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Synthesis, Characterization, and Reactivity of Alkyldisulfanido Zinc Complexes

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The alkyldisulfanido zinc complexes $Tp^{iPr,iPr}Zn(SSR)$ and $Tp^{Ph,Me}Zn(SSR)$ where $Tp^{iPr,iPr}$ is hydridotris-((3,5-isopropyl) pyrazolyl)borate, $Tp^{Ph,Me}$ is hydridotris-((3-phenyl,5-methyl)pyrazolyl)borate, and (SSR) is *tert*-butyldisulfanido or triphenylmethanedisulfanido were synthesized by reaction between the corresponding hydroxo complexes TpZn(OH) and the synthetic persulfide RSSH. All the complexes were characterized by elemental analysis and ^{1}H NMR spectroscopy, and representative members of the class were also structurally characterized. The reactivity of the alkyldisulfanido TpZn(SSR) complexes with thiols was studied. In the absence of base, a simple exchange reaction between the alkyldisulfanido ligand and the thiol was observed in dichloromethane; when in the presence of base, the corresponding hydrogen(sulfido) complexes TpZn(SH) were obtained. The mechanism of the latter reaction has been studied and does not involve the coordinated alkyldisulfanido group. Reaction of the hydrogen(sulfido) complexes $Tp^{iPr,iPr}Zn(SH)$ with the thiosulfonate $PhCH_2S\text{-}SO_2CF_3$ did not yield the expected alkyldisulfanido complex but benzyltrisulfide and a new complex tentatively assigned as $Tp^{iPr,iPr}Zn(O_2SCF_3)$.

Introduction

The role of oxidized sulfur species in biology is now well documented, and in that regard oxidized disulfides have been recently proposed to be involved in the regulation of various physiological processes.[1,2] Disulfide monoxides and dioxides, while usually produced under oxidative stress conditions, are also involved in the signaling pathways of eukaryotic cells.[3−6] Another emerging class of oxidized sulfur species are the persulfides (or hydrodisulfides) R−S−S−H,[7] which predominantly serve as sulfur donors to various biomolecules.[8,9] In biology, hydrodisulfides are generated by several enzymatic systems,[8,9] including cysteine desulfurases, the physiological implication of which is now clearly assessed. They use the cofactor pyridoxal 5′-phosphate to convert cysteine to a protein-based cysteinyl persulfide and generate alanine. The terminal sulfur of the hydrodisulfide, once transferred to another cysteine in more specific acceptor proteins, is finally used in the biosynthesis of several cofactors (thiamin, iron−sulfur clusters,...) or thionucleosides (4-thiouridine,...).[8,9] Crystal structures analysis of the oxidized form of the hybrid cluster protein from sulfate reducing bacteria,[10,11] of the SoxAX protein present in photosynthetic sulfur bacteria[12] as well as of the CO deshydrogenase from *Moorella thermoacetica*[13] reveals a direct interaction between a persulfide and a metal center. This finding opens a new

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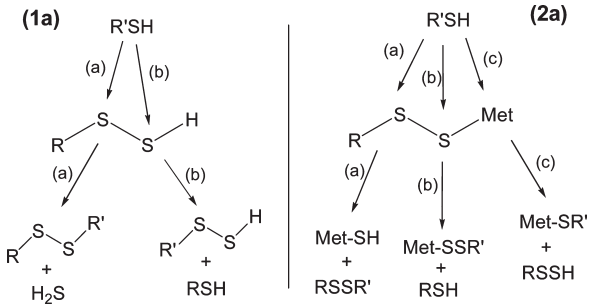
challenging field of investigation for bioinorganic chemists, since organic persulfides are generally unstable[14−17] and rapidly degraded under the conditions commonly used in inorganic synthesis, including the presence of redox active metal cations and the use of basic conditions or of polar solvents. As part of our ongoing work on the reactivity of oxidized sulfur species toward metals,[18,19] we wish to report our first results on the study of the interaction between hydrodisulfides and inorganic complexes. A number of alkyl- or aryldisulfanido derivatives have been reported in the literature,[20−29] but to the best of our knowledge this work describes the first direct rational synthesis of alkyldisulfanido complexes by the simple reaction of a metal complex with a synthetic persulfide, as well as the first alkyldisulfanido complexes of zinc to be structurally characterized.

Thiols can react with organic persulfides either at the sulfenyl (inner) sulfur (Scheme 1a, path (a)) or at the sulfhydryl (terminal) sulfur[14,15] (Scheme 1a, path (b)) leading to the formation of a disulfide (RSSR′) with release of hydrogen sulfide, or to a sulfur transfer from the hydrodisulfide (RSSH) to the thiol (R′SH) with formation of a new hydrodisulfide (R′SSH). In biology, this rich chemistry (hydrodisulfides are also nucleophiles) make the persulfide group a versatile reagent for incorporating sulfur along many metabolic pathways.[9] For instance, the release of hydrogen sulfide upon reduction of the persulfide bond by a thiol is related to the biosynthesis of 4-thiouridine and of iron−sulfur clusters[30,31] or to the vasoactivity of garlic,[32] when path (b) is related to the transfer of the active sulfur, generated by cysteine desulfurases, to the cysteine of a protein acceptor until the incorporation of the sulfur atom into an end product.[9] Binding the organic persulfide to a metal to give an alkyldisulfanido complex leads to a more complex situation with three electrophilic centers, the two sulfurs of the persulfide as described above, and the metal center, thus adding the possible formation of thiolato complexes (Scheme 1b) and subsequent reactions. In this regard, the reactivity of our alkyldisulfanido zinc derivatives toward thiols is explored in the second part of this paper.

