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Structure of $[Ni(dippe)(\mu-S)]_2$ and its reaction products. The nucleophilicity of the Ni₂S₂ fragment

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Dedicated to the memory of Professor Luigi Venanzi

Abstract

The dimer $[(dippe)Ni(\mu-S)]_2$ reacts with organic electrophiles to give the alkylated species $[(dippe)_2Ni_2(\mu-S)(\mu-SR)]^+$. Stronger alkylating agents lead to double alkylation and cleavage of the dimer. Protonation similarly occurs with strong acids. The structures of several of these species have been determined. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Our group reported recently the desulfurization of dibenzothiophene by $[Ni(dippe)(\mu-H)]_2$ to produce



biphenyl [1]. Alkylated dibenzothiophenes also were found to be reactive. Four transition metal complexes were identified as intermediates in the reaction, two of which were observed to contain bridging sulfido ligands, $[Ni_2(dippe)_2(\mu-S)]$ and $[Ni(dippe)-(\mu-S)]_2-\mu-Ni-$ (2,2'-biphenyl) (Scheme 1). A third related bis- μ -sulfido complex $[Ni(dippe)(\mu-S)]_2$ was also prepared.

These dinuclear nickel bridging sulfido species proved to be quite interesting for several reasons. First, the structures of $[Ni_2(dippe)_2(\mu-S)]$ and $[Ni(dippe)(\mu-S)]_2$ most closely approximate the edge site of a heterogeneous MoCoS catalyst that is used in the large scale hydrodesulfurization of petroleum [2]. Second, we have suggested that $[Ni(dippe)(\mu-S)]_2$ results from the combination of two molecules of Ni(dippe)S, whose transient existence has been demonstrated to be possible (Eq. (1)) [3].



Third, its behavior as a bidentate metalloligand toward [Ni(2,2'-biphenyl)] suggests its utility as a reagent in the synthesis of more complex organometallic compounds. While the mechanism for formation of the adduct with [Ni(2,2'-biphenvl)] remains unclear, one analysis of analogous $[Pt_2(\mu-S)_2(PR_3)_4]$ compounds indicates that the bonding and antibonding combinations of the $(S_2)^{4-}$ fragment are responsible for its basicity toward other transition metal and main group element centers [4]. Fourth, our determination of the structure of $[Ni(dippe)(\mu-S)]_2$ shows it to be the only reported $Ni_2(\mu-S)$ $X)_2$ molecule (where X = O, S, Se, Te, F, Cl, Br or I) that is bent along the X-X axis [5]. It is mainly due to this last structural property that a series of alkylation and protonation experiments, such as those that in the past have been performed on Pt_2S_2 complexes [6–10], was conducted.

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2. Results and discussion

2.1. Preparation and characterization of $[Ni(dippe)(\mu-S)]_2$

The bis μ -sulfido dimer [Ni(dippe)(μ -S)]₂ (1) can be conveniently prepared by the reaction of the hydrido dimer [Ni(dippe)(μ -H)]₂ with cyclohexene sulfide (Eq. (2)).



Alternatively, the dimer forms upon loss of benzene from (dippe)Ni(Ph)(SH) in a reaction that is believed to generate [(dippe)Ni = S] (Eq (1)). The ¹H NMR spectrum for **1** shows two types of isopropyl methyl groups, each appearing as a doublet of doublets due to coupling to the methine hydrogen and the phosphorus. Only a single environment is observed for the methine and methylene hydrogen resonances. The ³¹P NMR spectrum shows a singlet for the 4 equiv. phosphorus. Note that the observation of two types of isopropyl methyl group (i.e. one kind of isopropyl group with different methyl environments) is consistent with either a planar structure for the dimer or a hinged structure in which inversion at the sulfurs renders the *exo* and *endo* isopropyl groups equivalent.

The single crystal X-ray structure of $[Ni(dippe)(\mu-S)]_2$ actually shows it to be an example of a bent M_2X_2 molecule (Fig. 1) [3]. While this type of bending is common in this class of molecules, it is quite rare in Ni_2X_2 molecules [11]. The molecule can be described in terms of two square planar Ni(II) centers joined and bent along the S–S edge, with a hinge angle of 140.2°. The average P–Ni–P angle of 89.9° is typical of a bidentate phosphine, but is slightly larger than what is found in platinum-aminothiolate dimers with diphos as the terminal ligand [11]. The Ni-Ni distance is 2.941 Å, approximately 0.44 Å greater than the sum of their van Der Waals radii, indicating the absence of any direct metal-metal interaction. The average Ni-S distance is typical of a single bond interaction at 2.197 Å.

While $[Ni(dippe)(\mu-S)]_2$ is the only known bent $Ni_2(\mu-S)_2$ molecule, the factors that determine its structure are



Fig. 1. ORTEP drawing of $[(dippe)Ni(\mu-S)]_2$ (1). Ellipsoids shown at 30% probability level. Hydrogen atoms are omitted for clarity. Selected distances: Ni(1)–Ni(2), 2.941(2), Ni(1)–P(1), 2.145(3), Ni(1)–P(2), 2.149(3), Ni(1)–S(1), 2.187(3), Ni(1)–S(2), 2.206(3), Ni(2)–P(3), 2.144(4), Ni(2)–P(4), 2.152(4), Ni(2)–S(1), 2.201(4), Ni(2)–S(2), 2.194(3).



