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Synthesis, Stability, and Reactivity of $[(TPA)Zn(SH)]^+$ in Aqueous and Organic Solutions

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Reaction of the complex $[(TPA)Zn(H_2O)]^{2+}$ [TPA = tris(2-pyridylmethyl)amine] with hydrogen sulfide in aqueous buffered solution gives the corresponding monomeric hydrogensulfido complex $[(TPA)Zn(SH)]^+$, which was fully characterized, including by XRD. This complex is stable at neutral pH, but decomposes under basic conditions to yield the free ligand and zinc sulfide, and under acidic conditions to give hydrogen sulfide and the starting aqua complex. In organic solvents, the coordinated sulfur atom reacts with electrophiles such as methylmethanethiosulfonate to yield methyltrisulfide. Reaction with the hydroxo complex $[(Tp^{Ph,Me})Zn(OH)]$ [$Tp^{Ph,Me}$ = hydridotris{(5-methyl-3-phenyl)pyrazolyl}borate] promotes the formation of the unsymmetrical dinuclear μ-sulfido species $[(TPA)Zn–S–Zn(Tp^{Ph,Me})]^+$, which, upon treatment with one molar equivalent of trifluoroacetic acid, dissociates into $[(Tp^{Ph,Me})Zn(SH)]$ and $[(TPA)Zn(CF_3CO_2)]^+$, resulting in the transfer of the hydrogensulfido ligand from one zinc center to another.

Introduction

Hydrogen sulfide (H_2S) is well known to be a major player in the metabolism of exotic organisms as a source of electrons or as the final product in the reduction of oxidized sulfur derivatives.[1] It has also emerged as a new gasotransmitter in mammals, along with nitric oxide and carbon monoxide. In living organisms, H_2S can react with several hemoproteins, such as haemoglobin, which can be converted to sulfhaemoglobin,[2] or cytochrome c oxidase, which has been proposed as a biomarker for H_2S exposure.[3] Apart from iron, zinc is also known to interact with hydrogen sulfide in biological systems. For instance, HS^- strongly inhibits isoforms of carbonic anhydrase,[4] and zinc has been proposed to be closely associated to sulfide binding and transport in some chemoautotrophic organisms.[5] However, the coordination chemistry of hydrogen sulfide has been essentially directed towards organometallic chemistry so far, with a strong interest in hydrodesulfurization processes (removal of sulfur from natural gas and refined petroleum products) and the catalytic conversion of hydrogen sulfide to hydrogen,[6] whereas bioinorganic studies are more scarce and focus on the interaction of hydrogen sulfide with hemoproteins.[7]

We, and others, have isolated hydrogensulfido zinc derivatives, either by direct reaction of a hydroxo derivative with hydrogen sulfide,[8] or as the end product of the reaction between an alkyldisulfanido complex and a thiolate in apolar aprotic solvents.[9] To date, isolation of stable hydrogensulfido zinc complexes has required bulky apolar ligands, based either on substituted hydridotris(pyrazolylborate)[8a,9,10] or hydridotris(thioimidazolyl)borate,[11] and using azamacrocyclic ligands only led to degradation.[12] Because hydrogen sulfide exists in three different forms (H_2S, HS^-, and S^{2-}), which can potentially bind transition metals, its biological properties involving interaction with a metal center are dependent on the presence of protons in the local environment. Here, we report that with a simple scaffold, such as tris(2-pyridylmethyl)amine (TPA, Figure 1), a stable hydrogensulfido zinc complex can be formed in aqueous buffered solution as well as in organic solvents.

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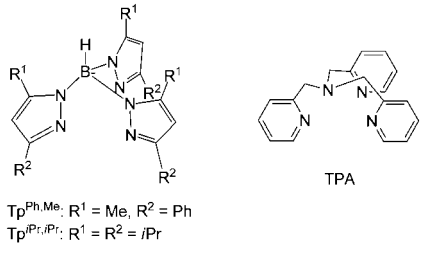


Figure 1. Ligands used or cited in this work.

The stability of the complex and its reactivity towards oxidized sulfur species and other zinc complexes is also discussed.