Scheme 1. Possible Reactions between a Thiol and a Free (**1a**) or Metal Bonded (**1b**) Organic Persulfide



Results and Discussion

Synthesis and Spectroscopic Characterization of the Alkyldisulfanido Complexes. Several alkyldisulfanido metal derivatives $L_nM(SSR)$ have been reported (many if trithioperoxycarboxylates are classified as persulfides). They mostly result from unexpected side reactions,[20−22] even if some rational routes have also been described, such as the nucleophilic attack of coordinated hydrogen (sulfido)[23,24] or disulfido[25] ligands on either electrophilic carbon or sulfur centers, sulfur insertion into metal−carbon bonds,[26] or redox processes.[27−29] However, to our knowledge, no alkyldisulfanido complex derived from the simple reaction of a metal hydroxo complex with a hydrodisulfide has been reported so far. Hydridotris-(pyrazolyl)borate (Tp) ligands containing a bulky substituent at the pyrazole 3-position are known to give access to the stable albeit reactive TpZn-(OH) species.[33,34] In these complexes, the hydroxide behaves as a base or a nucleophile. Following this strategy, we used as scaffold the two sterically restricting ligands $Tp^{iPr,iPr}K$[35] and $Tp^{Ph,Me}K$, previously reported to yield stable thiolato zinc complexes by reaction between TpZn(OH) and various thiols.[36−38] Reaction of equimolar amounts of the zinc derivatives $Tp^{iPr,iPr}Zn(OH)$[33] or $Tp^{Ph,Me}Zn(OH)$[39] with *tert*-butyl hydrodisulfide *t*BuSSH[40] or triphenylmethane hydrodisulfide $(Ph)_3CSSH$[41] in non-polar solvents (heptane or dichloromethane) readily affords the

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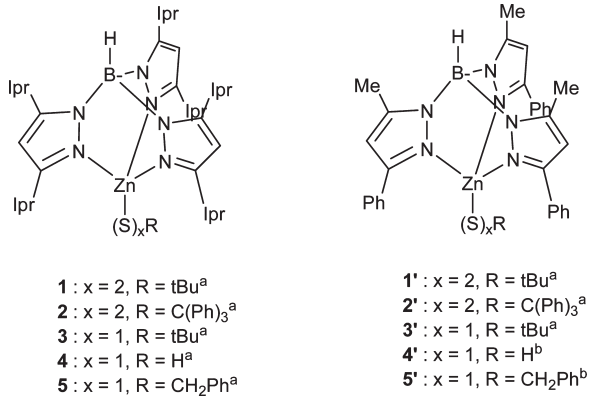

Figure 1. Complexes used in this work ([a]: this work,[b]: ref 42).

new alkyldisulfanido complexes **1**, **1′** and **2**, **2′**, respectively (Figure 1). *Deprotonation of the persulfide in the vicinity of the metallic cation is crucial to the success of this reaction*, since hydrodisulfides are rapidly decomposed into polysulfides under alkaline conditions.[16] In the case of **1′** and **2′**, ^{1}H NMR analysis of the crude mixtures only reveals the presence of the expected complexes which are isolated as analytically pure compounds in yields higher than 80%. For **1** and **2**, yields are lower because the starting complex $Tp^{iPr,iPr}Zn(OH)$ cannot be isolated in a pure form because of its very high solubility.[33] Analytically pure alkyldisulfanido complexes are nevertheless obtained by precipitation in heptane, with yields around 50%. For comparison, we also synthesized the thiolato complexes **3** and **3′** related to **1** and **1′** (Figure 1). The alkyldisulfanido complexes, like their thiolato counterparts, are stable for days in the solid state or in solution in non dissociating solvents.

As above-mentioned, ^{1}H NMR is a good spectroscopic method to characterize the new alkyldisulfanido complexes, and the analysis of their NMR spectra is straightforward. In addition to the classical features attributed to the $Tp^{iPr,iPr}$ and $Tp^{Phe,Me}$ ligands, a single peak integrating for 9H is observed and assigned to the *tert*-butyl groups in **1** (δ = 1.45 ppm in C_6D_6) and **1′** (δ = 0.56 ppm in $CDCl_3$). In **1′**, this signal is shifted upfield relative to the one in the free persulfide *t*BuSSH (δ = 1.37 ppm in $CDCl_3$) and is deshielded relative to the corresponding signal in the thiolato complex **3′** (δ = 0.38 ppm in $CDCl_3$). Shielding of the protons upon coordination of *t*BuSSH or *t*BuSH arises from the pocket created by the phenyl groups at the 3-pyrazolyl position.[42] In the thiolato complex **3′**, the protons of the *tert*-butyl group are clearly embedded inside the cavity, thus undergoing the strongest shielding; when in **1′** they lie slightly outside the cavity (see Supporting Information, Figure S4). Free rotation of the thiolate and hydrodisulfide in the pocket of the anionic tripod ligand in solution results in a C_3 symmetry, with three equivalent pyrazolyl groups and only one resonance for the *t*Bu moiety. Free rotation is also observed in **1** and **3**, but the coordination of the sulfur-containing ligands induces less variation of the chemical shifts of the *t*Bu protons. Spectra of $Tp^{iPr,iPr}Zn(SSC(Ph_3))$ **2** and $Tp^{iPr,iPr}Zn(SSC(Ph_3))$ **2′** are less informative because of the number of aromatic protons in these complexes.

