzymes in the xanthine oxidase family and is known to be requisite for enzyme function.⁶ Although not engaged in sulfur atom transfer in the normal functioning of the enzyme, xanthine oxidase is deactivated in the presence of CN⁻, which abstracts the sulfido ligand to produce SCN⁻.⁷ Indeed, this deactivation by sulfur atom transfer to CN⁻ is a distinctive assay for molybdoenzymes in the xanthine oxidase family. These enzymes, which in the desulfo form are inactive, can afterward be reconstituted by the addition of sulfide.⁷ A molybdoenzyme that may operate through bona fide sulfur atom transfer is polysulfide reductase, which catalyzes reduction of polysulfide with evolution of H₂S (reaction 1a).⁸ Other instances in which metal sulfido ligation and metal-mediated sulfur atom transfer may occur are among the tungstoenzymes, particularly as the organisms that make use of this metal are generally found in sulfur-rich environments.⁹ Much, however, remains to be learned about these systems.

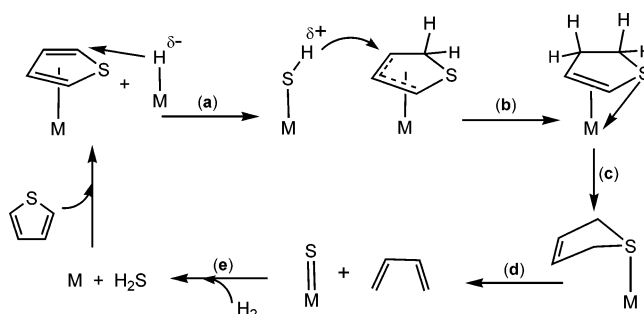


Other biological systems that may involve sulfur atom transfer reactions, although they are not metal-mediated transfers, are the reactions catalyzed by the ubiquitous mitochondrial enzyme rhodanese¹⁰ and other, related, enzymes such as mercatopyruvate sulfurtransferase.¹¹ Rhodanese catalyzes the *in vitro* transfer of a sulfur atom from thiosulfate to cyanide through the intermediacy of a persulfido cysteinate residue (reactions 1b and 1c). This reaction is believed to be a physiological defense mechanism to cyanide exposure, which occurs naturally at low levels in the metabolism of cyanogenic glycosides. Although rhodanese may have a biological function in cyanide detoxification, it is a multifunctional enzyme that appears to play critical roles in protein synthesis ranging from C–S bond forming reactions to the catalytic formation of prosthetic groups such as iron–sulfur clusters.¹²

1.3. Sulfur Atom Transfer in the Context of Petroleum Desulfurization

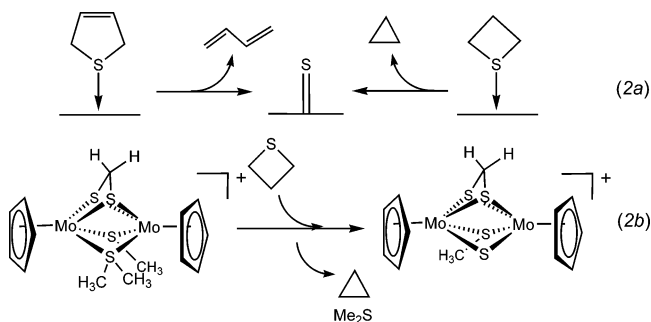
The commercial desulfurization of petroleum feedstocks is another important arena in which sulfur atom transfer reactions, especially their thermodynamic aspects, are of immediate relevance. This process has long been an essential part of the refining industry, and it generally involves a heterogeneous system employing Ni- or Co-doped molybdenum sulfide held on an alumina support.¹³ Although these systems are complex and have variable compositions, the work of several research groups has underscored the likelihood that bona fide sulfur atom transfer reactions are indeed operative in large-scale industrial hydrodesulfurizations. For instance, in his seminal studies upon thiophene desulfurization,¹⁴ Angelici has identified hydride and proton transfers [(a) and (b) in Scheme 1] as plausible initial steps that afford,

Scheme 1. Possible Mechanism for Thiophene Desulfurization^a



^a Step (d), as proposed by Angelici, is a sulfur atom abstraction by the metal. Reprinted with permission from ref 14a. Copyright 1988 American Chemical Society.

after an isomerization, an η^1 S-bound 2,5-dihydrothiophene species. This intermediate then undergoes sulfur atom transfer to the metal surface to liberate butadiene and form metal sulfide [(d) in Scheme 1].¹⁴ Studies by Friend on Mo(110) crystal surfaces¹⁵ and by Rakowski Dubois with homogeneous dinuclear molybdenum systems¹⁶ also have revealed sulfur atom abstraction from 2,5-dihydrothiophene as well as from small cyclic sulfides such as ethylene sulfide and thietane to form the corresponding hydrocarbons (reactions 2a and 2b).



The current technological challenge in this area lies in efficiently desulfurizing benzo- and dibenzothiophenes, especially those that bear sterically encumbering substituents, and the need for new ideas and innovations in this area is ongoing. Government standards for the sulfur content in refined petroleum are increasingly stringent and seek to minimize the environmental and health repercussions that

attend the release of sulfur oxides into the atmosphere when fossil fuels are burned.¹⁷

1.4. Sulfur Vulcanization of Polyolefins

The vulcanization of polyolefins with elemental sulfur, a process of historical and commercial significance dating back nearly 170 years, is also a system in which sulfur atom transfer reactions are operative. This process, represented pictorially in Figure 1, involves the cross-linking of linear

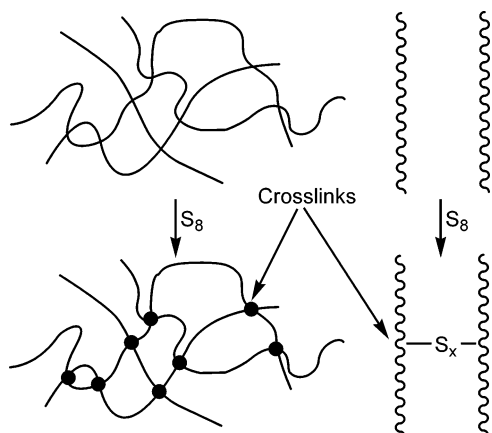


Figure 1. Representation of the sulfur vulcanization of polyolefins. Only when $x = 1$ can the process be called a sulfur atom transfer. This figure is modified from ref 18e with permission of the American Chemical Society.

polymers with sulfide, disulfide, or polysulfide connectors so as to form an elastomeric network. It is only when $x = 1$ in Figure 1, however, that sulfur atom transfer according to the narrow definition adopted in this review (vide infra) can be said to have occurred. The resulting networked polymer has greatly enhanced elasticity, tear strength, and fatigue life compared to the material before cross-linking. Although a variety of cross-linkers have found use as vulcanization agents, sulfur is still widely used for this purpose because of its cost-effectiveness and because it is amenable to a high degree of control in this very complex process. The interested reader is referred to more authoritative sources on this subject.¹⁸

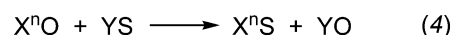
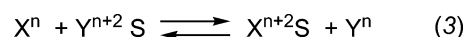
Placed in the light of these several broad-ranging interests, a current review of the existing body of information on sulfur atom transfer reactions has obvious and timely value. Furthermore, the usefulness of the thermodynamic scale for oxygen atom transfer reactions, which has been introduced by Holm and Donahue,¹⁹ makes it clear that analogous tables of thermodynamic data for sulfur atom donors and acceptors could have similarly broad utility. Related to the concept of an atom transfer reactivity scale is the idea of an atom exchange scale, which is also presented and discussed here inasmuch as many metal sulfido complexes derive from the corresponding oxo complexes by chalcogenide exchange. Certain aspects of metal sulfido chemistry have been dealt with previously by others,^{1f,20} and a limited sulfur atom transfer scale has been presented for reactions conducted in toluene or benzene solution.²¹

2. Definitions and Scope

This paper addresses thermodynamic aspects of sulfur atom transfer and oxo-for-sulfido exchange reactions chiefly when they involve transition metals. Some discussion of these

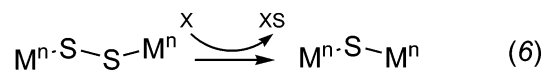
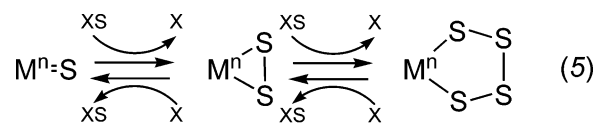
reaction types in main group and in purely organic systems is included, because it serves to call attention to potentially useful sulfur atom donors that are different from the reagents typically employed by inorganic chemists and also because it emphasizes the generality of these reaction types. Some aspects of sulfur atom transfer and oxo-for-sulfido exchange, for example, in thiirane synthesis and the preparation of thiones with Lawesson's reagent, are rather large subject areas in themselves. In these cases, the most current and comprehensive reviews are identified for the reader interested in further information. Not addressed here is any consideration of kinetics; that is, the information contained herein may suggest that a certain atom transfer or exchange reaction *can* occur but not necessarily that it *will* or in what time frame. Other molecular properties such as redox potentials and pK_a values can also offer predictive insight into the feasibility of atom transfer reactions but are outside the focus of this paper.

In their simplest conceptual form, sulfur atom transfer reactions and oxo-for-sulfido exchange reactions are depicted in reactions 3 and 4, respectively. In reaction 3, the sulfur



donor could be sulfur atom itself, in which case Y is absent. The term "oxo-for-sulfido exchange" upon X is used in the following discussion to refer specifically to reaction 4 as written, in which an oxygen atom bound to X is replaced by a sulfur atom bound to X, X being the substrate of interest. For clarity, reaction 4 is written in only the forward direction so as to emphasize the point that oxo-for-sulfido exchange upon X means the transformation of XO to XS through the agency of YS and not the reverse process. This review is limited to molecular species X or XS that are formed by oxidative addition or reductive elimination of sulfur atom or by pure chalcogenide exchange from the corresponding XO species without change in oxidation state (or valence state) and without other structural reorganization.

Not included in this review is any discussion of sulfur atom transfer to or from disulfide (S_2^{2-}) or polysulfide (e.g., S_4^{2-}) ligands (reactions 5 and 6), inasmuch as these reactions

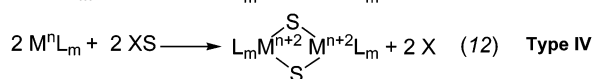
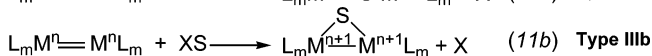
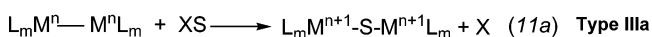
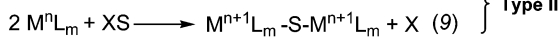
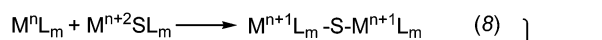


do not involve redox changes at the metal center. Such processes have been classified by Woo as "secondary" atom transfers,^{1f} although it is noted here that a different meaning has been applied to that term by Holm.^{1b} A further restriction placed upon the sulfido (S^{2-}) chemistry discussed herein is a limitation to systems with metal atom nuclearity of one or two. The formation of metal sulfide clusters from low-valent metal precursors and a source of sulfur atom can be viewed as occurring through sulfur atom transfer processes. However, because of some of the inherent complexities in systematizing such reactions, they are not considered here.

In the succeeding sections, many examples of transition metal and main group element sulfido (S^{2-}) compounds are

listed in table form. These tables do not represent an exhaustive catalogue of all known mono- and dinuclear sulfido species, but rather only those formed through the aforementioned atom transfer and chalcogenide exchange processes. Sulfido compounds may be prepared by a variety of other distinct methods, such as by the direct addition of sulfide,²² by deprotonation of hydrosulfido ligand(s),²³ by exchange of sulfide for 2 equiv of halide,²⁴ and by internal redox rearrangement with sulfur-containing ligands such as dithiolates^{25a} or dithiocarbamates.^{25b} These reaction types fall outside the purview of this paper.

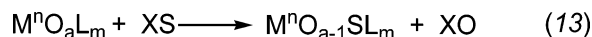
Several distinct types of sulfur atom transfer reactions can be described. Type I, *metal-mediated* sulfur atom transfer reactions (reaction 7), are those in which the oxidation state of the metal is changed by 2 units. The number of supporting ligands often is, but is not necessarily, the same, and other structural reorganization is minimal. This reaction type is strictly analogous to the *primary* oxygen atom transfer reaction defined by Holm.^{1b} A significant number of sulfur atom transfer reactions are of type I, and in most instances $a = 0$ in reaction 7. In type II sulfur atom transfer reactions (reaction 8), atom transfer is an incomplete intermetal process. A binuclear species is formed in which sulfide bridges two metal ions, each of which has undergone an oxidation state change by 1 unit. Type II sulfur atom transfer reactions may be alternatively, and perhaps more usefully, expressed by reaction 9 in which 2 equiv of M^nL_m react with 1 equiv of donor XS to form $L_mM^{n+1}-S-M^{n+1}L_m$. Such reactions may proceed by transient formation of $M^{n+2}SL_m$, which is a more reactive species than XS and quickly adds to a second equivalent of M^nL_m . If transfer of a sulfur atom between two transition metal complexes does not result in a bridged species, then the reaction is said to be complete (reaction 10), and the oxidation state change at each metal site is by 2 units. Reaction 10 is a particular instance of reaction 7 in which $XS = M^{n+2}SL'_m$.



A type III sulfur atom transfer reaction (reactions 11) involves the insertion of a sulfur atom into (11a) or across (11b) a metal–metal bond, the latter type being analogous to the episulfidation of an olefin. Type III reactions are distinctly different in that they combine features of both type I and type II reactions. As in type I sulfur atom transfer reactions, the nuclearity of the system does not change, but the oxidation state change is by 1 unit, and the sulfide is in a bridging mode as in type II reactions. Type IV sulfur atom transfer systems (reaction 12), which are comparatively less common, also combine aspects of reaction types I and II. The oxidation state change is by 2 units, as in type I atom transfer reactions, but the nuclearity of the system changes as in a type II reaction.

Reaction 13 represents a distinctly different reaction type than those given by reactions 7–12, namely, chalcogenide

exchange as opposed to chalcogen transfer. The terms

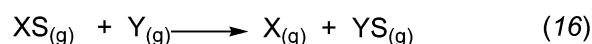
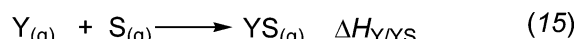
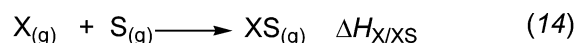


“transfer” and “exchange” refer specifically to the conceptually different reaction types illustrated by reactions 7–12 and 13, respectively, and are not used interchangeably. The defining distinction (cf. reactions 3 and 4) is that sulfur atom transfer reactions involve oxidative addition of sulfur, whereas a chalcogenide exchange reaction involves no oxidation state change at the metal center. Chalcogenide exchange reactions are considered here because reactions of this kind may also be organized onto a thermodynamic scale that may offer some predictive insights.

3. Tables of Thermodynamic Data

3.1. Thermodynamic Tables for Sulfur Atom Transfer

The feasibility of and driving force for a given sulfur atom transfer reaction may be assessed by organizing all of the available thermodynamic data for potential sulfur donors and acceptors onto a common scale. If the enthalpies of reaction with sulfur for two different elements or molecules X and Y are known in the same phase and at the same temperature (reactions 14 and 15), then the difference between these



$$\Delta H = \Delta H_{Y/YS} - \Delta H_{X/XS}$$



$$\Delta_f H^\circ (298.15) = 66.25 \pm 0.04 \text{ kcal/mol}$$

reaction enthalpies is a measure of the propensity for sulfur atom transfer between X and Y (reaction 16). A key aspect in the formulation of gas phase sulfur atom transfer couples, such as that shown in reaction 16, is the implicit use of reaction 17, the formation of gaseous atomic sulfur from the solid element, and its associated enthalpy of formation ($\Delta_f H^\circ$ at 298.15 K) of 66.25 kcal/mol.²⁶ The reported uncertainty for this number is ± 0.04 .²⁶ This value of $\Delta_f H^\circ$ for S(g) is used explicitly in the determination of reaction enthalpies $\Delta H_{X/XS}$ and $\Delta H_{Y/YS}$ (reactions 14 and 15), but it cancels when the difference between two such reaction enthalpies is taken to form a sulfur atom transfer couple such as reaction 16.

Assuming the reaction enthalpy to be the dominant term in the expression for free energy change, $\Delta G = \Delta H - T\Delta S$, which is useful at least as an approximation in the absence of free energy data, then $\Delta G \approx \Delta H$ and reaction 16 proceeds from left to right if $\Delta H_{X/XS} > \Delta H_{Y/YS}$. Furthermore, if the set of all elements and molecules X for which thermodynamic data on XS are available is arranged in line reactions such as 14 and 15 in order of decreasing (i.e., more negative) ΔH , then the resulting table serves as a predictor for the viability and direction of a wide range of possible sulfur atom transfer reactions. In other words, a molecule Y of a couple for which $\Delta H_{Y/YS}$ is more negative than the corresponding couple $\Delta H_{X/XS}$ for X is thermodynamically competent to accept a sulfur atom from XS. If structural changes are small, then ΔH for reaction 16 in the gas phase amounts to the

difference between corresponding X–S and Y–S bond energies. The utility of such a table is that it enables one to see at a glance the sets of reagents that may be capable of effecting a particular sulfur atom transfer and those that are not. Hence, a more judicious choice of reagent may be made at the outset.

Table 1 presents selected thermodynamic information for sulfur atom donor–acceptor reagents in the gas phase and, with one exception, is restricted to neutral species. These data are largely assembled from the leading compilations of general thermodynamic data,^{25–34} although some of the table entries are drawn from sources in the primary literature,^{35–39} some dealing specifically with sulfur compounds. The sulfur atom transfer couples are arranged in order of decreasing reaction enthalpies (i.e., more negative reaction enthalpies) for the reaction $X(g) + S(g) \rightarrow XS(g)$. When available, $\Delta G^{298}_{X/XS}$ values and estimated uncertainties are included. These $\Delta G^{298}_{X/XS}$ values are generally ~ 6 – 8 kcal/mol less negative than the corresponding $\Delta H^{298}_{X/XS}$ values because of the entropy decrease associated with forming one gaseous product from two gaseous reactants. When values for a particular couple are available from more than one source, they are usually, but not always, in close agreement. In the construction of Table 1, preference was given to sources that offered both ΔG and ΔH values for a particular couple or, when only enthalpy data were accessible, to the more recent source. Table 1 emphasizes couples with main group elements and with organic molecules most likely to be of potential use as sulfur atom donors or acceptors. A number of the couples listed, such as those for methanethiol, dibenzothiophene, and thiophene, are intended to serve as reference points.

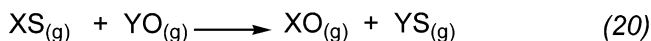
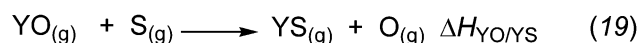
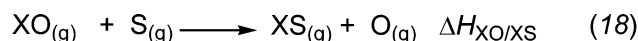
Figure 2 presents the gas phase enthalpies for the reaction $X(g) + S(g) \rightarrow XS(g)$ for all of the elements for which such data are available. Many of the data summarized in Figure 2 are also contained in Table 1. Many of the numbers in Figure 2 have high uncertainties (e.g., those for Be and Mg) or are not based upon measured values at all but originate from estimated values for $\Delta_f H^\circ$ at 298 K (e.g., that for Nb). The gaps and uncertainties in the data make difficult an identification of overarching trends or insights into the data beyond the observation that, for the main group elements in groups 13–16, for which $\Delta_f H(298)$ values are more accurately determined, the reaction enthalpies for the reaction $X(g) + S(g) \rightarrow XS(g)$ become less negative in proceeding down a given main group column of the periodic table. This trend is a plausible one because the light main group elements generally form the strongest bonds to all of the other elements. Less favorable overlap with the larger, more diffuse valence orbitals of the heavier elements probably accounts for the decrease in exothermicity as one proceeds down a given column.

Tables 2 and 3 list thermodynamic data for sulfur atom transfer couples in the solid and liquids states, respectively, and are likewise assembled from standard reference sources for thermodynamic data.^{27–30,34} The information in Table 2 may possibly be useful for heterogeneous systems or in high-temperature syntheses conducted in the solid phase. The general order of entries in Tables 2 and 3 parallels that in Table 1, because enthalpies of vaporization and sublimation for a given species tend to cancel one another. Table 4 presents data measured by Hoff^{21,40} and Nolan⁴⁰ for couples in aromatic hydrocarbon solution and includes entries for several species not found in the other tables. Tables 1 and 4

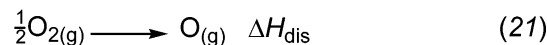
contain only a single entry in common, namely Ph_3PS , and reveal a difference in reaction enthalpies for $Ph_3P + S \rightarrow Ph_3PS$ that is >72 kcal/mol between the two phases. The significantly less negative value for the solution phase is likely due to a large enthalpy of solvation for sulfur atom in going from the gas phase to a benzene or toluene solution.

3.2. Thermodynamic Data for Oxo-for-Sulfido Exchange Reactions

In addition to atom transfer reactions, another general method for the preparation of transition metal sulfido complexes is by atom exchange, as represented in generic form in reaction 18. If enthalpies of formation for $X-O(g)$ and $X-S(g)$ are available in the same phase and at the same temperature, then $\Delta H_{XO/XS}$ offers a measure of the propensity for X to undergo oxo-for-sulfido exchange. The reaction enthalpy for reaction 18 thereby provides a measure for the difference in dissociation energies between X–O and X–S bonds. A set of reaction couples such as 18 and 19, when



$$\Delta H = \Delta H_{YO/YS} - \Delta H_{XO/XS}$$



placed in order of decreasing (i.e., more negative) ΔH , then provides a basis for anticipating the direction of a wide variety of chalcogen exchange reactions in a fashion completely analogous to the atom transfer reactivity scale just described. If $\Delta H_{XO/XS} > \Delta H_{YO/YS}$ (i.e., $\Delta H_{XO/XS}$ has a less negative value than $\Delta H_{YO/YS}$), then the driving force for reaction 20 is in the forward direction. In other words, a molecule Y for which the formation of Y–S from Y–O is a more negative (exothermic) process than the same process for molecule X will substitute sulfur in place of oxygen if Y–O and X–S are mixed (assuming kinetic considerations do not intervene). Such a chalcogen atom exchange table has the utility of permitting one to see the reagents most inclined to exchange oxygen in favor of sulfur (and vice versa) and therefore to select the reagent most suitable for the purpose at hand. These couples are all determined with the aid of reactions 17 and 21, which are the enthalpies of vaporization of elemental sulfur and of the dissociation of the O_2 bond in the gas phase.

Table 5 assembles the available data for oxo-for-sulfido exchange reactions. It is noteworthy that F_2S and Cl_2S are two species that have an appreciable thermodynamic basis for preferring sulfur over oxygen; that is, replacing sulfur with oxygen in these molecules is an *endothermic* process. In contrast, most of the light main group elements such as hydrogen and boron and carbon have a strong preference for bonding oxygen over sulfur. Data are presented for species in the gas phase because this state provides the most direct assessment of intrinsic bond strength differences without the additional effect of solvation. Several of the entries in Table 5 may function as sulfur atom donors, according to the stoichiometry of any of the reactions 7–12, or as oxo-for-sulfido exchange reagents, according to the stoichiometry of reaction 13, depending upon the particular system to which XS is introduced. The most important and widely used of these “dual” reagents is H_2S , for which X =

Table 1. Gas Phase S Atom Transfer Thermodynamic Reactivity Scale: $X(g) + S(g) \rightarrow XS(g)$

X	XS	$\Delta G^{298}_{X/XS}$ (kcal/mol)	$\Delta H^{298}_{X/XS}$ (kcal/mol)	ref	X	XS	$\Delta G^{298}_{X/XS}$ (kcal/mol)	$\Delta H^{298}_{X/XS}$ (kcal/mol)	ref
I	IS ^a		-19	28, 39	S ₅	S ₆		-71.7	27
Br	BrS ^a		-37	28, 39				-71.7 ± 0.6 ^c	28, 30
CH ₃ CN	CH ₃ SCN		-43.9	27	CO	COS	-63.3	-72.9 ± 0.4	28
Cd	CdS	-41.1	-47.4	28	Sb	SbS		[-73] ^{b,d}	33
Zn	ZnS	-42.6	-49.1	28	Bi	BiS	-67.9	-74.8	28
Hg	HgS	-44.2	-50.5	28	SiS	SiS ₂	-65.1	-75.1	28
H ₂ S	HS(S)H		[-51 ± 7] ^b	35	Fe	FeS	-69.6	-76.4	28
Me ₂ S	MeS(S)Me		[-53 ± 3] ^b	35	In ₂ S	In ₂ S ₂	-64.6	-76.9	28
CH ₄	CH ₃ SH	-47.0	-54.1	27	SO	S ₂ O	-68.4	-77.1	28
H ₃ CCH ₃	H ₃ CSCH ₃	-47.4	-55.3	27	F ₃ P	F ₃ PS	-68.1	-78.3	31
Br ₂ S	Br ₂ S ₂	-47.3	-55.8	28	Te	TeS	[-71.4] ^b	[-78.8] ^b	28
H ₂ S	H ₂ S ₂	-49.4	-57.1	28				-81.1 ± 0.5 ^c	28, 30
H ₃ CCH ₃	H ₃ CCH ₂ SH	-50.1	-57.3	27				-82.0 ± 0.7 ^c	28, 30
Cl	ClS	-51.0	-57.8	28	F	FS	-74.9	-82.1 ± 1.6	28
C ₆ H ₆	PhSH		-59.1 ± 0.5 ^c	28, 30				-82.9 ± 0.7 ^c	28, 30
			-59.0 ± 0.5 ^c	28, 29	B ₂ S ₂	B ₂ S ₃	-76.5	-84.5	28
			-59.5 ± 0.8 ^c	28, 30	SCL	S ₂ Cl	-76.8	-84.8	28
		-49.6	-60.0	28	H	HS	-78.8	-85.0	28
			-60.0 ± 0.8 ^c	28, 30	Al	AlS	-80.8	-88.0 ± 3.1	28
			-60.3 ± 0.5 ^c	28, 30	Cl ₃ P	Cl ₃ PS	-78.1	-88.2	31
			-61.4 ± 0.8 ^c	28, 30	Se	SeS	[-81.1] ^b	[-88.5] ^b	28
			-61.8 ± 0.8 ^c	28, 30	As	AsS	-82.0	-89.8	28
			-62.6 ± 0.8 ^c	28, 30	F ₂ S	FSSF	-81.8	-91.2	31
			-62.9	28	B ₂ S ₃	B ₂ S ₄	-74.6	-92.9	28
H ₂ S ₃	H ₂ S ₄		-63.0	28	Ph ₃ P	Ph ₃ PS		-93.5 ± 2.9 ^c	28, 36, 37
H ₂ S ₄	H ₂ S ₅		-63.1	28	Br ₃ P	Br ₃ PS	-84.1	-94.3	31
H ₂ S ₂	H ₂ S ₃		-63.4	27	S	S ₂	-94.0	-101.7 ± 0.2	28
H ₃ CSCCH ₃	H ₃ CSSCH ₃	-55.0	-64.0	27	CS	CS ₂	-95.3	-105.3 ± 6.2	28
S ₆	S ₇		-64.5 ± 0.6 ^c	28, 30	Al ₂ S	Al ₂ S ₂	[-94.3] ^b	-105.5	28
			-64.5 ± 0.6 ^c	28, 30	Al ₂ S	Al ₂ S ₂	[-94.3] ^b	-105.5	28
CH ₃ SCl	CH ₃ SSCl		[-65 ± 3] ^b	35	Sn	SnS	-106	-112	28
PhSCl	PhSSCl		[-65 ± 3] ^b	35	P	PS	-106.0	-112.9	28
S ₂	S ₃		-65.6	27	OCl	OSCl	-105.4	-116.2	32
S ₃	S ₄		-65.6	27	N	NS	-109	-116 ± 25	28
SCl ₂	ClSSCl	-57.3	-66.0 ± 1.8	28				-117.1 ± 1.2 ^c	28, 30
F ₂ S	FS(S)F	-56.8	-66.3	31	B	BS	-111.9	-119.4	27
HCN	HNCS	-58.6	-67.5	32	O	SO	-116.9	-124.6 ± 0.4	28
S ₇	S ₈		-69.3	27	Al ₂	Al ₂ S	[-118.5] ^b	-127.5	28
^t BuS ^t Bu	^t BuSS ^t Bu		-69.3 ± 0.9 ^c	28, 30	Ge	GeS	-123.2	-130.4	28
In	InS	-63.0	-69.4	28	O ₂	SO ₂	-128.3	-137.1 ± 0.1	28
S ₄	S ₅		-69.7	27	In ₂	In ₂ S		-143	27
Cl ₂	Cl ₂ S	-62.6	-70.4 ± 0.9	28	BS	BS ₂	[-134] ^b	-143.2	28
CH ₃ NC	CH ₃ NCS	-62.1	-70.9	27	Si	SiS	-138	-146	28
H ₂	H ₂ S	-64.5	-71.1	28				-153 ± 11 ^c	28, 29, 38
					H ⁺	HS ⁺		-158.6	27
					BH	BSH	-151.1	-160.0 ± 4.5	28
					C	CS	-162.3	-170.5 ± 6.2	28

^a $\Delta_f H^\circ(298)$ values for IS(g) and BrS(g) are from ref 39. ^b These numbers are based upon estimated $\Delta_f H^\circ$ values. ^c For these couples, $\Delta_f H^\circ(298.15\text{ K})$ for S(g) is taken from ref 28. ^d The $\Delta_f H^\circ(298)$ value for SbS(g) is listed as -44.40 kcal/mol in ref 34 but as ~56 kcal in ref 33. The latter value is preferred here because it is much more consistent with those of the surrounding elements (cf. Figure 2). The number from ref 34 appears to have a sign error, which, if simply taken as it is, produces -174.1 kcal/mol as the $\Delta H_{\text{rxn}}(298)_{X/XS}$ value for the couple Sb(g) + S(g) → SbS(g). In my opinion, this result is implausible.

H -85.0																	He
Li	Be -81±16											B -120.	C -170.5± 6.2	N -116± 25	O -124.6± 0.4	F -82.1± 1.6	Ne
Na	Mg -67±16											Al -88.0± 3.1	Si -146	P -112.9	S -101.7± 0.2	Cl -57.8	Ar
K	Ca -79.2± 2.3	Sc -113	Ti -100.4	V -106.9	Cr -78.2	Mn -68.9	Fe -76.4	Co -82.3	Ni -83.6± 6.1	Cu -70.3	Zn -49.1	Ga	Ge -130.4	As -89.8	Se [-88.5]	Br -37	Kr
Rb	Sr -79.5± 2.5	Y -126.5	Zr -138.0	Nb [-138]	Mo	Tc	Ru	Rh	Pd	Ag [-40.1]	Cd -47.4	In -69.4	Sn -112	Sb [-73]	Te [-78.8]	I -19	Xe
Cs	Ba -100.0± 4.3	La -141	Hf	Ta -130.	W	Re	Os	Ir	Pt	Au -99.2	Hg -50.5	Tl	Pb -81.4± 1.8	Bi -74.8	Po	At	Rn
Fr	Ra	Ac															
Ce -126.3	Pr -116.9	Nd -112.7	Pm	Sm -93.4	Eu -87.0	Gd -124.0	Tb -121.4	Dy -96.6	Ho -102.7	Er [-93.0]	Tm [-83.2]	Yb [-39.6]	Lu -120.1				
Th	Pa	U -118	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Figure 2. $\Delta H(298)$ in kcal/mol for the gas phase reaction $X(g) + S(g) \rightarrow XS(g)$. These numbers may be viewed as one way of expressing “thiophilicities” of the elements. Numbers in brackets are derived from estimated $\Delta_f H(298)$ values. $\Delta_f H(298)$ for $SbS(g)$ is taken from ref 33, and $\Delta_f H(298)$ for $BrS(g)$ and $IS(g)$ are from ref 39. All other data that have been used are from ref 28.

H +17.3± +1.6																	He
Li	Be +24±18											B +51.5	C +86.8± 25.6	N +34.8± 25.2	O -5.4± 0.4	F -29.6	Ne
Na	Mg +14±22											Al +34.4± 4.2	Si +42.7	P +32.1± 11.1	S +22.9± 0.5	Cl +6.5	Ar
K	Ca +12.4± 7.1	Sc +50.	Ti +59.3	V +45.4	Cr +31.3	Mn	Fe +22.0± 9.0	Co	Ni +4.8	Cu -3.3	Zn	Ga	Ge +29.7	As +55.5	Se [+12.5] ±0.4	Br +20.	Kr
Rb	Sr +22.4± 1.5	Y	Zr +53.3	Nb [+48.9]	Mo	Tc	Ru	Rh	Pd	Ag	Cd +19.5	In -42.7	Sn +14.4	Sb +74	Te [+13.6] ±0.1	I +36	Xe
Cs	Ba +32.0± 5.0	La +51.0	Hf	Ta +70.3	W	Re	Os	Ir	Pt	Au +13.8	Hg	Tl	Pb +8.1± 3.3	Bi	Po	At	Rn
Fr	Ra	Ac															
Ce +65.3	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Th	Pa	U +61	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Figure 3. $\Delta H(298)$ in kcal/mol for the gas phase reaction $XO(g) + S(g) \rightarrow XS(g) + O(g)$. These numbers may be viewed as an alternate way of expressing “thiophilicities” of the elements. Numbers in brackets are derived from estimated $\Delta_f H(298)$ values. $\Delta_f H(298)$ for $SbS(g)$ is taken from ref 33, and $\Delta_f H(298)$ for $BrS(g)$ and $IS(g)$ are from ref 39. For $X = In$ and U , the data used are taken from ref 27. All other data that have been used in the calculation of these $\Delta H(298)$ values are taken from refs 28 and 31.

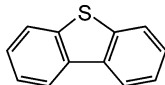
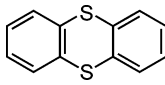
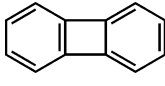
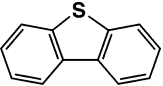
H_2 when it acts as pure sulfur atom donor, whereas $XO = H_2O$ when it serves as an exchange reagent.

The utility of Table 5 is that it permits one to identify at least an upper limit on the difference in strength of an $M=O$ bond versus an $M=S$ bond, where $M =$ a transition metal or main group element. If reaction 13 is a spontaneous process as written for a given chalcogenide exchange reagent, for instance, $XS = COS$ and $XO = CO_2$, then the 53.5 kcal/mol greater bond strength of the $C=O$ bond in CO_2 versus the $C=S$ bond in CS_2 indicates that the $M=S$ is only weaker than the corresponding $M=O$ bond by an amount ≤ 53.5 kcal/mol. If reaction 13 proceeds in the reverse direction with $XO = H_2O$, for instance, then a value of 45.5 kcal/mol is established as a lower limit on the difference between $M=O$

and $M=S$ bond strengths. In principle, with demonstrated reactivity involving a broad enough set of chalcogenide exchange reagents, upper and lower limits on $M=O/M=S$ bond strength differences could be reliably established.