Fig. 2. Critical orbital interactions in M₂S₂ structures.



Fig. 3. ^{31}P NMR spectrum of $[Ni_2(dippe)_2(\mu\text{-}S)(\mu\text{-}SCH_3)]Cl$ in acetone-d_6.

perhaps best explained by applying the conclusions of a theoretical study of platinum(II) dimers with a Pt_2S_2 ring by González-Duarte, Lledós and coworkers [4]. Their analysis also provides the basis for understanding the chemical reactivity of $[Ni(dippe)(\mu-S)]_2$ towards nucleophiles. Their work concludes that the factor that determines the preference for a hinged geometry in platinum(II) dimers with a Pt_2S_2 ring is the stabilization of the M–S MO's that are formed from the filled σ^* and π_{ll}^* orbitals of the $(S_2)^{4-}$ 'fragment' and the unfilled bonding and antibonding combinations of orbitals of the $[M_2L_4]^{4+}$ fragment. These orbitals are shown in Fig. 2. While the antibonding interaction within the $(S_2)^{4-}$ fragment π_{ll}^* orbital is not expected to be strong due to the distance between the two bridging sulfur atoms, the antibonding interaction within its σ^* orbital may be substantial. When the M_2S_2 core folds, mixing of $[M_2L_4]^{4+}$ xy orbitals and xz orbitals becomes symmetry allowed and the result is better $[M_2L_4]^{4+}$ xy-orbital overlap with the $(S_2)^{4-}$ σ^* and π_{ll}^* orbitals. Despite the fact that the metal xz orbitals are destabilized, distortion of the M2S2 core allows for greater stabilization of the S-S antibonding interactions. Furthermore, the change in geometry of the M_2S_2 core that takes place upon reaction is determined by the electronic demands of the $(S_2)^{4-}$ σ^* and π_{ll}^* orbitals.

2.2. Alkylation of $[Ni(dippe)(\mu-S)]_2$

[Ni(dippe)(μ -S)]₂ cleanly participates in an apparent $S_N 2$ reaction with CH₃Cl to form [Ni₂(dippe)₂(μ -S)(μ -SCH₃)]Cl (Eq. (3)).

Table 1

Selected bond lengths (Å) and bond angles (°) for $[(dippe)_2Ni_2(\mu-S)(\mu-SMe)][BPh_4]$ (2a), $[(dippe)_2Ni_2(\mu-S)(\mu-SEt)][BPh_4]$ (2b) and $[(dippe)_2-Ni_2(\mu-S)(\mu-S-i-Pr)][BPh_4]$ (2c)

	2a	2b	2c
Bond lengths			
Ni(1)–P(2)	2.1519(9)	2.1599(13)	2.1683(10)
Ni(1)–P(1)	2.1703(9)	2.1902(13)	2.1988(10)
Ni(1)-S(2)	2.1726(9)	2.1737(13)	2.1800(10)
Ni(1)–S(1)	2.2162(9)	2.2330(13)	2.2455(9)
Ni(1)–Ni(2)	2.9615(5)	2.9656(8)	2.9911(6)
Ni(2)–P(4)	2.1556(9)	2.1614(13)	2.1739(10)
Ni(2)–S(2)	2.1738(9)	2.1823(13)	2.1804(9)
Ni(2)–P(3)	2.1854(9)	2.1964(13)	2.1997(10)
Ni(2)–S(1)	2.2173(9)	2.2399(13)	2.2384(9)
S(1)–C(1)	1.863(4)	1.842(5)	1.870(4)
Bond angles			
P(1)-Ni(1)-P(2)	89.13(3)	88.69(5)	88.85(4)
S(1)-Ni(1)-S(2)	86.53(3)	86.16(5)	85.84(3)
P(1)-Ni(1)-S(1)	95.49(3)	97.59(5)	95.05(4)
P(1)-Ni(1)-S(2)	167.63(4)	164.58(6)	177.92(4)
P(2)-Ni(1)-S(1)	168.39(4)	166.71(6)	169.66(4)
P(2)-Ni(1)-S(2)	91.24(3)	90.87(5)	90.58(4)
P(3)–Ni(2)–P(4)	89.13(3)	89.10(5)	88.04(4)
S(1)-Ni(2)-S(2)	86.47(3)	85.79(5)	86.01(3)
P(3)-Ni(2)-S(1)	93.91(3)	94.66(5)	95.13(4)
P(3)-Ni(2)-S(2)	175.45(4)	176.51(6)	170.78(4)
P(4)-Ni(2)-S(1)	176.08(4)	173.00(6)	175.56(4)
P(4)-Ni(2)-S(2)	90.30(4)	90.11(5)	91.35(4)
C(1)-S(1)-Ni(1)	97.57(14)	102.83(18)	100.69(12)
C(1)-S(1)-Ni(2)	103.31(15)	100.74(17)	107.41(12)
Ni(1)-S(1)-Ni(2)	83.82(3)	83.06(5)	83.68(3)
Ni(1)-S(2)-Ni(2)	85.90(3)	85.82(5)	86.62(3)

The ³¹P NMR spectrum of the monomethylated product in acetone-d₆, shown in Fig. 3, consists of a pair of sextets at δ 82.99 and 77.04 ppm. The coupling pattern is consistent with an AA'BB' spin system. Counterion metathesis with NaBPh₄ yielded $[Ni_2(dippe)_2(\mu-S)(\mu-SCH_3)][BPh_4]$ (2a), from which Xray diffraction quality crystals were grown. In the ¹H NMR spectrum of $[Ni_2(dippe)_2(\mu-S)(\mu-SCH_3)][BPh_4]$, the thiolate proton signal overlaps the signal of the isopropyl methyne protons at 2.3 ppm. This chemical shift lies with the range of previously reported chemical shift values for μ -SMe protons [12].