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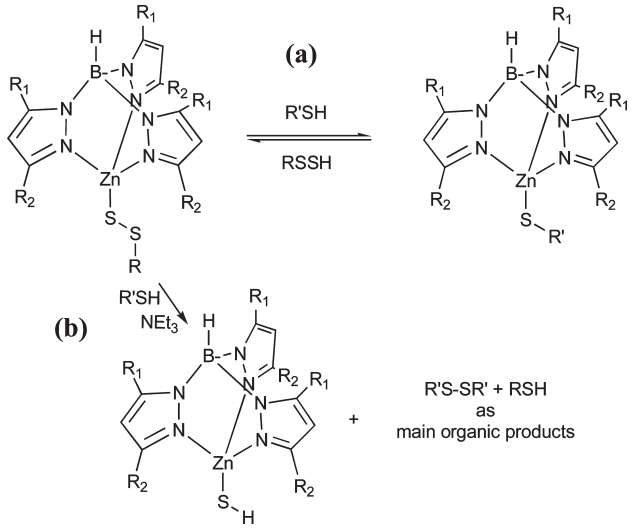
Scheme 2. Reaction of the Alkyldisulfanido Complexes with Thiols under Neutral and Basic Conditions



Structural Characterization of Complexes 2 and 2′. The crystal structures of complexes **2** and **2′** are displayed in Figure 2 (the structures of **1′** and **3′** are provided in Supporting Information, Figure S4). Crystal data and structure refinements are given in Table 1, and selected bond lengths and angles are listed in Table 2. In all the compounds, the zinc center is in a trigonally distorted tetrahedral environment, and bond lengths and angles are close to those reported for related thiolato complexes.[36,37] The Zn−S bonds distance are, however, significantly shorter (by at least 0.05 Å) than those observed in zinc trithioperoxycarboxylato derivatives.[43,44] The S−S bond distances in complexes **2** and **2′** (2.089 and 2.048 Å, respectively) are within known S−S distances for synthetic[45] or protein-bound hydrodisulfide.[46] They are also in the range of reported S−S bond lengths in disulfanido complexes.[11,20,21,24] Increasing the steric bulk of the persulfide or of the tripodal ligand leads to strongly distorted complexes, as exemplified by the structure of complex **2′**.

Reactivity of the Disulfanido Complexes with Thiols. The addition of 1 equiv of $PhCH_2SH$ to a dichloromethane solution of complex **1** or **1′** has been monitored by ^{1}H NMR (Supporting Information, Figure S1) and yields a mixture containing the starting alkyldisulfanido complex TpZn(SSR) and the thiolato complex TpZn(SCH_2Ph), as well as the free thiol $PhCH_2SH$ and the free hydrodisulfide RSSH (Scheme 2a). The closely related thiol/thiolate exchange in parent TpZn(SR) complexes has been studied in detail[36,37] and has been shown to take place via protonation of the coordinated thiolate by the competing thiol. We did not undertake such an extensive study but we propose a similar mechanism to explain our results. This is supported by the lack of

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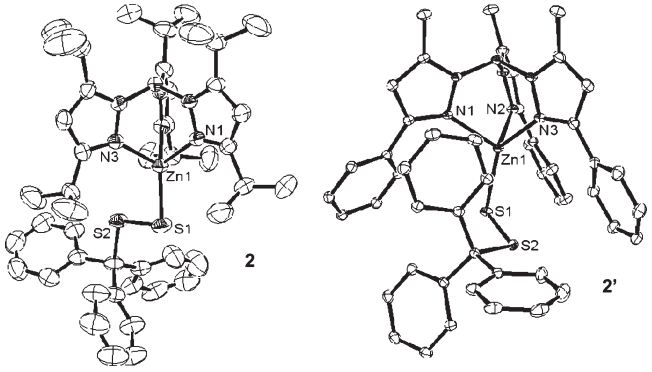

Figure 2. ORTEP views of complexes **2** and **2′** showing thermal ellipsoids at 50% probability and atom labeling. Hydrogen atoms have been omitted for clarity.

polysulfides formation during the exchange reaction, which goes against free deprotonated persulfides in solution. The relative ratio between the alkyldisulfanido and the thiolato complexes results mainly from steric interactions between the thiol and the pyrazolyl cavity: when 1 equiv of the bulky thiol *t*BuSH is added to **1** or **1′** in deuterated dichlomethane (Supporting Information, Figure S2), a strong preference is noticed for **1** and **1′** against **3** and **3′** (the ratios **1**/**3** and **1′**/**3′** are greater than 9), whereas with the less hindered $PhCH_2SH$, the *t*BuSSH hydrodisulfide is more or less displaced depending on the size of the cavity (the ratios **1**/**5** and **1′**/**5′**[42] are 0.5 and 2, respectively).