Figure 3 presents the gas phase enthalpies for the reaction $XO(g) + S(g) \rightarrow XS(g) + O(g)$ for all of the elements for which they can be formulated. Figure 3 incorporates information from Table 5 but includes additional data as well. As was the case with Figure 2, a high degree of uncertainty and gaps in the data complicate the identification of trends. A natural question posed by the data in Figures 2 and 3 is whether these numbers constitute any useful index of “thiophilicity.” One could argue that Figure 2 presents a measure of thiophilicity because the strength of the bond

Table 2. S Atom Transfer Thermodynamic Reactivity Scale in the Solid Phase: X(c) + S(c) → XS(c)

X	XS	$\Delta G^{298}_{X/XS}$ (kcal/mol)	$\Delta H^{298}_{X/XS}$ (kcal/mol)	ref	X	XS	$\Delta G^{298}_{X/XS}$ (kcal/mol)	$\Delta H^{298}_{X/XS}$ (kcal/mol)	ref
			+14.8 ± 0.8	30	Fe	FeS (α)	-24.4	-24.3 ± 0.2	28
PhCH ₂ CH ₂ Ph	PhCH ₂ SCH ₂ Ph		+11.4 ± 0.8	29	In	InS	-30.5	-32.0	28
K ₂ S ₄	K ₂ S ₅		0.2	27	TiS	TiS ₂	-31.6	-32.3	28
K ₂ S ₅	K ₂ S ₆		0.2	27	Cd (α form)	CdS	-37.3	-38.6	27
TiS	TiS ₂	[1.4] ^a	0	28	Cd (γ form)	CdS	-37.4	-38.7	27
K ₂ S ₃	K ₂ S ₄		-0.6	27	Cr	CrS	-37.8	-37.2	28
P ₄ S ₅	P ₄ S ₆	-1.6	-1.8	34	LaS	LaS ₂	-36.9	-38.0	28
PdS	PdS ₂	-1.7	-1.8	28	Si	SiS	[-38.2] ^a	-38.4	28
P ₄ S ₆	P ₄ S ₇	-2.2	-2.6	34	LiH	LiSH		-38.5	27
MnS	MnS ₂	-2.1	-2.9	28	CeS	CeS ₂	-37.9	-38.6	28
ReS ₂	ReS ₃	[-3.0] ^a	[-4.1] ^a	28	Zn	ZnS (wurtzite)		-40.0	27
US ₂	US ₃	-3.8	-4.1	28	NaH	NaSH		-43.2	27
TiS ₂	TiS ₃	-4.0	-5.4	28	Zn	ZnS (sphalerite)	-47.8	-49.0	28
TaS ₂	TaS ₃	-4.3	-5.4	28	KH	KSH		-49.6	27
As ₂ S ₂	As ₂ S ₃		-6.3	27	Ga	GaS	-48.9	-50.0	28
PtS	PtS ₂	-5.7	-6.6	28	US	US ₂	-50.0	-50.0	28
WS ₂	WS ₃	[-6.6] ^a	[-8.0] ^a	28				-51.2 ± 1.2	30
MoS ₂	MoS ₃	-6.6	-8.0	28	Mn (α form)	MnS (green, cr)	-52.2	-51.2	27
K ₂ S ₂	K ₂ S ₃		-8.4	27	RbH	RbSH		-51.3	27
HfS ₂	HfS ₃	[-8.2] ^a	[-9.0] ^a	28	Mn (γ form)	MnS (green, cr)	-52.5	-51.6	27
SnS	SnS ₂	-9.4	-10.9	28	CsH	CsSH		-52.7	27
ZrS ₂	ZrS ₃	[-10.6] ^a	-12.0	28	ThS	ThS ₂	-54.5	-55.1	28
K ₂ S	K ₂ S ₂		-12.3	27	Be	BeS	-55.7 ± 2.1	-56.0 ± 2.1	28
TcS ₂	TcS ₃	-11.1	-12.5	28	Ti (α)	TiS	-64.6	-65.0	28
SiS	SiS ₂	[-12.6] ^a	-12.6	28	Ti (β)	TiS	-65.7	-66.7	28
Cu	CuS	-12.9	-12.8	28	U	US	-75.7	-76.0	28
AgCN	AgSCN	-13.3	-13.9	27	Mg	MgS	-81.6 ± 1.0	-82.6 ± 1.0	28
Ge	GeS	-14.9	-14.6 ± 0.3	28	Th	ThS	-93.4	-94.5	28
Tl	TlS	[-14.6] ^a	[-15.0] ^a	28	Eu	EuS	-97.7	-100.0	28
FeS (α)	FeS ₂ (marcasite)	-13.0	-15.7 ± 0.7	28	Sm	SmS	-101.5	-103.0	28
FeS (α)	FeS ₂ (pyrite)	-13.9	-16.7 ± 0.7	28	Pu	PuS	-103.9	-104.3	28
Ni	NiS (precip)		-18.5	27	Pr	PrS	-106.0	-108.0	28
Pd	PdS	-15.9	-16.9	28	Sc	ScS	[-107.3] ^a	[-108.0] ^a	28
Pt	PtS	-18.2	-19.5	28	Y	YS	[-107.3] ^a	-108.0	28
Ni	NiS (cr)	-19.0	-19.6	27	Ce	CeS	-107.4	-109.1	28
Co (α form)	CoS		-19.8	27	Ba	BaS	-109.6 ± 0.5	-110.8 ± 0.5	28
Co (β form)	CoS		-19.9	27	La	LaS	-109.9	-111.0	28
KCN	KSCN	-18.1	-20.7	28	Ta	TaS		-111	27
GeS	GeS ₂	-22.0	-22.9	28	Nd	NdS	-109.0	-111.1	28
Sn (gray)	SnS	-23.5	-23.4	27	Sr	SrS	-110.6 ± 4.1	-112.0 ± 4.1	28
Pb	PbS	-23.1 ± 0.5	-23.5 ± 0.5	28	Ca (α)	CaS	-111.9	-113.1	28
Sn (white)	SnS	-23.5	-23.9	27	Ca (β)	CaS	-112.0	-113.4	28

^a These values are based upon estimated $\Delta_f H^\circ$ values.

formed in XS(g) by oxidative addition of S(g) to X(g) reflects a greater or lesser affinity for sulfur. However, a more intuitive and perhaps more conventional idea of thiophilicity could be formulated along the lines of the hard–soft acid–base concepts that have been advanced by Pearson.⁴¹ This conceptualization of thiophilicity involves pairing “soft” bases such as S²⁻ with “soft” (or at least borderline soft) acids such as Pb²⁺ without any change in redox states. In the language of hard–soft acid–base ideas, thiophilicity is not really an absolute, determinable number but rather a preference by some species for sulfur (or sulfide, S²⁻) vis-à-vis something else, such as oxide, O²⁻. Polarizability is a property often correlated to the “softness” or “hardness” of a particular chemical species.⁴²

Some of the data contained in Figure 3 appear to be consistent with the idea of “thiophilicity” expressed in the sense of hard–soft acid–base ideas. For example, the group 14 elements all show the XO(g) + S(g) → XS(g) + O(g) process to be endothermic, but the endothermicity decreases

significantly in moving down the column and suggests an increasing affinity for sulfur relative to oxygen. The group 13 elements, notwithstanding the missing datum for gallium, reveal a similar trend and indicate that the oxo-for-sulfido exchange process is *exothermic* for indium. According to this notion of interpreting thiophilicity as a preference for sulfur over oxygen, the data in Table 5 and Figure 3 show oxygen and fluorine themselves to be rather thiophilic elements. These elements are not typically thought of as thiophilic, but their high electronegativities probably enable them to form stronger, more polarized bonds with sulfur than with oxygen.

3.3. Bond Dissociation Energies

The reverse of reaction 14 is sulfur bond dissociation, and the associated reaction enthalpy is a bond dissociation energy (BDE). Table 6 presents sulfur bond dissociation energies for a range of organic and inorganic sulfides, and these data have been determined several different ways as emphasized

Table 3. Sulfur Atom Transfer Thermodynamic Reactivity Scale in the Liquid Phase: X(l) + S(l) → XS(l)

X	XS	$\Delta G^{298}_{X/XS}$ (kcal/mol)	$\Delta H^{298}_{X/XS}$ (kcal/mol)	ref
CH ₃ CN	CH ₃ SCN		+20.4 ^a	27, 28
PhPh	PhSPh		+10.9 ^a	28, 30
cyclohexane	hexamethylene sulfide		+9.9 ^a	28, 30
C ₆ H ₅ CH ₃	C ₆ H ₅ SCH ₃		+6.9 ^a	28, 30
CH ₃ C(CH ₃) ₂ CH ₃	(CH ₃) ₃ CCH ₂ SH		+5.5 ^a	28, 30
CH ₃ CH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CH ₂ CH ₂ SH		+4.8 ^a	28, 30
CH ₃ CH ₂ SH	HSCH ₂ CH ₂ SH		+4.3 ^a	27, 28
C ₆ H ₆	PhSH		+3.1 ^a	28, 30
			+2.7 ^a	28, 30
(CH ₃) ₃ CH	^t BuSH		+2.7 ^a	28, 30
			+1.8 ^a	28, 30
Cl ₂ S ₃	Cl ₂ S ₄		+1.8 ^a	27, 28
			+1.4 ^a	28, 30
Cl ₂ S ₂	Cl ₂ S ₃		+1.3 ^a	27, 28
Cl ₂ S ₄	Cl ₂ S ₅		+1.0 ^a	27, 28
			+0.8 ^a	28, 30
			+0.3 ^a	28, 30
H ₂ S ₂	H ₂ S ₃		+0.3 ^a	27, 28
CH ₃ SCH ₃	CH ₃ SSCH ₃	+2.4	+0.3 ^a	27, 28
H ₂ S ₃	H ₂ S ₄		+0.1 ^a	27, 28
H ₂ S ₄	H ₂ S ₅		+0.05 ^a	27, 28
H ₂ S ₅	H ₂ S ₆		+0.05 ^a	27, 28
			-0.7 ^a	28, 30
ⁿ BuS ⁿ Bu	ⁿ BuSS ⁿ Bu		-1.0 ^a	28, 30
NiS	NiS ₂	-2.4	-1.4	28
Cl ₂ S	Cl ₂ S ₂	-2.7	-2.5	28
^t BuS ^t Bu	^t BuSS ^t Bu		-5.9 ^a	28, 30
CH ₃ C(O)H	CH ₃ C(O)SH		-6.6 ^a	27, 28
			-10.2 ^a	28, 30
Na ₂ S	Na ₂ S ₂	-14.4	-13.9	28
			-18.7 ^a	28, 29
Ni	NiS	-19.2	-19.6	28
Pb	PbS	-21.0	-21.6	28

^a For these couples, $\Delta_f H^\circ$ (298.15 K) for S(l) = 1.9 kJ/mol is taken from ref 28.

by their placement in different columns. In the second column are numbers that have recently been produced as computational estimates by Jenks and co-workers using G3 (Gaussian 3) methods.⁴³ In the third column are numbers that are the reverse of entries in Table 1 for the corresponding XS molecule. These sulfur bond dissociation energies are indirectly determined from independent experimental measurements of $\Delta_f H(298)$ for X(g), XS(g), and S(g) and, as such, are experimentally determined numbers themselves. The $\Delta_{rxn} H(298)$ for XS(g) → X(g) + S(g), which is the X–S bond dissociation energy, is then simply taken as $\Delta_f H(X) + \Delta_f H(S) - \Delta_f H(XS)$ at 298 K. The numbers determined by this approach are possibly the more accurate experimental numbers in Table 6 because they avoid the need to account for solvation enthalpies.

In the fourth column of Table 6 are X–S bond dissociation energies determined through direct calorimetric measurement of $\Delta_{rxn} H(298)$ for X + S → XS. $\Delta_{rxn} H(298)$ values obtained by Chernick, Pedley, and Skinner were obtained in excess liquid phosphine and subsequently coupled to enthalpies of vaporization for R₃P, R₃PS, and atomic sulfur and to the enthalpy of solvation of R₃PS in liquid R₃P.⁴⁴ In contrast, Hoff and co-workers measured $\Delta_{rxn} H(298)$ values for R₃P + S → R₃PS in benzene or toluene solution.²¹ They obtained X–S bond dissociation energies by coupling these $\Delta_{rxn} H(298)$ values to $\Delta_f H(298)$ for S(g) and using the simplifying assumption that $\Delta_{vap} H$ for X and XS have similar values and therefore can be neglected because they offset one another. In turn, bond dissociation energies for Ph₃AsS and Ph₃SbS were obtained by measurement of $\Delta_{rxn} H(298)$ for Ph₃AsS + Ph₃P → Ph₃As + Ph₃PS and Ph₃SbS + Ph₃P → Ph₃Sb + Ph₃PS. Uncertainties in these numbers reported by Hoff are of the order of ±3 kcal/mol. Carbon–sulfur bond dissociation energies for the sulfides (thiones) of the mesityl and adamantyl substituted Arduengo carbenes were determined by Hoff and Nolan in a similar manner through sulfur atom abstraction reactions by these carbenes from Ph₃AsS and Ph₃SbS.⁴⁰ The fourth column of Table 6 also contains the few known values for transition metal sulfide bond dissociation energies that have been either measured calorimetrically⁴⁵ or at least estimated.⁴⁶

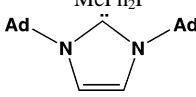
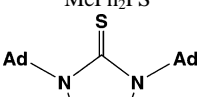
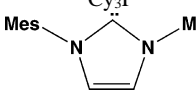
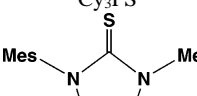
For only one compound, namely Ph₃P, have bond dissociation energies been determined by all of the aforementioned approaches. The values for the phosphorus–sulfur bond dissociation energy in Ph₃PS by these experimental methods [93.5 ± 2.9 from $\Delta_f H(298)$ values and 88 ± 3 from $\Delta_{rxn} H$ measurements; see Table 6] are therefore the same within the given uncertainties. The somewhat lower value obtained by computational estimate is attributed in part to intrinsic limitations of the G3 method in dealing with sulfide bonds of this type.

The phosphorus–sulfur bond dissociation energies in phosphine sulfides generally correlate with electron richness as governed by the nature of the substituents on the phosphorus atom. Thus, F₃PS, with highly electronegative fluorine atoms, has a bond dissociation energy ~20 kcal/mol less than the phosphine sulfides with electron-rich alkyl groups. A trend in olefin sulfide bond dissociation energies is more difficult to identify and likely reflects a competition between two distinct effects. More electron-rich olefins, that is, those with more alkyl substituents, ought to favor oxidative addition of sulfur and have the higher bond dissociation energies, but at the same time increased substitution disfavors the addition of sulfur because of steric crowding. The net result appears to be that the intermediate degree of alkyl substitution found in *trans*-2-butene produces the greatest stabilization in the corresponding olefin sulfide.

4. Compounds Prepared by Sulfur Atom Transfer Reactions

Well-defined sulfur atom transfer reactions involving the transition metals, main group elements in groups 13–15, and the f-block elements are collected in Table 7 and, where classification is unambiguous, designated according to the reaction types defined in reactions 7–12. The use of bold-faced type in the donor/acceptor column of Table 7 is intended to draw a clearer distinction for the instances of desulfurization versus sulfuration. Complexes prepared by or desulfurized by type I sulfur atom transfer (reaction 7) are designated as such in Table 7. Similarly, molecules prepared by secondary

Table 4. Sulfur Atom Transfer Thermodynamic Scale in C₆H₆ or C₆H₅CH₃ Solution: X(sol) + S(sol) → XS(sol)

X	XS	$\Delta G^{298}_{X/XS}$ (kcal/mol)	$\Delta H^{298}_{X/XS}$ (kcal/mol)	ref
Ph ₃ Sb	Ph ₃ SbS		0 ^a	21
BzSSBz	BzSSSBz		-1.9 ^b	21
Ph ₃ As	Ph ₃ AsS		-3.8 ^c	21
Ph ₃ P	Ph ₃ PS		-21.5	21
MePh ₂ P	MePh ₂ PS		-23.8	21
			-24.1 ^d	40
Me ₂ PhP	Me ₂ PhPS		-26.0	21
Me ₃ P	Me ₃ PS		-27.1	21
Bu ₃ P	Bu ₃ PS		-28.9	21
Cy ₃ P	Cy ₃ PS		-30.9	21
			-35.0 ^e	40

^a Determined indirectly from $\Delta_{rxn}H$ for Ph₃SbS + Ph₃P → Ph₃Sb + Ph₃PS. ^b Determined indirectly from $\Delta_{rxn}H$ for BzSSSBz + Cy₃P → BzSSBz + Cy₃PS. ^c Determined indirectly from $\Delta_{rxn}H$ for Ph₃AsS + Ph₃P → Ph₃As + Ph₃PS. ^d Determined indirectly from $\Delta_{rxn}H$ for Ph₃AsS + X → Ph₃As + XS, X = carbene. ^e Determined indirectly from $\Delta_{rxn}H$ for Ph₃AsS + X → Ph₃As + XS and from $\Delta_{rxn}H$ for Ph₃SbS + X → Ph₃Sb + XS, X = carbene.

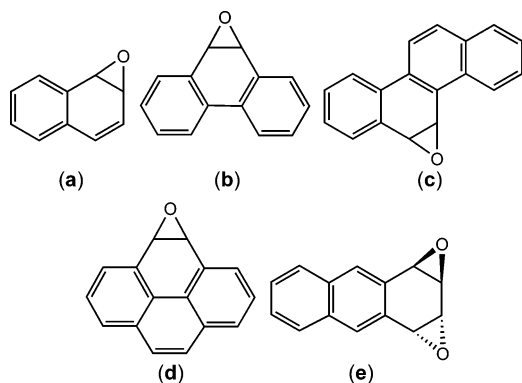
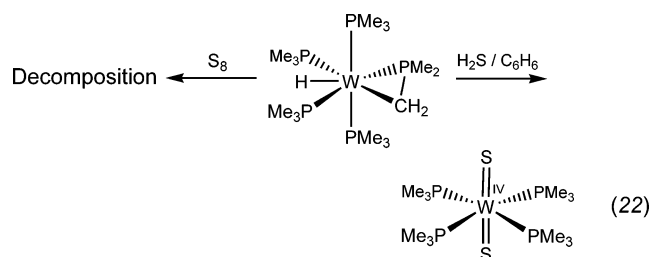


Figure 4. Examples of known arene epoxides: (a) naphthalene-1,2-oxide;⁴⁸ (b) phenanthrene-9,10-oxide;⁴⁹ (c) chrysene-5,6-oxide;⁵⁰ (d) pyrene-4,5-oxide;⁵¹ (e) anthracene-1,2,3,4-dioxide.⁵²

sulfur atom transfer processes are denoted by II, tertiary processes are indicated by IIIa or IIIb, and quaternary reactions are denoted IV. In each case, the reagents used as sulfur atom donor or acceptor are also indicated. All ligand abbreviations are fully defined in section 11.

In many cases, a variety of sulfur atom donors are competent to effect the same reaction. In other instances, for reasons that are not necessarily clear a priori, some (or even only one) sulfur atom donor agents will work to effect a particular sulfur atom transfer, but others will not. For instance, Parkin has noted that the *trans*-W^{IV}S₂(PMe₃)₄ complex is cleanly prepared from W(PMe₃)₄(η^2 -CH₂PMe₂)H using H₂S, with concomitant evolution of H₂, whereas elemental sulfur results in immediate and complete decomposition (reaction 22).⁴⁷ Observations such as these empha-



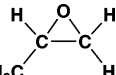
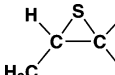
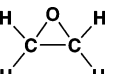
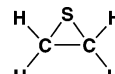
size the value in testing more than one donor reagent if an initial choice does not produce the desired sulfur atom transfer or does not do so cleanly. In the following sections, a variety of sulfur atom donors is discussed in an effort to identify their relative advantages and disadvantages. Some of these reagents are molecules that have been frequently employed as sulfur atom donors, whereas others have not been used at all. With regard to the potential usefulness of these sulfur atom donors, some aspects of the following discussion are speculative. The intent herein is merely to suggest possibilities to the reader who is interested in synthesis by sulfur atom transfer.

5. Sulfur Atom Donors

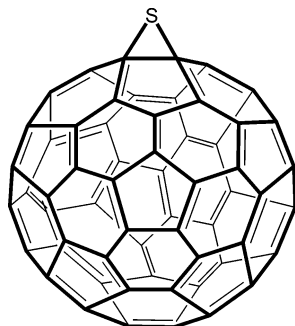
A scarcity of strong sulfur atom donors is immediately apparent from a cursory inspection of Tables 1–4. In contrast to the gas phase table for oxygen atom transfer reagents,¹⁹ Table 1 contains no entry for which XS → X + S is an exothermic process. This paucity of strong sulfur atom donors may be attributed in some degree to the readiness by which sulfur bonds with itself. Whereas molecules such as H₂O₂, Bu^tOObu^t, and O₃ are active, indeed often indiscriminate, oxygen atom donors, the analogous sulfur compounds do not have similar atom transfer ability. The electron lone-pair–lone pair repulsions that activate peroxy species are mitigated by the larger, more diffuse nature of the valence sulfur p atomic orbitals.

Another reason for the scant number of strong sulfur atom donors is that many reagents XS that are of conceivable use tend to be too unstable toward elimination of elemental sulfur and formation of X. Sulfur analogues of species such as trimethylamine *N*-oxide (Me₃NO), iodosyl benzene (C₆H₅-IO), and the hypochlorite anion (OCI⁻) appear to be unknown species, probably for this reason. A class of compounds that is generally interesting as reagents for chalcogen transfer is the family of arene chalcogenides. The strong driving force for chalcogen atom transfer arises from the formation of arene, a relatively innocent byproduct that is easily separated from other species. Although numerous arene epoxides are known^{48–52} (Figure 4) and many have even been structurally characterized by X-ray crystallography, the corresponding

Table 5. Oxo-for-Sulfido Exchange Thermodynamic Scale: $XO(g) + S(g) \rightarrow XS(g) + O(g)$

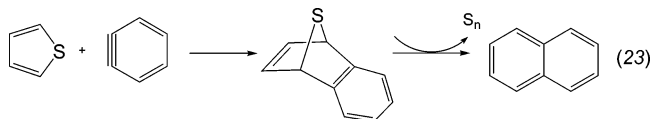
XO	XS	$\Delta G^{298}_{XO/XS}$ (kcal/mol)	$\Delta H^{298}_{XO/XS}$ (kcal/mol)	ref
CO	CS	+86.3	+86.8	31
B ₂ O ₃	B ₂ S ₃		+65 ^a	27
Me ₃ SiOSiMe ₃	Me ₃ SiSSiMe ₃		~ +61 ^b	31, 189
COS	CS ₂	+54.4	+54.4	31
CO ₂	COS	+53.5	+54.3	31
F ₃ PO	F ₃ PS	+51.5	+52.0	31
BO	BS	+51.0	+51.5	31
OSO	OSS	+47.7	+50.8	31
Al ₂ O ₂	Al ₂ S ₂	+48.7	+48.4 ^c	28
H ₂ O	H ₂ S	+45.5	+46.3	31
Ph ₃ PO	Ph ₃ PS		+41.9	31, 36, 37
SiO	SiS	+42.3	+42.7	31
In ₂ O	In ₂ S	+41.1	+42.1	28
Cl ₃ PO	Cl ₃ PS	+35.8	+36.2	31
NO	NS	+34.4	+34.8	31
AlO	AlS	+34.0	+34.4 ± 4.0	28
PO	PS	+31.8	+32.1	31
CLOS	ClS ₂		+30.9	d
GeO	GeS	+29.4	+29.7	28
F ₂ SO	F ₂ SS	+26.9	+27.4	31
			+26.6	27, 29
		+24.7	+25.2	27
Br ₃ PO	Br ₃ PS	+22.9	+23.4	31
HO	HS	+17.0	+17.3 ± 1.6	28
SnO	SnS	+14.2	+14.4	28
PbO	PbS	+7.7	+8.1 ± 3.3	28
ClO	ClS	+6.1	+6.5	31
O=O	S=O	-6.2	-5.4 ± 1.7	28
FO	FS	-29.8	-29.6	31
Cl ₂ O	Cl ₂ S	-32.1	-32.4	31
InO	InS		-42.7	27
F ₂ O	F ₂ S	-83.7	-83.4	31

^a This value is one-third the value of the couple $B_2O_3(g) + 3S(g) \rightarrow B_2S_3(g) + 3O(g)$. The other entries in the table are for single chalcogen atom exchanges, so this couple must be "normalized" so as to be fitted into a meaningful position in the table. Data are not available for the single atom exchange couples $B_2O_3(g) + S(g) \rightarrow B_2O_2S(g) + O(g)$ or $B_2O_2S(g) + S(g) \rightarrow B_2OS_2(g) + O(g)$ or $B_2OS_2(g) + S(g) \rightarrow B_2S_3(g) + O(g)$, but +65 kcal/mol could be taken as a rough estimate for the value of each of these reactions. Inasmuch as the nearest other couples are ± several kcal/mol, it is likely that the position for B_2S_3 in this table is not out of place. ^b This value is estimated from the difference in approximate Si–O and Si–S bond strength energies given in ref 189. The difference between $\Delta H_f(298)$ for O(g) and $\Delta H_f(298)$ for S(g) is taken into consideration for this estimate. ^c A "normalization" similar to that described in footnote *a* is performed here. ^d Takacs, G. A. J. *Chem. Eng. Data* **1978**, 23, 174.

**Figure 5.** Structure of C₆₀S.

sulfur analogues are unknown due to their instabilities relative to those of the aromatic molecules and elemental sulfur. Similarly, molecules such as 1,4-dihydro-1,4-thionaphthalene⁵³ can be generated and detected at low temper-

ature but are too unstable to permit their isolation (reaction 23).



5.1. Allotropes of Sulfur

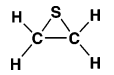
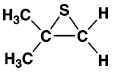
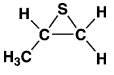
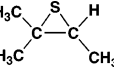
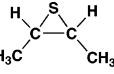
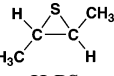
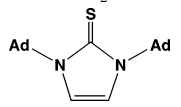
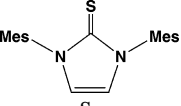
The thermodynamic data in Table 1 involving S₃–S₈ presumably all refer to cyclic species rather than to linear or cage species. These data do not suggest any of these species to be especially active sulfur atom donors, at least not to weak acceptors. This fact notwithstanding, commercially available elemental sulfur (~99% S₈) has found frequent use as a sulfur atom donor agent, principally because it is coupled to strong sulfur atom acceptors (vide infra). It bears mention here that many other allotropes of sulfur have been prepared, structurally authenticated by X-ray crystallography, and characterized by other means. Of these allotropes, which include S₆,⁵⁴ S₇,⁵⁵ S₉,⁵⁶ S₁₀,^{55a,57} S₁₁,⁵⁸ S₁₂,⁵⁹ S₁₃,^{58bc} S₁₄,⁶⁰ S₁₅,⁶¹ S₁₈,^{55e,59d,62} and S₂₀,^{55e,59d,62a,63} S₆ is most amenable to preparative scale synthesis.^{54ab} In general, these species may be produced through kinetically controlled syntheses of the type $H_2S_x + Cl_2S_y \rightarrow 2HCl + S_{x+y}$ or $Cp_2TiS_x + Cl_2S_y \rightarrow Cp_2TiCl_2 + S_{x+y}$.

It has been noted that S₆ and S₇ are more reactive allotropes of sulfur than is S₈, with S₇ being quite prone to decomposition even at ambient temperature. Both S₆ and S₇ are known to be in equilibrium with S₈ in solution and combined account for approximately 1.2% of total sulfur by mass.⁶⁴ As single sulfur atom transfer agents that would result in cyclic S_{n-1} byproducts, S₆ is weaker by 2.4 kcal/mol, whereas S₇ is stronger by 5.3 kcal/mol, than S₈ in terms of the thermodynamic data presented in Table 1. The more meaningful comparison between these allotropes, however, is to view each S_n species as a source of *n* S atoms. Considered in this "normalized" way, for instance, $8S_6(g) \rightarrow 48S(g)$ is more favorable enthalpically than $6S_8(g) \rightarrow 48S(g)$ by 49.3 kcal/mol, which is consistent with S₈ being the most stable S_n allotrope. Cycloheptasulfur (and S₁₂ also) has been observed to react with triarylphosphine to form the corresponding phosphine sulfide at rates that are ~10² greater than that shown by S₈, whereas the rate of reaction of S₆ is even faster still by a factor of ~10⁴.⁶⁵ In these systems, it is quite likely that kinetic effects are contributing significantly to the observed rates. Although it has not (as yet) been synthesized and isolated, the fullerene sulfide C₆₀S (Figure 5) has been suggested by semiempirical energy calculations to be a stable species. Its formation according to the stoichiometry $nC_{60} + S_n \rightarrow nC_{60}S$ is calculated to be more favorable for *n* = 6 over *n* = 8 by 32.5 kcal/mol.⁶⁶ Despite its accessibility and these indications that its reactivity is appreciably greater than that of S₈, S₆ does not appear to have ever been used synthetically as a sulfur atom donor agent.

5.2. Oxathiiranes, Dithiiranes, and Sulfines

Possible strong sulfur atom donors for which no thermodynamic data are available are the oxathiiranes and dithiiranes, the general structures of which are given as (a) and (c), respectively, in Figure 6. Oxathiiranes as such are too reactive to permit isolation but may be generated photolytically⁶⁷ or thermally⁶⁸ from their isomeric form, the thione

Table 6. Bond Dissociation Energies for the Gas Phase, $\text{XS(g)} \rightarrow \text{X(g)} + \text{S(g)}$, in Kilocalories per Mole

XS	computational estimate	from $\Delta_f H$ values	from $\Delta_{\text{rxn}} H$ values	ref
H_3AsS	48.3 ^a			43
HS(S)H		$[51 \pm 7]^b$		35
MeS(S)Me		$[53 \pm 4]^b$		35
ClS		57.8		28
		59.0 ± 0.5		28, 29
		59.5 ± 0.8		28, 30
		60.0 ± 0.8		28, 30
		61.4 ± 0.8		28, 30
		61.8 ± 0.8		28, 30
		62.6 ± 0.8		28, 30
H_3PS	63.7 ^a			43
S_3		65.6		27
FS(S)F		66.3		31
Ph_3SbS			67	21
Ph_3AsS	68.4 ^{a,43}		70 ²¹	43, 21
Me_3AsS	69.5 ^a			43
CH_3NCS		70.9		27
O=C=S		72.9 ± 0.4		28
S_2O		77.1		28
F_3PS		78.3 ^c		31
S_2Cl		84.8		28
HS		85.0		28
Cl_3PS		88.2 ^c		31
$(\text{EtO})_3\text{PS}$			90.6	44
Ph_3PS	82.4 ^{a,43}	$93.5 \pm 2.9^{28,36,37}$	88 ²¹	43, 28, 36, 37, 21
Br_3PS		94.3 ^c		31, ^d
MePh_2PS			91	21
			91	40
Me_2PhPS			93	21
Me_3PS	87.5 ^{a,43}		94 ²¹	43, 21
Pr_3PS			91.6	44
Bu_3PS			91.5, ⁴⁴ 96 ²¹	44, 21
Cy_3PS			98	21
			102	40
S_2		101.7 ± 0.2		28
$([\text{R}(\text{ArN})_3\text{Mo}=\text{S}]^e$			104.4 ± 1.2	45
$\text{S}=\text{C}=\text{S}$		105.3 ± 6.2		28
$\text{L}_3\text{Cl}_2\text{W}=\text{S}^f$			≥ 105	46
$\text{O}=\text{S}$		124.6 ± 0.4		28
SiS		146		28
CS		170.5 ± 6.2		28

^a These computational estimates are for the gas phase at 0 °C. ^b Values are based on estimated numbers. ^c The reference given in footnote ^d lists BDEs of 100 and 68 kcal/mol for F_3PS and Cl_3PS , respectively. These numbers are appreciably different from the numbers obtained from ref 31, which is the source preferred here. Both sources have the same value for $\text{Br}_3\text{P}=\text{S}$. ^d Lou, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: New York, 2003; p 286. ^e $\text{R} = \text{C}(\text{CD}_3)_2\text{CH}_3$, $\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$. ^f $\text{L} = \text{PMe}_3$ or PMe_2Ph .

S-oxide or sulfine [(b) in Figure 6]. Sulfines are considerably more stable than oxathiiranes, and the preparation and characterization of a variety of examples have been described.⁶⁹ Aryl-substituted oxathiiranes generated in situ by photolysis of sulfines have been shown to effectively transfer a sulfur atom to olefins such as norbornene and *trans*-cyclooctene to produce the corresponding episulfide.⁷⁰ Curiously, thermolysis of fluorene-thione *S*-oxide in the presence

of olefinic substrate also resulted in efficient sulfur atom transfer but through the agency of an intermediate different from the expected oxathiirane.⁷¹ Beyond the episulfidation of olefins, the sulfur atom transfer capabilities of in situ generated oxathiiranes do not appear to have been systematically investigated. It is unclear how much synthetic value they will have as general sulfur atom donor reagents in reactions with other types of acceptors. Because any species

Table 7. Metal and Organic Sulfides Prepared or Desulfurized by Sulfur Atom Transfer Reactions

	compound	sulfur atom donor/acceptor	rxn type	ref
Ti^{IV}S	(TpTP)TiS	(OEP)Ti ^{IV} (η^2 -S ₂), ^a Ph ₃ PS, ^b ^t BuNCS, ^c CS ₂ , ^c Cy ₃ PS ^c	I	a, b, c
	Cp* ₂ TiS(py)	S ₈	I	d
Ti^{IV}(μ-S)₂Ti^{IV}	[(η^5 -C ₅ H ₅)Ti(μ -S)] ₂ (μ - η^5 : η^5 -C ₁₀ H ₈) ^e	S ₈	IV	f
	[Me ₂ NC(N ⁱ Pr) ₂] ₂ Ti(μ -S) ₂ Ti[Me ₂ NC(N ⁱ Pr) ₂] ₂	propylene sulfide	IV	g
Zr^{IV}S	Cp* ₂ ZrS(py)	S ₈ , H ₂ S, ^h SC ₂ H ₄ , ⁱ Ph ₃ PS	I	j, 137
	CpEt* ₂ ZrS(py)	S ₈	I	j
Zr^{IV}(μ-S)Zr^{IV}	Cp* ₂ Zr(SH)(μ -S)Zr(SH)Cp* ₂ ^k	H ₂ S	II	138
Zr^{IV}(μ-S)(μ-O)Zr^{IV}	Cp' ₂ Zr(μ -S)(μ -O)ZrCp' ₂ ^l	S ₈	III	m
Zr^{IV}(μ-S)₂Zr^{IV}	Cp ₂ Zr(μ -S) ₂ ZrCp ₂	H ₂ S	IV	139
	Cp' ₂ Zr(μ -S) ₂ ZrCp' ₂	S ₈	IV	n
	Cp* ₂ Zr(μ -S) ₂ ZrCp* ₂	S ₈	IV	140
Zr^{IV}(μ-S)Ir^{III}	Cp ₂ Zr(μ -N- ^t Bu)(μ -S)IrCp*	Me ₃ PS, S ₈ , H ₂ S, <i>cis</i> - or <i>trans</i> -2-butene sulfide, 2-methylpropene sulfide, propylene sulfide, ethylene sulfide	III	o
Hf^{IV}S	Cp* ₂ HfS(py)	S ₈	I	p
V^I(μ-S)V^I	[V(CO) ₃ (dppe)] ₂ (μ -S)	SO ₃ ²⁻ /H ₂ O/H ⁺ ; ^q Na ₂ S/H ⁺ or H ₂ S ^r		q, r
V^{IV}S	(Por)VS (Por = OEP, TPP, TmTP, TpTP)	S ₈	I	s, t
	(BzMe ₃ N) ₂ [VS(SPh) ₄] ^u	S ₈		v
	(Ph ₄ P)Na[VS(edt) ₂], (Et ₄ N)Na[VS(edt) ₂] ^u	S ₈		w
V^{IV}(μ-S)V^{IV}	CpV(μ -N- ^t Bu) ₂ (μ -S)VCp	S ₈	II	x
V^{IV}(μ-S)₂V^{IV}	Cp*ClV(μ -S) ₂ VClCp*	S ₈		y
	[(Me ₃ Si) ₂ N] ₂ V(μ -S) ₂	S ₈		z
V^{IV}(μ-S)₂V^V(S)₂	(Et ₄ N) ₂ Na[(edt)V(E)(μ -S) ₂ V(S) ₂ (E = O, S)]	S ₈		w, aa
V^VS	(Ph ₃ SiO) ₃ VS	S ₈		ab
	(^t BuO) ₃ VS ^{ac}	S ₈		155
	[N ₃ N]VS [N ₃ N] = [(Me ₃ SiNCH ₂ CH ₂) ₃ N] ³⁻	S ₈ , ethylene sulfide	I	ad
	[(Me ₃ Si) ₂ N] ₂ V(S)(ESiR ₃) (E = Se, Te; R = SiMe ₃ , Ph)	propylene sulfide	I	ae
	[(3,5-Me ₂ Ph)N(Ad)] ₃ VS	S ₈	I	af
V^V(S)₂	(Me ₃ NBz) ₂ [V(S) ₂ (S ₂)(SPh)]	S ₈		aa, ag
Nb^{III}(μ-S)₂Nb^{III}	[Cp(CO) ₂ Nb] ₂ (μ -S) ₂	H ₂ S	IV	ah
Nb^{IV}(μ-S)₂Nb^{IV}	[Cp ₂ Nb] ₂ (μ -S) ₂	^t BuSH, [CpCr(S ^t Bu)] ₂ S	IV	ai
Nb^{IV}(μ-S)₃Nb^{IV}	[Cp(CO) ₂ Nb] ₂ (μ -S) ₃	H ₂ S		ah
Nb^VS	Cp*Nb(NAr)(S)(PMe ₃) (Ar = 2,6-C ₆ H ₃ Pr ₂)	S ₈	I	aj
	(N[Np]Ar) ₃ NbS (Np = neopentyl, Ar = 3,5-Me ₂ Ph)	Me ₃ PS	I	ak
Ta^{IV}(μ-S)Ta^{IV}	[Cp ₂ Ta(Me)] ₂ (μ -S) ^{al}	ethylene sulfide, Me ₃ PS	II	am, an
Ta^VS	Cp ₂ TaS(Me) ^{al}	ethylene sulfide, Me ₃ PS	I	am, an
	Cp ₂ TaS(SMe) ^{al,ao}	ethylene sulfide	I	am, an
Cr^{II}(μ-S)Cr^{II}	[CpCr(CO) ₂] ₂ S	N ₃ S ₃ Cl ₃ , ^{ap,aq} SO ₃ ²⁻ /H ₂ SO ₄ ^r		aq, r
		S ₈	II	ar, as
Cr^{III}(μ-S)Cr^{III}	[CpCr] ₂ (μ -S)(μ -S ^t Bu) ₂	^t BuSH	II	at
Cr^{IV}(μ-S)₂Cr^{IV}	[(Cy ₂ N) ₂ Cr] ₂ (μ -S) ₂ , [(Ad(3,5-Me ₂ Ph)N) ₂ Cr] ₂ (μ -S) ₂	S ₈		au
Mo^{II}(μ-S)Mo^{II}	[(HB(3,5-Me ₂ pz) ₃)Mo(CO) ₂] ₂ (μ -S)	N ₃ S ₃ Cl ₃ , ^{ap,av} S ₈ ^{aw}		av, aw
Mo^{III}(μ-S)Mo^{III}	Mo(PMe ₃) ₃ Cl(μ -Cl)(μ -S)Mo(PMe ₃) ₂ Cl ₂	Me ₃ PS ^{ax,46a,46b} Ph ₃ PS, ^{46b} ^t BuSH, ^{46b} ethylene sulfide ^{ax,46b}	II	ax, 46a, 46b
	Mo(PMe ₃) ₃ Cl(μ -Cl)(μ -S)Mo(PMe ₃)Cl ₂	Me ₃ PS, ethylene sulfide	II	ax
Mo^{III}(μ-S)W^{III}	MoW(μ -Cl)(μ -S)Cl ₃ (PMe ₃) ₅	M ^{IV} (S)Cl ₂ (PMe ₃) ₃ (M = Mo, W)	II	46b
Mo^{IV}S	(TpTP)MoS	S ₈ , Cp ₂ Ti(η^2 -S ₅), (TpTP)SnS	I	ay
	MoSCl ₂ (PMe ₃) ₃	SC ₂ H ₄ , PMe ₃ ^{az}	I	ax, 46a, 46b
trans-Mo^{IV}(S)₂	(<i>syn</i> -Me ₈ [16]aneS ₄)Mo(S) ₂	S ₈ , ^t BuSH	I	ba
	(Me ₃ P) ₄ Mo(S) ₂	H ₂ S	I	136
	(dppe) ₂ Mo(S) ₂	BzSSSBz ^{bb}	I	132
	(dppe) ₂ Mo(S) ₂	BzSSSBz ^{bb}	I	132
trans-Mo^{IV}(O)(S)	(dppe) ₂ Mo(O)(S)	SO ₂	I	bc
Mo^{IV}(S)-Mo^{IV}(S)	Cp*Mo(S)(μ -S) ₂ Mo(S)Cp*	S ₈		bd
Mo^{IV}(μ-S)Mo^{IV}	[(Cp)Mo(μ -S ₂ CH ₂)(μ -SMe)(μ -S)Mo(Cp)] ⁺	SC ₂ H ₄ , <i>cis</i> -stilbene sulfide, thietane, 2,5-dihydrothiophene		16
Mo^{IV}(μ-S)₂Mo^{IV}	Cp*Mo(μ -S) ₂ (μ -S) ₂ MoCp*	S ₈	III	bd
Mo^VS	(N[R]Ar) ₃ Mo(S) (R = C(CD ₃) ₂ CH ₃ , Ar = 3,5-C ₆ H ₃ Me ₂)	S ₈ , propylene sulfide, CS ₂ , ^{be} SO ₂ ^{bf}	I	bg
Mo^VO(μ-O,S)Mo^VO	<i>syn</i> - and <i>anti</i> -CpMoO(μ -O)(μ -S)MoOCp from [CpMo(CO) ₂] ₂	As ₄ S ₄		bh
	<i>anti</i> -(MeCp)MoO(μ -O)(μ -S)MoO(MeCp)			bh
Mo^VO(μ-S)₂Mo^VO	<i>anti</i> -CpMoO(μ -S) ₂ MoOCp from [CpMo(CO) ₃] ₂	cyclohexene sulfide followed by air oxidation		bi, bj
Mo^VS(μ-S)₂Mo^VO	(R ₂ NCS ₂)Mo(S)(μ -S) ₂ Mo(O)(S ₂ CNR ₂) (R = Me, Et)	Ph₃P , CN ⁻ ^{bk}	I	bl