 $[Ni_2(dippe)_2(\mu-S)(\mu-SCH_3)][BPh_4]$ crystallizes in the space group $P\overline{1}$. Bond lengths and angles are given in





Fig. 4. ORTEP drawing of $[(dippe)_2Ni_2(\mu-S)(\mu-SMe)][BPh_4]$ (2a). Ellipsoids are shown at 30% probability level. Hydrogen atoms and the BPh₄ counterion are omitted for clarity.



Fig. 5. ORTEP drawing of $[(dippe)_2Ni_2(\mu-S)(\mu-SEt)][BPh_4]$ (2b). Ellipsoids are shown at 30% probability level. Hydrogen atoms and the BPh₄ counterion are omitted for clarity.



Fig. 6. ORTEP drawing of $[(dippe)_2Ni_2(\mu-S)(\mu-S'Pr)][BPh_4]$ (2c). Ellipsoids are shown at 30% probability level. Hydrogen atoms and the BPh₄ counterion are omitted for clarity.

Table 1, and a structural diagram is shown in Fig. 4. The structure is typical of d^8 metal dimers that contain mixed sulfido-thiolato ligands in that the hinge geometry is maintained, presumably for the same reasons that hold for dimers with two sulfido ligands [4]. The hinge angle [5], θ , of $[Ni_2(dippe)_2(\mu-S)(\mu-SCH_3)]^+$ is 136.5°, while the angles for $[Pt_2(\mu-S)(\mu-SCH_3)(PH_3)_4]^+$ and

 $[Pt_2(\mu-S)(\mu-SCH_3)(PPh_3)_4]^+$ are 136.9 and 138.0°, respectively. Furthermore, among the four isomers that mixed sulfido-thiolato d⁸ metal dimers can assume, it has the bent-*exo* form, which is the most common member of the group [13]. The sum of the angles around the thiolato sulfur atom in $[Ni_2(dippe)_2(\mu-S)(\mu-SCH_3)]^+$ is 284.6°, which is slightly less than in $[Pt_2(\mu-S)(\mu-SCH_3)(PH_3)_4]^+$ and $[Pt_2(\mu-S)(\mu-SCH_3)(PPh_3)_4]^+$. The values fall in the range that is to be expected for a μ -alkylthiolato sulfur [13].

Both the ethyl (2b) and ⁱpropyl (2c) mono-alkylated dinuclear species can be prepared similarly. The initial disappearance of $[Ni(dippe)(\mu-S)]_2$ and formation of $[Ni_2(dippe)_2(\mu-S)(\mu-SEt]C]$ is facile at room temperature, and follows bimolecular kinetics $(k = 8.8 \times 10^{-3})$ M^{-1} s⁻¹). Both display NMR spectra similar to that of **1a**, with the addition of new alkyl group resonances. Compounds 2b and 2c were also characterized structurally, as shown in Figs. 5 and 6. The molecules both are hinged at angles of 134.2 and 135.5°, respectively, virtually identical to that observed in 2a. The sum of the angles around the thiolato sulfur atom is 286.6° for **2b** and 291.8° for **2c**, showing a slight tendancy towards flattening with the larger alkyl group (Table 1). Bending at the hinge is a low energy process, and consequently only large differences in the hinge angle are associated with significant energy differences.

One aspect of the structural characteristics of $[Ni(dippe)(\mu-S)]_2$ (2a-2c) is inconsistent with the treatment of these types of dimers as reported by González-Duarte, Lledós and coworkers. Alkylation of a sulfido ligand should force the p-orbital of sulfur that is used in the formation of the σ^* orbital in the (S₂)⁴⁻ fragment out of the S-S direction, thereby reducing the amount of antibonding interaction. Consequently, the hinge angle should increase (i.e. flatten out) in moving from a bis-sulfido dimer to a mixed sulfido-thiolato dimer [4]. To the contrary, alkylation of [Ni(dippe)(μ -S)]₂ decreases the hinge angle slightly from 140 to ~ 135°. It is possible that the smaller hinge angle in **2a** could be due to steric interactions between the phosphorus substituents and the thiolate group.

In the reaction that produced $[Ni_2(dippe)_2(\mu-S)(\mu-SCH_3)]^+$, the ratio of reagents $[Ni(dippe)-(\mu-S)]_2$ and CH₃Cl was approximately 1:5. However, the dialkylated product $[Ni(dippe)(\mu-SCH_3)_2]Cl_2$ did not form. This same behavior was first reported by Chatt and Mingos [6] and then by Ugo [7] in regard to the reaction of organic halides with $[Pt_2(\mu-S)_2(PMe_2Ph)_4]$ and $[Pt_2(\mu-S)_2(PPh_3)_4]$, respectively.