A different result is obtained when using, in place of a thiol, a mixture of a thiol and a base. Addition of 1 equiv of an equimolar solution of $PhCH_2SH$ and Et_3N to the $Tp^{iPr,iPr}Zn(SSR)$ complexes **1** or **2** results after 18 h in the formation of the corresponding hydrogen(sulfido) complexes $Tp^{iPr,iPr}Zn(SH)$ **4** in 40 and 60% yields, respectively (Scheme 2b). Increasing the ratio $PhCH_2SH/Et_3N$ to 2 leads to increased yields (74% from **1**, 70% from **1′**, 95% from **2** and 90% from **2′**) in **4** or **4′**. Complex **4′** has already been reported and thoroughly characterized by Vahrenkamp and al.,[42] and **4** is a new member of the TpZn(SH) family.[42,47,48] As all the other TpZn(SH) derivatives, **4** is easily identified by the highly shielded S*H* proton in ^{1}H NMR (−1.43 ppm in *d2*-dichloromethane) and its structure has been confirmed by X-ray diffraction (XRD) analysis (Figure 3). It shows the longest Zn−S distance (2.230 Å) in the series (average TpZn-SH[42,48] bond lengths of 2.212 Å), and other distances and angles are usual. As already noticed for this family of compounds,[42,47] no ν(SH) is observed by IR spectroscopy. In addition to the formation of **4** or **4′**, the analysis of the reaction mixture by ^{1}H NMR reveals the presence of several organic products, among which the main components are the disulfide $PhCH_2SSCH_2Ph$ and the thiol RSH. When an attractive mechanism to explain these results would be a nucleophilic attack of the deprotonated thiol on the sulfenyl sulfur of the alkyldisulfanido complex followed by protonation of the resulting sulfido zinc complex (route (a) in Scheme 1b, with R_2S^- instead of R_2SH), the traces of complexes $TpZn(SCH_2Ph)$ **5** or **5′**[42] observed at the end of each reaction goes against this explanation. Actually, monitoring the reaction by ^{1}H NMR shows that the conversion of TpZn(SSR) into TpZn(SH) proceeds in two steps (Figure 4). A first and rapid exchange reaction between the alkyldisulfanido ligand and $PhCH_2SH$ affords, as described above, the complexes **5** or **5′**. However, under basic conditions, the released hydrodisulfide is unstable and further reacts to yield polysulfides (see below), thus making this exchange an irreversible process in contrast to the equilibrium observed in the absence of base. These polysulfides have been reported to generate hydrogen sulfide by a complex mechanism.[16,32] So, in the second step, the thiolato ligand is exchanged by hydrogen sulfide and the resulting complex **4** or **4′** is the thermodynamically most stable product of the reaction since among all the sulfur-containing organic products in the mixture, hydrogen sulfide is the most acidic and the less sterically demanding. Additional support for this mechanism arises from the reaction between the thiolato complex $Tp^{iPr,iPr}Zn(SCH_2Ph)$ (**5**) and a 1/1 mixture of triphenylmethane hydrodisulfide and Et_3N (1 equiv.), which produces complex **4** in a 50% yield. Moreover, no effect of the cavity is observed on the yields in **4** and **4′** obtained from either **1** and **1′** or **2** and **2′**, essentially reflecting the different reactivities of the intermediate polysulfides. Triphenylmethane hydrodisulfide appears under our conditions to be the most efficient precursor of H_2S.

Reactivity of the Hydrogen(sulfido) Complexes with Electrophilic Sulfur-Containing Reagents. The goal of this study was to investigate the reverse reaction between the (hydrogen)sulfido complex TpZn(SH) **4** and an electrophilic sulfur-containing molecule to prepare the related alkyldisulfanido complexes. While such reactions are well documented in organometallic chemistry,[23,24,49] no such example has been reported for complexes based on nitrogen-containing ligands. For instance, the reaction of hydrogen(sulfido) ruthenium or tungsten complexes based on the cyclopentadienyl ligand with alkylthioisoindoline-1,3-dione appears a convenient route to access the corresponding alkyldisulfanido complexes. For this study, we chose three organic compounds previously used to transfer the [RS] moiety to a nucleophilic sulfur atom: the alkylthioisoindoline-1,3-dione $PhCH_2S$-Phth,[22] the thiosulfonate $PhCH_2S$-SO_2CF_3,[50] and the sulfenylthiocarbonate $PhCH_2S$-SCO_2Me.[51] Reaction of these compounds with the hydrogen(sulfido) complexes should promote the intermediate formation of a zinc-bonded protonated persulfide (Scheme 3) which could be easily deprotonated by the released phthalimido anion from $PhCH_2S$-Phth or methylthiocarbonate from $PhCH_2S$-SCO_2Me, while with the thiosulfonate the addition of an external base will be needed. The hydrogen(sulfido) zinc complexes based on hydridotris-(pyrazolyl)borate ligands have earlier been reported to be rather inert toward electrophiles.[42] However, complex **4** was found to be reactive toward the thiosulfonate, while no reaction occurred in dichloromethane with the two other substrates, even after several days. The reaction of

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Table 1. - Crystal Data and Structure Refinements for Complexes **2**, **2′**, and **4**