Table 7. (Continued)

	compound	sulfur atom donor/acceptor	rxn type	ref
Mo^VS(μ-S)₂Mo^VS	<i>anti</i> -Cp*Mo ^V (S)(μ-S) ₂ Mo ^V (S)Cp* from [Cp*(CO) ₂ Mo] ₂	S ₈	I and III	<i>bd</i>
	<i>anti</i> -Cp*Mo ^V (S)(μ-S) ₂ Mo ^V (S)Cp* from Cp*Mo(CO) ₃ H	S ₈		<i>bm</i>
	<i>anti</i> -(MeCp)Mo ^V (S)(μ-S) ₂ Mo ^V (S)(MeCp) from [(MeCp)Mo(CO) ₃] ₂	S ₈	I and III	<i>bm</i>
Mo^{VI}S	[Et ₃ N][MoS(O- <i>p</i> -C ₆ H ₄ X')(S ₂ C ₂ Me ₂) ₂] (X' = Me, OMe, H, Br, COMe, CN)	Ph ₃ AsS, Ph ₃ SbS (only for X' = H) ^{bn}	I	<i>bo</i>
Mo^{VI}OS	[(HB(3,5-Me ₂ pz) ₃)MoOS(η ¹ -S ₂ P(^{<i>i</i>} Pr) ₂)]	propylene sulfide, CN ⁻	I	<i>bp</i>
	[(HB(3- ^{<i>i</i>} Prpz) ₂ (5- ^{<i>i</i>} Prpz))MoOS(η ¹ -S ₂ PR ₂)] (R = ^{<i>i</i>} Pr, Ph)	propylene sulfide	I	165
	[(HB(3- ^{<i>i</i>} Prpz) ₃)MoOS(OPh)]	propylene sulfide, Ph ₃ P, CN ⁻	I	<i>bq</i>
	[MoOS(OSiPh ₃) ₂ (Me ₄ phen)]	Ph₃P	I	<i>br</i>
	[(Et ₂ NCS) ₂ MoOS]	RNC (R = various substituent), olefins, allenes (various)^{bs}	I	3, 4
	[(EtO) ₂ PS ₂) ₂ MoOS]	olefins and allenes (various)^{bs}	I	3b, 3c
W^{II}(μ-S)W^{II}	[(HB(3,5-Me ₂ pz) ₃)W(CO) ₂] ₂ (μ-S)	N ₃ S ₃ Cl ₃ ^{ap}		<i>av</i>
W^{III}(μ-S)W^{III}	W(PMe ₃) ₃ Cl(μ-Cl)(μ-S)W(PMe ₃) ₂ Cl ₂	Me ₃ PS	II	46b
W^{IV}S	W(S)(PhCCPh)(S ₂ CNEt ₂) ₂	cyclohexene sulfide	I	<i>bt</i>
	[(HB(3,5-Me ₂ pz) ₃)WS(S ₂ CNEt ₂)]	cyclohexene sulfide	I	<i>bu</i>
	W(S)Cl ₂ (PMePh ₂) ₂ L (L = PMePh ₂ , CO, CN ^{<i>n</i>} Bu, H ₂ C=CH ₂)	MePh ₂ PS, OCS, ^{<i>n</i>} BuNCS, ethylene sulfide, ^{<i>n</i>} BuSH ^{bv}	I	124, 125, <i>bv</i>
	W(S)Cl ₂ (PMe ₃) ₃	Me ₃ PS, SC ₂ H ₄	I	46a
	[(HB(3,5-Me ₂ pz) ₃)W ^{IV} S(CO)X]	propylene sulfide	I	<i>bw, bx</i>
	(X = halide or η ¹ -S ₂ PR ₂ ¹⁻ ; R = Ph, OEt, O ^{<i>n</i>} Pr, (-)-mentholate)			
	[(HB(3,5-Me ₂ pz) ₃)W ^{IV} S(py)Cl]	PPH₃ (S abstraction from [(HB(3,5-Me₂pz)₃)W^{VI}S₂Cl] in py	I	<i>by, bz</i>
	[(HB(3,5-Me ₂ pz) ₃)W ^{IV} S(η ² -S ₂ PPh ₂)]	PPH₃ (S abstraction from [(HB(3,5-Me₂pz)₃)W^{VI}S₂(η¹-S₂PPh₂)]	I	<i>by, bz</i>
<i>trans</i> -W ^{IV} (S) ₂	W(S) ₂ (Me ₃ P) ₄	H ₂ S ^{ca}	I	47
W^{III}(μ-S)₂W^V(S)	Cp*W ^{III} (CO) ₂ (μ-S) ₂ W ^V (S) Cp* from [Cp*W(CO) ₂] ₂	S ₈	I and III	<i>bd</i>
W^{IV}(S)—W^{IV}(S)	Cp*W(S)(μ-S) ₂ W(S)Cp* from [Cp*W(CO) ₂] ₂	S ₈		<i>bd</i>
W^V(μ-S)W^V	(^{<i>n</i>} BuCH ₂ O) ₃ W(μ-S)(μ-OCH ₂ ^{<i>n</i>} Bu) ₂ W(OCH ₂ ^{<i>n</i>} Bu) ₃	S ₈	IIIb	<i>cb</i>
W^V(S)(μ-S)₂W^V(S)	<i>anti</i> -Cp*W(S)(μ-S) ₂ W(S)Cp* from Cp*W ^V (S)(μ-S) ₂ W ^{III} (CO) ₂ Cp*	S ₈	I	<i>bd</i>
W^VS	[(HB(3,5-Me ₂ pz) ₃)W ^V S ₂ Cl]	PPH₃ (S abstraction from [(HB(3,5-Me₂pz)₃)W^{VI}S₂Cl] in CH₂Cl₂ followed by Cl atom abstraction from CH₂Cl₂		<i>by</i>
W^{VI}S	WS ₂ Cl ₄ (from W(CO) ₆ with <i>hv</i>)	S ₂ Cl ₂	I	<i>cc</i>
	WS ₂ Cl ₄	Ph₃P	I	<i>cd</i>
	[Et ₃ N][W(S)(OSi ^{<i>n</i>} BuPh ₂)(bdt) ₂]	BzSSSBz	I	129
	[Et ₃ N][W(S)(OPh)(S ₂ C ₂ Me ₂) ₂]	BzSSSBz	I	130
	[Et ₃ N][W(S)(SC ₆ H ₂ -2,4,6- ^{<i>i</i>} Pr ₃)(S ₂ C ₂ Me ₂) ₂]	BzSSSBz	I	131
	[Et ₃ N][W(S)(O- <i>p</i> -C ₆ H ₄ X')(S ₂ C ₂ Me ₂) ₂]	Ph ₃ AsS, Ph ₃ SbS (only for X' = H)	I	<i>bo</i>
	(X' = Me, OMe, H, Br, COMe, CN)			
cis -W ^{VI} OS	[WS(OPh)(S ₂ C ₂ Me ₂) ₂] ¹⁻	Ph₃P	I	<i>bo</i>
	[(HB(3,5-Me ₂ pz) ₃)WOS(η ¹ -S ₂ P(Ph) ₂)]	S ₈ , propylene sulfide, ^{bz} PMe₂Ph, Ph₃P^{bz}	I	<i>by, bz</i>
	[(HB(3,5-Me ₂ pz) ₃)WOS(η ¹ -SP(O)(Ph) ₂)]	internal S transfer from η²-S₂PPh₂ followed by oxidation of η¹-SPPH₂ ligand	I	<i>by</i>
cis -W ^{VI} (S) ₂	[(HB(3,5-Me ₂ pz) ₃)WS ₂ Cl]	Ph₃P	I	<i>by, bz</i>
	[(HB(3,5-Me ₂ pz) ₃)WS ₂ (η ¹ -S ₂ P(Ph) ₂)]	propylene sulfide, Ph₃P	I	<i>by</i>
	[(HB(3,5-Me ₂ pz) ₃)WS ₂ (η ¹ -SP(O)(Ph) ₂)]	internal S transfer from η²-S₂PPh₂ followed by oxidation of η¹-SPPH₂ ligand	I	<i>by</i>
Mn^I(μ-S)Rh^I	[(CO) ₃ Mn(μ-S)(dppm) ₂ Rh(CO)]	H ₂ S	IIIa	143
Mn^{II}(μ-S)Mn^{II}	[CpMn(CO) ₂] ₂ (μ-S)	ethylene sulfide	II	<i>ce, cf</i>
	[CpMn(CO) ₂] ₂ (μ-S)	S ₈	II	<i>cg</i>
	[Cp* ^{<i>n</i>} Mn(CO) ₂] ₂ (μ-S)	S ₈	II	<i>cg</i>
Re^{II}(μ-S)Re^{II}	[CpRe(CO) ₂] ₂ (μ-S)	S ₈ , COS ^{ch}	II	<i>cg, ch</i>
	[Cp* ^{<i>n</i>} Re(CO) ₂] ₂ (μ-S)	S ₈	II	<i>cg, ci</i>
Re^{III}(μ-S)Re^{III}	Re ₂ (μ-S)(μ-X)X ₃ (CS)(μ-dppm) ₂ (X = Cl, Br),	CS ₂	III	<i>cj</i>
	Re ₂ (μ-S)(μ-Br)Br ₃ (CS)(μ-dpam) ₂	CS ₂	III	<i>cj</i>
Re^VS	[Re ^V S(S ₂ C ₂ R ₂) ₂] ¹⁻ (R = Me, Ph, Me ₃ Si) ^{ck}	S ₈ /RC≡CR	I	<i>cl</i>
Re^{VII}O₂S	ReMeO ₂ S	propylene sulfide, Ph₃P	I	203
Re^{VIII}(μ-S)₂Re^{VII}	(ArN) ₂ MeRe(μ-S) ₂ ReMe(NAr) ₂	Me₂PhP, MePh₂P, (MeO)₃P, (MeO)₂PhP, (MeO)Ph₂P, (^{<i>i</i>}Pr)₃P, dmpm, CN^{<i>n</i>}Bu, CN^{<i>n</i>}Bu	III	<i>cm</i>

Table 7. (Continued)

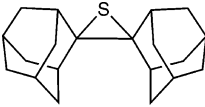
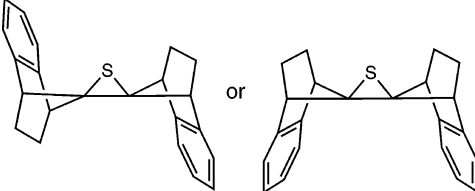
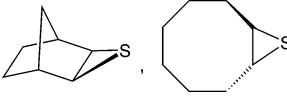
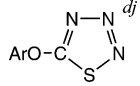
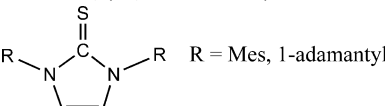

	compound	sulfur atom donor/acceptor	rxn type	ref
Fe^{II}(μ-S)Fe^{II}	[(HC(CMeN(2,6- ⁱ Pr ₂ -C ₆ H ₃)) ₂)] ₂ (μ -S)	S ₈	II	<i>cn</i>
Fe^{III}(μ-S)Fe^{III}	(salen)Fe(μ -S)Fe(salen)	S ₈ , Cp* ₂ V ^{IV} (S ₂) ^y	II	<i>co, y</i>
	(acen)Fe(μ -S)Fe(acen)	S ₈	II	<i>cp</i>
	(η^4 -Me ₄ taa)Fe(μ -S)Fe(η^4 -Me ₄ taa)	S ₈	II	<i>cq</i>
Ru^I(μ-S)Ru^I	[Ru ₂ (CO) ₄ (μ -S)(μ -dppm) ₂]	S ₈ (1 equiv), H ₂ S, propylene sulfide	III	144
Ru^{III}(μ-S)Ru^{III}	[(OEP)Ru] ₂ (μ -S)	ethylene sulfide, CS ₂		<i>cr</i>
Co^I(μ-S)Co^I	[Co ₂ (CO) ₂ (μ -CO)(μ -S)(dppm) ₂]	ethylene sulfide	III	<i>cs</i>
Co^{II}(μ-S)₂Co^{II}	(Me ₃ P) ₃ Co(μ -S) ₂ Co(PMe ₃) ₃	S ₈	IV	<i>ct</i>
Co^{III}(μ-S)Co^{III}	CpCo(μ -PMe ₂) ₂ (μ -S)CoCp	S ₈	IIIa	<i>cu</i>
Rh^I(μ-S)Re^I	[RhRe(CO) ₄ (μ -S)(dppm) ₂]	H ₂ S	III	145
Rh^I(μ-S)Rh^I	[Rh ₂ (CO) ₂ (μ -S)(dppm) ₂]	H ₂ S, ¹⁴⁶ ethylene sulfide ^{cv}	III	146, <i>cv</i>
Rh^{III}(μ-S)₂Rh^{III}	[(triphos)Rh(μ -S) ₂ Rh(triphos)](Ph ₄ B) ₂	H ₂ S	IV	147
Ir^I(μ-S)Ir^I	[Ir ₂ (CO) ₂ (μ -S)(dppm) ₂]	H ₂ S	III	146
Pd^{II}(μ-S)Pd^{II}	Pd ₂ X ₂ (μ -S)(μ -dppm) ₂ (X = Cl, Br, I) ^{cw}	S ₈ , ¹⁴¹ propylene sulfide ¹⁴¹ H ₂ S ¹⁴²	III	141, 142
Pt^I(μ-S)Pt^I	(Ph ₃ P) ₂ Pt-S-Pt(CO)PPh ₃	COS		122, 123
	(η^1 -dppm)Pt(μ -dppm)(μ -S)Pt(η^1 -dppm)	COS, ^{cx,cy} S ₈ ^{cy}	III	<i>cx, cy</i>
Pt^{II}(μ-S)M	[(dppe)Pt(R)(μ -S)M(CO) ₅] (M = Mn, R = Me, Et, Np; M = Re, R = Me, Et) ^{da}	ethylene sulfide, propylene sulfide, isobutylene sulfide, <i>cis</i> - and <i>trans</i> -2-butene sulfide	III	<i>cz</i>
Al^{III}(μ-S)Al^{III}	[(Me ₃ Si ₂ CH) ₂ Al] ₂ (μ -S)	CS ₂	IIIa	<i>db</i>
Ga^{III}S	(HB(3,5- ⁱ Bu ₂ pz) ₃)GaS	S ₈ , (HB(3,5- ⁱ Bu ₂ pz) ₃)In(η^2 -S ₄)	I	<i>dc</i>
Ga^{III}(μ-S)Ga^{III}	[(Me ₃ Si ₂ CH) ₂ Ga] ₂ (μ -S)	Et ₃ PS	III	<i>dd</i>
	((Me ₃ Si) ₂ HC)Ga(μ -O ₂ CCH ₃) ₂ (μ -S)-Ga(CH(SiMe ₃) ₂)	propylene sulfide	IIIa	<i>de</i>
Ga^{III}(μ-S)₂Ga^{III}	[[HC(CMeN(2,6- ⁱ Pr ₂ -C ₆ H ₃)) ₂]] ₂ Ga] ₂ (μ -S) ₂	S ₈	IV	<i>df</i>
In^{III}(μ-S)In^{III}	[(Me ₃ Si ₂ CH) ₂ In] ₂ (μ -S)	propylene sulfide	III	<i>dg</i>
C^{III}(μ-S)C^{III}		S ₈	IIIb	<i>dh</i>
		S ₈ , S ₂ Cl ₂	IIIb	<i>di</i>
			IIIb	151, 152
	Ar = <i>p</i> -C ₆ H ₄ X, X = H, CH ₃ , OCH ₃ , Cl, NO ₂			
	cyclohexene sulfide	"BuLi, PhLi, "BuMgBr, BzMgBr	I	<i>dk</i>
	<i>cis</i> - and <i>trans</i> -2-butene sulfide	PhLi, P(OEt)₃	I	<i>dl</i>
	ethylene sulfide, propylene sulfide	S (¹ D and ³ P) ^{dm}	I	<i>dn</i>
	1,1-difluoroethylene sulfide	S (¹ D and ³ P) ^{dm}	I	<i>do</i>
	1-butene sulfide, <i>cis</i> - and <i>trans</i> -2-butene sulfide	S (¹ D and ³ P) ^{dm}	I	<i>dp</i>
	isobutylene sulfide, vinylthiacyclopropane (from 1,3-butadiene)			
C^{IV}=S	HC(=S)CO ₂ Et, (<i>p</i> -MeO-C ₆ H ₄) ₂ C=S R ₁ R ₂ C=S, (R ₁ , R ₂ = various)	cyclohexene sulfide ^{dq} propylene sulfide ^{ds}	I I	<i>dr</i> <i>dt</i>
	 R = Mes, 1-adamantyl	S ₈ , Ph ₃ AsS, Ph ₃ SbS	I	40
C^{IV}(μ-S)S		Ph₃P	I	72b
Si^{III}-S-Si^{III}	(Mes) ₂ Si-S-Si(Mes) ₂ <i>cis</i> - or <i>trans</i> -[(ⁱ Bu)(Mes)Si-S-Si(ⁱ Bu)(Mes)] <i>cis</i> - or <i>trans</i> -[(ⁱ Bu)(Tip)Si-S-Si(ⁱ Bu)(Tip)]	S ₈ , cyclohexene sulfide ^{dv} S ₈ , ethylene sulfide ^{dx} S ₈ , propylene sulfide	IIIb IIIb IIIb	<i>du, dv, dw</i> <i>dv, dx</i> <i>dx</i>
Si^{IV}(μ-S)₂Si^{IV}	Cp* ₂ Si(μ -S) ₂ SiCp* ₂	S ₈	IV	<i>dy</i>
Ge^{IV}S	[η^2 -{(μ -BuN) ₂ (SiMeN ⁱ Bu) ₂ }]GeS (Tb)(Tip)GeS (Tb)((Me ₃ Si) ₂ CH)GeS (η^4 -Me ₈ taa)GeS	S ₈ styrene sulfide S ₈ S ₈ , ^{ec} (η^4 -Me ₈ taa)SnS ^{ed}	I I I I	<i>dz</i> <i>ea</i> <i>eb</i> <i>ec, ed</i>

Table 7. (Continued)

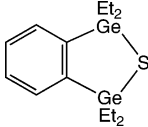
	compound	sulfur atom donor/acceptor	rxn type	ref
Ge^{IV}(μ-S)Ge^{IV}	$[\eta^2\text{-}[2\text{-}(\text{Me}_3\text{Si})_2\text{C}]\text{C}_5\text{H}_4\text{N}]_2\text{GeS}$	S ₈	I	<i>ee</i>
	$[\eta^1\text{-}(\text{CyNC}(\text{R})\text{NCy})][\eta^2\text{-}(\text{CyNC}(\text{R})\text{NCy})]\text{GeS}$ (R = Me, 'Bu)	styrene sulfide	I	<i>ef</i>
	$[\eta^1\text{-}(\text{CyNC}(\text{'Bu})\text{NCy})][\eta^2\text{-}(\text{CyNC}(\text{'Bu})\text{NCy})]\text{GeS}$ (Tbp) ₂ GeS	(CyNC('Bu)NCy) ₂ SnS S ₈ ^{eh}	I I	<i>eg</i> <i>ei</i>
		S ₈	IIIa	<i>ej</i>
	(C ₆ F ₅) ₃ GeSGe(C ₆ F ₅) ₃ (C ₆ F ₅) ₃ GeSGeEt ₃	S ₈ S ₈	IIIa IIIa	<i>ek, el</i> <i>em</i>
Ge^{IV}(μ-S)HgGe^{IV} Ge^{IV}(μ-S)₂Ge^{IV} Sn^{IV}S	(C ₆ F ₅) ₃ GeSHgGe(C ₆ F ₅) ₃	S ₈	IIIa	<i>ek, el</i>
	(C ₆ F ₅) ₃ GeSHgGeEt ₃	S ₈	IIIa	<i>em</i>
	(C ₆ F ₅) ₃ GeSHgGe(C ₆ F ₅) ₃	S ₈	IIIa	<i>el</i>
	$[(\text{MeSi})_2\text{N})_2\text{Ge}]_2(\mu\text{-S})_2$ ^{en} (Tb)(Tip)SnS	S ₈ styrene sulfide	IV I	<i>eo</i> <i>ep</i>
	(Por)Sn=S (Por = TPP, TmTP, TpTP, TMP, OEP) (η ⁴ -Me ₈ taa)SnS (CyNC('Bu)NCy) ₂ SnS	Cp ₂ Ti(η ² -S ₅) ^{eq} (TPP)SnS ^{er} S ₈ , (η ⁴ -Me ₈ taa)Ge ^{II} styrene sulfide, ^{et} $[\eta^1\text{-}(\text{CyNC}(\text{'Bu})\text{NCy})][\eta^2\text{-}$ $\text{CyNC}(\text{'Bu})\text{NCy}]\text{Ge}^{eg}$	I I	<i>eq, er^{es}</i> <i>ed</i> <i>eg, et</i>
Sn^{IV}(μ-S)Sn^{IV}	Me ₃ Sn(μ-S)SnMe ₃	S ₈	IIIa	<i>eu</i>
	Ph ₃ Sn(μ-S)SnPh ₃ , Bz ₃ Sn(μ-S)SnBz ₃ ^{ev}	Me ₃ SbS, Ph ₃ SbS	IIIa	84
Sn^{IV}(μ-S)₂Sn^{IV}	$[(\text{Tb})(\text{Mes})\text{Sn}](\mu\text{-S})_2[\text{Sn}(\text{Tb})(\text{Mes})]$, both <i>cis</i> and <i>trans</i> isomers	styrene sulfide	IV	<i>ep</i>
	$[(\text{C}_9\text{H}_6\text{N})(\text{Me}_3\text{Si})\text{CH}]_2\text{Sn}(\mu\text{-S})_2\text{Sn}-$ $[(\text{C}_9\text{H}_6\text{N})(\text{Me}_3\text{Si})\text{CH}]_2$ (CyNC(Me)NCy) ₂ Sn(μ-S) ₂ Sn- (CyNC(Me)NCy) ₂	S ₈ styrene sulfide	IV IV	<i>ew</i> <i>et</i>
Pb^{IV}(μ-S)Pb^{IV}	$[(\text{Me}_3\text{Si})_2\text{N})_2\text{Sn}]_2(\mu\text{-S})_2$ Ar ₃ Pb(μ-S)PbAr ₃ (Ar = Ph, <i>p</i> -tolyl)	S ₈ Ph ₃ SbS, ⁸⁵ (<i>p</i> -tolyl) ₃ SbS, ⁸⁵ (C ₆ F ₅) ₃ SbS ⁸⁶	IV IIIa	<i>eo, ex</i> 85, 86
	Ph ₃ Pb(μ-S)PbPh ₃	S ₈	IIIa	<i>ey</i>
Pb^{IV}(μ-S)₂Pb^{IV} P^{II}(μ-S)P^{II}	$[(\text{Tip})(\text{Tip})\text{Pb}]_2(\mu\text{-S})_2$	S ₈	IV	<i>ez</i>
	<i>trans</i> -(Me ₃ Si) ₃ Cp-S-PC(SiMe ₃) ₃	S ₈ or MeSSMe	IIIb	<i>fa</i>
	<i>trans</i> -(Tbp)P-S-P(Ar) (Ar = Tbp, 2,4-'Bu-6-MeC ₆ H ₂ , or Mes) ^{fb}	S ₈	IIIb	<i>fc, fd, fe, ff</i>
	<i>trans</i> -(Tbp)P-S-P(Ar) (Ar = 2,4-'Bu ₂ -6-MeO-C ₆ H ₂)	S ₈	IIIb	<i>fg</i>
	<i>trans</i> -(Bbt)P-S-P(Bbt)	S ₈	IIIb	<i>fh</i>
P^I=P^{III}(S)	<i>trans</i> -(Cr(CO) ₅)PhP-S-P(Cr(CO) ₅)Ph	S ₈	IIIb	<i>fi, fj</i>
	(Tbp)P=P(S)(Ar) (Ar = Tbp, 2,4-'Bu-6-MeC ₆ H ₂ , or Mes) ^{fb}	S ₈ , P(NMe ₂) ₃ ^{fc, fe}	I	<i>fc, fe, ff</i>
P^VS	(Tbp)P(S)=P(Ar) (Ar = 2,4-'Bu ₂ - 6-MeO-C ₆ H ₂)	S ₈	I	<i>fg</i>
	(Tbp)P(S)H ₂	S ₈	I	<i>fe, fk</i>
	Ar ₃ PS, Ar ₁ Ar ₂ PS (Ar = Ph, <i>p</i> -tolyl, <i>p</i> -Cl-C ₆ H ₄ ; Ar ₁ , Ar ₂ = Ph, <i>p</i> -Cl-C ₆ H ₄)	S ₈	I	<i>fl</i>
	Et ₃ PS	ethylene sulfide, propylene sulfide, chloropropylene sulfide	I	<i>fm</i>
	ⁿ Bu ₃ PS	isobutylene sulfide, cyclohexene sulfide	I	<i>fn</i>
	(EtO) ₃ PS	<i>cis</i> - and <i>trans</i> -2-butene sulfide	I	<i>fm, fo</i>
	EtSSEt	cyclohexene sulfide	I	<i>fp</i>
	RSH (R = <i>n</i> -octyl, benzyl) ^{fq}	EtSSEt	I	<i>fr</i>
	'BuSH, ^{fs} 'BuSS'Bu ^{ft}	RSH (R = <i>n</i> -octyl, benzyl) ^{fq}	I	<i>fr</i>
	ethylene sulfide, propylene sulfide, ^{fv} styrene sulfide, cyclohexene sulfide, (XX'CH)CH-S-CH ₂	'BuSH, ^{fs} 'BuSS'Bu ^{ft}	I	<i>fu</i>
	X = Cl, ^{fv} MeO, ^{fv} EtO, ⁿ PrO, ⁱ PrO, ⁿ BuO, or PhO and X' = H; X = X' = OEt	ethylene sulfide, propylene sulfide, ^{fv} styrene sulfide, cyclohexene sulfide, (XX'CH)CH-S-CH ₂	I	<i>fv, fw</i>
	H ₂ C-S-CH ₂ -CHCl	X = Cl, ^{fv} MeO, ^{fv} EtO, ⁿ PrO, ⁱ PrO, ⁿ BuO, or PhO and X' = H; X = X' = OEt	I	<i>fx</i>
	Ph ₃ PS	H ₂ C-S-CH ₂ -CHCl	I	<i>fx</i>
	(Me ₂ NCS) ₂ S ₂ , (PhCO) ₂ S ₂ , (Me ₂ N- <i>p</i> -C ₆ H ₄) ₂ S ₂ , (1-C ₁₀ H ₇ CS) ₂	(Me ₂ NCS) ₂ S ₂ , (PhCO) ₂ S ₂ , (Me ₂ N- <i>p</i> -C ₆ H ₄) ₂ S ₂ , (1-C ₁₀ H ₇ CS) ₂	I	<i>fy, fz</i>
	<i>cis</i> - and <i>trans</i> -2-butene sulfide, 1-butene sulfide	<i>cis</i> - and <i>trans</i> -2-butene sulfide, 1-butene sulfide	I	<i>fn</i>
cyclohexene sulfide, propylene sulfide ^{fo}	cyclohexene sulfide, propylene sulfide ^{fo}	I	<i>fm, fo</i>	
H ₂ C-S-CH ₂ -CHCl	H ₂ C-S-CH ₂ -CHCl	I	<i>fx</i>	
SCL ₂ , S ₂ Cl ₂	H ₂ C-S-CH ₂ -CHCl	I	<i>fx</i>	
5-ethoxy-1,2,3,4-thiazazole ^{dj}	SCL ₂ , S ₂ Cl ₂	I	<i>ga</i>	
	5-ethoxy-1,2,3,4-thiazazole ^{dj}	I	153	

Table 7. (Continued)

	compound	sulfur atom donor/acceptor	rxn type	ref
		Na ₂ S ₂ O ₃ (sodium thiosulfate)	I	<i>gb</i>
		P ₄ S ₁₀	I	103b
		α-P ₄ S ₉	I	104, 105
		α-P ₄ S ₈	I	105
		α-P ₄ S ₇	I	106, 107
		α-P ₄ S ₅	I	108
	Ar ₃ PS (Ar = various)	Na ₂ S _n (sodium polysulfide)	I	<i>gc</i>
	Ph ₃ PS, (MeO) ₃ PS	Lawesson's reagent	I	<i>gd</i>
P^{II}(μ-S)As^{II}	<i>trans</i> -(Me ₃ Si) ₃ CP-S-AsC(SiMe ₃) ₃	S ₈	IIIb	<i>ge</i>
	<i>trans</i> -(Tbp) ₃ P-S-As(Tbp)	S ₈	IIIb	<i>gf</i>
	[Cp(CO)(Ph ₃ P)]FeAs-S-P(Tbp), [Cp*(CO) ₂]FeAs-S-P(Tbp), [Cp*(CO) ₂]FeP-S-As(Tbp),	S ₈	IIIb	<i>gg</i>
P^V(S)(μ-S)As^{II}	[Cp*(CO) ₂ Fe]P(S)-S-As(Tbp)	S ₈	I	<i>gg</i>
As^{II}(μ-S)As^{II}	<i>trans</i> -(Me ₃ Si) ₃ CAs-S-AsC(SiMe ₃) ₃	S ₈	IIIb	<i>gh</i>
	<i>trans</i> -(Tbp)As-S-As(Tbp)	S ₈	IIIb	<i>gg</i>
As^VS	Ph ₃ AsS	SCl ₂ , S ₂ Cl ₂	I	<i>ga</i>
		P ₄ S ₁₀	I	81
		5-ethoxy-1,2,3,4-thiaziazole ^{<i>dj</i>}	I	153
Sb^{III}(μ-S)₂Sb^{III}	Ph ₂ As(S)-E-AsPh ₂ (E = O, S)	S ₈	I	<i>gi</i>
	(Bbt)Sb(μ-S) ₂ Sb(Bbt)	S ₈	IIIb	<i>gj</i>
Sb^{III}(μ-S)Sb^{III}	R ₂ Sb(μ-S)SbR ₂ (R = Me, ^{<i>gk-gn</i>} Et, ^{<i>gk</i>} Pr, ^{<i>gk</i>} Ph ^{<i>gk</i>})	S ₈	IIIa	<i>gk, gl, gm, gn</i>
Sb^VS	R ₃ SbS (R = Et, ^{<i>n</i>} Pr, ^{<i>n</i>} Bu, Cy)	S ₈	I	83
	Ph ₃ SbS	5-ethoxy-1,2,3,4-thiaziazole ^{<i>dj</i>}	I	153
	(C ₆ F ₅) ₃ SbS	S ₈ , Ar ₃ Pb ₂ (Ar = Ph, <i>p</i> -tolyl)	I, IIIa	86
	Me ₃ SbS, Ph ₃ SbS	R ₃ SnSnR ₃ (R = Ph, Bz) ^{<i>ev</i>}	IIIa	84
Bi^{III}(μ-S)Bi^{III}	R ₂ Bi(μ-S)BiR ₂ (R = Me, ^{<i>go</i>} ^{<i>go</i>} Pr, ^{<i>gp</i>} <i>p</i> -tolyl ^{<i>gq</i>})	S ₈	IIIa	<i>go, gp, gq</i>
Sm^{III}(μ-S)Sm^{III}	Cp* ₂ (THF)Sm(μ-S)Sm(THF)Cp* ₂	Ph ₃ PS	II	<i>gr</i>
Yb^{III}(μ-S)Yb^{III}	(Cp*) ₂ Yb(μ-S)Yb(Cp*) ₂	Ph ₃ PS, As ₂ S ₃ , COS	II	126
U^{IV}(μ-S)U^{IV}	(MeC ₅ H ₄) ₃ U(μ-S)U(MeC ₅ H ₄) ₃	COS, Ph ₃ PS	II	<i>gs</i>
	(ArO) ₃ U(μ-S)U(OAr) ₃ (ArO ⁻ = 2,6-di- <i>tert</i> -butylphenoxide)	COS, Ph ₃ PS, S ₈ , ^{<i>gt</i>} SO ₂ ^{<i>gt</i>}	II	127