Results and Discussion

Formation and Stability of the Hydrogensulfido Complex in Aqueous Solution

Mixing TPA with one equivalent of hydrated zinc nitrate in 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer affords the corresponding aqua complex $[(TPA)Zn(H_2O)](NO_3)_2$ [**1**$(NO_3)_2$],[13] the reactivity of which can be easily monitored by ^{1}H NMR spectroscopy.[14] Indeed, addition of KSH to a buffered solution of **1**$(NO_3)_2$ in HEPES (50 mM, pH = 7.1) results in a clear shift of the *ortho*-H of the pyridine moieties from 8.62 to 8.76 ppm after addition of 1 equiv. of KSH (see Figure 2), indicating the formation of a new species **2**(NO_3). However, addition of more than one equivalent of hydrogen sulfide leads to the appearance of signals of free TPA (Figure 2) along with the precipitation of zinc sulfide.

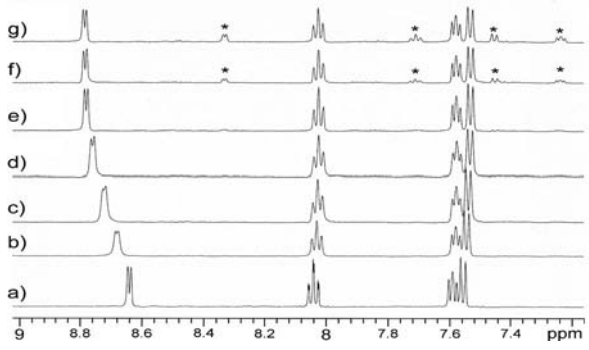


Figure 2. Aromatic region of the ^{1}H NMR spectra recorded at 500 MHz of complex **1**$(NO_3)_2$ (4 mM in HEPES buffer 50 mM, pH = 7.1) after addition of 0 (a), 0.25 (b), 0.50 (c), 0.75 (d), 1.00 (e), 1.25 (f), and 2.00 (g) equiv. of KSH. * indicates the signals from the free ligand TPA.

The new complex **2**(NO_3) has been characterized by mass spectrometry and NMR spectroscopy. It shows a peak at m/z = 387 (100%) by ESI$^+$-MS, corresponding to $[(TPA)Zn(SH)]^+$. Its ^{1}H NMR spectrum, recorded in H_2O instead of D_2O, shows a typical signal at –0.86 ppm integrating for one proton assigned to the S*H* proton, as in previous hydrogensulfido zinc complexes.[8b,9] We also separately synthesized **2**(ClO_4) by reaction of TPA, $Zn(ClO_4)_2{\cdot}6H_2O$, and KSH in methanol. This complex was obtained as analytically pure microcrystals, and it displays the same ^{1}H NMR and MS spectra as **2**(NO_3). For full characterization, we exchanged the perchlorate anion to a tetraphenylborate anion, which yielded crystals suitable for XRD analysis.

The ORTEP view of **2**(BPh_4) is displayed in Figure 3 and shows a mononuclear complex in which the zinc center is in a slightly distorted trigonal bipyramidal N_4S geometry. The Zn–S bond is the longest reported for hydrogensulfido zinc derivatives, probably because the metal is in a N_3S environment in the other complexes.[8a,9,10] However, it is within the range of reported Zn–S distances for N_4S thiolate containing complexes.[12,15] As in the other hydrogensulfido zinc derivatives, no ν(SH) is observed by IR spectroscopy.

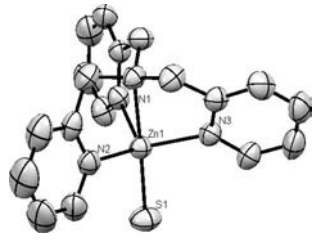
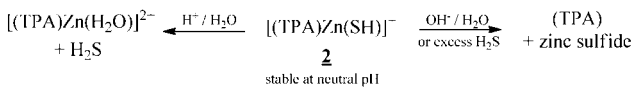


Figure 3. ORTEP view of complex **1**(BPh_4) showing thermal ellipsoids at 50% probability and atom labeling. Hydrogen atoms and the BPh_4 anion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–N1 2.0985, Zn1–N2 2.114, Zn1–N3 2.1169, Zn1–N4 2.2968, Zn1–S1 2.3060, N1–Zn1–N2 113.92, N2–Zn1–N3 115.94, N1–Zn1–N3 112.69, N1–Zn1–S1 104.91, N2–Zn1–S1 102.26, N3–Zn1–S1 105.45, N4–Zn1–S1 178.17, N1–Zn1–N4 75.78, N2–Zn1–N4 75.92, N3–Zn1–N4 75.69.