	2	**2′**	**4**
formula	$C_{46}H_{61}BN_6S_2Zn$	$C_{49}H_{43}BN_6S_2Zn$	$C_{27}H_{47}BN_6SZn$
fw	838.31	856.19	563.95
T(K)	296(2)	173(2)	173(2)
wavelenght (Å)	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
unit cell dimension			
a (Å)	9.713(1)	11.977(1)	9.950(1)
b (Å)	14.894(1)	12.926(1)	16.036(1)
c (Å)	16.308(1)	14.842(1)	19.411(1)
α (deg)	84.45(1)	98.18(2)	90
β (deg)	89.09(1)	111.25(2)	104.71(2)
γ (deg)	84.25(1)	97.77(2)	90
V (Å^3)	2336.3(3)	2075.8(3)	2995.7(4)
Z	2	2	4
d(calc) (Mg/m^3)	1.192	1.370	1.250
abs coeff (mm^{-1})	0.652	0.736	0.915
crystal size (mm^3)	0.50 × 0.40 × 0.25	0.35 × 0.30 × 0.20	0.54 × 0.25 × 0.12
crystal color	colorless	colorless	Colorless
θ range for data collection (deg)	1.77 − 27.00	1.50 − 33.28	1.67 − 31.70
index ranges	$-11 < h < 12$	$-18 < h < 18$	$-14 < l < 13$
	$-19 < k < 19$	$-19 < k < 19$	$-23 < k < 23$
	$-20 < l < 20$	$-22 < l < 22$	$-28 < l < 28$
reflns collected	50349	83486	79888
indep reflns	10162	15830	10131
	[R(int) = 0.045]	[R(int) = 0.0496]	[R(int) = 0.0376]
completness to θ max	99.5%	99.0%	99.7%
abs correction	none	none	none
data/restraints/params	10162/1/520	15830/4/547	10131/5/353
GOF on F^2	1.022	1.068	1.033
final R indices	R1 = 0.043	R1 = 0.028	R1 = 0.028
[$I > 2\sigma(I)$][a,b]	wR2 = 0.1214	wR2 = 0.0806	WR2 = 0.0699
R indices (all data)[a,b]	R1 = 0.066	R1 = 0.0331	R1 = 0.0420
	wR2 = 0.1377	wR2 = 0.0824	wR2 = 0.0758
largest peak and hole (e Å^{-3})	0.881 and −0.487	0.563 and −0.282	0.454 and −0.508

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; where $w = q/\sigma^2(F_O^2) + (qp)^2 + bp$. GOF $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	2	**2′**	**4**
Zn−S1	2.2447(7)	2.2598(4)	2.2300(4)
S1−S2	2.089(1)	2.0485(5)	
Zn1−N1	2.034(2)	2.0896(9)	2.0327(9)
Zn1−N2	2.035(1)	2.1084(9)	2.039(1)
Zn1−N3	2.037(1)	2.053(1)	2.032(1)
S2−S1−Zn1	92.36(3)	107.37(2)	
N1−Zn1−S1	124.06(6)	113.40(3)	124.69(3)
N2−Zn1−S1	125.09(6)	123.68(3)	123.56(5)
N3−Zn1−S1	121.38(6)	133.65(3)	124.04(3)
N1−Zn1−N2	92.68(8)	89.23(3)	92.57(4)
N2−Zn1−N3	92.14(8)	84.88(4)	91.09(4)
N1−Zn1−N3	92.47(8)	101.32(4)	91.24(4)

sulfenylthiocarbonate with thiols has been proposed to take place via a 6-membered ring transition state[51] which is probably not favored with our bulky complex, and the steric crowding around the metal may also contribute to the lack of reaction with $PhCH_2S$-Phth. Studies in more polar solvents such as methanol or DMSO were precluded because the starting complex is poorly soluble in these solvents. Complex **4** reacts rapidly with an equimolar quantity of the thiosulfonate $PhCH_2S$-SO_2CF_3 in the presence of Et_3N to give a 1/1/1 mixture of the starting complex, the trisulfide $PhCH_2S-S-SCH_2Ph$ and a new zinc derivative, as detected by ^{1}H NMR (Supporting Information, Figure S3). Addition of a second equivalent of thiosulfonate leads to a complete conversion of **4** into the trisulfide and the new zinc complex $Tp^{iPr,iPr}ZnX$, tentatively assigned as $Tp^{iPr,iPr}Zn(O_2SCF_3)$ since $CF_3SO_2^-$ is the only nucleophile remaining in solution. To support this hypothesis, trifluoromethanesulfonate, a more weakly coordinating ligand than trifluoromethanesulfinate, has been described to bind a closely related hydridotris-(pyrazolyl)borate zinc derivative to form the corresponding $TpZn(O_3SCF_3)$ complexes, although no crystal structure of this product was reported.[52] The formation of the trisulfide deserves additional comments: its formation can be rationalized by the mechanism depicted in Scheme 3, in which the hydrogen(sulfido) ligand first reacts with the thiosulfonate to give the expected protonated alkyldisulfanido complex. However, the lack of accessibility of the zinc-bonded $PhCH_2SSH$ ligand prevents its rapid deprotonation, and thus $PhCH_2SSH$ is exchanged with the trifluoromethane sulfinate anion. Once released in solution, $PhCH_2SSH$ is deprotonated with Et_3N and upon reaction with the remaining thiosulfonate yields the trisulfide. The reaction of the thiosulfonate with the persulfide anion is faster than with **4**, leading to the observed ratios.

This result highlights the complexity of the synthesis of alkyldisulfanido complexes, and validates our approach based on complexes which possess a base *within the coordination sphere of the metal* to deprotonate the per-

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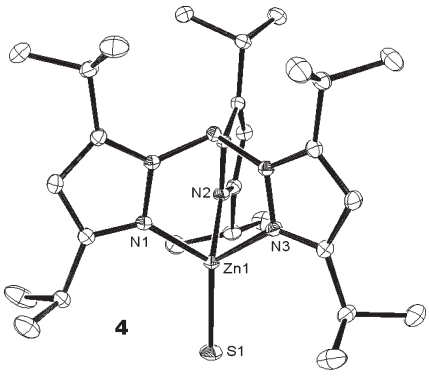


Figure 3. ORTEP views of **4** showing thermal ellipsoids at 50% probability and atom labeling. Hydrogen atoms have been omitted for clarity.

sulfide in the vicinity of the metal center and not in the bulk solution.