^{*a*} Woo, L. K.; Hays, J. A. *Inorg. Chem.* **1993**, *32*, 2228. ^{*b*} Woo, L. K.; Hays, J. A.; Young, Jr., V. G.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186. ^{*c*} Thorman, J. L.; Young, Jr., V. G.; Boyd, P. D. W.; Guzei, I. A.; Woo, L. K. *Inorg. Chem.* **2001**, *40*, 499. ^{*d*} Sweeney, Z. K.; Polse, J. L.; Andersen, R. A.; Bergman, R. G.; Kubinec, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 4543. ^{*e*} If loss of H₂S from a possible [(η⁵-C₅H₅)Ti(μ-H)]₂(μ-S)(μ-η⁵-η⁵-C₁₀H₈) intermediate is viewed as a two-electron reductive elimination at each metal center, then the oxidative addition of two additional equivalents of S atom allow one to classify the reaction as a type IV sulfur atom transfer process. ^{*f*} Cuenca, T.; Herrmann, W. A.; Ashworth, T. V. *Organometallics* **1986**, *5*, 2514. ^{*g*} Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6952. ^{*h*} Excess H₂S produced Cp*₂Zr(SH)₂ as the final product. ^{*i*} Ethylene sulfide produced Cp*₂ZrS(py) but only as one component in a mixture of products. ^{*j*} Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606. ^{*k*} This compound was originally formulated as Cp*₂Zr(μ-S)₂ZrCp*₂ in ref 139 but was subsequently shown to be a mono-μ-sulfido species. ^{*l*} Classification of this molecule as resulting from a type III sulfur atom transfer reaction assumes reductive elimination of C₂H₆ from Cp*₂Zr(CH₃)(μ-O)Zr(CH₃)Cp*₂ followed by oxidative addition of elemental sulfur. ^{*m*} Tainturier, G.; Gautheron, B.; Fahim, M. *J. Organomet. Chem.* **1985**, *290*, C4. ^{*n*} Erker, G.; Mühlhner, T.; Bann, R.; Ruffiniska, A.; Tainturier, G.; Gautheron, B. *Organometallics* **1986**, *5*, 1023. ^{*o*} Baranger, A. M.; Hanna, T. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 10041. ^{*p*} Howard, W. A.; Parkin, G. *J. Organomet. Chem.* **1994**, *472*, C1. ^{*q*} Schiemann, J.; Hübener, P.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 980. ^{*r*} Albrecht, N.; Hübener, P.; Behrens, U.; Weiss, E. *Chem. Ber.* **1985**, *118*, 4059. ^{*s*} Poncet, J.-L.; Guillard, R.; Friant, P.; Goulon, J. *Polyhedron* **1983**, *2*, 417. ^{*t*} Poncet, J. L.; Guillard, R.; Friant, P.; Goulon-Ginet, C.; Goulon, J. *Nouv. J. Chim.* **1984**, *8*, 583. ^{*u*} Strictly speaking, these systems do not involve pure sulfur atom transfer reactions because one of the reducing equivalents for S to go to S²⁻ comes from excess thiolate. ^{*v*} Nicholson, J. R.; Huffman, J. C.; Ho, D. M.; Christou, G. *Inorg. Chem.* **1987**, *26*, 3030. ^{*w*} Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1988**, *27*, 507. ^{*x*} Billen, M.; Hornung, G.; Wolmerschäuser, G.; Preuss, F. *Z. Naturforsch.* **2003**, *58*, 237. ^{*y*} Floriani, C.; Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2099. ^{*z*} Moore, M.; Feghali, K.; Gambarotta, S. *Inorg. Chem.* **1997**, *36*, 2191. ^{*aa*} Money, J. K.; Nicholson, J. R.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4072. ^{*ab*} Chamberlain, M. M.; Jabs, G. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1962**, *27*, 3321. ^{*ac*} This system also does not involve a pure S atom transfer reaction because the oxidation state change from the starting material, V(O^{*t*}Bu)₄, is only one unit. The other reducing equivalent for the sulfur atom apparently originates from displaced ^{*t*}BuO⁻. ^{*ad*} Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448. ^{*ae*} Gerlach, C. P.; Arnold, J. *Inorg. Chem.* **1996**, *35*, 5770. ^{*af*} Rupp, K. B. P.; Desmangles, N.; Gambarotta, S.; Yap, G.; Rheingold, A. L. *Inorg. Chem.* **1997**, *36*, 1194. ^{*ag*} Sendlinger, S. C.; Nicholson, J. R.; Lobkovsky, E. B.; Huffman, J. C.; Rehder, D.; Christou, G. *Inorg. Chem.* **1993**, *32*, 204. ^{*ah*} Herrman, W. A.; Biersack, H.; Ziegler, M. L.; Balbach, B. *J. Organomet. Chem.* **1981**, *206*, C33. ^{*ai*} Skripkin, Y. V.; Eremenko, I. L.; Pasynskii, A. A.; Struchkov, Y. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285. ^{*aj*} Siemeling, U.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1670. ^{*ak*} Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 4020. ^{*al*} These reactions occur under photolytic conditions. ^{*am*} Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7953. ^{*an*} Proulx, G.; Bergman, R. G. *Organometallics* **1996**, *15*, 133. ^{*ao*} Cp₂Ta=S(SMe) is generated from a transient Cp₂Ta(SMe) intermediate formed by migration of the Me group in Cp₂Ta=S(Me) to the sulfido ligand. ^{*ap*} N₃S₃Cl₃ = trithiazyl chloride. See Jolly, W. L.; Maguire, K. D.; Martin, D. F.; Gano, J. E.; Woehle, R.; Yoshida, C. *Inorg. Synth.* **1967**, *9*, 102. ^{*aq*} Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3543. ^{*ar*} Goh, L. Y.; Hambley, T. W.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1458. ^{*as*} El-Hinnawi, M. A.; El-Quaseer, A. K. *J. Organomet. Chem.* **1985**, *296*, 393. ^{*at*} Pasynskii, A. A.; Eremenko, I. L.; Rakitin, Y. V.; Novotortsev, V. M.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1979**, *165*, 57. ^{*au*} Reardon, D.; Kovacs, I.; Rupp, K. B. P.; Feghali, K.; Gambarotta, S.; Petersen, J. *Chem. Eur. J.* **1997**, *3*, 1482. ^{*av*} Lichtenberger, D. L.; Hubbard, J. L. *Inorg. Chem.* **1984**, *23*, 2718. ^{*aw*} Lincoln, S.; Soong, S.-L.; Koch, S. A.; Sato, M.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1355. ^{*ax*} Hall, K. A.; Critchlow, S. C.; Mayer, J. M. *Inorg. Chem.* **1991**, *30*, 3593. ^{*ay*} Berreau, L. M.; Young, Jr., V. G.; Woo, L. K. *Inorg. Chem.* **1995**, *34*, 3485. ^{*az*} S atom abstraction from MoSCl₂(PME₃)₃ by PME₃ leads to the dinuclear species Mo(PME₃)₃Cl(μ-Cl)(μ-S)Mo(PME₃)₂Cl₂. ^{*ba*} Yoshida, T.; Adachi, T.; Matsumura, K.; Kawazu, K.; Baba, K. *Chem. Lett.* **1991**, 1067. ^{*bb*} This reference also describes

Table 7. (Continued)

Continuation of References for Table 7.

the synthesis and crystal structure of (dppee)Mo(O)(S), but the preparation involves use of MoCl₃(THF)₃/NaHS/dppee and does not appear to occur by bona fide S atom transfer. ^{bc} Lorenz, I.-P.; Walter, G.; Hiller, W. *Chem. Ber.* **1990**, *123*, 979. ^{bd} Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107. ^{be} Formation of Mo^V(S)(N[R]Ar)₃ from CS₂ is attended by the formation of [Mo(N[R]Ar)₃]₂(μ-CS). ^{bf} Formation of Mo^V(S)(N[R]Ar)₃ from SO₂ is accompanied by the formation of 2 equiv of Mo^V(O)(N[R]Ar)₃. ^{bg} Johnson, A. R.; Davis, W. M.; Cummins, C. C.; Serron, S.; Nolan, S. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 2071. ^{bh} Gorzellik, M.; Bock, H.; Gang, L.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1991**, *412*, 95. ^{bi} Treichel, P. M.; Wilkes, G. R. *Inorg. Chem.* **1966**, *5*, 1182. ^{bj} Stevenson, D. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 3721. ^{bk} The presence of NCS⁻ byproduct, which confirmed the sulfur atom transfer, was proven by treating the reaction mixture with 1% aqueous ferric chloride. ^{bl} Newton, W. E.; McDonald, J. W.; Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1979**, *18*, 1621. ^{bm} Rakowski DuBois, M.; Dubois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064. ^{bn} These Mo^{VI}S complexes are generated transiently in solution and are prone to internal reduction leading to [(Me₂C₂S₂)₂Mo^V]₂(μ-S)₂²⁻ as the isolable species. ^{bo} Wang, J.-J.; Kryatova, O. P.; Rybak-Akimova, E. V.; Holm, R. H. *Inorg. Chem.* **2004**, *43*, 8092. ^{bp} Eagle, A. A.; Laughlin, L. J.; Young, C. G.; Tiekink, E. R. T. *J. Am. Chem. Soc.* **1992**, *114*, 9195. ^{bq} Smith, P. D.; Slizys, D. A.; George, G. N.; Young, C. G. *J. Am. Chem. Soc.* **2000**, *122*, 2946. ^{br} Thapper, A.; Donahue, J. P.; Musgrave, K. B.; Willer, M. W.; Nordlander, E.; Hedman, B.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 4104. ^{bs} These systems are catalytic, with S₈ or a thiirane serving as sulfur source. Regeneration of oxidized catalyst appears to involve the intermediacy of a Mo^{VI}O(η²-S₂) complex. Because a sulfido (S²⁻) species is not the immediate product formed by sulfur atom transfer to Mo^{IV}, the sulfur atom donors that constitute the other half of the catalytic cycle are not included in the table. ^{bt} Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745. ^{bu} Young, C. G.; Bruck, M. A.; Enemark, J. H. *Inorg. Chem.* **1992**, *31*, 593. ^{bv} Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413. ^{bw} Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Organometallics* **1996**, *15*, 2428. ^{bx} Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Inorg. Chem.* **2006**, *45*, 352. ^{by} Eagle, A. A.; Gable, R. W.; Thomas, S.; Sproules, S. A.; Young, C. G. *Polyhedron* **2004**, *23*, 385. ^{bz} Eagle, A. A.; Tiekink, E. R. T.; George, G. N.; Young, C. G. *Inorg. Chem.* **2001**, *40*, 4563. ^{ca} Reference 47b also describes the preparation of W^{IV}(S)(Se)(Me₃P)₄ from H₂S and W^{IV}Se(H₂(Me₃P)₄), but because no +2 change in oxidation state at the metal centers occurs, this system does not fit the description of a sulfur atom transfer reaction. ^{cb} Bollinger, J. C.; Chisholm, M. H.; Click, D. R.; Folting, K.; Hadad, C. M.; Tiedtke, D. B.; Wilson, P. J. *J. Chem. Soc., Dalton Trans.* **2001**, 2074. ^{cc} Hughes, D. L.; Lane, J. D.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1627. ^{cd} Drew, M. G. B.; Page, E. M.; Rice, D. A. *J. Chem. Soc., Dalton Trans.* **1983**, 61. ^{ce} Lorenz, I.-P.; Messelhäuser, J.; Hiller, W.; Conrad, M. *J. Organomet. Chem.* **1986**, *316*, 121. ^{cf} Beuter, G.; Drobnik, S.; Lorenz, I.-P.; Lubik, A. *Chem. Ber.* **1992**, *125*, 2363. ^{cg} Herberhold, M.; Schmidkonz, B. *J. Organomet. Chem.* **1988**, *358*, 301. ^{ch} Herberhold, M.; Reiner, D.; Ackermann, K.; Thewalt, U.; Debaerdemaeker, T. Z. *Naturforsch., B: Chem. Sci.* **1984**, *39*, 1199. ^{ci} Herberhold, M.; Schmidkonz, B.; Thewalt, U.; Razavi, A.; Schöllhorn, H.; Herrmann, W. A.; Hecht, C. *J. Organomet. Chem.* **1986**, *299*, 213. ^{cj} Qi, J.-S.; Schrier, P. W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 258. ^{ck} In this system, addition of 1 equiv of RC≡CR to ReS₄⁻ produces a [Re^V(S)₂(S₂C₂R₂)]¹⁻ intermediate to which elemental sulfur adds in a two-electron oxidation addition process. Subsequent addition of a second equivalent of RCCR across two terminal sulfide ligands effects a second two-electron reduction to give [Re^V(S₂C₂R₂)]¹⁻. ^{cl} Goodman, J. T.; Inomata, S.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1996**, *118*, 11674. ^{cm} Wang, W.-D.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **2002**, *41*, 4780. ^{cn} Vela, J.; Stoian, S.; Flaschenriem, C. J.; Münck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2004**, *126*, 4522. ^{co} Floriani, C.; Fachinetti, G. *Gazz. Chim. Ital.* **1973**, *103*, 1317. ^{cp} Corazza, F.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Dalton Trans.* **1987**, 709. ^{cq} Berno, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 551. ^{cr} Yee, G. T.; Noll, B. C.; Williams, D. K. C.; Sellers, S. P. *Inorg. Chem.* **1997**, *36*, 2904. ^{cs} Heyke, O.; Beuter, G.; Lorenz, I.-P. *J. Chem. Soc., Dalton Trans.* **1992**, 2405. ^{ct} Klein, H.-F.; Gass, M.; Koch, U.; Eisenmann, B.; Schäfer, H. Z. *Naturforsch., B: Chem. Sci.* **1988**, *43*, 830. ^{cu} Hofman, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1014. ^{cv} Neher, A.; Heyke, O.; Lorenz, I.-P. *Z. Anorg. Allg. Chem.* **1989**, *578*, 185. ^{cw} Reference 141 deals with only the Pd₂(dpm)₂(μ-S)Cl₂ compound. ^{cx} Hadj-Bagheri, N.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1269. ^{cy} Hadj-Bagheri, N.; Puddephatt, R. J. *Inorg. Chem.* **1989**, *28*, 2384. ^{cz} Komiya, S.; Muroi, S.; Furuya, M.; Hirano, M. *J. Am. Chem. Soc.* **2000**, *122*, 170. ^{da} For R = Np and M = Mn, evidence supports a concerted mechanism. For all other complexes, intermediates are isolated that implicate heterolytic Pt–Mn(Re) bond dissociation, coordination of thiirane to a [(dppe)Pt(R)]⁺ cation, and S_N2 attack by [M(CO)₅]⁻. ^{db} Uhl, W.; Vester, A.; Hiller, W. *J. Organomet. Chem.* **1993**, *443*, 9. ^{dc} Kuchta, M. C.; Parkin, G. J. *J. Chem. Soc., Dalton Trans.* **1998**, 2279. ^{dd} Uhl, W.; Gerding, R.; Hahn, I.; Pohl, S.; Saak, W. *Polyhedron* **1996**, *15*, 3987. ^{de} Uhl, W.; Cuyper, L.; Spies, T.; Weller, F.; Harbrecht, B.; Conrad, M.; Greiner, A.; Puchner, M.; Wendorff, J. H. Z. *Anorg. Allg. Chem.* **2003**, *629*, 1124. ^{df} Hardman, N. J.; Power, P. P. *Inorg. Chem.* **2001**, *40*, 2474. ^{dg} Uhl, W.; Graupner, R.; Reuter, H. *J. Organomet. Chem.* **1996**, *523*, 227. ^{dh} Nakayama, J.; Ito, Y.; Mizumura, A. *Sulfur Lett.* **1992**, *14*, 247. ^{di} Sugihara, Y.; Noda, K.; Nakayama, J. *Tetrahedron Lett.* **2000**, *41*, 8913. ^{dj} The sulfur atom donor ability of this reagent type is driven by the liberation of N₂. ^{dk} Bordwell, F. G.; Andersen, H. M.; Pitt, B. M. *J. Am. Chem. Soc.* **1954**, *76*, 1082. ^{dl} Neureiter, N. P.; Bordwell, F. G. *J. Am. Chem. Soc.* **1959**, *81*, 578. ^{dm} Singlet and triplet sulfur are generated via photodissociation of COS. ^{dn} Strausz, O. P.; Gunning, H. E. *J. Am. Chem. Soc.* **1962**, *84*, 4080. ^{do} Wiebe, H. A.; Knight, A. R.; Strausz, O. P.; Gunning, H. E. *J. Am. Chem. Soc.* **1965**, *87*, 1443. ^{dp} Sidhu, K. S.; Lown, E. M.; Strausz, O. P.; Gunning, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 254. ^{dq} The carbene to which the sulfur atom is transferred is generated thermally via a diazonium salt. ^{dr} Hata, Y.; Watanabe, M.; Inoue, S.; Oae, S. *J. Am. Chem. Soc.* **1975**, *97*, 2553. ^{ds} The carbenes to which the sulfur atom is transferred are generated photolytically as transient species. ^{dt} Pezacki, J. P.; Wood, P. D.; Gadosy, T. A.; Luszyk, J.; Warkentin, J. *J. Am. Chem. Soc.* **1998**, *120*, 8681. ^{du} Michalczuk, M. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1525. ^{dv} West, R.; De Young, D. J.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 4942. ^{dw} Mangette, J. E.; Powell, D. R.; West, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1348. ^{dx} Mangette, J. E.; Powell, D. R.; West, R. *Organometallics* **1995**, *14*, 3551. ^{dy} Jutz, P.; Möhrke, A.; Müller, A.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1518. ^{dz} Veith, M.; Becker, S.; Huch, V. *Angew. Chem.* **1989**, *101*, 1287; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. ^{ea} Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. ^{eb} Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811. ^{ec} Kuchta, M. C.; Parkin, G. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1351. ^{ed} Kuchta, M. C.; Parkin, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 8372. ^{ee} Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2116. ^{ef} Foley, S. R.; Bensimon, C.; Richeson, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 10359. ^{eg} Foley, S. R.; Richeson, D. S. *J. Chem. Commun.* **2000**, 1391. ^{eh} The germathione generated by sulfur atom transfer is a transient species that quickly reacts with one C–H bond of one of the pendant 'Bu groups. ^{ei} Lange, L.; Meyer, B.; du Mont, W.-W. *J. Organomet. Chem.* **1987**, *329*, C17. ^{ej} Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K. *Organometallics* **1996**, *15*, 2014. ^{ek} Bochkarev, M. N.; Razuvaev, G. A.; Vyazankin, N. S.; Semenov, O. Y. *J. Organomet. Chem.* **1974**, *74*, C4. ^{el} Bochkarev, M. N.; Maiorova, L. P.; Vyazankin, N. S.; Razuvaev, G. A. *J. Organomet. Chem.* **1974**, *82*, 65. ^{em} Bochkarev, M. N.; Vyazankin, N. S.; Bochkarev, L. N.; Razuvaev, G. A. *J. Organomet. Chem.* **1976**, *110*, 149. ^{en} The reference given in footnote *eo* formulates this sulfide as $1/2[\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-S})]_n$, but it is most likely a dimer. ^{eo} Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Leung, W.-P.; Rai, A. K.; Taylor, R. E. *Polyhedron* **1991**, *10*, 1203. ^{ep} Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065. ^{eq} Guillard, R.; Ratti, C.; Barbe, J.-M.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 1537. ^{er} Berreau, L. M.; Woo, L. K. *J. Am. Chem. Soc.* **1995**, *117*, 1314. ^{es} The reference given in footnote *er* deals only with the TPP and TpTP complexes. ^{et} Zhou, Y.; Richeson, D. S. *J. Am. Chem. Soc.* **1996**, *118*, 10850. ^{eu} Kraus, C. A.; Sessions, W. V. *J. Am. Chem. Soc.* **1925**, *47*, 2361. ^{ev} Bz₃SnBz₃ is sulfurized by Me₃SbS but not by Ph₃SbS. ^{ew} Leung, W.-P.; Kwok, W.-H.; Law, L. T. C.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Commun.* **1996**, 505. ^{ex} Hitchcock, P. B.; Jang, E.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1995**, 3179. ^{ey} Krebs, A. W.; Henry, M. C. *J. Org. Chem.* **1963**, *28*, 1911. ^{ez} Kano, N.; Shibata, K.; Tokitoh, N.; Okazaki, R. *Organometallics* **1999**, *18*, 2999. ^{fa} Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satge, J.; Jaud, J. *Phosphorus Sulfur* **1983**, *17*, 221. ^{fb} The references given in footnotes *fc* and *fd* concern only the symmetrically substituted bis(Tbp) compound. ^{fc} Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Chem. Soc., Chem. Commun.* **1983**, 862. ^{fd} Yoshifuji, M.; Ando, K.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 418. ^{fe} Yoshifuji, M.; Shibayama, K.; Shima, I.; Inamoto, N. *Phosphorus Sulfur* **1983**, *18*, 11. ^{ff} Yoshifuji, M.; Shibayama, K.; Inamoto, N. *Heterocycles* **1984**, *22*, 681. ^{fg} Yoshifuji, M.; An, D.-L.; Toyota, K.; Yasunami, M. *Chem. Lett.* **1993**, 2069.

Table 7. (Continued)

Continuation of References for Table 7.

^{fj} Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Phys. Org. Chem.* **2003**, *16*, 450. ^{fk} Borm, J.; Huttner, G.; Orama, O.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *282*, 53. ^{fl} Borm, J.; Huttner, G.; Orama, O. *J. Organomet. Chem.* **1986**, *306*, 29. ^{fm} Yoshifuji, M.; Shibayama, K.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1983**, *24*, 4227. ^{fn} Bartlett, P. D.; Meguerian, G. *J. Am. Chem. Soc.* **1956**, *78*, 3710. ^{fo} Culvenor, C. C. J.; Davies, W.; Heath, N. S. *J. Chem. Soc.* **1949**, 282. ^{fp} Denney, D. B.; Boskin, M. J. *J. Am. Chem. Soc.* **1960**, *82*, 4736. ^{fq} Davis, R. E. *J. Org. Chem.* **1958**, *23*, 1767. ^{fr} Jacobsen, H. I.; Harvey, R. G.; Jensen, E. V. *J. Am. Chem. Soc.* **1955**, *77*, 6064. ^{fs} Thiol desulfurization in this system is catalyzed by UV radiation. ^{ft} Hoffmann, F. W.; Ess, R. J.; Simmons, T. C.; Hanzel, R. S. *J. Am. Chem. Soc.* **1956**, *78*, 6416. ^{fu} Desulfurization is catalyzed by 2 mol % azobisisobutyronitrile. ^{fv} Desulfurization is catalyzed by 2 mol % ^tBuOO^tBu. ^{fw} Walling, C.; Rabinowitz, R. *J. Am. Chem. Soc.* **1957**, *79*, 5326. ^{fx} Schuetz, R. D.; Jacobs, R. L. *J. Org. Chem.* **1958**, *23*, 1799. ^{fy} Schuetz, R. D.; Jacobs, R. L. *J. Org. Chem.* **1961**, *26*, 3467. ^{fz} Dittmer, D. C.; Kotin, S. M. *J. Org. Chem.* **1967**, *32*, 2009. ^{ga} Schönberg, A. *Chem. Ber.* **1935**, *68*, 163. ^{gb} Schönberg, A.; Barakat, M. Z. *J. Chem. Soc.* **1949**, 892. ^{gc} Glidewell, C. *J. Organomet. Chem.* **1976**, *116*, 199. ^{gd} Shcherbaov, V. I.; Grigor'eva, I. K.; Sarycheva, N. A.; Razuvaev, G. A. *Metalloorg. Khim.* **1988**, *1*, 700. ^{ge} Miranda, R.; Salas, I.; Mondragón, J.; Velasco, L. *Synth. Commun.* **1992**, *22*, 1077. ^{gf} Shabana, R.; El-Kateb, A. A.; Osman, F. H. *Chem. Ind. (London)* **1984**, *15*, 553. ^{gg} Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Wolf, J.-G. *Tetrahedron Lett.* **1983**, *24*, 3625. ^{gh} Smit, C. N.; Nemansky, M.; Bickelhaupt, F. *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 806. ^{gi} Weber, L.; Sonnenberg, U. *Chem. Ber.* **1989**, *122*, 1809. ^{gj} Couret, C.; Escudie, J.; Madaule, Y.; Ranaivonjatovo, H.; Wolf, J.-G. *Tetrahedron Lett.* **1983**, *24*, 2769. ^{gk} Silaghi-Dumitrescu, L.; Gibbons, M. N.; Silaghi-Dumitrescu, I.; Zukerman-Schpector, J.; Haiduc, I.; Sowerby, D. B. *J. Organomet. Chem.* **1996**, *517*, 101. ^{gl} Sasamori, T.; Mieda, E.; Takeda, N.; Tokitoh, N. *Chem. Lett.* **2004**, *33*, 104. ^{gm} Breunig, H. J.; Jawad, H. Z. *Naturforsch., B: Chem. Sci.* **1982**, *37*, 1104. ^{gn} Haaland, A.; Sokolov, V. I.; Volden, H. V.; Breunig, H. J.; Denker, M.; Rösler, R. Z. *Naturforsch., B: Chem. Sci.* **1997**, *52*, 296. ^{go} Haaland, A.; Shorokhov, D. J.; Volden, H. V.; Breunig, H. J.; Denker, M.; Rösler, R. Z. *Naturforsch., B: Chem. Sci.* **1998**, *53*, 381. ^{gp} Breunig, H. J.; Lork, E.; Rösler, R.; Becker, G.; Mundt, O.; Schwarz, W. Z. *Angew. Chem.* **2000**, *626*, 1595. ^{gq} Wieber, M.; Sauer, I. Z. *Naturforsch., B: Chem. Sci.* **1984**, *39*, 887. ^{gr} Breunig, H. J.; Müller, D. Z. *Naturforsch., B: Chem. Sci.* **1986**, *41*, 1129. ^{gs} Wieber, M.; Sauer, I. Z. *Naturforsch., B: Chem. Sci.* **1987**, *42*, 695. ^{gt} Evans, W. J.; Rabe, G. W.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1994**, *33*, 2719. ^{gu} Brennan, J. G.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1986**, *25*, 1761. ^{gv} Use of S₈ or SO₂ is accompanied by the formation of other, unidentified species.

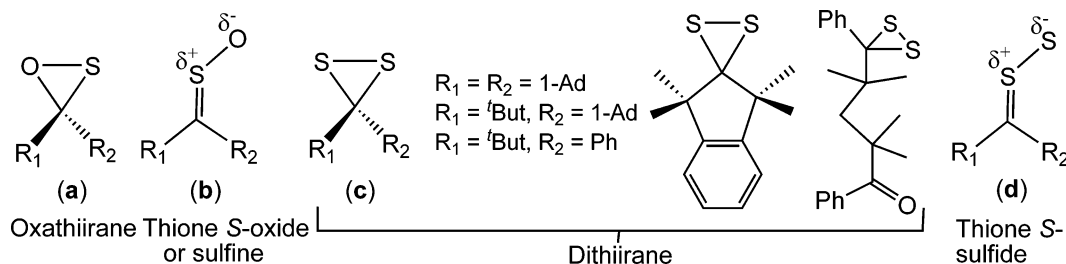


Figure 6. Illustration of the oxathiirane, sulfine, dithiirane, and thione S-sulfide structures.

that would be a good sulfur atom acceptor from an oxathiirane would likely also be a good oxygen atom acceptor, oxygen atom transfer from an oxithiirane might be competitive with, or conceivably even preferred to, the desired sulfur atom transfer.

Dithiiranes [(c) in Figure 6], although relatively scarce and unusual molecules, are considerably more amenable to isolation and application as potential sulfur atom donor reagents. In contrast, thiocarbonyl S-sulfides [(d) in Figure 6] are highly reactive isomeric forms of dithiiranes, which are too unstable to permit isolation but which have been trapped in 1,3-dipolar cycloaddition reactions with an appropriate electrophile.⁷² The current body of knowledge on dithiiranes, thiocarbonyl S-sulfides, and related compounds has been recently reviewed.⁷³

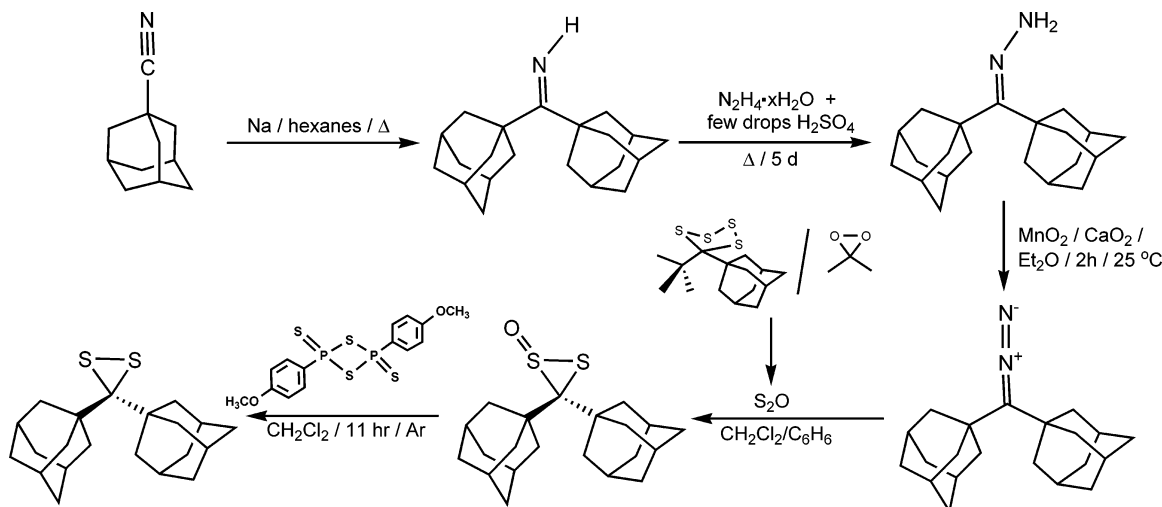
Several examples of dithiiranes have now been well-characterized spectroscopically^{72b,74} and by X-ray crystallography^{74ad} (Figure 6). These molecules are lightly orange-colored due to a $n_{\pi} \rightarrow \sigma^*$ (S–S, S–C) transition at 438–455 nm. When stabilized by the presence of bulky alkyl substituents such as *tert*-butyl and 1-adamantyl groups, dithiiranes may be handled at ambient temperature in the open air and be purified by column chromatography. With less sterically protecting groups, dithiiranes are susceptible to decomposition to elemental sulfur and the corresponding thione when subjected to chromatography on silica.⁷⁵ Apart from one report of the desulfurization of a dithiirane by Ph₃P,^{72b} the S atom donor ability of these molecules has not been systematically examined. The sulfur atom donor activity of dithiiranes is likely to be quite high, and although they are not commercially available molecules, they represent intriguing possibilities as potent but clean sulfur atom donor reagents. Their principal disadvantage is their relative

inaccessibility due to the multiple-step syntheses^{74d,76–78} through which they are prepared (Scheme 2).

5.3. R₃ES Compounds (E = P, As, Sb)

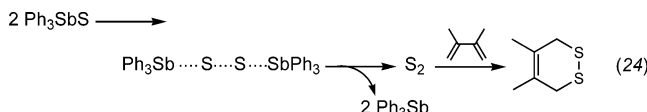
Sulfur atom transfer reactions between triaryl]pnictogen sulfides R₃ES (E = P, As, Sb) and triaryl- or trialkyl]pnictogens R'₃E are processes that are readily rationalized by the relative basicities of the pnictogen centers. Thus, phosphines are rapid and clean acceptors of sulfur atom from R₃AsS and R₃SbS complexes, whereas R₃As compounds are themselves in turn facile acceptors of a sulfur atom from R₃SbS.⁷⁹ Sulfur atom transfer between phosphine compounds or between arsine compounds occurs in the direction that favors placement of sulfur on the more alkyl substituted, and therefore more electron rich, pnictogen center. These reactions typically exhibit clean second-order kinetics consistent with the bimolecular mechanism that is presumed to be operative in these atom transfers.⁷⁹ Recent thermochemical measurements by Hoff²¹ on the reactions of elemental sulfur with a variety of phosphines in benzene or toluene solutions have verified earlier measurements by Chernick, Pedley, and Skinner^{44a} and established a range of reaction enthalpies for R₃P + S → R₃PS that extends from –30.9 kcal/mol for Cy₃P to –21.5 kcal/mol for Ph₃P (Table 4).²¹ Associated PS bond dissociation energies trend in the same manner (Table 6) and range from 98 to 88 kcal/mol. Thermodynamic data for Ph₃E + S → Ph₃ES (E = As, Sb) were derived indirectly from calorimetric measurements of sulfur transfer reactions to Ph₃P. The value obtained for Ph₃SbS indicates that elimination of sulfur is an approximately thermoneutral process in benzene or toluene solutions (Table 4).

Although sulfur atom transfer from Ph₃SbS to α-P₄S₄ has been reported to produce new phosphorus sulfides (γ-P₄S₅,

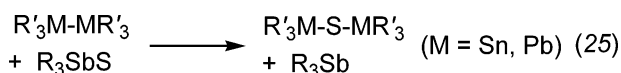
Scheme 2. Illustration of the Multistep Synthesis of Di(1-adamantyl)dithiirane Starting from Commercially Available 1-Cyanoadamantane^a


^a For step 1, cf. ref 76; for steps 2 and 3, ref 77; for step 4, ref 78; for step 5, ref 74d.

δ -P₄S₆, and ϵ -P₄S₆)⁸⁰ that have not been accessible by thermal reactions of the elements or by sulfur atom abstractions with phosphines, others have noted that facile decomposition of Ph₃SbS to Ph₃Sb and elemental sulfur in solution limits the utility of this compound as a synthetic reagent and greatly complicates kinetics studies. The sulfur extruded appears to be singlet disulfur resulting from a bimolecular disproportionation process.⁸¹ Evidence for the presence of transient singlet S₂ arises from spectroscopic detection of 3,6-dihydro-4,5-dimethyl-1,2-dithiin when solutions of Ph₃SbS are introduced to 2,3-dimethylbutadiene (reaction 24).



A variety of other R₃SbS compounds are known, including Me₃SbS,⁸² Et₃SbS,⁸³ ⁿPr₃SbS,⁸³ ⁿBu₃SbS,⁸³ and Cy₃SbS.⁸³ Of these, Me₃SbS warrants particular mention because it is a crystalline compound that is easily prepared and very amenable to purification and handling. The greater electron richness of methyl versus phenyl substitution probably renders Me₃SbS somewhat less prone to spontaneous extrusion of elemental sulfur, possibly placing it closer to Ph₃AsS in terms of its stability. R₃SbS has been found to be competent to insert a sulfur atom into the metal–metal bond in R'₃M–MR'₃ (R = Me, R' = Ph or Bz, M = Sn;⁸⁴ R = R' = Ph, M = Sn;⁸⁴ R = R' = Ph, M = Pb;⁸⁵ R = C₆F₅, R' = Ph, M = Pb;⁸⁶ R = C₆F₅, R' = *p*-C₆H₄CH₃, M = Pb⁸⁶) compounds (reaction 25), which generally places R₃SbS

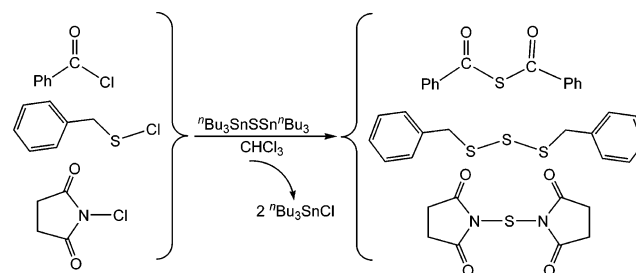


compounds above R₃Sn–S–SnR₃ reagents in terms of sulfur donor reactivity. The reactions illustrated in reaction 25 are of type IIIa as defined in reaction 11a. Interestingly, no sulfur atom transfer is observed to occur when Me₃SbS is treated with Ph₃M–MPh₃ species where M = Si or Ge.⁸⁴

5.4. Bis(tri-*n*-butylstannyl)sulfide, ⁿBu₃SnSSnⁿBu₃

Bis(tri-*n*-butylstannyl)sulfide, known also as Harpp's reagent, has several particular attributes that render it to be

Scheme 3. Examples of the Use of Harpp's Reagent^a



^a See ref 93.

an attractive candidate as a sulfur atom donor. It is commercially available and inexpensive.⁸⁷ The Sn–S bond dissociation energy is probably quite modest, although specific thermodynamic information on tin compounds is quite limited. The putative byproduct from sulfur atom donation, ⁿBu₃Sn–SnⁿBu₃, is unlikely to pose complications by further acting as an oxidizing agent or as a ligand if used as a sulfur atom donor in a transition metal system.⁸⁸ Hexabutyl-distannane should in most instances be readily separable from the desired sulfided product by extraction with an alkane solvent. Other hexaalkyl-distannylsulfides are known,⁸⁹ readily prepared according to literature methods, and offer some degree of tunability from the sulfur atom donor capacity of ⁿBu₃SnSSnⁿBu₃.

Bis(tri-*n*-butylstannyl)sulfide has found scant use thus far as a sulfur atom donor or chalcogenide exchange reagent in inorganic or organometallic systems. It has been used as a source of sulfur in the preparation of the cuboidal tungsten sulfide, [W(NTol)(S₂P(OEt)₂S)₄] (NTol = *N*-tolylimido),⁹⁰ although the complexity and low yield of the preparation leave it unclear as to whether ⁿBu₃SnSSnⁿBu₃ is a source of either sulfur atom or sulfide, S²⁻. Depending upon reaction conditions and stoichiometry, ⁿBu₃SnSSnⁿBu₃ has been demonstrated to be highly effective in transforming primary alkyl halides to thiols⁹¹ or to dialkyl sulfides.⁹² In the presence of acyl chlorides, sulfonyl chlorides (RSCl), or *N*-chlorosuccinimide as substrates, corresponding diacyl sulfides, organic dialkyl trisulfides, and bis(dialkylaminocarbonyl) sulfides are similarly formed (Scheme 3).⁹³ With these systems, the net reaction is effectively halide-for-sulfide exchange between ⁿBu₃SnSSnⁿBu₃ and the organic chloride. This point suggests

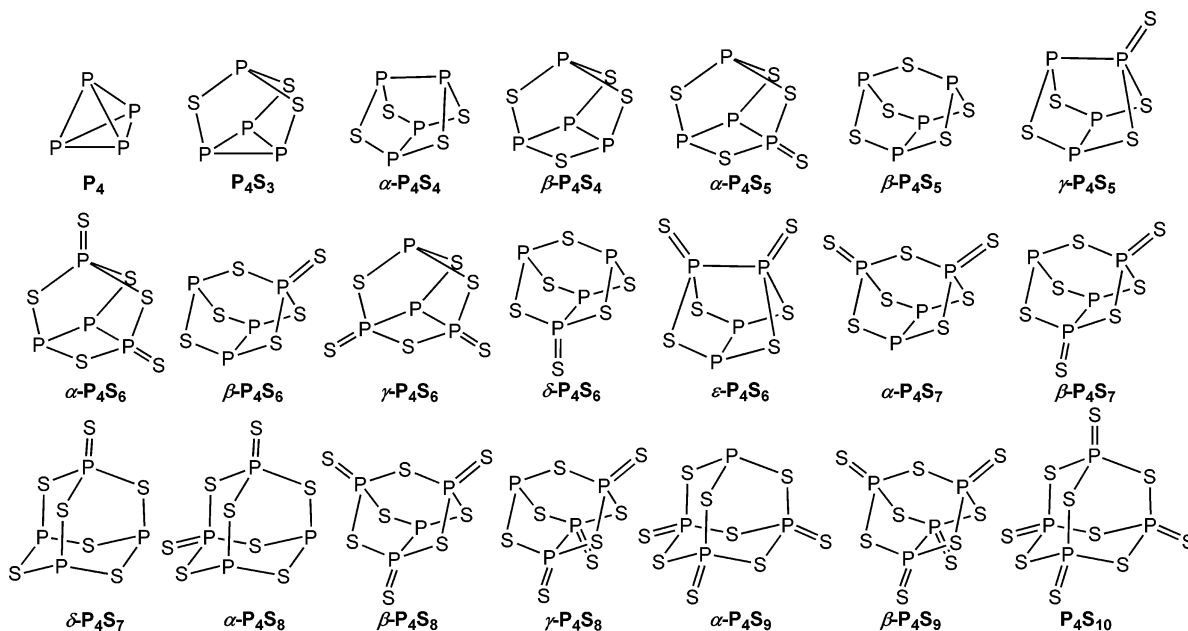
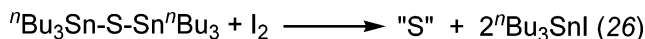


Figure 7. Known sulfides of phosphorus.

that the ability of ${}^n\text{Bu}_3\text{SnSn}^n\text{Bu}_3$ to engage in bona fide atom transfer may be improved in the presence of halogen so as to form a thermodynamically stable tin halide product and thereby drive the liberation of atomic sulfur (reaction 26).