In order to overcome the decreased nucleophilicity at the remaining sulfido group, $[Ni(dippe)(\mu-S)]_2$ was reacted with the more potent methylating agent, methyl triflate. The dialkylated product, $[Ni_2(dippe)_2(\mu-SCH_3)_2][OTf]_2$ (3), forms immediately upon addition of 4 equiv. of methyl triflate to an acetone solution of $[Ni(dippe)(\mu-S)]_2$ (Eq. (4)).



The ³¹P NMR spectrum of $[Ni_2(dippe)_2(\mu-SCH_3)_2]$ -[OTf]₂ consists of a singlet at δ 92.7 ppm, and the ¹H NMR spectrum displays the thiolate protons as a singlet at δ 2.37. The isopropyl methyl groups appear as two doublets of doublets centered at δ 1.37 and 1.24, consistent with either a planar structure, or more likely one with a rapidly inverting Ni₂S₂ core. [Ni₂(dippe)₂(μ -SCH₃)₂][OTf]₂ is an oil, but in this case anion exchange with NaBPh₄ also produces an oil, precluding structural studies.

Chatt and Mingos reported the formation of *cis*-[PtBr₂(PMe₂Ph)₂] when [Pt₂S₂(PMe₂Ph)₄] was reacted with and excess of CH₃Br [6]. A similar result was obtained when [Ni(dippe)(μ -S)]₂ was reacted with 1,2dichloroethane. The ³¹P NMR spectrum displayed a pair of sextets whose coupling patterns are reminiscent of those for [Ni₂(dippe)₂(μ -S)(μ -SCH₃)]⁺. The ultimate products of the reaction are Ni(dippe)(η^2 -S₂C₂H₄) (**4a**) and Ni(dippe)Cl₂, both of which steadily increased in concentration over an 18-h period as the intermediate [Ni₂(dippe)₂(μ -S)(μ -SC₂H₄Cl)]Cl diminished (Eq. (5)).



Similar results are obtained when $[Ni(dippe)(\mu-S)]_2$ was reacted with 1,3-dichloropropane, giving $Ni(dippe)(\eta^2-S_2C_3H_6)$ (**4b**), which indicates that strain is most likely



Fig. 7. ORTEP drawing of (dippe)Ni($S_2C_2H_4$) (4a). Ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity.

not the reason for the instability of $[Ni_2(dippe)_2(\mu - S_2C_nH_{2n})]Cl_2$ relative to its decomposition monomers.

(4)

The X-ray structures of **4a** and **4b** were determined (Figs. 7 and 8). Both are square planar Ni(II) complexes with very little distortion around the nickel (Table 2). The ethane bridge in **4a** is slightly puckered, whereas that in **4b** is highly puckered.

2.3. Protonation of $[Ni(dippe)(\mu-S)]_2$

[Ni(dippe)(μ -S)]₂ reacts immediately with 1 equiv. of HBF₄·Et₂O to form [Ni₂(dippe)₂(μ -S)(μ -SH)][BF₄]. The NMR data demonstrate the acidic nature of the sulfhydryl proton. In the room temperature ¹H NMR spectrum, no sulfhydryl signal is seen. However, at -50 °C, a broad triplet at $\delta - 0.16$ is observed. Line-broadening also occurs in the ³¹P NMR spectrum, as seen in Fig. 9. The pair of pseudo triplets at δ 86.97 and 82.62 seen at 25 °C resolves into a pair of quintets at -30 °C.



In the presence of excess acid, $[Ni_2(dippe)_2(\mu-S)(\mu-SH)][BF_4]$ is involved in an equilibrium with $[Ni_2(dippe)_2(\mu-SH)_2][BF_4]_2$, as is described by Eq. (6).



Fig. 8. ORTEP drawing of (dippe)Ni($S_2C_3H_6$) (4b). Ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2

Selected bond lengths (Å) and bond angles (°) for $(dippe)Ni(S_2C_2H_4)$ (4a) and $(dippe)Ni(S_2C_3H_6)$ (4b)

	4 a	4b
Bond lengths		
Ni(1)–P(2)	2.154(2)	2.1648(7)
Ni(1)–P(1)	2.156(2)	2.1729(6)
Ni(1)-S(2)	2.179(2)	2.1950(7)
Ni(1)–S(1)	2.181(2)	2.2089(7)
S(1)–C(1)	1.820(7)	1.829(3)
S(2)–C(2/3)	1.810(8)	1.823(3)
Bond angles		
P(1)-Ni(1)-P(2)	89.17(7)	88.66(2)
S(1)–Ni(1)–S(2)	93.41(8)	95.42(3)
P(1)-Ni(1)-S(1)	165.19(8)	173.12(3)
P(1)-Ni(1)-S(2)	90.54(8)	89.45(3)
P(2)-Ni(1)-S(1)	90.70(8)	87.28(2)
P(2)-Ni(1)-S(2)	164.80(9)	170.77(3)
C(1)-S(1)-Ni(1)	101.5(3)	102.95(9)
C(2/3)-S(2)-Ni(1)	101.4(3)	106.97(9)



Fig. 9. ^{31}P NMR spectrum of $[Ni_2(dippe)_2(\mu\text{-}S)(\mu\text{-}SH)][BF_4]$ in acetone-d_6.