Conclusion

This work demonstrates that alkyldisulfanido complexes can be rationally synthesized by the direct reaction of a synthetic persulfide and an inorganic complex. The success of this strategy relies on the nature of the starting complex, which must contain a base as ligand of the metal center to avoid the formation of free deprotonated hydrodisulfide in solution and its further degradation. The alkyldisulfanido complexes react with thiols under neutral conditions to give simple exchange reactions; when under basic conditions, the formation of the corresponding hydrogen(sulfido) derivatives is observed. However, this reaction does not involve the coordinated alkyldisulfanido group, and further work needs to be done to direct the reactivity of the nucleophilic reactants toward the S−S bond rather than the metal center, to more closely reproduce biologically relevant processes. Attempts to realize the opposite reaction were unsuccessful, and we did not observe the formation of alkyldisulfanido zinc complexes by nucleophilic attack of the zinc-bound hydrogen (sulfido) ligand on substrates containing activated sulfur.

Experimental Section

Physical Measurements. ^{1}H NMR spectra were recorded at 300 K on a Bruker ARX-250 or ADVANCED II-500 spectrometer, and chemical shifts are reported in ppm downfield from TMS. IR spectra were obtained with a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with a MIRacleTM single reflection horizontal ATR unit (Zirconium−Selenium crystal). Elemental analyses were carried out by the microanalysis service at Gif-sur-Yvette CNRS.

Materials. Solvents were distilled using standard techniques and treated under argon prior to use when necessary. Chemicals were purchased from Aldrich or Acros and used as received. Hydrogen sulfide was purchased from Praxair. *tert*-Butyl hydrodisulfide tBuSSH[40] and triphenylmethane hydrodisulfide $(Ph)_3CSSH$[41] were synthesized as previously described. $Tp^{Ph,-Me}Zn(OH)$[39] and $Tp^{iPr,iPr}Zn(OH)$[33] were prepared as previously reported. $PhCH_2S\text{-}SO_2CF_3$ and $PhCH_2S\text{-}SCO_2Me$ were synthesized according to reported procedures.[50,53] $PhCH_2S$-Phth was synthesized by reaction of $PhCH_2SSO_2CF_3$ with potassium phtalimide in methanol.

Synthesis. Disulfanido Complexes 1 and 2. The crude hydroxo complex $Tp^{iPr,iPr}Zn(OH)$ was dissolved in heptane under argon at −20 °C (typically 50 mg in 1 mL), and 1 equiv of the corresponding persulfide was added. After stirring for 1 h, the white precipitate was filtrated and dried. Pure products were thus obtained, as indicated by ^{1}H NMR and elemental analysis. Yields were around 50%, depending on the purity of the starting hydroxo complexes. **$Tp^{iPr,iPr}Zn(SStBu)$ (1)**: Anal. Calcd (found) for $C_{31}H_{55}BN_6S_2Zn$: C, 57.09 (56.75); H, 8.50 (8.53); N, 12.89 (12.89). ^{1}H NMR (δ, C_6D_6): 5.84 (s, 3H), 3.46 (m, 6H), 1.45 (s, 9H), 1.28 (m, 36H). FT-IR (ATR, cm^{-1}): 2545 (ν_{BH}). **$Tp^{iPr,-iPr}Zn(SSC(Ph)_3)$ (2)**: Anal. Calcd (found) for $C_{46}H_{61}BN_6S_2Zn$: C, 65.90 (66.12); H, 7.33 (7.33); N, 10.02 (9.79). ^{1}H NMR (δ, CD_2Cl_2): 7.49 (m, 6H), 7.29 (m, 9H), 5.90 (s, 3H), 3.48 (sept, 3H, $^3J_{H-H}$ = 6.8 Hz), 3.39 (sept, 3H, $^3J_{H-H}$ = 6.8 Hz), 1.28 (d, 18H, $^3J_{H-H}$ = 6.8 Hz), 1.15 (d, 18H, $^3J_{H-H}$ = 6.8 Hz). FT-IR (ATR, cm^{-1}): 2547 (ν_{BH}).