Stability of 2 in Aqueous Solution

Once formed, the hydrogensulfido complex **2**(NO_3) is stable in aqueous solution for days. Although the affinity constant between the zinc complex and HS^- could not be directly deduced from the NMR spectroscopic data,[16] a K_{app} value has been evaluated by competition experiments with sodium phenyl phosphate, a substrate of known affinity,[14] and was found in the same order ($\log K_{app}$ = 3.9 ± 0.2).

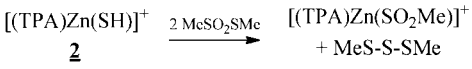
This behavior is different under acidic or basic conditions (Scheme 1). On addition of one equivalent of perchloric acid to a solution of **2**(ClO_4) in a 1:9 mixture of $[D_6]$-DMSO and D_2O, the ^{1}H NMR spectrum reverts back to the spectrum of the aqua derivative, indicating that the resulting $[(TPA)Zn(SH_2)]^{2+}$ complex is not stable, which leads to the subsequent release of H_2S in solution (see Figure S1 in the Supporting Information). Similarly, under the same conditions, addition of one equivalent of sodium hydroxide to **2**(ClO_4) leads to the release of the TPA ligand in solution as the major identified process (75%), with concomitant precipitation of zinc sulfide (Figure S2). This is in accordance with the reported instability of hydrogensulfido zinc derivatives in the presence of strong bases in organic solvents.[8b]



Scheme 1. Stability of **2** in aqueous solution.

Reactivity of the 2 towards Electrophiles or Other Zinc Complexes in Organic Solvents

Our previous study on the reactivity of the hydrogensulfido zinc complex Tp^{iPr,iPr}Zn(SH) [Tp^{iPr,iPr} = hydridotris{(3,5-isopropyl)pyrazolyl}borate] was hampered by its lack of solubility in polar solvents.[9] In contrast **2**(ClO_4) is soluble in CH_2Cl_2 and DMSO, and its reactivity could be more thoroughly investigated. Although the outcome of the reaction between **2**(ClO_4) and the thiosulfonate MeS–SO_2Me (Scheme 2 and Figure S3) is not affected by the solvent, replacing CH_2Cl_2 with DMSO in the reaction with the less reactive sulfenylthiocarbonate $PhCH_2S$–SCO_2Me has a dramatic impact. Indeed, there is no reaction in CH_2Cl_2 between **2**(ClO_4) and 2 equiv. of $PhCH_2S$–SCO_2Me [a result that recalls our previous work with Tp^{iPr,iPr}Zn(SH)].[9] However, **2**(ClO_4) quickly reacts in DMSO to quantitatively yield the corresponding trisulfide $(PhCH_2S)_2S$.

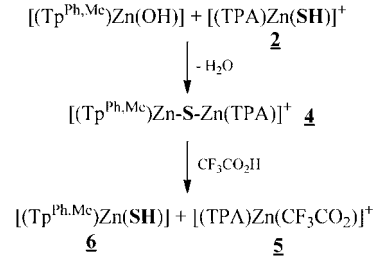


Scheme 2. Reactivity of **2** with MeS–SO_2Me.