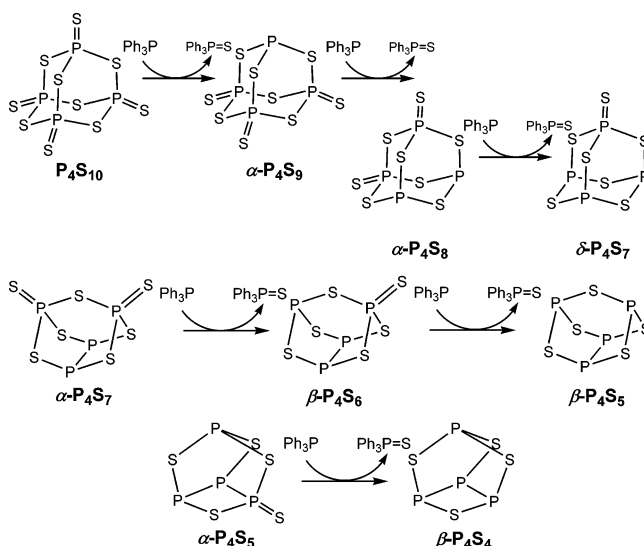
On balance, the currently available information on ${}^n\text{Bu}_3\text{SnSn}^n\text{Bu}_3$ indicates that it may offer wider utility as a sulfur atom donor reagent than has been thus far demonstrated.

5.5. Phosphorus Sulfides, P_4S_n

Numerous sulfides of phosphorus are known, well characterized, and available either commercially or through clear preparative procedures. All phosphorus sulfides are of the general composition P_4S_n ($n = 3-10$) and conceptually may be derived from the P_4 tetrahedron through sulfur atom oxidative addition to a phosphorus lone electron pair to form a terminal thiophosphoryl group ($\text{P}=\text{S}$) and/or insertion into a $\text{P}-\text{P}$ single bond.⁹⁴ For sulfides where $n = 4-9$, more than one isomer may be prepared or at least detected spectroscopically (Figure 7). Those phosphorus sulfides that are available directly from melt reactions of the elements in the proper ratios are P_4S_3 ,^{95,96} $\alpha\text{-P}_4\text{S}_7$,^{95,97,98} and P_4S_{10} .^{95,97,99} Small quantities of $\beta\text{-P}_4\text{S}_6$ have also been identified in and isolated from phosphorus-sulfur melts.¹⁰⁰ Another long-known and well-characterized phosphorus sulfide is $\alpha\text{-P}_4\text{S}_5$,^{95,97,101} which is obtained photochemically from CS_2 solutions of P_4S_3 and elemental sulfur with catalytic traces of I_2 .

From the scant thermodynamic data that have been obtained either experimentally^{33,34} or computationally,¹⁰² indications are that phosphorus sulfides are potentially useful sulfur atom donors. The couples $\text{P}_4\text{S}_7(\text{s}) \rightarrow \text{P}_4\text{S}_6(\text{s}) + \text{"S"}(\text{s})$ and $\text{P}_4\text{S}_6(\text{s}) \rightarrow \text{P}_4\text{S}_5(\text{s}) + \text{"S"}(\text{s})$ are exothermic processes (Table 2) and among the few available that apparently favor sulfur atom donation. Unfortunately, it is unclear which of the various isomers of P_4S_7 , P_4S_6 , and P_4S_5 correspond to the data presented in the original sources. The only plausible couples are obviously those that interconvert topologically similar $\text{P}_4\text{S}_{n+1}/\text{P}_4\text{S}_n$ species (e.g., $\alpha\text{-P}_4\text{S}_7/\beta\text{-P}_4\text{S}_6$ in Figure 7

Scheme 4. Sulfur Atom Abstraction Reactions from P_4S_n Molecules by Ph_3P



and Scheme 4) so that structural reorganization is minimized. Nevertheless, these data offer at least an approximate idea of where the sulfur atom couples connecting structurally related P_4S_n species might occur. It has been suggested that sulfur-binding energies decrease in P_4S_n compounds as the proportion of sulfur increases.¹⁰² It is unfortunate that a lack of thermochemical data on the P_4S_8 and P_4S_9 phosphorus sulfides prevents couples involving these higher sulfides from being formulated.

A point that further adduces the potential for P_4S_n compounds to serve as sulfur atom donor agents is the fact that many of the other known P_4S_n species are derived from $\alpha\text{-P}_4\text{S}_5$, $\alpha\text{-P}_4\text{S}_7$, and P_4S_{10} by sulfur atom abstraction with phosphines. By this synthetic approach, $\alpha\text{-P}_4\text{S}_9$ may be obtained from P_4S_{10} ,¹⁰³ $\delta\text{-P}_4\text{S}_7$ from $\alpha\text{-P}_4\text{S}_9$ ¹⁰⁴ through the intermediacy of $\alpha\text{-P}_4\text{S}_8$,¹⁰⁵ $\beta\text{-P}_4\text{S}_6$ ¹⁰⁶ and $\beta\text{-P}_4\text{S}_5$ ¹⁰⁷ from $\alpha\text{-P}_4\text{S}_7$, and $\beta\text{-P}_4\text{S}_4$ from $\alpha\text{-P}_4\text{S}_5$ (Scheme 4).¹⁰⁸ Even a relatively modest sulfur atom acceptor such as Ph_3As may be readily oxidized to Ph_3AsS by sulfur atom transfer from P_4S_{10} .⁸¹

One significant advantage to the use of P_4S_{10} and P_4S_6 as sulfur atom donor agents is their commercial availability,¹⁰⁹ but it should be noted that they are typically formulated incorrectly as P_2S_5 and P_2S_3 species. Conceivable disadvantages to their use are issues of solubility, which may render the reaction system to be heterogeneous rather than homogeneous, and their potential for forming MS_2 (S_2^{2-} , disulfide) products in reactions with transition metal complexes.

5.6. Sulfur Diimides

A class of molecules with potential usefulness as sulfur atom donor agents is the family of molecules known as dialkyl and diaryl sulfur diimides, $R-N=S=N-R$ (R = alkyl, aryl) (Figure 8). When these intriguing molecules were

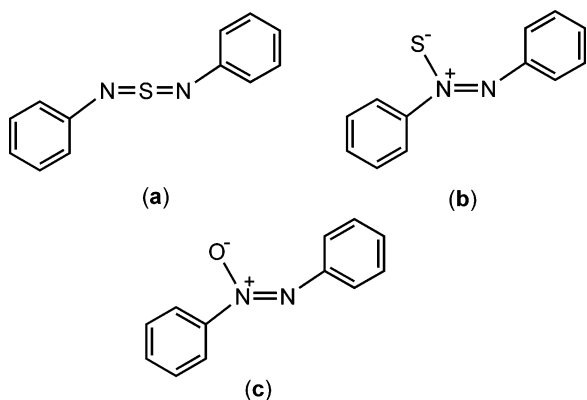
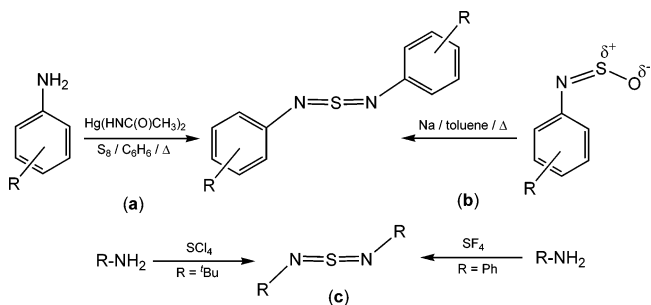


Figure 8. Structures of diphenyl sulfur diimide (a), diphenyl diazene *N*-sulfide (azothiobenzene) (b), and diphenyl diazene *N*-oxide (azoxybenzene) (c).

first synthesized and studied, they were misidentified by some researchers as their structural isomers, the diazene *N*-sulfides¹¹⁰ (Figure 8). It was not until a later structural characterization by X-ray crystallography¹¹¹ that their correct identity was clearly established. The initial formulation of these molecules as diazene *N*-sulfides was not unreasonable because the oxygen analogue of this molecule type, the diazene *N*-oxide (Figure 8), was a known molecule type and because they were observed to undergo facile desulfurization, either on basic alumina^{110b} or in the presence of metallic zinc,^{110ab,112} to afford the corresponding diazenes. Notwithstanding the erroneous stereochemical conclusions to which they led, these observations of facile desulfurization suggest the possibility of applying these sulfur diimides as sulfur atom donor agents.

A conspicuous advantage to these molecules is their ready availability (in gram quantities) by several synthetic routes, as illustrated in Scheme 5. Diaryl sulfur diimides may be synthesized directly from elemental sulfur and the corresponding aniline through the mediation of mercuric acetamide,^{112,113} although this method appears to work best with electron-donating para substituents. Reductive coupling of *N*-sulfinyl amine by sodium metal in refluxing toluene^{110a,112,114} has also been reported to produce sulfur diimides, which can either be vacuum distilled or purified with column chromatography silica gel.¹¹² Phenyl *N*-sulfinyl amine is not only available commercially¹¹⁵ but can also be readily prepared from the anilinium chloride and thionyl chloride.¹¹⁶ A third route to $R-N=S=N-R$ compounds involves treating primary amine with either SCl_4 (R = *t*Bu)¹¹⁷ or SF_4 (R = Ph) in Me_3N as solvent.¹¹⁴ A further advantage to the use of sulfur

Scheme 5. Synthetic Routes to Sulfur Diimides^a

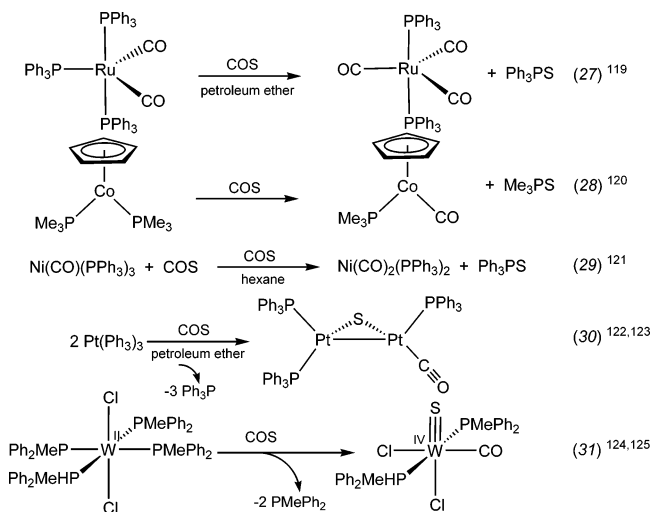


^a See text for literature citations.

diimides is the possibility of achieving some tunability to their reactivity by appropriate variation of the *R* group. One disadvantage to their use is that, in sulfur atom transfer to metal complexes, the diazene byproduct could persist as an unwanted ligand.

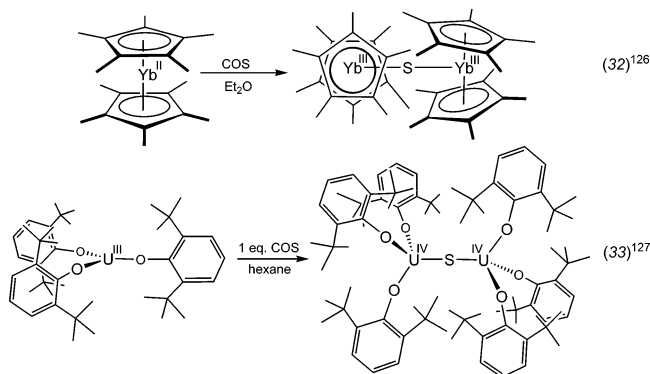
5.7. Carbonyl Sulfide, COS

The transition metal chemistry of COS consists predominantly of the formation of $M-\eta^2-COS$ species, the formation of dithiocarbonate ligand (COS_2^{2-}) via reductive disproportionation, and insertion into metal–ligand bonds.¹¹⁸ In metal complexes with phosphine ligands, the formation of an η^2-COS carbonyl sulfide adduct is often attended by sulfur atom abstraction by displaced phosphine (reactions 27–29).^{119–121}



Nevertheless, carbonyl sulfide has in a variety of instances been observed to act as a sulfur atom donor to transition metal centers in reactions of types I and II. Carbonyl sulfide is a considerably better sulfur atom donor than CS_2 owing to the ~ 30 kcal/mol greater stability of $C=O$ versus $C\equiv S$ as the byproduct, the latter of which is not an isolable molecule. The first study in which COS was found to act as a sulfur atom transfer agent involved its reaction with $Pt(PPh_3)_3$,¹²² a reaction that is of the secondary type (reaction 30). Identification of the product as a dinuclear μ -sulfido species was later established by structural characterization by X-ray crystallography.¹²³ Carbonyl sulfide has also been found to react by primary atom transfer with W^{II} complexes to afford species to which the CO byproduct is also bound (reaction 31).^{124,125} In other instances, COS is observed to cleanly transfer sulfur atom with complete elimination of CO, as with Cp^*Yb^{II} and $(ArO)_3U^{III}(THF)$, which react by

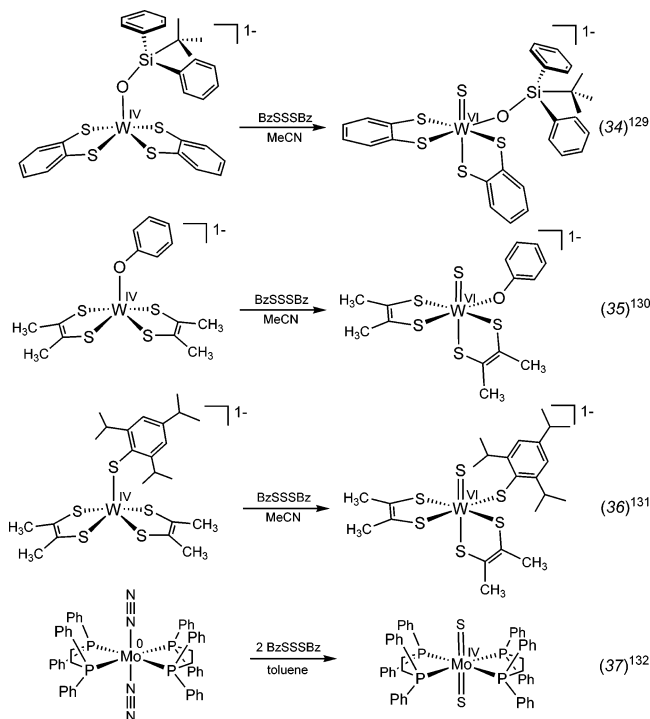
type II atom transfer to produce the corresponding $\text{Cp}^*_2\text{Yb}^{\text{III}}-\text{S}-\text{Yb}^{\text{III}}\text{Cp}^*_2$ ¹²⁶ and $(\text{ArO})_3\text{U}^{\text{IV}}-\text{S}-\text{U}^{\text{IV}}(\text{OAr})_4$ ¹²⁷ dinuclear species, respectively (reactions 32 and 33). Al-



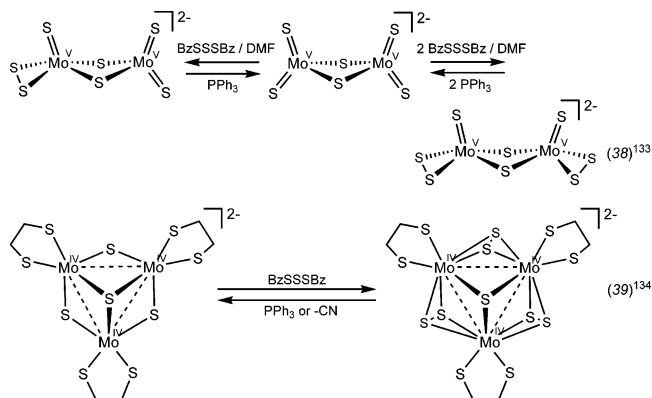
though it has not been widely used as a sulfur atom donor agent, COS does have the convenience of being a gas, which can be used in excess and readily swept away. Although commercially available, it may also be generated conveniently and inexpensively in the laboratory.¹²⁸ Disadvantages to the use of COS include the possible formation of undesired (η^2 -COS) products and binding of CO to the M^{n+2}S product.

5.8. Dibenzyl Trisulfide

Dibenzyl trisulfide has been determined by measurement of reaction enthalpies to be a relatively good sulfur atom transfer agent that falls between Ph_3AsS and SPh_3SbS in donor strength.²¹ It has been used by Holm in the preparation of a series of $\text{W}^{\text{VI}}\text{S}$ complexes in couples of the type $\text{W}^{\text{IV}} + [\text{S}] \rightarrow \text{W}^{\text{VI}}\text{S}$ (reactions 34–36)^{129–131} as well as by Cotton in the synthesis of *trans*-(*dppe*)₂ $\text{Mo}^{\text{IV}}\text{S}_2$ (reaction 37) and



trans-(*dppee*)₂ $\text{Mo}^{\text{IV}}\text{S}_2$ complexes.¹³² In a number of instances, BzSSSBz has been applied in the transformation of terminal or bridging sulfide ligands into the corresponding disulfide ligands (S_2^{2-}) (reactions 38 and 39),^{133,134} a conversion that

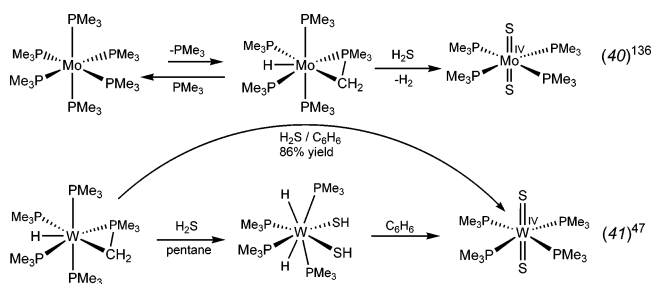


may generally be reversed by a strong sulfur atom acceptor such as Ph_3P . However, the interconversions illustrated by reactions 38 and 39 are reactions of the type depicted in reaction 5 and are not oxidative addition or reductive elimination atom transfer processes as defined in reactions 7–12.

Advantages to the use of BzSSSBz are its commercial availability, the fact that it is easily prepared,¹³⁵ and its stability as a solid in the open air, which makes it convenient in applications in which stoichiometric precision is essential. A potential disadvantage to the use of BzSSSBz is the formation of BzSSBz byproduct, which might undergo further oxidative addition to the intended product to form thiolate ligated species.

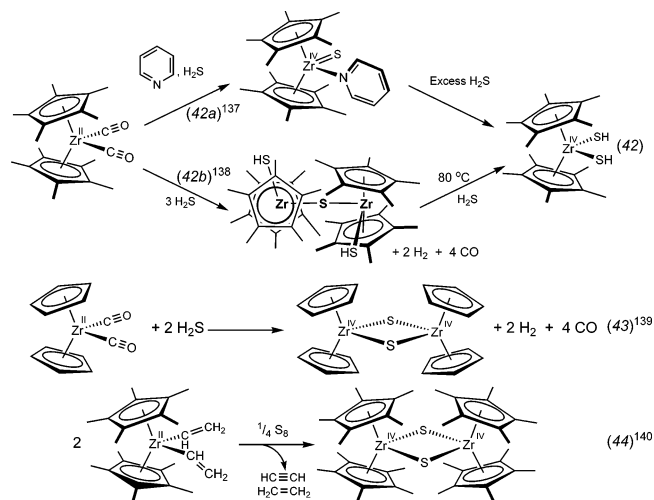
5.9. Hydrogen Sulfide, H_2S

H_2S is not commonly employed as a sulfur atom donor reagent, presumably because of the inconveniences associated with working quantitatively with a corrosive gas, which also has a highly offensive odor. When H_2S functions as a bona fide sulfur atom donor, an equivalent of H_2 gas is generated as byproduct. Mononuclear systems that show well-defined reactivity with hydrogen sulfide are the cyclometalated phosphine complexes $\text{M}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ of molybdenum¹³⁶ and tungsten⁴⁷ described by Parkin, which oxidatively add 2 equiv of H_2S and eliminate 2 equiv of H_2 to form the corresponding *trans*- $\text{M}^{\text{IV}}\text{S}_2(\text{PMe}_3)_4$ complexes (reactions 40 and 41). In the tungsten system, a bis-



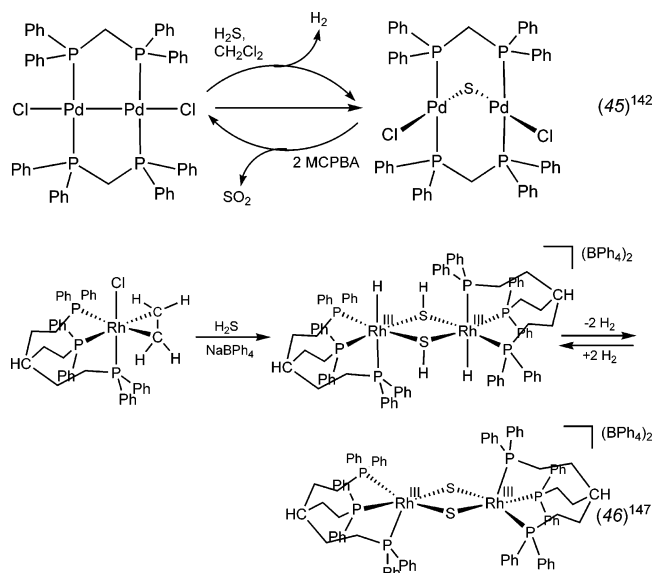
(hydrosulfide) bis(hydrido) intermediate was isolated and identified analytically and spectroscopically by comparison with its deuterio counterpart. Formation of H_2 was confirmed by conducting the reaction in the presence of 2 equiv of the oxametallacycle $\text{W}(\text{PMe}_3)_4\text{H}_2(\eta^2\text{-OC}_6\text{H}_4)$, which functions as a hydrogen trap.^{47b}

Primary sulfur atom transfer by H_2S to $\text{Cp}^*_2\text{Zr}(\text{CO})_2$ has also been observed but only under conditions of substoichiometric H_2S in the presence of pyridine¹³⁷ (reaction 42a). In the absence of pyridine and in the presence of limiting H_2S (3 equiv) the monosulfido complex $[(\text{Cp}^*_2\text{Zr}(\text{SH}))_2(\mu\text{-$



S) may be isolated¹³⁸ (reaction 42b), a compound that was previously formulated as the bis(μ -S) dimer, $[\text{Cp}^*_2\text{Zr}]_2(\mu\text{-S})_2$.¹³⁹ With the less sterically crowded $\text{Cp}_2\text{Zr}(\text{CO})_2$ system, reaction with H_2S does lead to the formation of $[\text{Cp}_2\text{Zr}]_2(\mu\text{-S})_2$, a product that was characterized structurally by X-ray crystallography (reaction 43).¹³⁹ It bears mention that although $[\text{Cp}^*_2\text{Zr}]_2(\mu\text{-S})_2$ does not result from reaction between $\text{Cp}^*_2\text{Zr}(\text{CO})_2$ and H_2S , presumably because of steric considerations, its formation by alternate routes is not necessarily precluded. Although they did not confirm its identity with a crystal structure, Thiele and Beckhaus have reported the synthesis of $[\text{Cp}^*_2\text{Zr}]_2(\mu\text{-S})_2$ from $\text{Cp}^*_2\text{Zr}(\text{CH}=\text{CH}_2)_2$ using elemental sulfur (reaction 44).¹⁴⁰

Most other instances of sulfur atom transfer involving H_2S fall under the type III classification (reactions 11) because reductive elimination of H_2 is facilitated in dinuclear complexes where each metal center can bear a hydride ligand. The most thoroughly studied such system is that of $\text{Pd}_2(\text{dppe})_2\text{X}_2$ ($\text{X} = \text{Cl}^-$, Br^- , I^-), which is most reactive when $\text{X} = \text{Cl}^-$ (reaction 45). The sulfido-bridged compound $\text{Pd}_2(\mu\text{-S})$



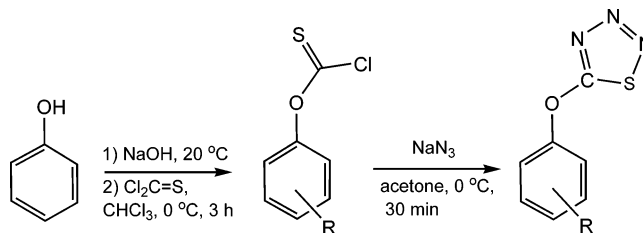
$[\text{Pd}_2(\mu\text{-S})(\mu\text{-dppe})_2\text{Cl}_2]$ was first prepared by Balch by oxidative addition of elemental sulfur or abstraction of sulfur from propylene sulfide.¹⁴¹ Subsequently, James discovered facile formation of $\text{Pd}_2(\mu\text{-S})(\mu\text{-dppe})_2\text{Cl}_2$ from H_2S as well and undertook a thorough study of the kinetics of this reaction.¹⁴²

Balch had noted that the μ -sulfido ligand could be oxidized by MCPBA to $\mu\text{-SO}_2$, which readily dissociates to regenerate the starting $\text{Pd}_2(\text{dppe})_2\text{Cl}_2$ complex. This reactivity scheme thus provides a conceptual basis for a catalytic cycle of reduction of H_2S to H_2 . Since the studies done by James, a number of related dinuclear μ -bis(phosphine) complexes of late transition metals have been observed to accept the sulfur atom from H_2S and eliminate H_2 . These systems include zerovalent MnRh ,¹⁴³ Ru_2 ,¹⁴⁴ RhRe ,¹⁴⁵ Rh_2 ,¹⁴⁶ and Ir_2 ,¹⁴⁶ complexes with bridging dppe ligands. An interesting and unusual example of reversible elimination/addition of H_2 to a dinuclear bis(μ -S) complex is the $[(\text{triphos})\text{Rh}^{\text{III}}(\mu\text{-S})_2\text{Rh}^{\text{III}}(\text{triphos})]^{2+}$ system, which is formed in a type IV reaction from $(\text{triphos})\text{RhCl}(\text{H}_2\text{C}=\text{CH}_2)$ and 2 equiv of H_2S (eq 46).¹⁴⁷

5.10. 5-Aryloxy-1,2,3,4-thiaziazoles

Molecules with potential usefulness as clean, powerful sulfur atom donors are 5-aryloxy-1,2,3,4-thiaziazoles. These molecules are readily prepared by reaction of aryloxy with thiophosgene¹⁴⁸ and subsequent treatment of the resulting *O*-arythionochloroformate with azide¹⁴⁹ (Scheme 6). These

Scheme 6. Synthesis of 5-Aryloxy-1,2,3,4-thiaziazoles^a



^a See refs 148, 149, and 151.

5-aryloxythiaziazoles undergo thermolysis under mild conditions to liberate aryl cyanate and, ultimately, elemental sulfur and dinitrogen. The irreversible formation of dinitrogen gas provides the strong thermodynamic impetus for sulfur atom donation. Vacuum flash pyrolysis experiments and matrix isolation of the labile species formed have identified dinitrogen sulfide, N_2S , as the reactive intermediate that donates sulfur atom in the presence of a suitable substrate.¹⁵⁰

Aryloxy-1,2,3,4-thiaziazoles have been found to produce modest yields of the corresponding olefin sulfides when reacted with norbornene and *trans*-cyclooctene.^{151,152} Reactivity with triphenylpnictogens, Ph_3E ($\text{E} = \text{P}$, As , Sb) to produce triphenylpnictogen sulfide was somewhat cleaner and higher yielding.¹⁵³ Although these sulfur atom donors do not appear to have been used in any other instances as sulfur atom donors, they do have the advantages of being readily accessible on a preparative scale, of being stable when stored at low temperature, and of forming relatively benign, easily separated byproducts ($\text{ArOC}\equiv\text{N}$ and N_2) after atom transfer. Furthermore, their reactivity can be tuned to some degree by appropriate variation of the para substituents on the aryl ring.¹⁵¹ Other types of 1,2,3,4-thiaziazoles, such as 5-alkyl- and 5-amino-substituted variants, have been described and reviewed elsewhere.¹⁵⁴

6. Compounds Prepared by Oxo-for-Sulfido Exchange Reactions

Oxo-for-sulfido exchange is a second method for the synthesis of molecular sulfides and is arguably of greater historical and general significance than sulfur atom transfer

reactions. If oxo-for-sulfido exchange reactions are considered to include organic systems, such as the synthesis of thiiranes from epoxides and the conversion of ketones and aldehydes into the corresponding thiones, then the number of specific examples of chalcogenide exchange reactions would appreciably exceed the number of instances in which sulfur atom transfer has been described. Indeed, for the two cases just mentioned, chalcogen exchange remains the preferred preparative route to these types of compounds, many of which are biologically relevant or synthetically useful. In general, these oxo-for-sulfido exchange reactions work because light main group elements such as carbon and phosphorus generally form appreciably stronger bonds to oxygen than to sulfur in isostructural compounds. Thus chalcogen exchange is a thermodynamically favorable process. Table 8 summarizes known instances of oxo-for-sulfido exchange along with the exchange reagent used and the corresponding literature reference.

7. Oxo-for-Sulfido Exchange Reagents

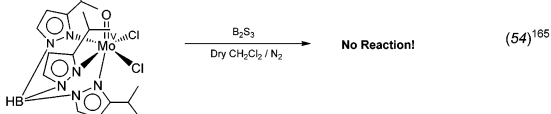
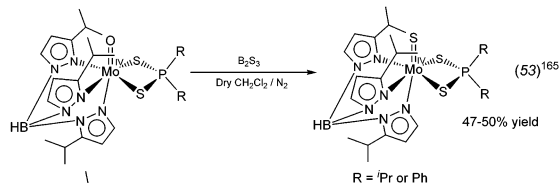
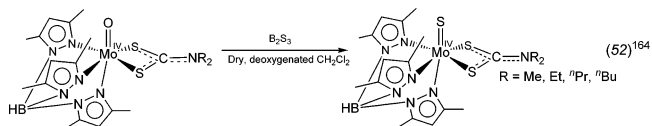
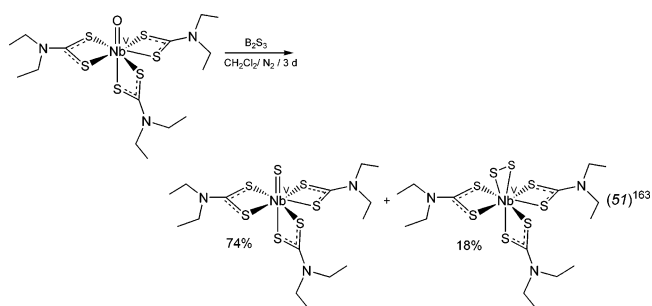
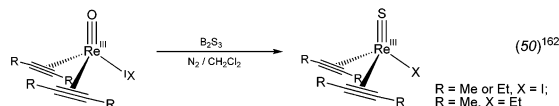
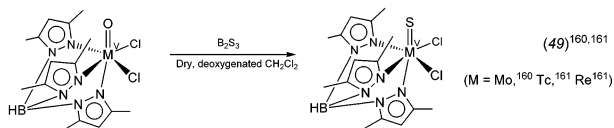
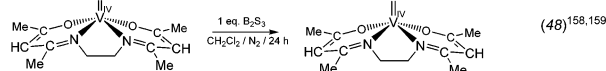
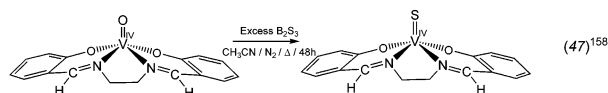
7.1. Lawesson's Reagent, [2,4-Bis-(*p*-methoxyphenyl)-1,3-dithiaphosphetane-2,4-disulfide]

Although it has been almost exclusively under the domain of organic chemistry, the most convenient, versatile, and probably most effective oxo-for-sulfido exchange reagent is [2,4-bis(*p*-methoxyphenyl)-1,3-dithiaphosphetane-2,4-disulfide], which is commonly known as Lawesson's reagent. Lawesson's reagent enjoys the advantages of being commercially available and inexpensive. Its ready solubility in common organic solvents renders it effective under mild conditions (e.g., ambient temperature, short reaction times) compared to heterogeneous reagents such as B_2S_3 . The mechanism through which Lawesson's reagent is known to operate involves dissociation to the highly reactive dithiophosphorus ylid, which then reacts with carbonyl substrate (Scheme 7). The thioxaphosphetane intermediate that forms then decomposes to liberate thioketone and phosphoryl byproduct in a manner completely analogous to the Wittig reaction. This mechanism very likely extends to other types of substrates such as phosphoryl and metal oxo groups. To date, the only instances in the literature in which Lawesson's reagent has been used to prepare a metal sulfido moiety from the corresponding metal oxo group are the syntheses of $(t\text{-BuO})_3\text{V}=\text{O}$ ¹⁵⁵ and $(\text{Bu}'_3\text{tach})\text{MS}_3$ ($M = \text{Mo}, \text{W}$).¹⁵⁶ Lawesson's reagent should find wider application in the future among synthetic inorganic chemists and will likely prove to be effective in cases where B_2S_3 or $\text{Me}_3\text{SiSSiMe}_3$ have been previously used. An extensive body of literature on applications of Lawesson's reagent in thiocarbonyl synthesis has been built over the past 40 years, and further discussion is beyond the focus of this review. The interested reader is referred to several leading reviews.¹⁵⁷

7.2. Boron Trisulfide, B_2S_3

The usefulness of B_2S_3 as an oxo-for-sulfido exchange reagent is suggested by its placement in Table 5, which calls attention to the fact that boron is significantly more oxophilic than thiophilic. The exchange ability that is suggested from the thermodynamic data has been amply demonstrated by the conversion of a variety of $M=\text{O}$ fragments in a variety of oxidation states into the corresponding $M=\text{S}$ moiety.

Indeed, the first thiovanadyl $\text{V}^{\text{IV}}=\text{S}$ compounds were prepared from corresponding oxo homologues with B_2S_3 (reactions 47 and 48).^{158,159} Similarly, the first mononuclear $\text{Mo}^{\text{V}}=\text{S}$,¹⁶⁰ $\text{Tc}^{\text{V}}=\text{S}$,¹⁶¹ and $\text{Re}^{\text{III}}=\text{S}$ ¹⁶² complexes were prepared and isolated with B_2S_3 as the chalcogen exchange reagent (reactions 49 and 50). Other types of $M=\text{S}$ complexes prepared with this reagent include $\text{Nb}^{\text{V}}=\text{S}$,¹⁶³ $\text{Mo}^{\text{IV}}=\text{S}$,^{164,165} $\text{Mo}^{\text{VI}}\text{OS}$,¹⁶⁶ $\text{W}^{\text{VI}}\text{OS}$,^{167–170} $\text{W}^{\text{VI}}\text{S}_2$,^{167–171} $\text{W}^{\text{VI}}\text{OS}_2$,¹⁶⁶ and $\text{Re}^{\text{V}}=\text{S}$ ¹⁶¹ (reactions 49, 51–53, and 55–60). In one



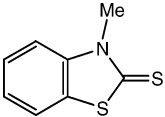
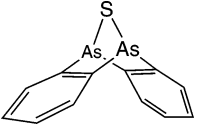
instance, B_2S_3 has been reported to convert nonenolizable ketones to corresponding thiones.¹⁷² A notable case in which B_2S_3 fails to react in an exchange reaction is with $[\text{HB}(3\text{-}i\text{Prpz})_3]\text{Mo}^{\text{V}}\text{OCl}_2$, an observation that is attributed to the steric shielding of the $\text{Mo}^{\text{V}}=\text{O}$ group that is presented by the three isopropyl substituents on the pyrazole rings (reaction 54).¹⁶⁵ The lessened crowding found in the $[\text{HB}(3\text{-}i\text{Prpz})_2(5\text{-}i\text{Prpz})]\text{Mo}^{\text{V}}\text{OCl}_2$ isomer is sufficient to permit the exchange reaction to occur (reaction 53).