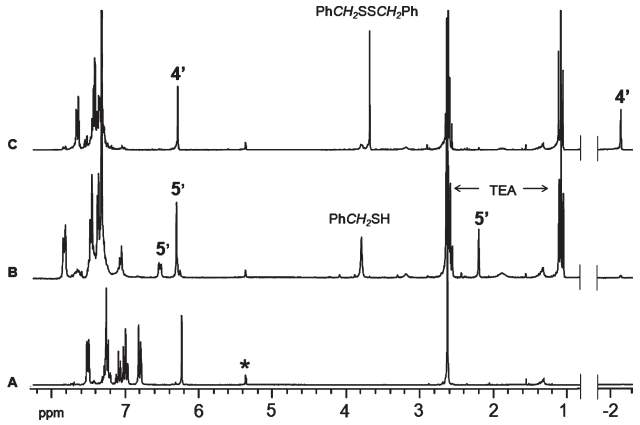


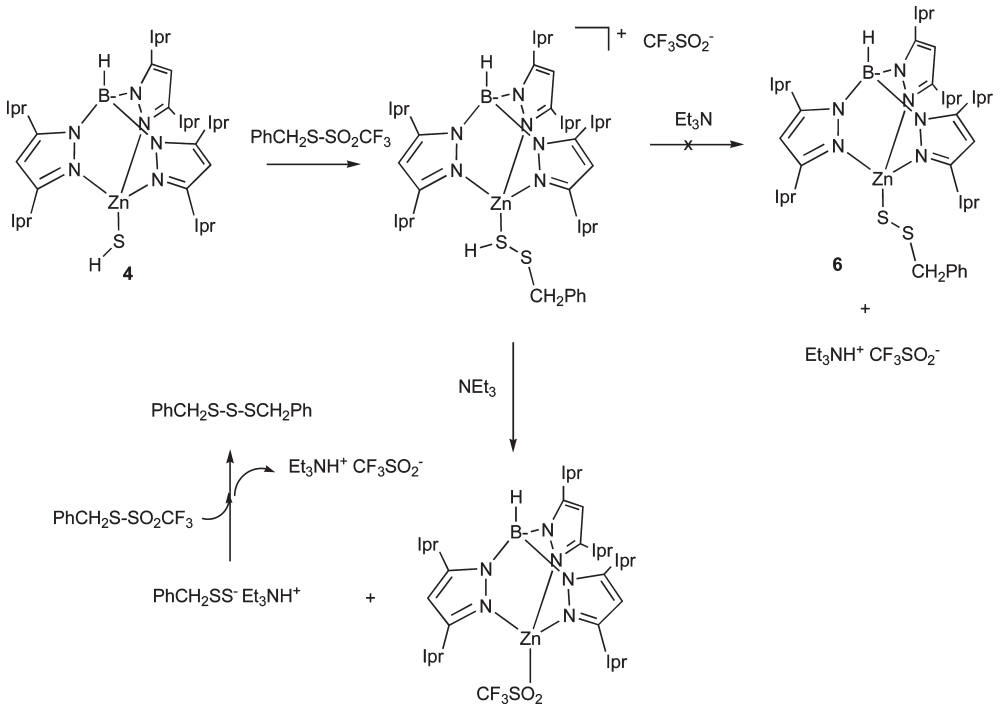
Figure 4. ^{1}H NMR monitoring of the reaction between $PhCH_2SH$ and complex **2′** under basic conditions: (**A**) spectrum of complex **2′** (400 μL of a 15 mM solution in CD_2Cl_2) recorded at 500 MHz; (**B**) spectrum recorded 2 min after the addition of $PhCH_2SH$ (2 equiv.) and Et_3N (1 equiv) (complex **5′** represents approximately 75% of the total content of zinc complexes); (**C**) spectrum recorded after 18 h (complex **4′** represents approximately 90% of the total content of zinc complexes). * indicates the residual solvent peak, TEA the signals corresponding to the Et_3N, and **4′** and **5′** the characteristic signals from the corresponding complexes.

Disulfanido Complexes 1′ and 2′. The hydroxo complex $Tp^{Ph,Me}Zn(OH)$ was dissolved in dichloromethane under argon at −20 °C (typically 50 mg in 1 mL), and 1 equiv of the corresponding persulfide was added. After stirring for 1 h, the solvent was removed, and the white powder washed with pentane. Pure products were thus obtained, as indicated by ^{1}H NMR and elemental analysis. Yields were higher than 80%. Crystals of **1′** and **2′** suitable for XRD studies were obtained by layering a benzene solution of the disulfanido complex with heptane. **$Tp^{Ph,Me}Zn(SStBu)$ (1′)**: Anal. Calcd (found) for $C_{34}H_{37}BN_6S_2Zn$: C, 60.95 (61.10); H, 5.57 (5.50); N 12.54 (12.75). ^{1}H NMR (δ, $CDCl_3$): 7.93 (m, 6H), 7.63 (m, 9H), 6.26 (s, 3H), 2.83 (s, 9H), 0.56 (s, 9H). FT-IR (ATR, cm^{-1}): 2545 (ν_{BH}). **$Tp^{Ph,Me}Zn(SSC(Ph)_3)$ (2′)**: Anal. Calcd (found) for $C_{49}H_{43}BN_6S_2Zn$: C, 68.73 (68.42); H, 5.06 (5.17); N 9.82 (9.69). ^{1}H NMR (δ, CD_2Cl_2): 7.51 (m, 6H), 7.26 (m, 9H), 7.03 (m, 9H), 6.81 (m, 6H), 6.24 (s, 3H), 2.63 (s, 18H). FT-IR (ATR, cm^{-1}): 2546 (ν_{BH}).

$Tp^{iPr,iPr}Zn(StBu)$ (3). A 63 mg portion (0.11 mmol) of $Tp^{iPr,iPr}Zn(OH)$ was dissolved in 2 mL of heptane under argon at 0 °C, and 1 equiv of *tert*-butyl mercaptan (12 μL, 0.11 mmol) added. After stirring for 1 h, the white precipitate was filtered and dried to give 41 mg of **3** (60%). Anal. Calcd (found) for $C_{31}H_{55}BN_6SZn\cdot 1.3H_2O$: C, 60.05 (59.94); H, 8.94 (9.11); N, 13.55 (13.61). ^{1}H NMR (δ, C_6D_6): 5.99 (s, 3H), 4.08 (sept, 3H, $^3J_{H-H}$ = 6.7 Hz), 3.64 (sept, 3H, $^3J_{H-H}$ = 6.7 Hz), 1.97 (s, 9H), 1.39 (d, 18H, $^3J_{H-H}$ = 6.7 Hz), 1.25 (d, 18H, $^3J_{H-H}$ = 6.7 Hz). FT-IR (ATR, cm^{-1}): 2541 (ν_{BH}).