As detailed above, the stability of **2** in aerated aqueous buffer or organic solvents suggests a tight binding of the hydrogensulfido group to the metal center, precluding a simple exchange with another complex in solution. However, the transfer of the hydrogensulfido ligand from one zinc center to another metallic center is an attractive target that maybe relevant in the sulfide binding to the tubeworm hemoglobin reported by Flores et al.,[5] and we anticipated that it could take place by the formation of a dinuclear μ-sulfido derivative. In this regard, we used a strategy that we had previously used to isolate alkyldisulfanido complexes from the corresponding hydrodisulfide,[9] which are, like complex **2**, sensitive to basic conditions. Indeed, reaction of [(Tp^{Ph,Me})Zn(OH)][17] [Tp^{Ph,Me} = hydridotris{(5-methyl-3-phenyl)pyrazolyl}borate] with one molar equivalent of **2**(ClO_4) or **2**(BPh_4) in a mixture of acetone and CH_2Cl_2, gave rise to the formation of a new product identified as [(TPA)Zn–S–Zn(Tp^{Ph,Me})]$^+$ (**4**) by MS and NMR spectroscopy, as well as elemental analysis. The mass spectrum (Figure S4) of the crude mixture displays a peak at *m*/*z* = 937 (ESI$^+$, 100%), with the isotopic pattern expected for the dinuclear cation of **4**. This structure is further confirmed by NMR spectroscopy. The aromatic protons at the 5-position of the pyrazolyl groups are strongly shifted upfield relative to those of the mononuclear species, a feature observed in all dinuclear zinc derivatives bearing aromatic groups on a Tp backbone.[8a] Furthermore, the $^1H^1H$ NOESY experiment shows that the two ligands TPA and Tp are in close proximity (Figure S5). Finally, this dinuclear structure is also in accordance with the elemental analysis obtained for **4**(BPh_4). To the best of our knowledge, **4** is the first nonsymmetrical μ-sulfido zinc species reported. The only other noncluster example is Tp^{Cum,Me}Zn–S–ZnTp^{Cum,Me} [Tp^{Cum,Me} = hydridotris{(3-*p*-cumenyl-5-methyl)pyrazolyl}borate] reported by Vahrenkamp et al., which was obtained by thermal condensation of the corresponding hydrogensulfido derivatives.[8a,18]

This new species is sensitive to traces of acid, and addition of one equivalent of trifluoroacetic acid to **4** leads to the formation of a 1:1 mixture of [(TPA)Zn(CF_3CO_2)]$^+$ (**5**) (see Figure S6 and Exp. Sect.) and of the known hydrogensulfido complex Tp^{Ph,Me}Zn(SH) (**6**).[8b] The striking selectivity in favor of the formation of **6** can be rationalized on the basis of a higher affinity of the N_3Zn site than the N_4Zn one for the anionic hydrogensulfido ligand, a result that is in agreement with the shorter Zn–S distance observed in **6**[8b] than **2**. Complex **6** has already been described as a thermodynamic sink in previous studies.[8b,9]

Thus, the transfer of the hydrogensulfido ligand from one metal center to another is possible through the formation of a μ-sulfido dinuclear species (Scheme 3).



Scheme 3. Reactions leading to hydrogensulfido transfer from one zinc center to the other.

Conclusions

We have shown that in aqueous buffered solution hydrogen sulfide binds the zinc center of the complex [(TPA)-$Zn(H_2O)]^{2+}$ strongly to give the corresponding monomeric hydrogensulfido complex [(TPA)Zn(SH)]$^+$ (**2**). Regarding the possible role of zinc in the sulfide binding in hydrothermal vent tubeworms, we have identified two possible pathways leading to the cleavage of the zinc–sulfur bond: i) hydrogen sulfide can be released in solution in acidic media; ii) more interestingly, the hydrogensulfido ligand can be transferred to a zinc center of higher affinity through the intermediate formation of a μ-sulfido dinuclear species. This transfer can be very selective as the relative affinities of the two cations for HS^- are markedly different. Moreover, the requirement of only one equivalent of an acid supports the idea that this transfer could be regulated by the local proton environment in biological systems.

Experimental Section

General: ^1H NMR spectra were recorded at 300 K with a Bruker ARX-250 spectrometer or at 500 MHz with an AVANCE II-500 spectrometer and chemical shifts are calibrated by the residual solvent peak.[19] Elemental analyses were carried out by the microanalysis service at Gif-sur-Yvette CNRS. Solvents were distilled

using standard procedures. Chemicals were purchased from Aldrich or Acros and used as received. TPA, $Tp^{Ph,Me}Zn(OH)$, and potassium hydrosulfide were synthesized as described previously.[17,18,20] Deuterated HEPES buffer was prepared by dissolving HEPES free acid in D_2O and adjusting the pH with NaOD.