With approximately 2 equiv. of acid, the pair of triplets that is seen in the ³¹P NMR spectrum at room temperature coalesces to a broad singlet at δ 89.31. It is also shifted downfield from the average of the pair of triplets, apparently as a result of the increased polarity of the solvent. With the addition of approximately 10 equiv. of acid, the broad singlet sharpens considerably and is shifted to 92.5 ppm.

To determine whether the equilibrium between $[Ni_2(dippe)_2(\mu-S)(\mu-SH)][BF_4]$ and ~ 10 H⁺ and $[Ni_2(dippe)_2(\mu-SH)_2][BF_4]_2$ lies to the left or to the right, an acetone-d₆ solution of the reagents was cooled to -95 °C. Two sets of broad resonances are observed, a singlet at δ 100.07 and a 'doublet' centered at δ 86.90.

(6)

The equilibrium, even with such a large excess of acid, lies far to the left for the ratio of signal intensities between $[Ni_2(dippe)_2(\mu-S)(\mu-SH)][BF_4]$ and $[Ni_2(dippe)_2(\mu-SH)_2][BF_4]_2$ is approximately 11 to 1. The fact that dimethylation of $[Ni(dippe)-(\mu-S)]_2$ is facile with a good methylating agent, but that diprotonation is extremely difficult, again demonstrates the acidic nature of the sulfhydryl proton–sulfur bond.

2.4. Inversion of the Ni_2S_2 core

There are many examples of M_2S_2 fluxionality in molecules that contain bridging sulfido, thiolato, and sulfhydryl ligands [14–18]. This behavior can be due to either ring inversion (analogous to inversion of cyclohexane) along the X-X axis or to the cleavage and re-formation of an M–X bond during which the sulfur atom rotates. Ring inversion is much more facile than is bond cleavage/sulfur rotation. As an example, for *trans*-[{Ru(CO)(μ -SCH₂Ph)(η -C₅H₅)}₂], ring inversion is fast on the NMR timescale even at -100 °C, while sulfur rotation is fast only above 100 °C [12].

There is no evidence that suggests that sulfur rotation is occurring in $[Ni(dippe)(\mu-S)]_2$ and its products. However, ¹H NMR spectra of $[Ni(dippe)(\mu-S)]_2$, and $[Ni_2(dippe)_2(\mu-S)(\mu-SCH_3)]^+$ indicate that all of these complexes undergo rapid ring inversion at room temperature. Specifically, the dippe isopropyl methyl resonances point to this behavior. When the dippe ligand is chelated to a square planar metal center, one expects to observe two separate resonances for the inequivalent sets of methyl groups. Furthermore, the methyl protons couple to the isopropyl methine proton, and to the α -phosphorus atom, as well, leading to two doublets of

doublets. In the ¹H NMR spectrum of the square-planar Ni(dippe)(SCH₃)₂, these two sets of methyl groups produce two doublets of doublets that are centered at δ 1.37 and 1.24. The bent molecule [Ni(dippe)(μ -S)]₂ should have four distinct types of methyl groups, but rapid ring inversion leads to the observation of only two resonances, each a doublet of doublets.

For a bent, static molecule of the type $[Ni_2(dippe)_2(\mu-S)(\mu-SR)]^+$ one expects two see eight distinct methyl group resonances. Only four doublets of doublets are observed as a result of rapid ring inversion. Analysis of $[Ni(dippe)(\mu-SCH_3)]_2^+$ is more complex than the previous two cases. There is no crystal structure to indicate

the geometry that most likely corresponds to an energy minimum in solution. [Ni(dippe)(μ -SCH₃)]⁺ has a large number of possible isomers depending on whether the Ni_2S_2 core is planar or bent, and whether the alkyl groups are syn or anti. It could very well exist in solution as a planar molecule with rapid interconversion between syn and anti isomers, as is the case with $[{Pt(NH_3)_2(accysH_2-\mu-S)_2}^2]^2 +$ [14]. However, the analogous complex $[Pt_2(\mu$ -SCH₃)₂ $(PH_3)_4]^{2+}$ is probably a better model for the behavior of [Ni2(dippe)2(µ- $SCH_3_2^{+}$ in solution. When the geometry of $[Pt_2(\mu SCH_{3}_{2}(PH_{3})_{4}^{2+}$ is optimized for the *anti* configuration of thiolate methyl groups, the complex prefers to be planar. Yet, when it is optimized for the syn configuration, a bent geometry is favored. The energy difference between the planar-anti and the bent-syn isomers is 0.7 kcal mol⁻¹ in favor of the latter so it is reasonable to expect facile interconversion between the two of them in solution. Is there evidence of this behavior in $[Ni_2(dippe)_2(\mu$ -SCH₃)₂]⁺? The answer is yes. The planar-anti and the bent-syn isomers of [Ni2(dippe)2(µ- $SCH_{3}_{2}^{+}$ would produce four doublets of doublets in the ¹H NMR spectrum should the molecule be static at room temperature. However, it gives rise to two doublets of doublets for the isopropyl methyl groups, indicative of interconversion, probably via ring inversion.