An advantage to the use of B_2S_3 is the fact that the $B_2O_mS_{3-n}$ byproducts are generally insoluble and conveniently removed by filtration or column chromatography. A disadvantage to the use of B_2S_3 is the possible formation of

Table 8. Metal and Organic Sulfides Prepared by Oxo-for-Sulfido Exchange Reactions

	compound	oxo-for-sulfido exchange reagent	ref
Ti^{IV}=S	(η^4 -Me ₄ taa)Ti=S	H ₂ S/Et ₃ N, ^a COS, ^{192b} CS ₂ ^{192,b}	a, 192
V^{IV}=S	(acen)V=S	B ₂ S ₃ , ^{158,159} Me ₃ SiSSiMe ₃ ¹⁷⁶	158, 159, 176
	(salen)V=S	B ₂ S ₃	158
	[(edt) ₂ V=S] ²⁻	Me ₃ SiSSiMe ₃	175
V^V=S	(^t BuO) ₃ V=S	Lawesson's reagent	155
[V^VO_xS_{4-x}]³⁻	(NH ₄) ₃ [V ^V O _x S _{4-x}] ³⁻ (x = 1-3) ^c	H ₂ S/NH ₄ OH	d, e
[V^VS₄]³⁻	(NH ₄) ₃ [VS ₄]	H ₂ S/NH ₄ OH	e, f, g, h, i
Nb^V=S	(Et ₂ NCS ₂) ₃ Nb=S	Me ₃ SiSSiMe ₃ , ^{176,177} B ₂ S ₃ ¹⁶³	163, 176, 177
	(C ₇ H ₅ O ₂) ₃ Nb=S (C ₇ H ₅ O ₂ = tropolonato anion)	Me ₃ SiSSiMe ₃	178
	[Bu ₄ N] ₃ [NbW ₅ O ₁₈ S]	Me ₃ SiSSiMe ₃	179
	[Bu ₄ N] ₄ [PW ₁₁ O ₃₉ NbS]	Me ₃ SiSSiMe ₃	180
Ta^V=S	[Bu ₄ N] ₃ [TaW ₅ O ₁₈ S]	Me ₃ SiSSiMe ₃	179
	[Bu ₄ N] ₄ [PW ₁₁ O ₃₉ TaS]	Me ₃ SiSSiMe ₃	180
Mo^{IV}=S	[(HB(3,5-Me ₂ pz))MoS(η^2 -S ₂ CNR ₂)] (R = Me, Et, ⁿ Pr, ⁿ Bu)	B ₂ S ₃	164
	[(HB(3- ⁱ Prpz) ₂ (5- ⁱ Prpz))MoS(η^2 -S ₂ PR ₂)] (R = ⁱ Pr, Ph)	B ₂ S ₃	165
Mo^V=S	[(HB(3,5-Me ₂ pz))MoSCL ₂]	B ₂ S ₃	160
Mo^VO(μ-O,S)Mo^VO	(R ₂ NCS ₂)MoO(μ -O)(μ -S)MoO(S ₂ CNR ₂) (R = Et, ^{i,k} ⁿ Pr ⁱ)	H ₂ S, ^{i,k} P ₄ S ₁₀ ^l	j, k, l
	(ⁿ Pr ₂ PS ₂)MoO(μ -O)(μ -S)MoO(S ₂ P ⁿ Pr ₂)	H ₂ S in ClCH ₂ CH ₂ Cl, 80 °C	k
Mo^VO(μ-S)₂Mo^VO	(Et ₂ NCS ₂)MoO(μ -S) ₂ MoO(S ₂ CNEt ₂)	H ₂ S in ClCH ₂ CH ₂ Cl, ^j H ₂ S/HCl in CHCl ₃ ^k	j, k
	(ⁿ Bu ₂ NCS ₂)MoO(μ -S) ₂ MoO(S ₂ CN ⁿ Bu ₂)	P ₄ S ₁₀	m
	[(cysteinate)MoO(μ -S) ₂ MoO(cysteinate)] ²⁻	H ₂ S	n, o
	(histidine)MoO(μ -S) ₂ MoO(histidine)	H ₂ S	n, p
	[Mo ₂ O ₂ S ₂ (edta)] ²⁻	H ₂ S	o
Mo^VO(μ-O,NR)Mo^VS	(MeCp)MoO(μ -O)(μ -NPh)MoS(MeCp)	H ₂ S	q
Mo^VO(μ-S)₂Mo^VS	(R ₂ NCS ₂)MoO(μ -S) ₂ MoS(S ₂ CNR ₂) (R ₂ = Me ₂ , ^r Et ₂ , ^{k,r} (CH ₂) ₅ , ^r ⁿ Bu ₂ ^r)	H ₂ S	k, r
	<i>syn</i> -(MeCp)Mo(O)(μ -S) ₂ Mo(S)(MeCp), ^s	Me ₃ SiSSiMe ₃	181
	<i>anti</i> -(MeCp)Mo(O)(μ -S) ₂ Mo(S)(MeCp) ^s		
Mo^VS(μ-S)₂Mo^VS	<i>anti</i> -(MeCp)Mo(S)(μ -S) ₂ Mo(S)(MeCp) ^r	Me ₃ SiSSiMe ₃	181
	(R ₂ NCS ₂)MoS(μ -S) ₂ MoS(S ₂ CNR ₂) (R = Et, ^{i,k,t} ⁱ Pr, ^t ⁿ Bu, ^{t,u} ⁱ Bu ^t)	P ₄ S ₁₀	j, k, t, u
Mo^{VI}OS	Cp*MoOS(CH ₂ SiMe ₃)	H ₂ S/CS ₂	v
	MoOS(R ₂ NO) ₂ (R = Et, CH ₂ Ph)	H ₂ S in C ₆ H ₆ /Na ₂ SO ₄	w, x
	MoOS(C ₅ H ₁₀ NO) ₂ (C ₅ H ₁₀ NO = piperidine <i>N</i> -oxido)	H ₂ S, ^y B ₂ S ₃ ¹⁶⁶ , Me ₃ SiSSiMe ₃ ¹⁸²	y, 166, 182 ^z
	MoOS(Et ₂ NO) ₂	Me ₃ SiSSiMe ₃	182 ^z
[Mo^{VI}O₃S]²⁻	Na ₂ [MoO ₃ S], ^{aa} K ₂ [MoO ₃ S] ^{ab}	KOH/H ₂ S	aa, ab
	[Et ₄ N] ₂ [MoO ₃ S]	(Ph ₃ C)PF ₆ /HS ⁻	186
Mo^{VI}O₂S	[Et ₄ N][MoO ₂ S(OSiPh ₃)]	Ph ₃ SiSH	186
[Mo^{VI}O₂S₂]²⁻	K ₂ [MoO ₂ S ₂], ^{aa} [NH ₄] ₂ [MoO ₂ S ₂] from Na ₂ MoO ₄ ^{aa,ac-af}	H ₂ S/NH ₄ OH in H ₂ O	aa, ac, ad, ae, af, ag
	[NR ₄] ₂ [MoO ₂ S ₂] (R = H, Et) from Mo ₇ O ₂₄ ^{6-,ag}		
Mo^{VI}S₂	MoS ₂ (R ₂ NO) ₂ (R = Et, CH ₂ Ph)	H ₂ S in C ₆ H ₆ / Na ₂ SO ₄	w, x, y ^{ah}
	MoS ₂ (C ₅ H ₁₀ NO) ₂ (C ₅ H ₁₀ NO = piperidine <i>N</i> -oxide)	H ₂ S, ^y B ₂ S ₃ ¹⁶⁶ , Me ₃ SiSSiMe ₃ ¹⁸²	y, 166, 182 ^z
	MoS ₂ (Et ₂ NO) ₂	Me ₃ SiSSiMe ₃	182 ^z
Mo^{VI}S₃	[Ph ₄ P][Me ₃ SiO)MoS ₃]	Me ₃ SiSSiMe ₃	183
	[(Bu ^t tach)MoS ₃]	Lawesson's reagent	156
[Mo^{VI}OS₃]²⁻	CS ₂ [MoOS ₃]	H ₂ S	ag, ai
	[R ₄ N] ₂ [MoOS ₃] (R = H, Et), from Na ₂ [MoO ₄]	H ₂ S/NH ₄ OH in H ₂ O	ag
	[Et ₂ NH ₂] ₂ [MoOS ₃] from H ₂ MoO ₄	H ₂ S/Et ₂ NH ₂ in H ₂ O	aj
[Mo^{VI}S₄]²⁻	K ₂ [MoS ₄]	H ₂ S/KOH in H ₂ O	aa
	[R ₄ N] ₂ [MoS ₄] from [MoO ₄] ²⁻ (R = H ^{aa,ac,ad,af,ag,ak,al} E ^{t,ag,am})	H ₂ S/NH ₄ OH in H ₂ O	aa, ac, ad, af, ag, ak, al, am
W^{VI}=S	[Et ₄ N][W(S)(OSiBu ^t Ph ₂)(bdt) ₂]	Me ₃ SiSSiMe ₃	129
cis-W^{VI}OS	[(HB(3,5-Me ₂ pz))WOSCl]	B ₂ S ₃ , P ₄ S ₁₀ ¹⁶⁷	167, 168
	Cp*WOSR (R = Me, CH ₂ SiMe ₃)	H ₂ S/CS ₂ , ^v B ₂ S ₃ /CS ₂ ¹⁶⁹	v, 169
	WOSL (L = <i>N,N'</i> -dimethyl- <i>N,N'</i> -bis(2-thiophenolate)ethylenediamine)	B ₂ S ₃	170
	WOS(C ₅ H ₁₀ NO) ₂ (C ₅ H ₁₀ NO = piperidine <i>N</i> -oxido)	B ₂ S ₃	an
cis-W^{VI}(S)₂	[W(S) ₂ (sap)] (sap = 2-(salicylideneamino)phenolate)	Me ₃ SiSSiMe ₃	184
	[W(S) ₂ (5- <i>t</i> -Busap)(DMF)] (5- <i>t</i> -Busap = 2-(5- <i>t</i> -Busalicylideneamino)phenolate)	Me ₃ SiSSiMe ₃	184
	[W(S) ₂ (ssp)] (ssp = 2-(salicylideneamino)-benzenethiolate)	Me ₃ SiSSiMe ₃	184
	[(HB(3,5-Me ₂ pz))W(S) ₂ Cl]	B ₂ S ₃ , P ₄ S ₁₀ ¹⁶⁷	167, 168
	[(HB(3,5-Me ₂ pz))W(S) ₂ (η^1 -S ₂ P(Ph) ₂)]	B ₂ S ₃	167, 171
	W(S) ₂ L (L = <i>N,N'</i> -dimethyl- <i>N,N'</i> -bis(2-thiophenolate)ethylenediamine)	B ₂ S ₃	170
	Cp*W(S) ₂ R (R = Me, CH ₂ SiMe ₃)	B ₂ S ₃ /CS ₂	169
	W(S) ₂ (R ₂ NO) ₂ (R = Et, Bz; R ₂ NO = piperidine <i>N</i> -oxido)	B ₂ S ₃	an

Table 8. (Continued)

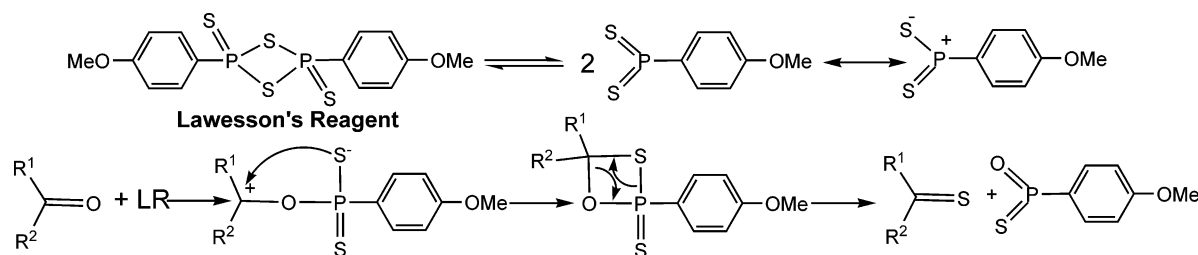
	compound	oxo-for-sulfido exchange reagent	ref
$[\text{W}^{\text{VI}}\text{O}_3\text{S}]^{2-}$	$\text{K}_2[\text{WO}_3\text{S}]$, ^{ao} $[\text{Et}_4\text{N}]_2[\text{WO}_3\text{S}]^{186}$	H_2S , ^{ao} $(\text{Ph}_3\text{C})\text{PF}_6/\text{HS}^{-186}$	ao, 186
$\text{W}^{\text{VI}}\text{OS}_2$	$[(\text{Bu}'_5\text{tach})\text{WO}(\text{S})_2]$	B_2S_3	156
$[\text{W}^{\text{VI}}\text{O}_2\text{S}_2]^{2-}$	$\text{K}_2[\text{WO}_2\text{S}_2]$, ^{ao} $[\text{NH}_4]_2[\text{WO}_2\text{S}_2]$, ^{ag,ao,ap} $[\text{Et}_4\text{N}]_2[\text{WO}_2\text{S}_2]$ ^{ag} from $[\text{WO}_4]^{2-}$	$\text{H}_2\text{S}/\text{NH}_4\text{OH}$ in H_2O	ag, ao, ap
$\text{W}^{\text{VI}}(\text{S})_3$	$[\text{Et}_4\text{N}][(\text{CH}_3)_3\text{CCH}_2\text{W}(\text{S})_3]$ $[(\text{Bu}'_5\text{tach})\text{W}(\text{S})_3]$	$\text{Me}_3\text{SiSSiMe}_3$ Lawesson's reagent	185 156
$[\text{W}^{\text{VI}}\text{OS}_3]^{2-}$	$\text{K}_2[\text{WOS}_3]$, ^{ao} $[\text{R}_4\text{N}]_2[\text{WOS}_3]$ (R = H, Et) ^{ag}	$\text{H}_2\text{S}/\text{NH}_4\text{OH}$ in H_2O	ag, ao
$[\text{W}^{\text{VI}}\text{S}_4]^{2-}$	$\text{Na}_2[\text{WS}_4]$, ^{ao} $\text{K}_2[\text{WS}_4]$, ^{ao} $[\text{NH}_4]_2[\text{WS}_4]$, ^{ag,ao} $[\text{Et}_4\text{N}]_2[\text{WS}_4]$ ^{ag} from WO_4^{2-}	$\text{H}_2\text{S}/\text{NH}_4\text{OH}$ in H_2O	ag, ao
$\text{Tc}^{\text{V}}=\text{S}$	$[(\text{HB}(3,5\text{-Me}_2\text{pz}))\text{TcSCl}_2]$	B_2S_3	161
$\text{Re}^{\text{III}}=\text{S}$	$\text{Re}(\text{S})\text{I}(\text{RC}\equiv\text{CR})_2$ (R = Me, Et)	B_2S_3 , $\text{H}_2\text{S}^{\text{aa}}$	162
	$\text{Re}(\text{S})(\text{Et})(\text{MeC}\equiv\text{CMe})_2^{\text{ar}}$	B_2S_3	162
$\text{Re}^{\text{V}}=\text{S}$	$[(\text{HB}(3,5\text{-Me}_2\text{pz}))\text{ReSCl}_2]$ $[(\text{C}_6\text{H}_4\text{S}(\text{CH}_2\text{S}))\text{ReSMe}(\text{PPh}_3)]$ $[(\text{C}_6\text{H}_4\text{S}(\text{CH}_2\text{S}))\text{ReSMe}(\text{py})]$	B_2S_3 P_4S_{10} P_4S_{10}	161 as as
$\text{Re}^{\text{VO}}(\mu\text{-S})_2\text{Re}^{\text{VO}}$	<i>anti</i> -Cp* $\text{ReO}(\mu\text{-S})_2\text{ReOCp}^*$	CS_2	at
$\text{Re}^{\text{VI}}(\mu\text{-O,S})\text{Re}^{\text{VI}}$	<i>syn</i> - $\text{Re}_2(\mu\text{-O})(\mu\text{-S})\text{O}_2(\text{CH}_2\text{CMe}_3)_4$	H_2S	au
$\text{Re}^{\text{VI}}(\mu\text{-S})_2\text{Re}^{\text{VI}}$	<i>syn</i> -, <i>anti</i> - $\text{Re}_2(\mu\text{-S})_2\text{O}_2(\text{CH}_2\text{CMe}_3)_4$	H_2S	au
$[\text{Re}^{\text{VII}}\text{O}_3\text{S}]^-$	$\text{M}^+[\text{ReO}_3\text{S}]$ ($\text{M}^+ = \text{Tl}^+$, ^{av,aw,K}+} , ^{av,ax} Rb^+ , ^{av,ax,ay} Cs^+ , ^{av,ax})	H_2S	av, aw, ax, ay
	$[\text{NH}_4][\text{ReO}_3\text{S}]$	H_2S	av
	$[\text{Et}_4\text{N}][\text{ReO}_3\text{S}]$	$\text{Me}_3\text{SiSSiMe}_3$	186
$[\text{Re}^{\text{VII}}\text{S}_4]^-$	$[\text{ReS}_4]^-$ $[\text{Bu}_4\text{N}][\text{ReS}_4]$ from Re_2O_7	H_2S $\text{H}_2\text{S}/\text{NH}_4\text{OH}$ in $\text{H}_2\text{O}/\text{KOH}$	az, ba f
$\text{Fe}^{\text{III}}(\mu\text{-S})\text{Fe}^{\text{III}}$	$[\text{Fe}(\text{salen})]_2\text{S}$	$\text{Me}_3\text{SiSSiMe}_3$	187
$\text{Fe}^{\text{III}}(\mu\text{-S})_2\text{Fe}^{\text{III}}$	$[\text{Fe}(5\text{-Busalen})]_2\text{S}$	$\text{Me}_3\text{SiSSiMe}_3$	188
$\text{Fe}^{\text{III}}(\mu\text{-S})_2\text{Fe}^{\text{III}}$	$[\text{Cl}_2\text{Fe}(\mu\text{-S})_2\text{FeCl}_2]^{2-}$	$\text{Me}_3\text{SiSSiMe}_3$	176
$\text{C}^{\text{III}}(\mu\text{-S})\text{C}^{\text{III}}$	$\text{R}_2\text{C-S-CR}_2$	$-\text{SCN}$, ^{bb} $\text{H}_2\text{NC}(\text{S})\text{NH}_2$, ^{bb} $\text{HC}(\text{S})\text{NMe}_2$, ^{bc}	bb, bc bd, be
		$\text{R}_3\text{PS}^{\text{bc}}$ (R = Ph, ⁿ Bu)	
$\text{C}^{\text{IV}}=\text{S}$	$\text{RC}(=\text{S})\text{R}'$ (R, R' = various) $\text{RC}(=\text{S})\text{R}'$ ($\text{RC}(=\text{O})\text{R}'$ = nonenolizable ketone, 2-pyrone, or 4-pyrone)	Lawesson's reagent B_2S_3 , SiS_2	157 172
	$\text{RC}(=\text{S})\text{R}'$ (R, R' = various)	$\text{BCl}_3/\text{Cy}_3\text{SnSSnCy}_3^{\text{bf}}$	89c
$\text{C}^{\text{IV}}\text{SH}$	ArSH Ph_3CSH	$\text{Et}_2\text{NC}(\text{S})\text{Cl}$ $\text{H}_2\text{S}/\text{H}_2\text{SO}_4$, ^{bg} Lawesson's reagent ^{bh,bi}	193 bg, bh, bi
	$\text{R}_1\text{R}_2\text{R}_3\text{CSH}$ (R ₁ , R ₂ , R ₃ = aryl, alkyl, H)	Lawesson's reagent	bh, bi
$\text{P}^{\text{V}}\text{S}$	Ph_3PS	Lawesson's reagent	bj
	$(\text{RO})_2\text{P}(\text{S})\text{H}$ (R = Me, Et)	Lawesson's reagent	bj
$\text{As}^{\text{III}}(\mu\text{-S})\text{As}^{\text{III}}$	$\text{RR}'\text{R}''\text{PS}$	B_2S_3 H_2S	bk bl, bm
			
$\text{As}^{\text{V}}\text{S}$	Ph_3AsS	Lawesson's reagent, ^{bj} $\text{Me}_3\text{SiSSiMe}_3$, ^{bm}	bj, bn
$\text{Sb}^{\text{V}}\text{S}$	Me_3SbS Ph_3SbS	H_2S Lawesson's reagent	82 bj

^a Goedken, V. L.; Ladd, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 142. ^b The $(\eta^4\text{-Me}_4\text{taa})\text{Ti}=\text{S}$ that initially forms from the reaction of $(\eta^4\text{-Me}_4\text{taa})\text{Ti}=\text{O}$ with CS_2 reacts with a second equivalent of CS_2 to yield $(\eta^4\text{-Me}_4\text{taa})\text{Ti}(\eta^2\text{-[S}_2\text{]-CS}_3)$ as the ultimate product. ^c These mixed oxothiovanadates salts were generated in solution and observed spectroscopically but were not isolated. ^d Ranade, A. C.; Müller, A.; Diemann, E. *Z. Anorg. Allg. Chem.* **1970**, 373, 258. ^e Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1986**, 1405. ^f Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, 24, 4635. ^g Krüss, G.; Ohnmais, K. *Chem. Ber.* **1890**, 23, 2547. ^h Krüss, G.; Ohnmais, K. *Justus Liebigs Ann. Chem.* **1891**, 263, 39. ⁱ Krüss, G. *Z. Anorg. Chem.* **1893**, 3, 264. ^j Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1976**, 98, 5387. ^k Schultz, F. A.; Ott, V. R.; Rolison, D. S.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1978**, 17, 1758. ^l Dirand-Colin, J.; Ricard, L.; Weiss, R. *Inorg. Chim. Acta* **1976**, 18, L21. ^m Winograd, R.; Spivack, B.; Dori, Z. *Cryst. Struct. Commun.* **1976**, 5, 373. ⁿ Spivack, B.; Dori, Z. *Chem. Commun.* **1970**, 1716. ^o Ott, V. R.; Swieter, D. S.; Schultz, F. A. *Inorg. Chem.* **1977**, 16, 2538. ^p Spivack, B.; Gaughan, A. P.; Dori, Z. *J. Am. Chem. Soc.* **1971**, 93, 5265. ^q Fletcher, J.; Hogarth, G.; Tocher, D. A. *J. Organomet. Chem.* **1991**, 405, 207. ^r Newton, W. E.; McDonald, J. W.; Yamanouchi, K.; Enemart, J. H. *Inorg. Chem.* **1979**, 18, 1621. ^s These compounds were detected spectroscopically but not isolated when generated by this method. ^t Sakurai, T.; Okabe, H.; Isoyama, H. *Bull. Jpn. Pet. Inst.* **1971**, 13, 243. ^u Spivack, B.; Dori, Z.; Stiefel, E. I. *Inorg. Nucl. Chem. Lett.* **1975**, 11, 501. ^v Fallor, J. W.; Ma, Y. *Organometallics* **1989**, 8, 609. ^w Hofer, E.; Holzbach, W.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 282. ^x Gheller, S. F.; Hambley, T. W.; Traill, P. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1982**, 35, 2183. ^y Wieghardt, K.; Hahn, M.; Weiss, J.; Swiridoff, W. Z. *Anorg. Allg. Chem.* **1982**, 492, 164. ^z The formation of these bis(dialkyl-N-oxido)MoOS and -MoS₂ species from $\text{Me}_3\text{SiSSiMe}_3$ was observed by ⁹⁵Mo NMR. Reaction products were not isolated. ^{aa} Krüss, G. *Justus Liebigs Ann. Chem.* **1884**, 225, 1. ^{ab} Müller, A.; Dornfeld, H.; Schulze, H.; Sharma, R. C. *Z. Anorg. Allg. Chem.* **1980**, 468, 193. ^{ac} Moore, F. W.; Larson, M. L. *Inorg. Chem.* **1967**, 6, 998. ^{ad} Harmer, M. A.; Sykes, A. G. *Inorg. Chem.* **1980**, 19, 2881. ^{ae} Kutzler, F. W.; Scott, R. A.; Berg, J. M.; Hodgson, K. O.; Doniach, S.; Cramer, S. P.; Chang, C. H. *J. Am. Chem. Soc.* **1981**, 103, 6083. ^{af} Brule, J. E.; Hayden, Y. T.; Callahan, K. P.; Edwards, J. O. *Gazz. Chim. Ital.* **1988**, 118, 93. ^{ag} McDonald, J. W.; Friesen, G. D.; Rosenheim, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, 72, 205. ^{ah} The reference given in footnote y describes preparation of the R = Et compound but not the R = Bz compound. ^{ai} Krebs, B.; Müller, A.; Kindler, E. *Z. Naturforsch., B: Chem. Sci.* **1970**, 25, 222. ^{aj} Ansari, M. A.; Chandrasekaran, J.; Sarkar, S. *Inorg. Chim. Acta* **1987**, 133, 133.

Table 8. (Continued)

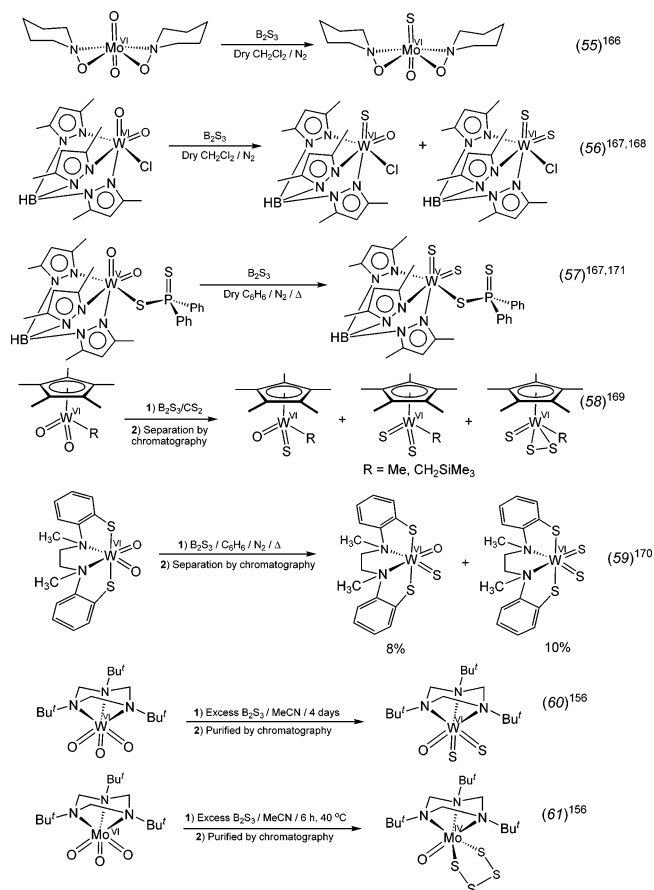
Continuation of References for Table 8.

^{ak} *Handbook of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic Press: New York, 1965; Vol. 2. ^{al} Schäfer, H.; Schäfer, G.; Weiss, A. Z. *Naturforsch., B: Chem. Sci.* **1964**, *19*, 76. ^{am} Kanatzidis, M. G.; Coucouvanis, D. *Acta Crystallogr., Sect. C* **1983**, *39*, 835. ^{an} McDonnell, A. C.; Vasudevan, S. G.; O'Connor, M. J.; Wedd, A. G. *Aust. J. Chem.* **1985**, *38*, 1017. ^{ao} Corleis, E. *Justus Liebigs Ann. Chem.* **1886**, 232, 244. ^{ap} Gonschorek, W.; Hahn, T.; Müller, A. Z. *Kristallogr.* **1973**, *138*, 380. ^{aq} Use of H₂S will generate the sulfido compound but is attended by the formation of other species due to further reaction with H₂S. ^{ar} This compound was observed spectroscopically at low temperature but not isolated due to its thermal sensitivity. ^{as} Jacob, J.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 3266. ^{at} Herrmann, W. A.; Jung, K. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2041. ^{au} Cai, S.; Hoffman, D. M.; Wierda, D. A. *Inorg. Chem.* **1991**, *30*, 827. ^{av} Feit, W. Z. *Anorg. Allg. Chem.* **1931**, *199*, 262. ^{aw} Müller, A.; Krebs, B. Z. *Anorg. Allg. Chem.* **1966**, *342*, 182. ^{ax} Krebs, B.; Müller, A.; Beyer, H. Z. *Anorg. Allg. Chem.* **1968**, *362*, 44. ^{ay} Krebs, B.; Kindler, E. Z. *Anorg. Allg. Chem.* **1969**, *368*, 293. ^{az} Müller, A.; Krebs, B.; Diemann, E. Z. *Anorg. Allg. Chem.* **1967**, *353*, 259. ^{ba} Diemann, E.; Müller, A. Z. *Naturforsch., B: Chem. Sci.* **1976**, *31*, 1287. ^{bb} Sander, M. *Chem. Rev.* **1966**, *66*, 297 and references cited therein. ^{bc} Takido, T.; Kobayashi, Y.; Itabashi, K. *Synthesis* **1986**, 779. ^{bd} Calò, V.; Lopez, L.; Marchese, L.; Pesce, G. *J. Chem. Soc., Chem. Commun.* **1975**, 621. ^{be} Chan, T. H.; Finkenbine, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 2880. ^{bf} This system functions by generating in situ a very active form of B₂S₃. ^{bg} Senning, A. *Sulfur Lett.* **1991**, *12*, 183. ^{bh} Nishio, T. *J. Chem. Soc., Chem. Commun.* **1989**, 205. ^{bi} Nishio, T. *J. Chem. Soc., Perkin Trans. I* **1993**, 1113. ^{bj} Shabana, R.; El-Kateb, A. A.; Osman, F. H. *J. Chem. Ind. (London)* **1984**, *15*, 553. ^{bk} Maryanoff, B. E.; Tang, R.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1973**, 273. ^{bl} Allen, D. W.; Coppola, J. C.; Kennard, O.; Mann, F. G.; Motherwell, W. D. S.; Watson, D. G. *J. Chem. Soc. C* **1970**, 810. ^{bm} Kennard, O.; Wampler, D. L.; Coppola, J. C.; Motherwell, W. D. S.; Mann, F. G.; Watson, D. G.; MacGillavry, C. H.; Stam, C. H.; Benci, P. *J. Chem. Soc. C* **1971**, 1511. ^{bn} Wang, J.-J.; Kryatova, O. P.; Rybak-Akimova, E. V.; Holm, R. H. *Inorg. Chem.* **2004**, *43*, 8092.

Scheme 7. Structure of Lawesson's Reagent and Mechanism for the Oxo-for-Sulfido Exchange Reaction^a

^a Reprinted with permission from Jesberger, M.; Davis, T. P.; Barner, L. *Synthesis* **2003**, 1929–1958. Copyright 2003 Georg Thieme Verlag, Stuttgart, Germany.

undesired disulfide S₂²⁻ or tetrasulfide S₄²⁻ species (reactions 51, 58, and 61) rather than terminal sulfido complexes by pure chalcogenide exchange. In cases when the products are

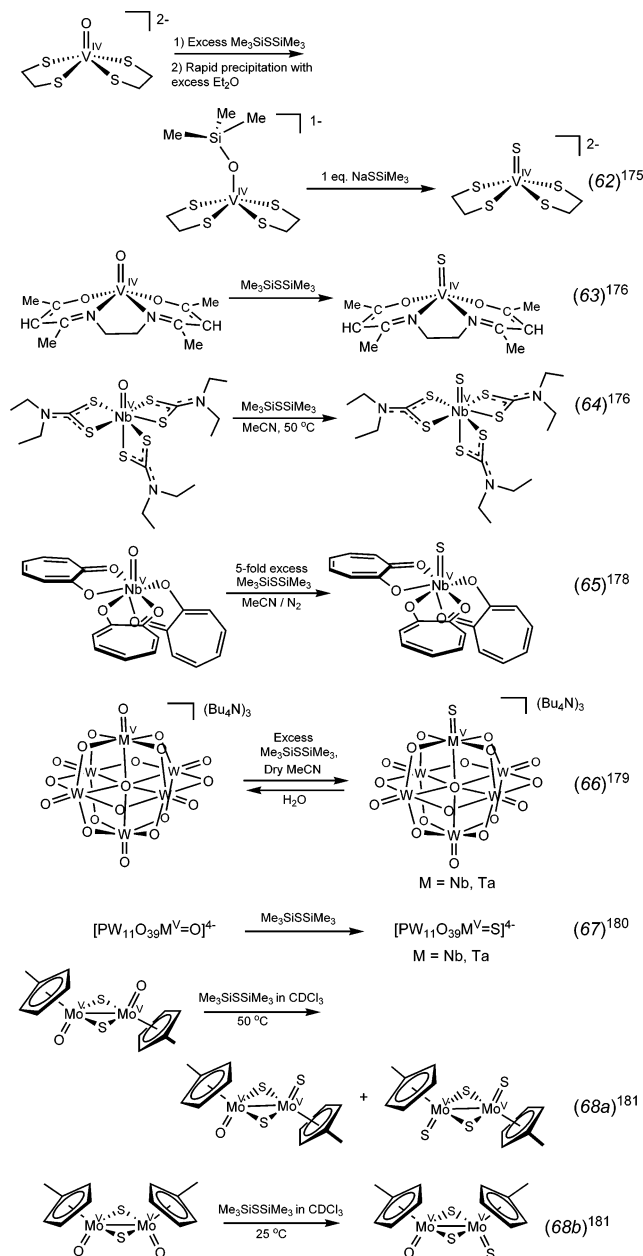


amenable to purification by column chromatography, these disulfide or tetrasulfide species may be separated if they constitute only minor byproducts. A further disadvantage to the use of B₂S₃ is the fact that it no longer appears to be sold commercially, although literature procedures describing its synthesis are readily available.^{95,173} Other main group sulfides that are commercially available and inexpensive, such as SiS₂, Al₂S₃, P₄S₆, P₄S₁₀, and As₂S₃, may presumably be substituted for B₂S₃ in many oxo-for-sulfido exchange reactions.

7.3. Hexamethyldisilathiane, Me₃SiSSiMe₃

The ability of hexamethyldisilathiane (Me₃SiSSiMe₃), which is also commonly referred to as bis(trimethylsilyl)sulfide, to effect oxo-for-sulfido exchange in metal oxides appears to have been first noted by Lebedev et al. in 1974.¹⁷⁴ This versatile reagent has since been used to transform terminal oxo ligands into corresponding sulfido ligands in a variety of metal complexes. Well-defined examples include V^{IV}S,^{175,176} Nb^VS,^{176–180} Ta^VS,^{179,180} Mo^VS,¹⁸¹ Mo^{VI}OS,¹⁸² Mo^{VI}S₂,¹⁸² Mo^{VI}S₃,¹⁸³ W^{VI}S,¹²⁹ W^{VI}S₂,¹⁸⁴ W^{VI}S₃,¹⁸⁵ and [Re^{VII}O₃S]^{1–}¹⁸⁶ (reactions 62–74). In at least one system, Me₃SiSSiMe₃ has been found to exchange bridging oxide for sulfide as well (reaction 75).^{187,188} Hexamethyldisilathiane has been observed to operate by initial silylation of terminal oxo ligand to form a trimethylsilyloxy species, an intermediate that in one instance has been isolated and characterized.^{175b} Subsequent steps are less clear but may involve a second silylation with concomitant nucleophilic displacement of Me₃-SiOSiMe₃ by the Me₃SiS⁻ anion. In cases when the M=O group is sufficiently protected by sterically encumbering ligands, such as in [HB(3-*i*-Prpz)₃Mo^{VO}Cl₂], chalcogenide exchange may not occur (reaction 54).¹⁶⁵

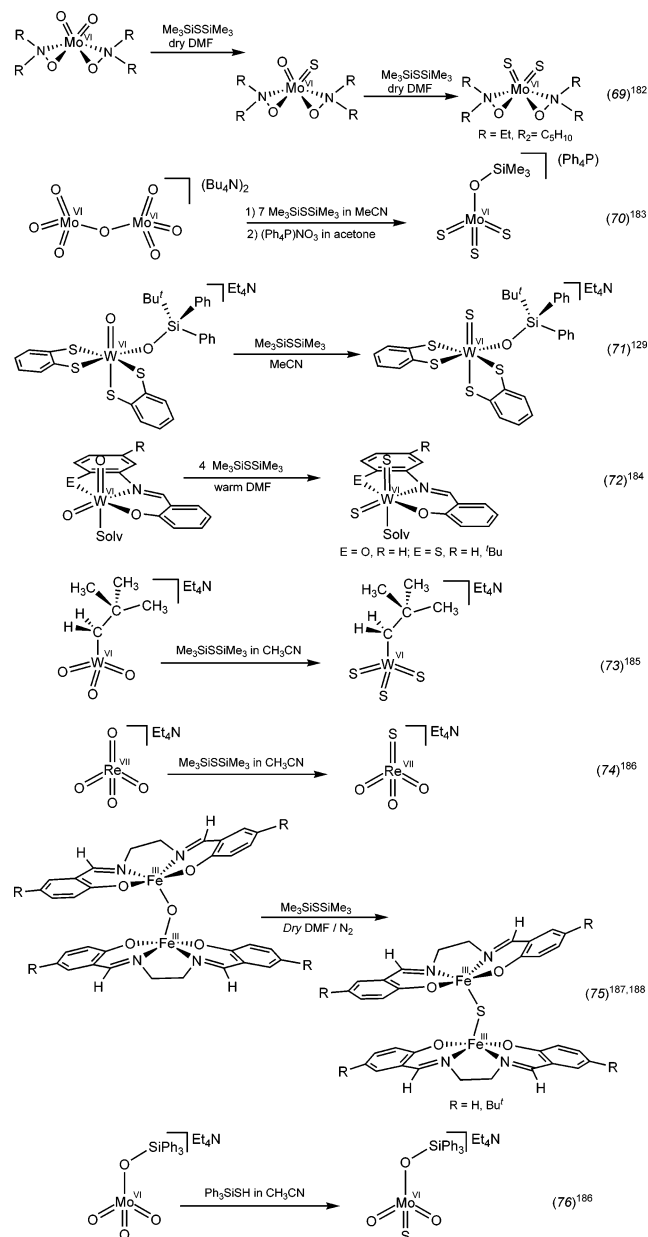
In general, Me₃SiSSiMe₃ appears to be effective in chalcogenide exchange reactions wherever B₂S₃ is useful.