[(TPA)Zn(SH)]ClO_4 [2(ClO_4)]: TPA (500 mg, 1.72 mmol) and $Zn(ClO_4)_2·6H_2O$ (641 mg, 1.72 mmol) were stirred for 5 min in methanol (20 mL) at room temp. KSH (124 mg, 1.72 mmol) was added, and the reaction mixture stirred for 1 h. After filtration of the slightly yellow precipitate, the organic phase was concentrated and left to stand at room temp., to give yellow crystals of **2**(ClO_4) (320 mg, 38%). ^{1}H NMR (DMSO): δ = 8.91 (d, $^3J_{H,H}$ = 4.8 Hz, 3 H), 8.13 (t, $^3J_{H,H}$ = 7.7 Hz, 3 H), 7.68 (m, 6 H), 4.22 (s, 6 H), –1.37 (s, 1 H) ppm. MS (ESI$^+$): 387 [100%, {(TPA)Zn(SH)}$^+$]. $C_{18}H_{19}ClN_4O_4SZn·0.5H_2O$ (504.97): calcd. C 68.73, H 5.06, N 9.82; found C 68.42, H 5.17, N 9.69. The perchlorate anion was further exchanged for a tetraphenylborate by mixing equimolar amounts of **2**(ClO_4) and $NaBPh_4$ in methanol for 1 h, followed by filtration. Crystal suitable for XRD analysis were grown from a CH_2Cl_2/heptane mixture.

[(TPA)Zn(SO_2Me)]BPh_4 [3(BPh_4)]: TPA (70 mg, 0.24 mmol) and $Zn(ClO_4)_2·6H_2O$ (90 mg, 0.24 mmol) were stirred for 5 min in methanol (3 mL) at room temp. $MeSO_2Na$ (32 mg, 0.26 mmol) was added, and the reaction mixture stirred for 30 min. After filtration of the precipitate, a solution of $NaBPh_4$ (82 mg) in methanol (2 mL) was added and the slurry was stirred for 15 min. After filtration, **3**(BPh_4) was obtained as a pale yellow powder (125 mg, 69%). ^{1}H NMR (DMSO): δ = 8.95 (d, $^3J_{H,H}$ = 4.7 Hz, 3 H), 8.04 (t, $^3J_{H,H}$ = 7.9 Hz, 3 H), 7.61 (m, 3 H), 7.55 (d, $^3J_{H,H}$ = 7.9 Hz, 3 H), 7.18 (m, 8 H), 6.92 (t, $^3J_{H,H}$ = 7.3 Hz, 8 H), 6.79 (t, $^3J_{H,H}$ = 7.3 Hz, 4 H), 4.31 (s, 6 H), 2.47 (s, 3 H) ppm. MS (ESI$^+$): 433 [50%, {(TPA)Zn(SO_2Me)}$^+$]. $C_{43}H_{41}BN_4O_2SZn·0.7NaClO_4$ (839.39): calcd. C 61.50, H 4.92, N 6.67; found C 61.48, H 5.04, N 6.50.

[(TPA)Zn-S-Zn($Tp^{Ph,Me}$)]BPh_4 [4(BPh_4)]: Complex **3**·BPh_4 (45 mg, 0.06 mmol) was dissolved in distilled acetone (3 mL) and added at 0 °C to a solution of $Tp^{Ph,Me}Zn(OH)$ (36 mg) in distilled CH_2Cl_2 (1.5 mL). The mixture was stirred for 30 min, concentrated, and a white powder obtained after addition of pentane (51 mg, 60%). ^{1}H NMR ([D$_6$]acetone): δ = 9.10 (d, $^3J_{H\text{-}H}$ = 5.1 Hz, 3 H, H_{TPA}), 8.02 (dt, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.5 Hz, 3 H, H_{TPA}), 7.8 (m, 6 H, H_{Tp}), 7.51 (d, $^3J_{H,H}$ = 7.6 Hz, 3 H, H_{TPA}), 7.37 (m, 11 H, H_{TPA}, H_{BPh4}), 6.93 (t, $^3J_{H,H}$ = 7.1 Hz, 8 H, H_{BPh4}), 6.88 (m, 9 H, H_{Tp}), 6.78 (t, $^3J_{H,H}$ = 7.1 Hz, 4 H, H_{BPh4}), 6.33 (s, 3 H, H_{Tp}), 4.02 (s, 6 H, H_{TPA}), 2.68 (s, 9H H_{Tp}) ppm. MS (ESI$^+$): 937 [100%, {(TPA)Zn–S–Zn($Tp^{Ph,Me}$)}$^+$]. $C_{72}H_{66}B_2N_{10}SZn_2·1.5H_2O$ (1282.36): calcd. C 67.41, H 5.42, N 10.52; found C 67.46, H 5.29, N 10.92.