3. Conclusion

The results of this study of $[Ni(dippe)(\mu-S)]_2$ and its reaction products with electrophiles demonstrate that many of the conclusions that have been reached in regard to Pt₂S₂ compounds can be generalized to some nickel analogs. M₂S₂ dimers often are chelating ligands toward other transition metal and main group element centers, which makes them potentially useful as homogeneous catalyts in organic and organometallic syntheses. Should other relevant nickel analogs replicate the chemistry of Pt_2S_2 compounds, then, as a class, they will offer the organometallic chemist a cost-effective substitute for the latter in that function. More studies of [Ni(dippe)(µ-S)]₂ will follow, focussing on the chemistry that takes place at nickel rather than sulfur. These studies are aimed at providing models for mechanistic details of the hydrodesulfurization of petroleum that are currently little understood.

4. Experimental

4.1. General considerations

All operations were performed under a nitrogen atmosphere unless otherwise stated. Benzene, THF and hexanes were distilled from dark purple solutions of benzophenone ketyl. Chlorobenzene was dried and distilled over CaH₂. Neutral silica and alumina were heated to 200 °C under vacuum for two days and stored under nitrogen. Cyclohexene sulfide and sodium hydrosulfide hydrate were purchased from Aldrich Chemical Co. and used without further purification. A Siemens-SMART 3-Circle CCD diffractometer was used for X-ray crystal structure determination. Elemental analyses were obtained from Desert Analytics. All ¹H, ³¹P and ¹³C spectra were recorded on a Bruker AMX400 NMR spectrometer, and all ¹H chemical shifts are reported relative to the residual proton resonance in the deuterated solvent. [(dippe)NiH]₂ and (dippe)Ni(SH)₂ were synthesized according to procedures published previously [19].

4.2. Preparation of $[(dippe)Ni(\mu-S)]_2$ (1)

Cyclohexene sulfide (0.37 g, 3.26 mmol) in THF was added via syringe to a THF solution of [Ni(dippe)(µ-H)]2 (1.00 g, 1.55 mmol) and the reaction mixture was stirred for 24 h. The solvent was evaporated under vacuum, the remaining solid redissolved in a minimal amount of THF, and the sample placed on a neutral alumina column. The column was eluted with hexanes, the first fraction was collected, and the solvent removed to yield a brown solid. The product was recrystallized from hexanes at -30 °C, yielding 514 mg of 1 (47%). ¹H NMR (C₆D₆, 25 °C): δ 2.32 (oct, J = 5.9 Hz, 8H), 1.63 (dd, J = 14.5, 7.1 Hz, 24H), 1.08 (dd, J = 12.2, 7.0 Hz, 24 Hz), 0.99 (d, J = 10.0 Hz, 8H). ¹³C{¹H} NMR $(C_6D_6, 25 \text{ °C}): \delta 25.85 - 25.57 \text{ (m)}, 22.11 \text{ (quin, } J = 9.0 \text{ (C}_6D_6, 25 \text{ °C}): \delta 25.85 - 25.57 \text{ (m)}, 22.11 \text{ (quin, } J = 9.0 \text{ (C}_6D_6, 25 \text{ °C}): \delta 25.85 - 25.57 \text{ (m)}, 22.11 \text{ (quin, } J = 9.0 \text{ (quin, } J = 9.0$ Hz), 20.29 (s), 18.73 (s). ${}^{31}P{}^{1}H{}$ (THF-d₈, 25 °C, 162 MHz) δ 77.88 (s). *Anal.* Calc. (Found) for C₂₈H₆₄Ni₂P₄S₂: C, 47.62 (47.36); H, 9.13 (9.24)%.

4.3. Preparation of [Ni₂(dippe)₂(μ-S)(μ-SCH₃)][BPh₄] (**2a**)

Approximately 1 atm of CH₃Cl was placed above an acetone solution of [Ni(dippe)(µ-S)]₂ (0.103 g, 0.15 mmol). The color of the solution immediately turned orange-red and Na[BPh₄] (0.056 g, 0.165 mmol) was added. The reaction mixture was stirred for 15 min, filtered through neutral alumina to remove NaCl and excess Na[BPh₄], and the solvent then removed under vacuum. The remaining red solid was recrystallized from acetone at -30 °C and then dried under vacuum (68% yield). ¹H NMR (acetone-d₆, 25 °CC): δ 7.33 (br s, 8H), 6.91 (t, J = 7.4 Hz, 8H), 6.77 (t, J = 7.2 Hz, 4H), 2.42-2.33 (m, 11H), 1.53 (m, 8H), 1.53-1.28 (m, 48H). ¹³C{¹H} NMR (acetone-d₆, 25 °C): δ 136.09 (s), 125.02 (dd, J = 2.6 Hz), 121.26 (s), 26.47 (d, J = 27.4 Hz), 22.14 (m), 19.86 (dd, J = 13.7, 10.0 Hz), 19.41(s), 19.27 (s), 17.99 (s), 17.92 (s), 13.39 (s). ${}^{31}P{}^{1}H{}$ NMR (acetone-d₆, 25 °C): δ 82.99 (m), 77.04 (m). Anal. Calc. (Found) for $C_{53}H_{87}Ni_2P_4S_2B$: C, 61.2 (61.03); H, 8.4 (8.31)%.