Its efficacy arises from the substantially greater thermodynamic stabilization offered by the Si–O bond as compared to the Si–S bond. From estimates of relative bond strengths (~ 88 kcal/mol for Si–O vs ~ 54 kcal/mol for Si–S),¹⁸⁹ the $\text{Me}_3\text{SiSSiMe}_3(\text{g}) + \text{O}(\text{g}) \rightarrow \text{Me}_3\text{SiOSiMe}_3(\text{g}) + \text{S}(\text{g})$ couple can be placed at ~ -61 kcal/mol. The position of this couple is consistent with the fact that $\text{Me}_3\text{SiSiMe}_3$ is the strongest of known oxygen atom acceptors in couples of the type $\text{X} + \text{O} \rightarrow \text{XO}$ and outdoes Ph_3P by a full 25 kcal/mol!¹⁹ Unfortunately, experimentally determined thermochemical data for $\text{Me}_3\text{SiSSiMe}_3$ are unavailable owing to the technical difficulties inherent to combustion calorimetry measurements upon compounds containing both silicon and sulfur.¹⁹⁰

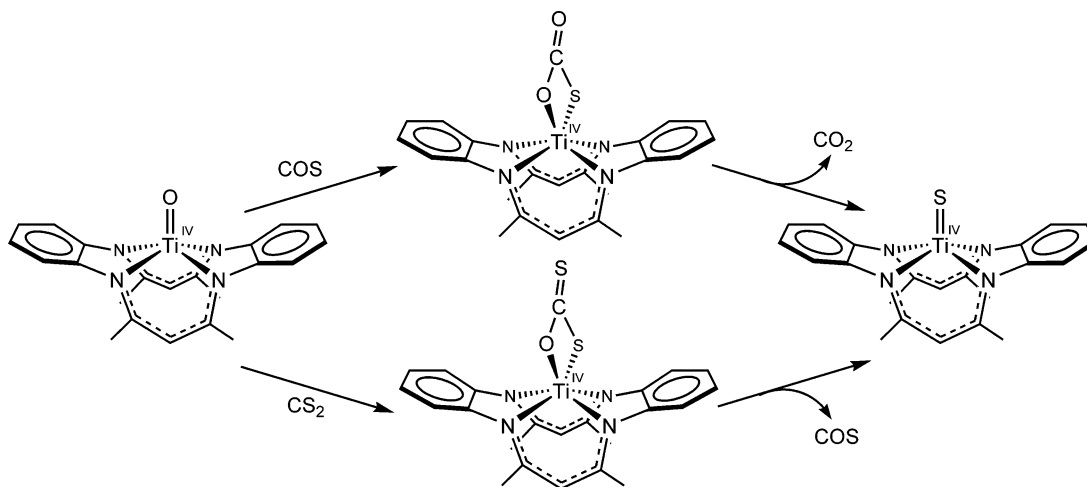
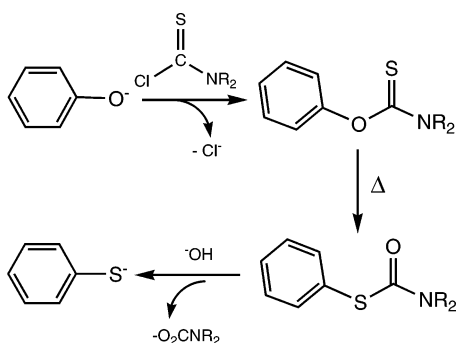
An advantage to the use of $\text{Me}_3\text{SiSSiMe}_3$ as chalcogen exchange reagent is its commercial availability, although it is quite easy to synthesize on a preparative scale.¹⁹¹ The fact that it is a liquid at standard temperature and pressure and freely miscible with common organic solvents enables it to be used in homogeneous solution. Consequently, it generally reacts appreciably more rapidly and under milder conditions than B_2S_3 . Unlike B_2S_3 , its use does not appear to be accom-

panied by the formation of disulfide or tetrasulfide byproducts. Both $\text{Me}_3\text{SiSSiMe}_3$ (if used in excess) and the $\text{Me}_3\text{-SiOSiMe}_3$ resulting from chalcogenide exchange are readily removed either by applying a vacuum or by washing with an appropriate organic solvent. The principal disadvantage to the use of $\text{Me}_3\text{SiSSiMe}_3$ is its highly offensive odor. In this regard, Ph_3SiSH or other, less volatile, silylthiols or thioethers may serve as convenient alternatives to $\text{Me}_3\text{SiSSiMe}_3$ in chalcogenide exchange reactions (reaction 76).¹⁸⁶



7.4. COS, CS₂, and R₂NC(S)Cl

The only documented instance in which COS or CS₂ has been observed to act as chalcogenide exchange agent is in reaction with $\text{Me}_4\text{taaTi}^{\text{IV}}=\text{O}$ (Scheme 8).¹⁹² These reactions proceed through η^2 -monothio- or η^2 -dithiocarbonate intermediates, which, although not isolated, are consistent with the products isolated in reactions of $\text{Me}_4\text{taaTi}^{\text{IV}}=\text{O}$ with a variety of other electrophiles. The reaction with COS illustrated in Scheme 8 produces CO₂, as detected spectroscopically. These reactions derive their thermodynamic impetus from the superior strength of the C=O bond versus

Scheme 8. Exchange of Oxo Ligand for Sulfido Ligand in $\text{Me}_4\text{taaTi}^{\text{IV}}=\text{O}^a$ ^a See ref 192.Scheme 9. Newman–Kwart Rearrangement Reaction ($\text{R} = \text{Me}$ or Et)^a^a See ref 193.

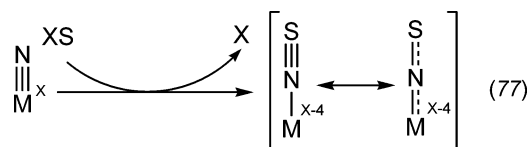
the C=S bond and identify an upper limit of 54.5 kcal/mol (Table 5) for the difference in strength between the Ti=O bond versus the Ti=S bond in $\text{Me}_4\text{taaTi}^{\text{IV}}=\text{E}$ ($\text{E} = \text{O}$ or S). Other transition metal oxo complexes of sufficient nucleophilicity to react with COS or CS_2 might very well undergo similar chalcogenide exchange reactions.

A reaction protocol that is generally useful for transforming aromatic alcohols into the corresponding thiols bears a conceptual similarity to the reactions of COS and CS_2 with $\text{Me}_4\text{taaTi}^{\text{IV}}=\text{O}$ in that it is driven (at least in part) by the formation of a strong C=O bond. Reported independently by Newman and Kwart^{193a,b} and commonly referred to as the Newman–Kwart rearrangement,¹⁹⁴ this reaction involves treatment of a phenolate anion with *N,N*-dialkylthiocarbonyl chloride (alkyl = Me, Et) to form a phenyl dialkylthionocarbonyl species (Scheme 9). A thermally induced rearrangement exchanges oxygen and sulfur, and subsequent base hydrolysis liberates the thiophenolate anion. This reaction type is particularly useful for the design of elaborated thiolate ligands for transition metal cations.¹⁹⁵ One limitation, however, of this reaction type is that it does not appear to work with alkyl-substituted alcohols, probably because the transition state through which it proceeds derives appreciable stabilization from the adjacent arene ring.

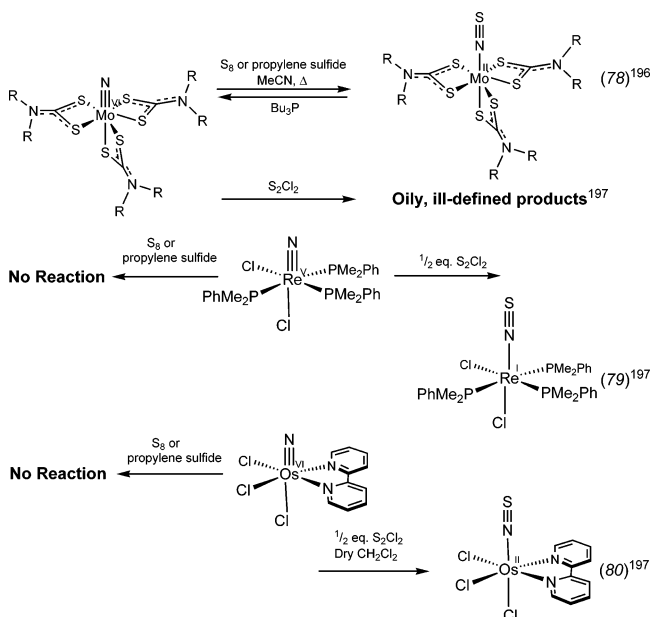
8. Ligand-Centered Sulfur Atom Transfer Reactions

In contrast to atom transfer reactions of the types illustrated in reactions 5 and 6, which interconvert sulfido, disulfido,

and tetrasulfide ligands without change in the oxidation state of the metal center, another distinctly different class of ligand-centered sulfur atom transfer reaction may be identified and defined by multielectron change induced at the metal center. The term “ligand-centered” is applicable because at all times the sulfur atom does not have a direct bond to the metal atom. These ligand-centered transfers are reactions of the type in which a multiply bonded terminal nitrido, phosphido, or carbido ligand is transformed into the corresponding thionitrosyl, thiophosphoryl, or thiocarbonyl ligand (reaction 77). This reaction type is noteworthy in several



respects. From a historical viewpoint, it is significant in that it was by this method that thionitrosyl complexes were first prepared by Chatt and Dilworth^{196,197} (reactions 78–80). It



remains a synthetic approach to thionitrosyl complexes with some general usefulness. These reactions are also unusual

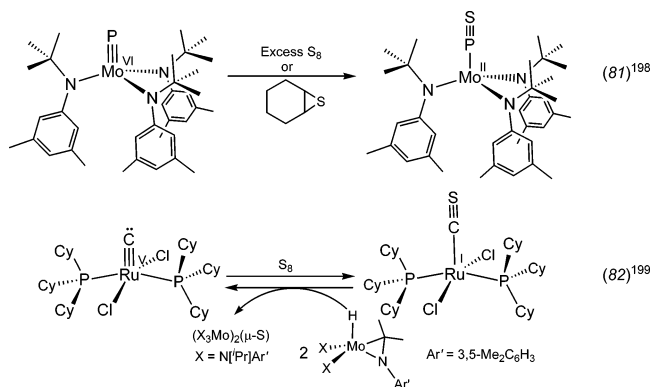
Table 9. Thionitrosyl, Thiophosphoryl, and Thiocarbonyl Complexes Prepared or Desulfurized by Sulfur Atom Transfer Reactions

	compound	sulfur atom donor/acceptor	ref
Mo^{II}NS	(R ₂ NCS ₂) ₃ Mo-NS [R ₂ = Me ₂ , Et ₂ , (CH ₂) ₄]	S ₈ , propylene sulfide, "Bu₃P	196, 197, <i>a</i>
	[(dppe) ₂ MoX(NS)] (X = N ₃ , Br)	propylene sulfide	<i>b</i>
	(TPP)Mo-NS	S ₈	<i>c</i>
W^{II}NS	[(dppe) ₂ WN ₃ (NS)]	propylene sulfide	<i>b</i>
Tc^INS	<i>mer</i> -(Me ₂ PhP) ₃ TcCl ₂ (NS)	S ₂ Cl ₂ (1 equiv)	<i>d, e</i>
	L ₃ TcCl ₂ (NS) (L = pyridine, 4-picoline, 3,5-lutidine)	Na ₂ (S ₂ O ₄)	<i>f</i>
	[(phen) ₂ TcCl(NS)] [PF ₆]	S ₂ Cl ₂	<i>g</i>
Tc^{II}NS	(Me ₂ PhP)(Me ₂ PhPO)TcCl ₃ (NS) ^{<i>h</i>}	S ₂ Cl ₂ (excess), Me₂PhP	<i>e</i>
	[TcCl ₄ (NS)] ⁻ⁱ	S ₂ Cl ₂	<i>j</i>
	LTcCl ₂ (NS)	S ₂ Cl ₂	<i>k</i>
	[L = anion of <i>N</i> -(<i>N''</i> -morpholinylthiocarbonyl)benzamide]		
Tc^{III}NS	(Et ₂ NCS ₂) ₂ TcCl ₂ (NS)	S ₂ Cl ₂ , SOCl ₂	<i>l</i>
	(Et ₂ NCS ₂) ₂ TcBr ₂ (NS)	SOBr ₂	<i>m</i>
Re^INS	<i>mer</i> -[(R ₂ R'P) ₃ ReCl ₂ (NS)] (R = Me or Et, R' = Ph; R = Ph, R' = Me)	S ₂ Cl ₂ (1/2 equiv)	<i>n, 197</i>
	<i>mer</i> -(Me ₂ PhP) ₃ ReCl ₂ (NS) ^{<i>o</i>}	S ₂ Cl ₂	<i>p</i>
	<i>mer</i> -[(R ₂ R'P) ₃ ReBrCl(NS)] (R = Me or Et, R' = Ph; R = Ph, R' = Me) ^{<i>q</i>}	S ₂ Cl ₂ (1/2 equiv)	<i>n, 197</i>
	<i>trans</i> -[(dppe) ₂ Re(NS)Cl]Cl ^{<i>r</i>}	S ₂ Cl ₂ (excess)	<i>n, 197</i>
	[Re(NS)(NCS) ₂ (Me ₂ PhP) ₃]	Me ₃ Si-NCS	<i>s</i>
	[(Me ₂ PhP) ₂ (Et ₂ NCS ₂)ReCl(NS)]	S ₂ Cl ₂	<i>t</i>
Re^{II}NS	[(R ₂ R'P) ₂ ReCl ₃ (NS)] (R = Me or Et, R' = Ph; R = Ph, R' = Me) ^{<i>u</i>}	S ₂ Cl ₂ (excess)	197
	<i>mer</i> -[(Me ₂ PhP) ₂ ReCl ₃ (NS)] ^{<i>o</i>}	S ₂ Cl ₂	<i>p</i>
	[(R ₂ R'P) ₂ ReCl ₃ (NS)] (R = R' = Ph; R = Ph, R' = <i>n</i> Pr) ^{<i>v</i>}	S ₂ Cl ₂ (1/2 equiv)	197
	<i>cis</i> -[Ph ₄ P][ReCl ₄ (NS)py], <i>trans</i> -[Ph ₄ P][ReCl ₄ (NS)py]	S ₂ Cl ₂	<i>j</i>
		(Ph ₄ P)(SCN) in aqueous acetone ^{<i>x</i>}	<i>y</i>
Os^{II}NS	[(Ph ₃ As) ₂ OsX ₂ Cl(NS)] (X = Br or Cl)	S ₂ Cl ₂ (1/2 equiv)	<i>n, 197</i>
	<i>mer</i> -[(Me ₂ PhP) ₂ OsCl ₃ (NS)] ^{<i>w</i>}	S ₂ Cl ₂ (1/2 equiv)	<i>n, 197</i>
	[(bipy)OsX ₂ Cl(NS)] (X = Br or Cl)	S ₂ Cl ₂ (1/2 equiv)	<i>n, 197</i>
	[(py) ₂ OsCl ₃ (NS)]	S ₂ Cl ₂ (1/2 equiv)	197
	<i>trans</i> -[Ph ₄ P][OsCl ₄ (NS)py], <i>trans</i> -[Hpy][OsCl ₄ (NS)py]	S ₂ Cl ₂	<i>j</i>
	[Ph ₄ P] ₂ [Os(NS)(NCS) ₅] (from [Ph ₄ P][OsNCl ₄])	(Ph ₄ P)(SCN) in aqueous acetone ^{<i>x</i>}	<i>y</i>
<i>trans</i> -[Os(tpy)Cl ₂ (NS)](SCN)	CS ₂ /N ₃ ^{-z}	<i>aa</i>	
Mo^{II}-PS	[(Mes)(<i>n</i> Bu)N] ₃ Mo(PS)	S ₈ , cyclohexene sulfide	198
Ru^I-CS	[(C ₃ P) ₂ Ru(CS)Cl ₂]	S ₈ , [X ₂ MoH[η ² -CMe ₂ (NAr')]]	200
		X = N[<i>i</i> -Pr]Ar', Ar' = 3,5-Me ₂ C ₆ H ₃	

^a Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1362. ^b Bevan, P. C.; Chatt, J.; Dilworth, J. R.; Henderson, R. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1982**, 821. ^c Kim, J. C.; Lee, B. M.; Shin, J. I. *Polyhedron* **1995**, *14*, 2145. ^d Kaden, L.; Lorenz, B.; Kirmse, R.; Stach, J.; Abram, U. *Z. Chem.* **1985**, *25*, 29. ^e Kaden, L.; Lorenz, B.; Kirmse, R.; Stach, J.; Behm, H.; Beurskens, P. T.; Abram, U. *Inorg. Chim. Acta* **1990**, *169*, 43. ^f Lu, J.; Clarke, M. J. *Inorg. Chem.* **1990**, *29*, 4123. ^g Lu, J.; Clarke, M. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1243. ^h This compound was earlier misidentified as (Me₂PhP)₂TcCl₃(NS) in the reference given in footnote *d* and in Abram, U.; Kirmse, R.; Köhler, K.; Lorenz, B.; Kaden, L. *Inorg. Chim. Acta* **1987**, *129*, 15. ⁱ This Tc compound was too unstable to isolate and could only be observed spectroscopically. ^j Reinel, M.; Höcher, T.; Abram, U.; Kirmse, R. *Z. Anorg. Allg. Chem.* **2003**, *629*, 853. ^k Abram, U.; Hartung, J.; Beyer, L.; Kirmse, R.; Köhler, K. *Z. Chem.* **1987**, *27*, 101. ^l Baldas, J.; Bonnyman, J.; Mackay, M. F.; Williams, G. A. *Aust. J. Chem.* **1984**, *37*, 751. ^m Baldas, J.; Colmanet, S. F.; Williams, G. A. *Aust. J. Chem.* **1991**, *44*, 1125. ⁿ Bishop, M. W.; Chatt, J.; Dilworth, J. R. *Chem. Commun.* **1975**, 780. ^o The Re starting material in this instance was [(Me₂PhP)₂ReNCl(R₂tcb)], where R₂tcb = the anion of *N*-(*N,N*-dialkylthiocarbamoyl)benzamide). ^p Abram, U.; Ritter, S. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1233. ^q These rhenium thionitrosyl compounds are formed from the corresponding [(R₂R'P)₃ReBr₂(N)] complexes. ^r The dppe ligands are in a *trans* configuration as well as the thionitrosyl and Cl⁻ ligands. ^s Hübener, R.; Abram, U.; Strähle, J. *Inorg. Chim. Acta* **1994**, *216*, 223. ^t Ritter, S.; Abram, U. *Z. Anorg. Allg. Chem.* **1996**, *622*, 965. ^u These [(R₂R'P)₂ReCl₃(NS)] complexes were prepared from the corresponding six-coordinate [(R₂R'P)₃ReCl₂(N)] complexes. ^v These [(R₂R'P)₂ReCl₃(NS)] compounds were formed from five-coordinate [(R₂R'P)₂ReCl₂(N)] precursors. ^w ³¹P NMR suggests a *trans* disposition of the phosphine ligands and therefore a *mer* configuration for the chloride ligands. ^x This compound was also prepared in low yield from OsNCl₃(AsPh₃)₂ with (Ph₄P)NCS and KNCS in aqueous acetone. ^y Wright, M. J.; Griffith, W. P. *Trans. Met. Chem.* **1982**, *7*, 53. ^z CS₂ and N₃⁻ react to form a 5-thio-1,2,3,4-thiazolato ring anion, which decomposes to generate an equivalent of sulfur atom, dinitrogen, and thiocyanate anion. ^{aa} Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 3610.

in that they are attended by a four-electron reduction, at least in a formal sense, at the metal center! The thionitrosyl ligand is generally formulated as a thionitrosonium cation (NS⁺). Such dramatic multielectron reorganizations are quite rare for such an ostensibly simple reaction. Furthermore, the sulfur transfer is in many instances fully reversible; that is, strong sulfur atom acceptors such as trialkyl phosphines can abstract the sulfur atom to regenerate the parent nitrido compound.

Table 9 summarizes known examples of type I ligand-centered sulfur atom transfer reactions involving terminal nitrido, phosphido, and carbido ligands. Only one example of sulfur atom transfer to a terminal phosphido ligand occurs in the literature (reaction 81¹⁹⁸), principally because of the



rarity of terminal phosphido complexes in general. An example of a μ^3 -PS ligand produced by the reaction of an in situ generated μ^3 -phosphido ligand with sulfur has also been described.¹⁹⁹ The first instance of sulfur atom transfer to a terminal carbido ligand has been recently reported by Johnson.²⁰⁰ The reverse process, desulfurization of thiocarbonyl ligand with a suitable sulfur atom acceptor, has been suggested to be a possible synthetic route of some generality for the synthesis of metal complexes bearing a terminal carbido ligand.²⁰⁰

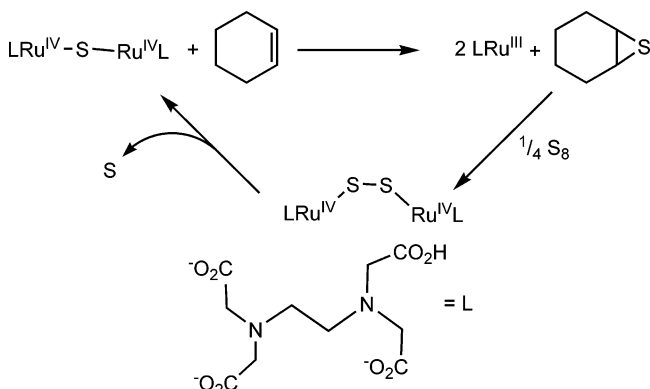
Also listed in Table 9 are the sulfur atom donors that were employed in the atom transfer reaction. It bears comment that, depending on the particular nitrido complex in question and its nucleophilicity, certain sulfur atom donors are effective and others not at all. For instance, whereas elemental sulfur and olefin sulfides are able to cleanly add sulfur atom to terminal nitrido ligands in $(R_2NCS_2)_3Mo\equiv N$ complexes (reaction 78), these same reagents do not work with Re or Os complexes (reactions 79 and 80). Conversely, whereas S_2Cl_2 and SCl_2 are able to effect sulfur atom transfer to terminal nitrido ligands in Re and Os compounds, these same sulfur atom donor agents result in messy, ill-defined products in the Mo system. These observations emphasize the point that it is generally worthwhile to test a different sulfur atom donor if one's initial choice does not result in clean atom transfer. Also noteworthy is the variety of sulfur atom donors that are collected in Table 9 for such an apparently narrow reaction type.

9. Catalytic Sulfur Atom Transfer Systems

The first report of catalytic sulfur atom transfer was by Khan and Siddiqui using a monoprotonated EDTA ruthenium complex in a mixed aqueous ethanol system.²⁰¹ These researchers observed turnovers of ~ 7 /mol of catalyst/h at 80 °C with cyclohexene as substrate. Although the turnover numbers observed are quite modest and the reaction conditions fairly vigorous, the significant point about their work is that cyclohexene is a particularly sluggish substrate. Other researchers,^{3b} however, have reported an inability to reproduce these results, and subsequent publications by Siddiqui and Khan that elaborate on their initial work have not yet appeared.

The catalytic scheme proposed by Khan and Siddiqui (Scheme 10) involves a sequential cycling through $Ru^{IV}(\mu-S_2)Ru^{IV}$, $Ru^{IV}(\mu-S)Ru^{IV}$, and monomeric Ru^{III} species, the last of which is then reoxidized by elemental sulfur to regenerate the disulfide-bridged $Ru^{IV}(\mu-S_2)Ru^{IV}$ complex.

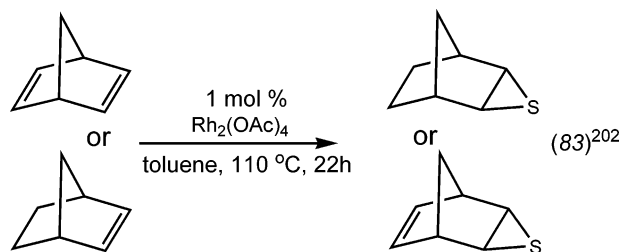
Scheme 10. Khan and Siddiqui's Ruthenium Catalytic System for the Sulfidation of Cyclohexene^a



^a See ref 200.

Both the disulfide- and sulfide-bridged complexes in Scheme 10, the latter of which appears to be the active sulfur atom donor species, were isolated and characterized by elemental analysis. Further insights into the working of this interesting system must await additional structural and spectroscopic characterization of these ruthenium compounds.

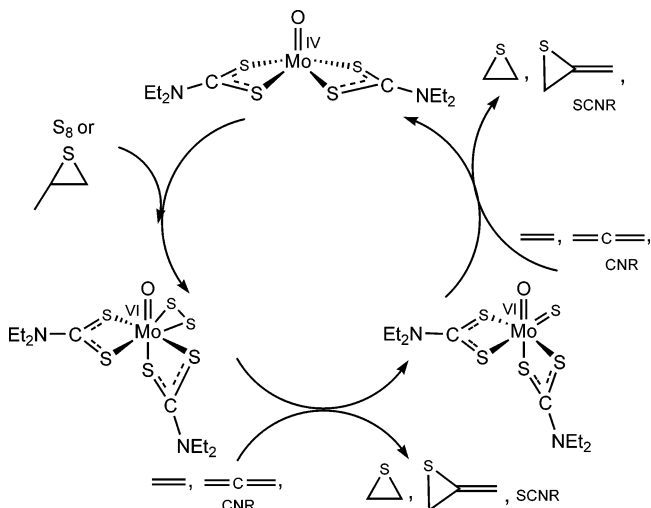
A brief paper describing thiirane metathesis using $Rh_2(OAc)_4$ as catalyst and propylene sulfide as sulfur source was described by Kendall and Simpkins (reaction 83).²⁰² The



substrates they examined were norbornene and norbornadiene, which were transformed to the corresponding olefin sulfides in 39 and 40% yields, respectively. The scope of this reaction and the mechanism by which it operates remain unclear, although it is well-known that $Rh_2(OAc)_4$ behaves essentially as a Lewis acid and catalyzes a variety of organic transformations.²⁰³

The most recent and significant work in the area of catalytic sulfur atom transfer reactivity is that reported by Adam and co-workers using a molybdenum catalyst with either dithiocarbamate or dithiophosphinate supporting ligands.^{3,4} In 2001, Adam reported that $(Et_2NCS_2)_2Mo^{VI}O(\eta^2-S_2)$ is competent to catalytically transfer a sulfur atom to a variety of olefinic substrates, with elemental sulfur acting as sulfur donor to regenerate active catalyst. This system is believed to proceed through a $Mo^{VI}OS$ intermediate, which delivers its sulfur atom to substrate in a distinct, separate step (Scheme 11). Adam extended his work to include

Scheme 11. Catalytic Cycle for Sulfur Atom Transfer to Olefins, Allenes, and Isonitriles through the Mediation of a $(Et_2NCS_2)_2Mo^{IV}O/(Et_2NCS_2)_2Mo^{VI}OS_2$ Catalyst (References 3 and 4)^a



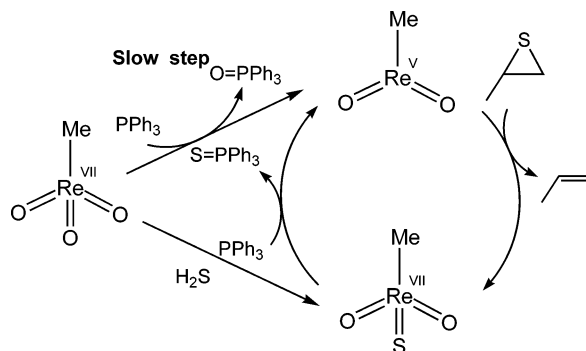
^a Adapted from ref 3b with permission from the American Chemical Society.

catalytic sulfuration of a range of isocyanides⁴ and allenenes.^{3b,c} Optimal catalytic efficiencies were reported with diethyldithiophosphate, $(EtO)_2PS_2^{1-}$, as supporting ligand and

propylene sulfide as sulfur source, but in this case the catalysis does not appear to involve a $\text{Mo}^{\text{VI}}(\eta^2\text{-S}_2)$ species in the oxidative half of the catalytic cycle.

Catalytic desulfurization of thiiranes substrates has also been reported by Espenson.²⁰⁴ Starting from MeReO_3 , which undergoes a slow activation by Ph_3P that is presumably an oxygen atom abstraction reaction, a highly reactive Re^{V} species is generated that quickly and stereospecifically excises sulfur from olefin sulfides (Scheme 12). Phosphine

Scheme 12. Catalytic Desulfurization of Thiiranes by a Methyl Rhenium Oxo Complex^a

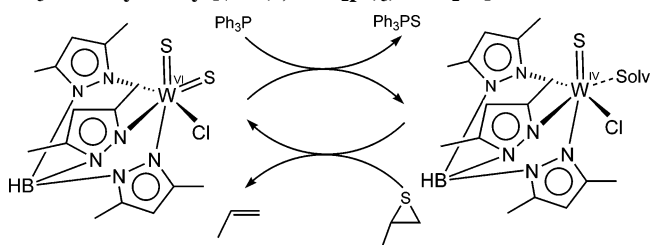


^a Adapted from ref 204 with permission from the Royal Society of Chemistry.

in turn removes sulfur from the Re^{VII} product to form phosphine sulfide and regenerate the active Re^{V} species. Strong evidence for the involvement of terminal sulfido ligation in the catalytic cycle is found in the observation that treating a MeReO_3 solution with H_2S , which would exchange an oxo for a terminal sulfido ligand, greatly reduces the induction period. Although this catalytic system for thiirane desulfurization is not one of special synthetic value, it is certainly relevant and interesting in the context of catalytic hydrodesulfurization of petroleum feedstocks.

Another, rather different, system for metal-mediated desulfurization of thiirane and transfer of the sulfur atom to phosphine was described by Young and co-workers.¹⁷¹ Using $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{WS}_2\text{X}$ complexes with variable X ($\text{X} = \text{Cl}^-$, PhO^- , PhS^-), they identified $\text{X} = \text{Cl}^-$ to be the optimal system. In the presence of 0.10 mol equiv of tungsten catalyst, 95% conversion of Ph_3P and propylene sulfide to Ph_3PS and propylene was observed spectroscopically over a three-day period (Scheme 13). The identity of the active,

Scheme 13. Sulfur Atom Transfer from Propylene Sulfide to Ph_3P Catalyzed by $[(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{W}^{\text{VI}}\text{S}_2\text{Cl}]^a$



^a See ref 171.

reduced W^{IV} species was not firmly established but may plausibly be formulated as a monosolvated complex resulting from abstraction of sulfide ligand by phosphine followed by coordination of solvent molecule. Significantly, no sulfur atom abstraction was observed in this system with $\text{C}\equiv\text{N}^-$. This observation demonstrates that reactivity with cyanide

cannot be used as a definitive assay for terminal sulfido ligation with tungsten as it has been with the molybdoenzymes.⁷

10. Summary and Conclusions

This review is intended as a resource for persons interested in the synthesis of new, interesting molecular sulfides, both organic and inorganic. The approach to this goal has been to organize sulfur atom donor/acceptor reagents onto a reactivity scale that identifies, at least in thermodynamic terms, the relative strengths of potential donors and acceptors. This review has also attempted to call attention to sulfur atom donor agents that are potentially very useful but somewhat outside the usual repertoire of reagents that are employed. Chief among these are hexasulfur (S_6), dialkyl dithiiranes, sulfur diimides, bis(tri-*n*-butylstannyl)sulfide, and 5-aryloxy-1,2,3,4-thiaziazoles. Similarly, oxo-for-sulfido exchange reagents such as SiS_2 , Ph_3SiSH , or Lawesson's reagent (for inorganic synthesis) have been little used but may be cleaner, milder, more selective, or more convenient alternatives in chalcogenide exchange reactions than B_2S_3 or $\text{Me}_3\text{SiSiMe}_3$.

The absence of many of these potentially useful reagents from the thermodynamic scales (Tables 1–6) identifies areas where experimental thermochemistry can contribute useful new information. The determination of standard molar enthalpies of formation for dialkyl dithiiranes (and also for thiones and thioaldehydes), for sulfur diimides, and for 5-aryloxy-1,2,3,4-thiaziazoles would be most helpful in quantifying their sulfur atom donor activity. Other areas of sulfide chemistry also represent opportunities for research. For instance, terminal sulfido complexes of ruthenium and osmium do not appear to be known, probably in part because no determined effort has been directed toward synthesizing such compounds. Terminal sulfido complexes of manganese and chromium are also unknown but pose greater synthetic challenges owing to the lesser stability of these first-row metals in the M^{IV} oxidation state that would be minimally required to support a terminal sulfido ligand. Organic sulfides such as C_{60}S and acenaphthalene sulfide have not yet been prepared and isolated but perhaps could be with the right choice of sulfur atom donor and reaction conditions. Catalytic sulfur atom transfer systems that extend and improve upon the pioneering work of Adam, for instance, by activating sluggish substrates such as cyclohexene or by performing enantioselective sulfur atom transfer to prochiral molecules, are also wide open areas for new chemical research.

11. Abbreviations

acen	<i>N,N'</i> -ethylenebis(acetylacetylideniminato)-(2-)
Ad	adamantyl
Ar	aryl
Bbt	2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl, 2,6-[CH(SiMe ₃) ₂]-4-[C(SiMe ₃) ₃]-C ₆ H ₂
bdt	benzene-1,2-dithiolate(2-)
ⁱ Bu	<i>iso</i> -butyl, -CH ₂ CH(CH ₃) ₂
Bu ^t ₃ tach	1,3,5-tri- <i>tert</i> -butyl-1,3,5-triazacyclohexane
Bz	benzyl, PhCH ₂ -
bipy	2,2'-bipyridine
Cp	cyclopentadienyl(1-), C ₅ H ₅ ⁻
Cp ^t	<i>tert</i> -butylcyclopentadienyl(1-), ^t Bu-C ₅ H ₄ ⁻
Cp*	pentamethylcyclopentadienyl(1-), Me ₅ C ₅ ⁻
CpEt*	ethyltetramethylcyclopentadienyl(1-), EtMe ₄ C ₅ ⁻

Cy	cyclohexyl
dmpm	bis(dimethylphosphino)methane, Me ₂ PCH ₂ PMe ₂
dpam	bis(diphenylarsino)methane, Ph ₂ AsCH ₂ AsPh ₂
dppe	1,2-bis(diphenylphosphino)ethane, Ph ₂ PCH ₂ CH ₂ -PPh ₂
dppee	1,2- <i>cis</i> -(diphenylphosphino)ethylene, <i>cis</i> -Ph ₂ PCH=CHPPh ₂
dppm	bis(diphenylphosphino)methane, Ph ₂ PCH ₂ PPh ₂
edt	ethane-1,2-dithiolate(2-)
edta	ethylenediaminetetraacetate(4-)
[HB(pz) ₃]	hydridotris(pyrazol-1-yl)borate(1-)
[HB(3,5- <i>t</i> -Bu- pz) ₃]	hydridotris(3,5-di- <i>tert</i> -butylpyrazol-1-yl)borate(1-)
[HB(3,5-Me ₂ - pz) ₃]	hydridotris(3,5-dimethylpyrazol-1-yl)borate(1-)
[HB(3- <i>i</i> Prpz) ₃]	hydridotris(3-isopropylpyrazol-1-yl)borate(1-)
[HB(3- <i>i</i> Prpz) ₂ - (5- <i>i</i> Prpz)]	hydridobis(3-isopropylpyrazol-1-yl)(5-isopropylpyrazol-1-yl)borate(1-)
Me ₄ phen	3,4,7,8-tetramethyl-1,10-phenanthroline
Me ₄ taa	tetramethyldibenzotetraaza[14]annulene(2-)
Me ₈ taa	octamethyldibenzotetraaza[14]annulene(2-)
<i>syn</i> -Me ₈ [16]- aneS ₄	3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathia-cyclohexadecane
MCPBA	<i>meta</i> -chloroperoxybenzoic acid
Mes	mesityl, 2,4,6-trimethylphenyl
Np	neopentyl, (CH ₃) ₃ CCH ₂ -
OEP	octaethylporphyrinate(2-)
phen	1,10-phenanthroline
por	porphyrinate(2-)
<i>i</i> Pr	isopropyl, -CH(CH ₃) ₂
<i>n</i> Pr	<i>n</i> -propyl, -CH ₂ CH ₂ CH ₃
py	pyridine
salen	1,2-bis(salicylideneamino)ethane(2-)
tacn	1,4,7-triazacyclononane
Tb	2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
Tbp	2,4,6-tri(<i>tert</i> -butyl)phenyl
Tip	2,4,6-tri(<i>iso</i> -propyl)phenyl
TMP	tetramesitylporphyrinate(2-)
TPP	tetraphenylporphyrinate(2-)
TmTP	tetra(<i>m</i> -tolyl)porphyrinate(2-)
TpTP	tetra(<i>p</i> -tolyl)porphyrinate(2-)
tpy	2,2':6',2''-terpyridine
triphos	MeC(CH ₂ PPh ₂) ₃
X	halide F ⁻ , Cl ⁻ , Br ⁻ , I ⁻

12. Acknowledgments

I gratefully acknowledge R. H. Holm for providing a preprint of the reference given in footnote *bo* of Table 7, which was helpful in the preparation of the manuscript. I thank Marcetta Y. Darensbourg and Kelly Reiter for their kind words of support during the writing of the manuscript, without which this work would not have been undertaken. I am deeply grateful for the generosity of F. A. Cotton, C. A. Murillo, Dave Jones, and Texas A&M University in providing me a place to work during the hiatus caused by Hurricane Katrina, during which time the manuscript was written. I thank Dr. Jim Mayer and the anonymous manuscript reviewers for their helpful commentary in the revision of the manuscript. Finally, I deeply appreciate the support of a Committee on Research Fellowship from Tulane University.