[(TPA)Zn(CO_2CF_3)]BPh_4 [5(BPh_4)]: TPA (70 mg, 0.24 mmol) and $Zn(ClO_4)_2·6H_2O$ (90 mg, 0.24 mmol) were stirred for 5 min in methanol (3 mL) at room temp. CF_3CO_2Na (36 mg, 0.26 mmol) was added, and the reaction mixture stirred for 30 min. After filtration of the precipitate, a solution of of $NaBPh_4$ (82 mg) in methanol (2 mL) was added and the slurry was stirred for 15 min. After filtration, **5**(BPh_4) was obtained as a white powder (117 mg, 62%). ^{1}H NMR (DMSO): δ = 8.67 (d, $^3J_{H,H}$ = 5.1 Hz, 3 H), 8.00 (dt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.5 Hz, 3 H), 7.56 (m, 3 H), 7.52 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H), 7.18 (m, 8 H), 6.93 (t, $^3J_{H,H}$ = 7.3 Hz, 8 H), 6.79 (t, $^3J_{H,H}$ = 7.3 Hz, 4 H), 4.40 (s, 6 H) ppm. MS (ESI$^+$): 467 [100%, {(TPA)Zn(CO_2CF_3)}$^+$]. $C_{44}H_{38}BF_3N_4O_2Zn·H_2O$ (805.71): calcd. C 65.57, H 5.00, N 7.07; Found C 65.51, H 4.86, N 6.94.

^{1}H NMR Experiments with 1(NO_3)$_2$:[13] $Zn(NO_3)_2·6H_2O$ (14.9 mg, 0.05 mmol) and TPA (14.5 mg, 0.05 mmol) were dissolved in deuterated HEPES buffer (5 mL, 50 mM, pH = 7.1). A portion of this solution (200 µL) was added to deuterated buffer (300 µL) in an NMR tube to make a 4 mmol solution of **1**(NO_3)$_2$, and a solution of KSH in deuterated HEPES buffer was added.

Competitive ^{1}H NMR Titration Experiment with Sodium Phenyl Phosphate:[14] To a solution of **1**(NO_3)$_2$ in HEPES buffer were added two equiv. of sodium phenyl phosphate, then increasing amounts of KSH in a buffer solution. The reverse reaction, in which two equiv. of KSH were added to **1**(NO_3)$_2$ and then increasing amounts of Na_2PP added was also performed. Fitting of the NMR spectroscopic data gave an equilibrium constant K_{app} = 2.0 ± 0.2 for the equation: [(TPA)Zn(PP)] + HS^- = [(TPA)Zn-(SH)]$^+$ + PP^{2-}.

Reactivity Studies of 2(ClO_4): to a solution of **2**(ClO_4) (400 µL, 15 mM) in DMSO was added the corresponding reactants. The progress of the reaction was monitored by ^{1}H NMR spectroscopy.

X-ray Data Collection and Structural Determination: Data collection on **2**(BPh_4) was performed with monochromated Mo-K_α radiation (λ = 0.71073 Å) with a Nonius Kappa detector at 293 K, using the HKL package for data collection and reduction.[21] Triclinic unit cell parameters: a = 9.5319(9), b = 20.0933(18), c = 21.3640(19) Å, α = 82.238(2), β = 83.042(2) γ = 79.536(2)°, V = 3967.2(6) Å^3, Z = 2 and d(calc) = 1.182 mg m^3, yielded 21035 total reflections to a $2\theta_{max}$ = 58.44°. The structure was solved by direct methods in the space group $P\bar{1}$ using SHELXS-97[22] and refined by least-squares methods on F^2 using SHELXL-97.[23] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically generated positions and were allowed to ride on their parent atom with an isotropic thermal parameter 1.2 times of those of the attached atoms. H atoms attached to S atoms were refined with an isotropic temperature factor. For all 21035 unique reflections and 889 variables, the final anisotropic full-matrix least-squares refinement on F^2 at $R1$ = 0.0451 and wR_2 = 0.1293 with a goodness of fit (Gof) of 1.081. In the final cycles of refinements, the peak pattern of electron density suggested that part of solvent was highly disordered; attempts to model this disorder were unsuccessful. In the final cycles of refinement, the contribution to electron density corresponding to the disordered solvent was removed from the observed data using the SQUEEZE option in PLATON.[24] The resulting data vastly improved the precision of the geometric parameters for the remaining structure.

CCDC-817629 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Figures S1–S6 and crystallographic data for **2**(BPh_4).

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