4.4. Titration of $[Ni(dippe)(\mu-S)]_2$ by CH_3Cl

Approximately 1 atm of CH₃Cl was placed in a resealable NMR tube that contained 0.7 ml of degassed acetone-d₆ that was spiked with 3 μ l (0.028 mmol) of toluene. The concentration of the resulting stock acetone-d₆ solution of CH₃Cl was determined by ¹H NMR spectroscopy by comparing the integration value for CH₃Cl to that of the toluene methyl protons. Aliquots of this stock solution were added to a known amount of [Ni(dippe)(μ -S)]₂ in acetone-d₆. The formation of [Ni₂(dippe)₂(μ -S)(μ -SCH₃)][Cl] occurred after approximately 1 equiv. of CH₃Cl was added.

4.5. Preparation of [Ni₂(dippe)₂(μ-S)(μ-SCH₂CH₃)][BPh₄] (**2b**)

Approximately 2 equiv. of C₂H₅Cl (2 M in *t*-butyl methyl ether, 0.26 ml, 0.52 mmol) was added by syringe to a stirred acetone solution of (2) (184 mg, 0.26 mmol). The solution was stirred for 6 days. Approximately 1 equiv. of NaBPh₄ (98 mg, 0.29 mmol) was placed in the reaction flask, and the mixture was stirred overnight. The solution was then vacuum filtered through neutral alumina and the solvent was removed under vacuum to yield an orange-red solid (64% yield). ¹H NMR (acetone-d₆, 25 °C): δ 7.33 (bs, 8H, $-C_6H_5$), 6.91 (m, 8H, $-C_6H_5$), 6.76 (t, J = 6.8 Hz, 4H, $-C_6H_5$), 3.15 - 3.06 (m, $2H_1 - SCH_2CH_3$, 2.48–2.29 (m, 8H, $-CH(CH_3)_2$), 1.98 -1.79 (m, 11H, $-PC_2H_4P-$, $-SCH_2CH_3$), 1.55–1.26 (m, 48H, $-CH(CH_3)_2$). ${}^{31}P$ {¹H} (THF-d₈, 25 °C): δ 83.30 (m), 76.39 (m). In a separate experiment using equimolar concentrations of 1 and chloroethane, a plot of 1/(1) versus time was linear with a slope that gave $k = 8.8 \times 10^{-3}$ M⁻¹ s⁻¹ (see Supplementary information).

4.6. Preparation of $[Ni_2(dippe)_2(\mu-S)(\mu-SCHMe_2)]$ -[BPh₄] (2c)

2-Tosylpropane (27 mg, 0.125 mmol) in THF was added by syringe to a stirred THF solution of **2**. The resulting solution was stirred for three days as the color changed from dark brown to dark crimson. The solvent was removed under vacuum to leave a red oil. The oil was redissolved in a minimal amount of THF, layered with hexanes, and chilled at -30 °C to yield a waxy dark red solid. This solid was placed in 25 ml of THF along with NaBPh₄ (43 mg, 0.125 mmol) and the mixture was stirred overnight. The mixture was vacuum filtered through neutral alumina and the solvent was removed under vacuum to yield a dark red waxy solid. All attempts to quantitatively exchange BPh₄ for tosylate were unsuccessful. ¹H NMR (acetone-d₆, 25 °C): δ 7.33 (b, 8H, C₆H₅), 6.91 (m, 8H, C₆H₅), 6.77 (m, 4H, C₆H₅), 2.45–2.35 (m, 9H, CH(CH₃)₂, SCH(CH₃)₂, 1.96–1.75 (bm, 8H, PC₂H₄P), 1.66 (d, J = 6.87 Hz, 6H, SCH(CH₃)₂), 1.51–1.31 (m, 48H, CH(CH₃)₂). ¹³C {¹H} NMR (acetone-d₆, 25 °C): δ 136.08 (s), 125.02 (m), 121.26 (s), 27.07 (s), 25.26 (s), 25.07 (s), 21.83 (m), 19.37 (m), 19.23 (bs), 17.88 (bs). ³¹P {¹H} NMR (acetone-d₆, 25 °C): 80.84 (m), 73.77 (m).

4.7. [Ni₂(dippe)₂(µ-SCH₃)]₂][OTf]₂

Neat methyl triflate (7.2 µl, 0.032 mmol) was added to an acetone solution of $[Ni(dippe)(\mu-S)]_2$ (0.011 g, 0.015 mmol). $[Ni_2(dippe)_2(\mu-SCH_3)_2][OTf]_2$ formed immediately following the methyl triflate addition. The solvent was removed by vacuum. The resulting oil was washed with hexanes and was then placed under vacuum for three days to remove excess methyl triflate. ¹H NMR (acetone-d₆, 25 °C): δ 2.78–2.53 (m, 8H), 2.37 (s, 6H), 2.26–2.23 (d, J = 13.7 Hz, 8H), 1.69–1.63 (dd, J = 9.4, 7.3 Hz, 24H), 1.43–1.38 (dd, J = 6.6 Hz, 24H). ³¹P{¹H} NMR (acetone-d₆, 25 °C): δ 92.71 (s).