13. References

- (1) (a) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (c) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165. (d) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (e) Bottomley, F. *Polyhedron* **1992**, *11*, 1707. (f) Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125. (g) Mehrotra, R. C.; Singh, A. *Chem. Soc. Rev.* **1996**, *25*, 1.
- (2) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905.
- (3) (a) Adam, W.; Bargon, R. M. *Chem. Commun.* **2001**, 1910. (b) Adam, W.; Bargon, R. M.; Schenk, W. A. *J. Am. Chem. Soc.* **2003**, *125*, 3871. (c) Adam, W.; Bargon, R. M. *Chem. Rev.* **2004**, *104*, 251.
- (4) Adam, W.; Bargon, R. M.; Bosio, S. G.; Schenk, W. A.; Stalke, D. *J. Org. Chem.* **2002**, *67*, 7037.
- (5) For representative examples of olefin epoxidation by transition metal oxo complexes, see: (a) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. (b) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. (c) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343. (d) Bailey, C. L.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1987**, 179. (e) Rajapakse, N.; James, B. R.; Dolphin, D. Selective Oxidations Catalyzed by Dioxo(porphyrinato)ruthenium(VI) Species. In *New Developments in Selective Oxidation*; Centi, G., Trifiró, F., Eds.; Elsevier: Amsterdam, The Netherlands, 1990; pp 109–117. (f) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063. (g) Bailey, A. J.; Griffith, W. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1833. (h) Brandes, B. D.; Jacobsen, E. N. *Tetrahedron Lett.* **1995**, *36*, 5123. (i) Al-Ajlouni, A. M.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 3969. (j) Copéret, C.; Adolffsson, H.; Sharpless, K. B. *Chem. Commun.* **1997**, 1565.
- (6) (a) Hille, R. *Chem. Rev.* **1996**, *96*, 2757. (b) Huber, R.; Hof, P.; Duarte, R. O.; Moura, J. J. G.; Moura, I.; Liu, M.-Y.; LeGall, J.; Hille, R.; Archer, M.; Romão, M. J. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 8846. (c) Romão, M. J.; Huber, R. *Struct. Bonding* **1998**, *90*, 69. (d) Enroth, C.; Eger, B. T.; Okamoto, K.; Nishino, T.; Nishino, T.; Pai, E. F. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 10723.
- (7) (a) Massey, V.; Edmondson, D. *J. Biol. Chem.* **1970**, *245*, 6595. (b) Wahl, R. C.; Rajagopalan, K. V. *J. Biol. Chem.* **1982**, *257*, 1354.
- (8) (a) Nagarajan, K.; Joshi, H. K.; Chaudhury, P. K.; Pal, K.; Cooney, J. J. A.; Enemark, J. H.; Sarkar, S. *Inorg. Chem.* **2004**, *43*, 4532. (b) Prisner, T.; Lyubenova, S.; Atabay, Y.; MacMillan, F.; Kröger, A.; Klimmek, O. *J. Biol. Inorg. Chem.* **2003**, *8*, 419.
- (9) (a) Chan, M. K.; Mukund, S.; Kletzin, A.; Adams, M. W. W.; Rees, D. C. *Science* **1995**, *267*, 1463. (b) Johnson, M. K.; Rees, D. C.; Adams, M. W. W. *Chem. Rev.* **1996**, *96*, 2817. (c) Hu, Y.; Faham, S.; Roy, R.; Adams, M. W. W.; Rees, D. C. *J. Mol. Biol.* **1999**, *286*, 899. (d) Raaijmakers, H.; Macieira, S.; Dias, J. M.; Teixeira, S.; Bursakov, S.; Huber, R.; Moura, J. J. G.; Moura, I.; Romão, M. J. *Structure* **2002**, *10*, 1261.
- (10) (a) Ploegman, J. H.; Drent, G.; Kalk, K. H.; Hol, W. G. J. *J. Mol. Biol.* **1979**, *127*, 149. (b) Bordo, D.; Deriu, D.; Colnaghi, R.; Carpen, A.; Pagani, S.; Bolognesi, M. *J. Mol. Biol.* **2000**, *298*, 691. (c) Bordo, D.; Bork, P. *EMBO Reports* **2002**, *3*, 741.
- (11) (a) Westley, J.; Adler, H.; Westley, L.; Nishida, C. *Fundam. Appl. Toxicol.* **1983**, *3*, 377. (b) Huxtable, R. J. *Biochemistry of Sulfur*; Plenum: New York, 1986; pp 124–129. (c) Nagahara, N.; Ito, T.; Minami, M. *Histol. Histopathol.* **1999**, *14*, 1277.
- (12) (a) Alexander, K.; Volini, M. J. *Biol. Chem.* **1987**, *262*, 6595. (b) Mihara, H.; Esaki, N. *Appl. Microbiol. Biotechnol.* **2002**, *60*, 12. (c) Saidu, Y. *Afr. J. Biotechnol.* **2004**, *3*, 370.
- (13) (a) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. Hydrodesulfurization. In *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; pp 390–447. (b) Prins, R.; de Beer, V. H. J.; Somorjai, G. A. *Catal. Rev.—Sci. Eng.* **1989**, *31*, 1. (c) Angelici, R. J. Hydrodesulfurization and Hydrodenitrogenation. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York, 1994; Vol. 3, pp 1433–1443. (d) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (e) Angelici, R. J. *Bull. Soc. Chim. Belg.* **1995**, *104*, 265. (f) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801. (g) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073. (h) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109. (i) Babich, I. V.; Mouljin, J. A. *Fuel* **2003**, *82*, 607. (j) Breyse, M.; Djega-Mariadassou, G.; Pessayre, S.; Geantet, C.; Vrinat, M.; Pérot, G.; Lemaire, M. *Catal. Today* **2003**, *84*, 129. (k) Bianchini, C.; Meli, A.; Vizza, F. *J. Organomet. Chem.* **2004**, *689*, 4277.
- (14) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Choi, M.-G.; Daniels, L. M.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3647.
- (15) (a) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394. (b) Liu, A. C.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 820. (c) Wiegand, B. C.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491.
- (16) Gabay, J.; Dietz, S.; Bernatis, P.; Rakowski Dubois, M. *Organometallics* **1993**, *12*, 3630.
- (17) (a) Stirling, D. *The Sulfur Problem: Cleaning up Industrial Feedstocks*; Royal Society of Chemistry: Cambridge, U.K., 2000. (b) U.S. Environmental Protection Agency Clean Air Act Tier 2; 1999.
- (18) (a) Parks, C. R.; Parker, D. K.; Chalfant, H. J. *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1974**, *19*, 325. (b) Coran, A. Y. *CHEMTECH* **1983**, *13*, 106. (c) Krejsa, M. R.; Koening, J. L. *Rubber Chem. Technol.* **1993**, *66*, 376. (d) Ignatz-Hoover, F. *Rubber World* **1999**, *220*, 24. (e) Nieuwenhuizen, P. J. *CATTECH* **2000**, *3*, 184.

- (19) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571.
- (20) (a) Diemann, E.; Müller, A. *Coord. Chem. Rev.* **1973**, *10*, 79. (b) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322. (c) Rice, D. A. *Coord. Chem. Rev.* **1978**, *25*, 199. (d) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934. (e) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. (f) Müller, A.; Diemann, E. Sulfides. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, pp 515–550. (g) Trnka, T. M.; Parkin, G. *Polyhedron* **1997**, *16*, 1031. (h) Kuchta, M. C.; Parkin, G. *Coord. Chem. Rev.* **1998**, *176*, 323. (i) Parkin, G. *Prog. Inorg. Chem.* **1998**, *47*, 1. (j) Rauchfuss, T. B. *Inorg. Chem.* **2004**, *43*, 14.
- (21) Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861.
- (22) Goddard, C. A.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5389.
- (23) Lundmark, P. J.; Kubas, G. J.; Scott, B. L. *Organometallics* **1996**, *15*, 3631.
- (24) Pawlicki, S. H.; Noll, B. C.; Kanney, J. A.; Rakowski Dubois, M. *Inorg. Chem.* **2003**, *42*, 1556.
- (25) (a) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Nicholson, T.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1339. (b) Gilletti, P. F.; Femecc, D. A.; Keen, F. I.; Brown, T. M. *Inorg. Chem.* **1992**, *31*, 4008.
- (26) Various sources list slightly different values for $\Delta_f H^\circ(298)$ for S(g), none of which would produce any significant differences in the tables of thermodynamic data presented in this paper. The number cited and its uncertainty are obtained from the National Institute of Standards website: <http://webbook.nist.gov/chemistry/>.
- (27) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C₁ and C₂ Organic Substances in SI Units*; Lide, Jr., D. R., Ed.; American Chemical Society and the American Institute of Physics: Washington, DC; *J. Phys. Chem. Ref. Data* **1982**, *11* (Suppl. 2).
- (28) Binnewies, M.; Milke, E. *Thermochemical Data of Elements and Compounds*; Wiley-VCH: Weinheim, Germany, 2002.
- (29) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.
- (30) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.
- (31) *NIST-JANAF Thermochemical Tables*, 4th ed.; Chase, Jr., M. W., Ed.; American Chemical Society and the American Institute of Physics: Washington, DC; *J. Phys. Chem. Ref. Data* **1998**, Monograph 9.
- (32) *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, P., Jordan, J., Eds.; Marcel Dekker: New York, 1985.
- (33) Mills, K. C. *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*; Butterworth: London, U.K., 1974.
- (34) Barin, I. *Thermochemical Data of Pure Substances*; VCH: Weinheim, Germany, 1993.
- (35) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.
- (36) Kirklin, D. R.; Domalski, E. S. *J. Chem. Thermodyn.* **1988**, *20*, 743.
- (37) Kirklin, D. R.; Chickos, J. S.; Liebman, J. F. *Struct. Chem.* **1996**, *7*, 355.
- (38) Deniz, A. A.; Peters, K. S.; Snyder, G. J. *Science* **1999**, *286*, 1119.
- (39) Dittmer, G.; Niemann, U. *Philips J. Res.* **1982**, *37*, 1.
- (40) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P.; Capps, K. B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **2000**, *39*, 1042.
- (41) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *Science* **1966**, *151*, 172. (c) Pearson, R. G. *Chem. Ber.* **1967**, *3*, 103. (d) Pearson, R. G. *Inorg. Chim. Acta* **1995**, *240*, 93.
- (42) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1993**, *97*, 4951.
- (43) Ibdah, A.; Espenson, J. H.; Jenks, W. S. *Inorg. Chem.* **2005**, *44*, 8426.
- (44) (a) Chernick, C. L.; Pedley, J. B.; Skinner, H. A. *J. Chem. Soc.* **1957**, 1851. (b) Hartley, S. B.; Holmes, W. S.; Jacques, J. K.; Mole, M. F.; McCoubrey, J. C. *Q. Rev. Chem. Soc.* **1963**, *17*, 204.
- (45) Johnson, A. R.; Davis, W. M.; Cummins, C. C.; Serron, S.; Nolan, S. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 2071.
- (46) (a) Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402. (b) Hall, K. A.; Mayer, J. M. *Inorg. Chem.* **1994**, *33*, 3289.
- (47) (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 5904. (b) Rabinovich, D.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 6341.
- (48) (a) Vogel, E.; Klärner, F.-G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 374. (b) Boyd, D. R.; Jerina, D. M.; Daly, J. W. *J. Org. Chem.* **1970**, *35*, 3170. (c) Akhtar, M. N.; Boyd, D. R.; Hamilton, J. G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2437.
- (49) (a) Cortez, C.; Harvey, R. G.; Jackson, J.; Chapman, O. L. *Org. Synth.* **1978**, *58*, 12. (b) Mello, R.; Ciminale, F.; Fiorentino, M.; Fusco, C.; Prencipe, T.; Curci, R. *Tetrahedron Lett.* **1990**, *31*, 6097.
- (50) Murray, R. W.; Singh, M.; Rath, N. P. *Struct. Chem.* **1999**, *10*, 419.
- (51) Rozen, S.; Bareket, Y.; Blum, J. *Tetrahedron Lett.* **1997**, *38*, 2333.
- (52) Rebelo, S. L. H.; Simões, M. M. Q.; Neves, M. Graca P. M. S.; Silva, A. M. S.; Cavaleiro, J. A. S. *Chem. Commun.* **2004**, 608.
- (53) (a) Reinecke, M. G.; Del Mazza, D.; Obeng, M. *J. Org. Chem.* **2003**, *68*, 70. (b) Reinecke, M. G.; Del Mazza, D. *J. Org. Chem.* **1989**, *54*, 2142. (c) Del Mazza, D.; Reinecke, M. G. *J. Org. Chem.* **1988**, *53*, 5799. (d) Callander, D. D.; Coe, P. L.; Tatlow, J. C. *Chem. Commun.* **1966**, 143.
- (54) (a) Bartlett, P. D.; Roderick, W. R.; Andersen, W. C. *Inorg. Synth.* **1966**, *8*, 100. (b) Mäusle, H.-J.; Steudel, R. Z. *Anorg. Allg. Chem.* **1980**, *463*, 27. (c) Donohue, J.; Caron, A.; Goldish, E. *J. Am. Chem. Soc.* **1961**, *83*, 3748. (d) Steidel, J.; Pickardt, J.; Steudel, R. Z. *Naturforsch., B: Chem. Sci.* **1978**, *33*, 1554.
- (55) (a) Schmidt, M.; Block, B.; Block, H. D.; Köpf, H.; Wilhelm, E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 632. (b) Kawada, I.; Hellner, E. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 379. (c) Steudel, R.; Reinhardt, R.; Schuster, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 715. (d) Steudel, R.; Steidel, J.; Pickardt, J.; Schuster, F.; Reinhardt, R. Z. *Naturforsch., B: Chem. Sci.* **1980**, *35*, 1378. (e) Steudel, R.; Mäusle, H.-J. *Z. Anorg. Allg. Chem.* **1981**, *478*, 156.
- (56) (a) Schmidt, M.; Wilhelm, E. *Chem. Commun.* **1970**, 1111. (b) Steudel, R.; Bergemann, K.; Buschmann, J.; Luger, P. *Inorg. Chem.* **1996**, *35*, 2184.
- (57) (a) Steudel, R.; Steidel, J.; Sandow, T.; Schuster, F. Z. *Naturforsch., B: Chem. Sci.* **1978**, *33*, 1198. (b) Reinhardt, R.; Steudel, R.; Schuster, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 57. (c) Steudel, R.; Steidel, J.; Reinhardt, R. Z. *Naturforsch., B: Chem. Sci.* **1983**, *38*, 1548.
- (58) (a) Steidel, J.; Steudel, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1312. (b) Sandow, T.; Steidel, J.; Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 794. (c) Steudel, R.; Steidel, J.; Sandow, T. Z. *Naturforsch., B: Chem. Sci.* **1986**, *41*, 958.
- (59) (a) Schmidt, M.; Wilhelm, E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 964. (b) Kutoglu, A.; Hellner, E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 965. (c) Schmidt, M.; Knippschild, G.; Wilhelm, E. *Chem. Ber.* **1968**, *101*, 381. (d) Steudel, R.; Mäusle, H.-J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 152. (e) Steidel, J.; Steudel, R.; Kutoglu, A. Z. *Anorg. Allg. Chem.* **1981**, *476*, 171.
- (60) Steudel, R.; Schumann, O.; Buschmann, J.; Luger, P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2377.
- (61) Strauss, R.; Steudel, R. Z. *Naturforsch., B: Chem. Sci.* **1988**, *43*, 1151.
- (62) (a) Schmidt, M.; Wilhelm, E.; Debaerdemaeker, T.; Hellner, E.; Kutoglu, A. Z. *Anorg. Allg. Chem.* **1974**, *405*, 153. (b) Debaerdemaeker, T.; Kutoglu, A. *Naturwissenschaften* **1973**, *60*, 49. (c) Debaerdemaeker, T.; Kutoglu, A. *Cryst. Struct. Commun.* **1974**, *3*, 611.
- (63) (a) Debaerdemaeker, T.; Hellner, E.; Kutoglu, A.; Schmidt, M.; Wilhelm, E. *Naturwissenschaften* **1973**, *60*, 300. (b) Steudel, R.; Strauss, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1775.
- (64) Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971.
- (65) (a) Bartlett, P. D.; Cox, E. F.; Davis, R. E. *J. Am. Chem. Soc.* **1961**, *83*, 103. (b) Fehér, F.; Kurz, D. Z. *Naturforsch., B: Chem. Sci.* **1969**, *24*, 1089.
- (66) Heymann, D.; Bachilo, S. M.; Weisman, R. B.; Marriotti, T.; Cataldo, F. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2002**, *10*, 37.
- (67) (a) Carlsen, L.; Harrit, N.; Holm, A. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1404. (b) Karlström, G.; Roos, B. O.; Carlsen, L. *J. Am. Chem. Soc.* **1984**, *106*, 1557.
- (68) (a) Snyder, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5005. (b) Carlsen, L.; Holm, A.; Koch, E.; Stikkerieg, B. *Acta Chem. Scand.* **1977**, *B31*, 679.
- (69) (a) Bonini, B. F.; Maccagnani, G.; Mazzanti, G. *J. Chem. Soc., Chem. Commun.* **1976**, 431. (b) Rindorf, G.; Carlsen, L. *Acta Crystallogr., Sect. B* **1979**, *35*, 1179. (c) Le Nocher, A. M.; Metzner, P. *Tetrahedron Lett.* **1991**, *32*, 747. (d) Huang, R.; Espenson, J. H. *J. Org. Chem.* **1999**, *64*, 6935.
- (70) Adam, W.; Deeg, O.; Weinkötz, S. *J. Org. Chem.* **1997**, *62*, 7084.
- (71) Adam, W.; Weinkötz, S. *J. Am. Chem. Soc.* **1998**, *120*, 4861.
- (72) (a) Huisgen, R.; Rapp, J. *J. Am. Chem. Soc.* **1987**, *109*, 902. (b) Ishii, A.; Hoshino, M.; Nakayama, J. *Pure Appl. Chem.* **1996**, *68*, 869. (c) Huisgen, R.; Rapp, J. *Tetrahedron* **1997**, *53*, 939.
- (73) Nakayama, J.; Ishii, A. *Adv. Heterocycl. Chem.* **2000**, *77*, 221.
- (74) (a) Ishii, A.; Akazawa, T.; Maruta, T.; Nakayama, J.; Hoshino, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 777. (b) Ishii, A.; Jin, Y.-N.; Nagaya, H.; Hoshino, M.; Nakayama, J. *Tetrahedron Lett.* **1995**, *36*, 1867. (c) Ishii, A.; Umezawa, K.; Nakayama, J. *Tetrahedron Lett.* **1997**, *38*, 1431. (d) Ishii, A.; Yamashita, R.; Saito, M.; Nakayama, J. *J. Org. Chem.* **2003**, *68*, 1555.
- (75) Shimada, K.; Kodaki, K.; Aoyagi, S.; Takikawa, Y.; Kabuto, C. *Chem. Lett.* **1999**, 695.
- (76) Wieringa, J. H.; Wynberg, H.; Strating, J. *Tetrahedron Lett.* **1972**, *13*, 2071.

- (77) Wieringa, J. H.; Wynberg, H.; Strating, J. *Tetrahedron* **1974**, *30*, 3053.
- (78) Ishii, A.; Kawai, T.; Tekura, K.; Oshida, H.; Nakayama, J. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1924.
- (79) Baechler, R. D.; Stack, M.; Stevenson, K.; Vanvalkenburgh, V. *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *48*, 49.
- (80) Nowotnick, H.; Blachnik, R. Z. *Anorg. Allg. Chem.* **1999**, *625*, 1966.
- (81) Jason, M. E. *Inorg. Chem.* **1997**, *36*, 2641.
- (82) Shindo, M.; Matsumura, Y.; Okawara, R. *J. Organomet. Chem.* **1968**, *11*, 299.
- (83) Zingaro, R. A.; Merijanjan, A. *J. Organomet. Chem.* **1964**, *1*, 369.
- (84) Otera, J.; Kadowaki, T.; Okawara, R. *J. Organomet. Chem.* **1969**, *19*, 213.
- (85) Bhattacharya, S. N.; Saxena, A. K. *Ind. J. Chem., Sect. A* **1979**, *17*, 307.
- (86) Raj, P.; Saxena, A. K.; Singhal, K.; Ranjan, A. *Polyhedron* **1985**, *4*, 251.
- (87) ${}^n\text{Bu}_3\text{SnSSn}^n\text{Bu}_3$ is available from Strem Chemicals, Pfaltz & Bauer, and Gelest, Inc.
- (88) One report has described Fe(III) and Cu(II) complexes with ${}^n\text{Bu}_3\text{SnSSn}^n\text{Bu}_3$ itself as a ligand coordinated to the metal through the sulfur atom. The identity of these complexes has not been established, as they have been characterized only by IR spectroscopy. See: Mikulski, C. M.; Karayannis, N. M. *Inorg. Chim. Acta* **1983**, *77*, L43.
- (89) (a) $\text{Me}_3\text{SnSSnMe}_3$; Capozzi, G.; Menichetti, S.; Ricci, A.; Taddei, M. *J. Organomet. Chem.* **1988**, *344*, 285. (b) ${}^n\text{Bu}_3\text{SnSSn}^n\text{Bu}_3$; Hänssgen, D.; Reuter, P.; Döllén, G. *J. Organomet. Chem.* **1986**, *317*, 159. Batchelor, R. J.; Einstein, F. W. B.; Jones, C. H. W.; Sharma, R. D. *Inorg. Chem.* **1988**, *27*, 4636. (c) $\text{Cy}_3\text{SnSSnCy}_3$; Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104. (d) $\text{Ph}_3\text{SnSSnPh}_3$; Glidewell, C.; Liles, D. C. *J. Organomet. Chem.* **1981**, *224*, 237. (e) $\text{Bz}_3\text{SnSSnBz}_3$; Kersch, S.; Wrackmeyer, B.; Männig, D.; Nöth, H.; Staudigl, R. Z. *Naturforsch., B: Chem. Sci.* **1987**, *42*, 387.
- (90) Sampson, M. L.; Richardson, J. F.; Noble, M. E. *Inorg. Chem.* **1992**, *31*, 2726.
- (91) Gingras, M.; Harpp, D. N. *Tetrahedron Lett.* **1990**, *31*, 1397.
- (92) Harpp, D. N.; Gingras, M. *Tetrahedron Lett.* **1987**, *28*, 4373.
- (93) Harpp, D. N.; Gingras, M.; Aida, T.; Chan, T. H. *Synthesis* **1987**, 1122.
- (94) Cowley, A. J. *Chem. Educ.* **1964**, *41*, 530.
- (95) *Handbook of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic Press: New York, 1963; Vol. 1.
- (96) (a) Leung, Y. C.; Waser, J.; van Houten, S.; Vos, A.; Wiegers, G. A.; Wiebenga, E. H. *Acta Crystallogr.* **1957**, *10*, 574. (b) Chattopadhyay, T. K.; May, W.; von Schnering, H. G.; Pawley, G. S. Z. *Kristallogr.* **1983**, *165*, 47.
- (97) Vos, A.; Olthoff, R.; van Bolhuis, F.; Botterweg, R. *Acta Crystallogr.* **1965**, *19*, 864.
- (98) Dixon, D. T.; Einstein, F. W. B.; Penfold, B. R. *Acta Crystallogr.* **1965**, *18*, 221.
- (99) Blachnik, R.; Matthiesen, J.; Müller, A.; Nowotnick, H.; Reuter, H. Z. *Kristallogr.* **1998**, *213*, 233.
- (100) Blachnik, R.; Peukert, U.; Czediwoda, A.; Engelen, B.; Boldt, K. Z. *Anorg. Allg. Chem.* **1995**, *621*, 1637.
- (101) van Houten, S.; Wiebenga, E. H. *Acta Crystallogr.* **1957**, *10*, 156.
- (102) Perkins, P. G. *Inorg. Chim. Acta* **1983**, *73*, 45.
- (103) Meisel, M.; Grunze, H. Z. *Anorg. Allg. Chem.* **1970**, *373*, 265.
- (104) Nowotnick, H.; Blachnik, R. Z. *Anorg. Allg. Chem.* **2000**, *626*, 611.
- (105) Barieux, J.-J.; Démarcq, M. C. *J. Chem. Soc., Chem. Commun.* **1982**, 176.
- (106) Bjorholm, T.; Jakobsen, H. J. *J. Am. Chem. Soc.* **1991**, *113*, 27.
- (107) Bues, W.; Somer, M.; Brockner, W. Z. *Anorg. Allg. Chem.* **1981**, *476*, 153.
- (108) Griffin, A. M.; Minshall, P. C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976**, 809.
- (109) P_4S_{10} is available from numerous suppliers, but P_4S_6 appears to be available only from the Aldrich Chemical Co.
- (110) (a) Leandri, G.; Rebora, P. *Experientia* **1957**, *13*, 71. (b) Leandri, G.; Rebora, P. *Gazz. Chim. Ital.* **1957**, *87*, 503. (c) Leandri, G.; Spinelli, D. *Ann. Chim.* **1959**, *49*, 1689. (d) Foffani, A.; Leandri, G.; Zanon, I.; Carpanelli, C. *Tetrahedron Lett.* **1959**, *1* (11), 21. (e) Jannelli, L.; Sciacovelli, O.; Carpanelli, C. *Ann. Chim.* **1963**, *53*, 1541.
- (111) Leandri, G.; Busetti, V.; Valle, G.; Mammi, M. *Chem. Commun.* **1970**, 413.
- (112) Bindra, A. P.; Elix, J. A.; Morris, G. C. *Aust. J. Chem.* **1969**, *22*, 2483.
- (113) For the preparation and crystal structure of mercury(II) acetamide, see: Kamenar, B.; Grdenić, D. *Inorg. Chim. Acta* **1969**, *3*, 25.
- (114) Cramer, R. *J. Org. Chem.* **1961**, *26*, 3476.
- (115) The best pricing for phenyl *N*-sulfinyllamine is from TCI America.
- (116) Al-Ajely, M. S.; Al-Rawi, J. M. A.; Elvidge, J. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1575.
- (117) Goehring, M.; Weis, G. *Angew. Chem.* **1956**, *68*, 678.
- (118) (a) Pandey, K. K.; Nigam, H. L. *Rev. Inorg. Chem.* **1984**, *6*, 69. (b) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.
- (119) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2851.
- (120) Werner, H.; Kolb, O. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 865.
- (121) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2860.
- (122) Baird, M. C.; Wilkinson, G. J. *J. Chem. Soc. A* **1967**, 865.
- (123) Skapski, A. C.; Troughton, P. G. H. *Chem. Commun.* **1969**, 170.
- (124) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826.
- (125) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261.
- (126) Berg, D. J.; Burns, C. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865.
- (127) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; McKee, S. D.; Smith, W. H. *Inorg. Chem.* **1994**, *33*, 4245.
- (128) (a) Ferm, R. *J. Chem. Rev.* **1957**, *57*, 621. (b) Neels, J.; Meisel, M.; Moll, R. Z. *Chem.* **1984**, *24*, 389. (c) Mizuno, T.; Nishiguchi, I.; Hirashima, T.; Sonoda, N. *Heteroat. Chem.* **1990**, *1*, 157.
- (129) Lorber, C.; Donahue, J. P.; Goddard, C. A.; Nordlander, E.; Holm, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 8102.
- (130) Sung, K.-M.; Holm, R. H. *Inorg. Chem.* **2001**, *40*, 4518.
- (131) Jiang, J.; Holm, R. H. *Inorg. Chem.* **2004**, *43*, 1302.
- (132) Cotton, F. A.; Schmid, G. *Inorg. Chem.* **1997**, *36*, 2267.
- (133) (a) Coucouvanis, D.; Hadjikyriacou, A. *Inorg. Chem.* **1986**, *25*, 4317. (b) Hadjikyriacou, A. I.; Coucouvanis, D. *Inorg. Chem.* **1987**, *26*, 2400.
- (134) Halbert, T. R.; McGauley, K.; Pan, W.-H.; Czernuszewicz, R. S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 1849.
- (135) (a) Sullivan, A. B.; Boustany, K. *Int. J. Sulfur Chem. A* **1971**, *1*, 207. (b) Coucouvanis, D.; Kanatzidis, M.; Simhon, E.; Baenziger, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 1874. (c) Hou, Y.; Abu-Yousef, I. A.; Doung, Y.; Harpp, D. N. *Tetrahedron Lett.* **2001**, *42*, 8607.
- (136) Murphy, V. J.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 3522.
- (137) Howard, W. A.; Trnka, T. M.; Waters, M.; Parkin, G. *J. Organomet. Chem.* **1997**, *528*, 95.
- (138) Howard, W. A.; Parkin, G. *Organometallics* **1993**, *12*, 2363.
- (139) Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986**, *5*, 1620.
- (140) Beckhaus, R.; Thiele, K.-H. Z. *Anorg. Allg. Chem.* **1989**, *573*, 195.
- (141) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.
- (142) (a) Lee, C.-L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1175. (b) Besenyei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987**, *26*, 3622. (c) Barnabas, A. F.; Sallin, D.; James, B. R. *Can. J. Chem.* **1989**, *67*, 2009. (d) Wong, T. Y. H.; Barnabas, A. F.; Sallin, D.; James, B. R. *Inorg. Chem.* **1995**, *34*, 2278.
- (143) (a) Heyke, O.; Hiller, W.; Lorenz, I.-P. *Chem. Ber.* **1991**, *124*, 2217. (b) Heyke, O.; Beuter, G.; Lorenz, I.-P. Z. *Naturforsch., B: Chem. Sci.* **1992**, *47*, 668.
- (144) Kuncheria, J.; Mirza, H. A.; Jenkins, H. A.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1998**, 285.
- (145) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 3339.
- (146) McDonald, R.; Cowie, M. *Inorg. Chem.* **1993**, *32*, 1671.
- (147) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1986**, *25*, 4617.
- (148) Reich, P.; Martin, D. *Chem. Ber.* **1965**, *98*, 2063.
- (149) Martin, D. *Chem. Ber.* **1964**, *97*, 2689.
- (150) (a) Wentrup, C.; Kambouris, P. *Chem. Rev.* **1991**, *91*, 363. (b) Wentrup, C.; Flammang, R. J. *Phys. Org. Chem.* **1998**, *11*, 350.
- (151) Adam, W.; Bargon, R. M. *Eur. J. Org. Chem.* **2001**, 1959.
- (152) Yu, Z.-X.; Wu, Y.-D. *J. Org. Chem.* **2003**, *68*, 6049.
- (153) Jensen, K. A.; Holm, A.; Høge-Jensen, E. *Acta Chem. Scand.* **1969**, *23*, 2919.
- (154) (a) Lieber, E.; Pillai, C. N.; Ramachandran, J.; Hites, R. D. *J. Org. Chem.* **1957**, *22*, 1750. (b) Lieber, E.; Oftedahl, E.; Rao, C. N. R. *J. Org. Chem.* **1963**, *28*, 194. (c) Kirmse, W. *Chem. Ber.* **1960**, *93*, 2353. (d) Jensen, K. A.; Pedersen, C. *Adv. Heterocycl. Chem.* **1964**, *3*, 263. (e) Jensen, K. A.; Holm, A.; Pedersen, C. T. *Acta Chem. Scand.* **1964**, *18*, 566. (f) Ikeda, S.; Murai, T.; Ishihara, H.; Kato, S. *Synthesis* **1990**, 415.
- (155) Preuss, F.; Noichl, H. Z. *Naturforsch., B: Chem. Sci.* **1987**, *42*, 121.
- (156) Partyka, D. V.; Staples, R. J.; Holm, R. H. *Inorg. Chem.* **2003**, *42*, 7877.
- (157) (a) Cherkasov, R. A.; Kutyrev, G. A.; Pudovik, A. N. *Tetrahedron* **1985**, *41*, 2567. (b) Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061. (c) Jesberger, M.; Davis, T. P.; Barner, L. *Synthesis* **2003**, 1929.

- (158) (a) Callahan, K. P.; Durand, P. J.; Rieger, P. H. *J. Chem. Soc., Chem. Commun.* **1980**, 75. (b) Callahan, K. P.; Durand, P. J. *Inorg. Chem.* **1980**, *19*, 3211.
- (159) Sato, M.; Miller, K. M.; Enemark, J. H.; Strouse, C. E.; Callahan, K. P. *Inorg. Chem.* **1981**, *20*, 3571.
- (160) Young, C. G.; Enemark, J. H.; Collison, D.; Mabbs, F. E. *Inorg. Chem.* **1987**, *26*, 2925.
- (161) (a) Duatti, A.; Tisato, F.; Refosco, F.; Mazzi, U.; Nicolini, M. *Inorg. Chem.* **1989**, *28*, 4564. (b) Tisato, F.; Bolzati, C.; Duatti, A.; Bandoli, G.; Refosco, F. *Inorg. Chem.* **1993**, *32*, 2042.
- (162) Tahmassebi, S. K.; Mayer, J. M. *Organometallics* **1995**, *14*, 1039.
- (163) Yan, X. F.; Fox, B. L.; Tiekink, E. R. T.; Young, C. G. *J. Chem. Soc., Dalton Trans.* **1994**, 1765.
- (164) Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938.
- (165) Young, C. G.; Laughlin, L. J.; Colmanet, S.; Scrofani, S. D. B. *Inorg. Chem.* **1996**, *35*, 5368.
- (166) Bristow, S.; Collison, D.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 2495.
- (167) Eagle, A. A.; Tiekink, E. R. T.; George, G. N.; Young, C. G. *Inorg. Chem.* **2001**, *40*, 4563.
- (168) Eagle, A. A.; Tiekink, E. R. T.; Young, C. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1746.
- (169) Faller, J. W.; Kucharczyk, R. R.; Ma, Y. *Inorg. Chem.* **1990**, *29*, 1662.
- (170) Barnard, K. R.; Gable, R. W.; Wedd, A. G. *J. Biol. Inorg. Chem.* **1997**, *2*, 623.
- (171) Eagle, A. A.; Gable, R. W.; Thomas, S.; Sproules, S. A.; Young, C. G. *Polyhedron* **2004**, *23*, 385.
- (172) Dean, F. M.; Goodchild, J.; Hill, A. W. *J. Chem. Soc. C* **1969**, 2192.
- (173) (a) Jerumanis, S.; Lalancette, J. M. *Can. J. Chem.* **1964**, *42*, 1928. (b) Greene, F. T.; Margrave, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 5555.
- (174) Lebedev, E. P.; Baburina, V. A.; Reikhsfel'd, V. O. *Zh. Obshch. Khim.* **1974**, *44*, 1212.
- (175) (a) Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1985**, *24*, 3297. (b) Money, J. K.; Folting, K.; Huffman, J. C.; Collison, D.; Temperley, J.; Mabbs, F. E.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4583.
- (176) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809.
- (177) Do, Y.; Holm, R. H. *Inorg. Chim. Acta* **1985**, *104*, 33.
- (178) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *Inorg. Chim. Acta* **1986**, *118*, 165.
- (179) Klemperer, W. G.; Schwartz, C. *Inorg. Chem.* **1985**, *24*, 4459.
- (180) Radkov, E.; Lu, Y.-J.; Beer, R. H. *Inorg. Chem.* **1996**, *35*, 551.
- (181) Tanner, L. D.; Haltiwanger, R. C.; Rakowski DuBois, M. *Inorg. Chem.* **1988**, *27*, 1741.
- (182) Minelli, M.; Enemark, J. H.; Wieghardt, K.; Hahn, M. *Inorg. Chem.* **1983**, *22*, 3952.
- (183) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831.
- (184) Yu, S.-B.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 4385.
- (185) Feinstein-Jaffe, I.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 1189.
- (186) Partyka, D. V.; Holm, R. H. *Inorg. Chem.* **2004**, *43*, 8609.
- (187) Dorfman, J. R.; Girerd, J.-J.; Simhon, E. D.; Stack, T. D. P.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 4407.
- (188) Mukherjee, R. N.; Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 1850.
- (189) Tacke, R.; Wannagat, U. *Top. Curr. Chem.* **1979**, *84*, 1.
- (190) Personal communication, Dr. William Steele, Oak Ridge National Laboratory and the University of Tennessee, Knoxville.
- (191) (a) So, J.-H.; Boudjouk, P. *Synthesis* **1989**, 306. (b) So, J.-H.; Boudjouk, P.; Hong, H. H.; Weber, W. P. *Inorg. Synth.* **1992**, *29*, 30.
- (192) (a) Housmekerides, C. E.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 563. (b) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453.
- (193) (a) Newman, M. S.; Karnes, H. A. *J. Org. Chem.* **1966**, *31*, 3980. (b) Kwart, H.; Evans, E. R. *J. Org. Chem.* **1966**, *31*, 410. (c) Kurth, H.-J.; Kraatz, U.; Korte, F. *Chem. Ber.* **1973**, *106*, 2419. (d) Kurth, H.-J.; Kraatz, U.; Korte, F. *Liebigs Ann. Chem.* **1976**, 1313. (e) Besserer, K.; Köhler, H.; Rundel, W. *Chem. Ber.* **1982**, *115*, 3678. (f) Corral, C.; Lissavetzky, J.; Valdeolmillos, A. M. *Synthesis* **1984**, 172. (g) Aslam, M.; Davenport, K. G. *Synth. Commun.* **1987**, *17*, 1761. (h) Beaulieu, F.; Snieckus, V. *Synthesis* **1992**, 112. (i) Gibbs, C. G.; Gutsche, C. D. *J. Am. Chem. Soc.* **1993**, *115*, 5389. (j) Fabbri, D.; Delogu, G.; De Lucchi, O. *J. Org. Chem.* **1993**, *58*, 1748. (k) Cossu, S.; De Lucchi, O.; Fabbri, D.; Valle, G.; Painter, G. F.; Smith, R. A. *J. Tetrahedron* **1997**, *53*, 6073. (l) Rao, P.; Hosseini, M. W.; De Cian, A.; Fischer, J. *Chem. Commun.* **1999**, 2169.
- (194) The Newman–Kwart rearrangement has also been referred to as the Newman–Karnes reaction in the literature.
- (195) See, for instance: Goddard, C. A. *Polyhedron* **1997**, *16*, 4273.
- (196) Chatt, J.; Dilworth, J. R. *J. Chem. Soc., Chem. Commun.* **1974**, 508.
- (197) Bishop, M. W.; Chatt, J.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1.
- (198) Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2042.
- (199) Lorenz, I.-P.; Pohl, W.; Polborn, K. *Chem. Ber.* **1996**, *129*, 11.
- (200) Caskey, S. R.; Stewart, M. H.; Kivela, J. E.; Sootsman, J. R.; Johnson, M. J. A.; Kampf, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 16750.
- (201) Khan, M. M. T.; Siddiqui, M. R. H. *Inorg. Chem.* **1991**, *30*, 1157.
- (202) Kendall, J. D.; Simpkins, N. S. *Synlett* **1998**, 391.
- (203) For further examples of organic transformations catalyzed by dirhodium paddlewheel compounds, see: (a) Doyle, M. P.; Phillips, I. M. *Tetrahedron Lett.* **2001**, *42*, 3155. (b) Doyle, M. P.; Phillips, I. M.; Hu, W. *J. Am. Chem. Soc.* **2001**, *123*, 5366. (c) Lee, D.; Otte, R. D. *J. Org. Chem.* **2004**, *69*, 3569. (d) Fruit, C.; Müller, P. *Tetrahedron: Asymmetry* **2004**, *15*, 1019. (e) Lou, Y.; Horikawa, M.; Kloster, R. A.; Hawryluk, N. A.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 8916. (f) Shi, W.; Zhang, B.; Zhang, J.; Liu, B.; Zhang, S.; Wang, J. *Org. Lett.* **2005**, *7*, 3103. (g) Doyle, M. P.; Morgan, J. P.; Fettingner, J. C.; Zavalij, P. Y.; Colyer, J. T.; Timmons, D. J.; Carducci, M. D. *J. Org. Chem.* **2005**, *70*, 5291.
- (204) Jacob, J.; Espenson, J. H. *Chem. Commun.* **1999**, *11*, 1003.

CR050044W