(53) Harpp, D. N.; Granata, A. *J. Org. Chem.* **1980**, *45*(2), 271.

Scheme 3. Proposed Mechanism for Reaction of **4** with the Thiosulfonate $PhCH_2S\text{-}SO_2CF_3$



$Tp^{Ph,Me}Zn(StBu)$ (3′). A 48 mg portion (0.085 mmol) of $Tp^{Ph,Me}Zn(OH)$ was dissolved in 3 mL of dichloromethane under argon at 0 °C, and 1 equiv of *tert*-butyl mercaptan (10 μL, 85 mmol) added. After stirring for 1 h, the volatiles were removed, and the product crystallized by slow diffusion of hexane in a benzene solution of **3′** to give 44 mg of colorless crystals (81%). Anal. Calcd (found) for $C_{34}H_{37}BN_6SZn$: C, 64.01 (63.77); H, 5.85 (5.77); N 13.17 (13.42). ^{1}H NMR (δ, $CDCl_3$): 7.71 (d, 6H, ^3J = 8.4 Hz), 7.40 (m, 9H), 6.20 (s, 3H), 2.58 (s, 9H), 0.38 (s, 9H). FT-IR (ATR, cm^{-1}): 2549 (ν_{BH}).

$Tp^{iPr,iPr}Zn(SH)$ (4). A 150 mg portion of crude $Tp^{iPr,iPr}$-Zn(OH) was dissolved in 3 mL of heptane under argon at 0 °C, and H_2S was passed through the solution for 1 min. The solution was then filtered, and the white precipitate dried under vacuum to give 94 mg of pure **5**. Crystals suitable for XRD studies were obtained by layering a benzene solution of **5** with heptane. Anal. Calcd (found) for $C_{27}H_{47}BN_6SZn$: C, 57.50 (57.76); H, 8.40 (8.38); N 14.90 (15.07). ^{1}H NMR (δ, CD_2Cl_2): 5.92 (s, 3H), 3.48 (sept, 3H, $^3J_{H-H}$ = 6.7 Hz), 3.36 (sept, 3H, $^3J_{H-H}$ = 6.7 Hz), 1.28 (d, 18H, $^3J_{H-H}$ = 6.7 Hz), 1.26 (d, 18H, $^3J_{H-H}$ = 6.7 Hz), −1.43 (s, 1H). FT-IR (ATR, cm^{-1}): 2545 (ν_{BH}).

$Tp^{iPr,iPr}Zn(SCH_2Ph)$ (5). A 91 mg portion of crude $Tp^{iPr,iPr}$-Zn(OH) was dissolved in 2 mL of heptane under argon at 0 °C, and 20 μL of benzyl mercaptan (0.17 mmol) were added. After stirring for 1 h, the solution was filtered, and the white precipitate dried under vacuum to give 48 mg of **5** (44% based on benzyl mercaptan). Anal. Calcd (found) for $C_{34}H_{53}BN_6SZn$: C, 62.43 (62.41); H, 8.17 (8.13); N 12.85 (12.89). ^{1}H NMR (δ, CD_2Cl_2): 7.51 (m, 2H), 7.36 (m, 2H), 7.28 (m, 1H), 5.94 (s, 3H), 4.04 (s, 2H), 3.50 (sept, 3H, $^3J_{H-H}$ = 6.7 Hz), 3.32 (sept, 3H, $^3J_{H-H}$ = 6.7 Hz), 1.29 (d, 18H, $^3J_{H-H}$ = 6.7 Hz), 1.27 (d, 18H, $^3J_{H-H}$ = 6.7 Hz). FT-IR (ATR, cm^{-1}): 2546 (ν_{BH}).

Reactivity of the Disulfanido Complexes. Reactivity studies were performed as follows: to a 15 mM solution (400 μL) of the disulfanido complex in CD_2Cl_2 were added the corresponding reactants. The progress of the reaction was monitored by ^{1}H NMR spectroscopy at 27 °C, and the yields determined after 18 h.

Reactivity of the Hydrogen(sulfido) Complexes. Reactivity studies were performed as follows: to a 15 mM solution (400 μL) of the hydrogen(sulfido) complex in CD_2Cl_2 were added the corresponding reactants. The progress of the reaction was monitored by ^{1}H NMR spectroscopy at 27 °C.

X-ray Data Collection and Structural Determination. Crystal data and experimental conditions are listed in Table 1. The drawings of the molecules were realized with ORTEP III.[54]

Structural Data for 2, 2′, and 4. Data were collected with a Bruker SMART APEX CCD diffractometer. The crystals were cooled to 173(2) K using the OXFORD CRYOSTREAM 700 low-temperature device for **2′** and **4**. Intensity measurements were performed using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data integration and global cell refinement were performed with the program SAINT.[55] The structure were solved by direct methods using SHELXS 97.[56] Refinement, based on F^2, were carried out by full matrix least-squares with SHELXL-97 software.[57] Non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were placed in their geometrically generated positions and allowed to ride on their parent atoms with an isotropic thermal parameter 20% higher to that of the atom of attachment. H atoms attached to B atoms were deduced from a difference Fourier map and were refined with isotropic temperature factor.

Supporting Information Available: Crystallographic data for complexes **1′**, **2**, **2′**, **3′**, and **4** in CIF format and Figures S1−S4 as a PDF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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