4.8. Preparation of Ni(dippe)(μ_2 -S₂C₂H₄)

One equiv. of 1,2-dichloroethane was added to an acetone-d₆ solution of $[Ni(dippe)(\mu-S)]_2$ to yield $[Ni_2(dippe)_2(\mu-S)(\mu-SC_2H_4Cl)][Cl]$. The intermediate $[Ni_2(dippe)_2(\mu-S)(\mu-SC_2H_4Cl)][Cl]$ decomposed over 18 h to form $Ni(dippe)(\eta^2-S_2C_2H_4)$ and $Ni(dippe)Cl_2$. $Ni(dippe)(\eta^2-S_2C_2H_4)$ was separated from $Ni(dippe)Cl_2$ and residual $[Ni_2(dippe)_2(\mu-S)(\mu-SC_2H_4Cl)][Cl]$ with a neutral alumina column, and its fraction was evaporated to yield a light red solid.

4.9. Alternative synthesis of Ni(dippe)(η^2 -S₂C₂H₄)

1,2-Ethanedithiol (0.108 g, 0.27 mmol) in THF was added to a stirred suspension of Ni(dippe)Cl₂ (26 mg, 0.28 mmol) in THF. NEt₃ (56 mg, 0.55 mmol) was added and the solution stirred until the color changed to a light red. The solution was filtered through neutral alumina and the solvent removed by vacuum. The resulting analytically pure red solid was washed with hexanes and dried under vacuum (60% yield). It was then redissolved in a minimal amount of THF, layered with hexanes, and chilled at -30 °C to yield crystals that were suitable for single crystal X-ray diffraction studies. ¹H NMR (acetone-d₆, 25 °C): δ 2.47 (s, 4H), 2.29 (m, 4H), 1.89 (d, J = 10.9 Hz, 4H), 1.37-1.18 (m, 24H). ¹³C{¹H} NMR: (acetone-d₆, 25 °C): δ 25.13– 24.59 (m), 22.32 (s), 22.80 to 20.40 (m), 18.39 (s), 17.70 (s). ${}^{31}P{}^{1}H$ NMR (acetone-d₆, 25 °C): δ 85.41 (s). Anal. Calc. (Found) for C₁₆H₃₆NiP₂S₂: C, 46.5 (46.67); H, 8.8 (8.75)%.

4.10. Preparation of Ni(dippe)(η^2 -S₂C₃H₆)

One equiv. of 1,2-dichloropropane was added to an acetone-d₆ solution of [Ni(dippe)(μ -S)]₂ to yield [Ni₂-(dippe)₂(μ -S)(μ -SC₃H₆Cl)][Cl], which decomposed over 36 h to form Ni(dippe)(η^2 -S₂C₃H₆) and Ni(dippe)Cl₂. Ni(dippe)(η^2 -S₂C₃H₆) was separated from Ni(dippe)Cl₂ and residual [Ni₂(dippe)₂(μ -S)(μ -SC₃H₆Cl)][Cl] on a neutral alumina column, and its fraction was evaporated to yield a red solid.

4.11. Alternative synthesis of Ni(dippe)(η^2 -S₂C₃H₆)

1,3-Propanedithiol (0.0593 g, 0.55 mmol) in THF was added to a stirred suspension of Ni(dippe)Cl₂ in THF. NEt₃ (0.111 g, 1.1 mmol) was added and the solution stirred until the color changed to dark red. The solution was filtered through neutral alumina and the solvent removed under vacuum. The resulting red solid was washed with hexanes, dried under vacuum, and then redissolved in a minimal amount of THF, layered with hexanes and chilled at -30 °C to yield crystals that were suitable for single crystal X-ray diffraction study. ¹H NMR (acetone-d₆, 25 °C): δ 2.42–2.32 (m, J = 7.1 Hz, 4H), 2.31-2.26 (m, J = 6.3 Hz, 4H, α -thiolate), 1.83–1.77 (quin, J = 6.5 Hz, 2H, β -thiolate), 1.80–1.77 (d, J = 11.1 Hz, 4H), 1.40 - 1.34 (dd, J = 7.3, 8.1 Hz, 12H), 1.26–1.21 (dd, J = 7.1, 5.9 Hz, 12H). ¹³C {¹H} NMR (acetone-d₆, 25 °C): δ 30.97 (s), 24.94 (m), 22.46 (s), 20.96 (t, J = 19.3 Hz), 19.29 (s), 17.94 (s). ${}^{31}P{}^{1}H{}$ NMR (acetone-d₆, 25 °C): δ 82.61 (s). Anal. Calc. (Found) for C₁₇H₃₈NiP₂S₂: C, 47.79 (47.44); H, 8.96 (9.24)%.

4.12. Preparation of Ni(dippe)(SCH₃)₂

Approximately 2 equiv (0.038 g, 0.54 mmol) of NaSCH₃ was added to a suspension of Ni(dippe)Cl₂ in THF. The reaction mixture was stirred for 15 min as a dark red color developed. It was filtered through neutral alumina and the solvent removed under vacuum. The resulting dark red solid was redissolved in a minimal amount of THF, layered with hexanes, and chilled at -30 °C to yield dark red crystals (61%). ¹H NMR (acetone-d₆, 25 °C): δ 2.54–2.45 (m, J = 7.1 Hz, 4H), 1.96 (d, J = 2.4 Hz, 6H), 1.76–1.74 (d, J = 11.6 Hz, 4H), 1.40–1.34 (dd, J = 8.5, 7.2 Hz, 12H), 1.26–1.21 (dd, J = 7.0, 5.9 Hz, 12H). ³¹P{¹H} NMR (acetone-d₆, 25 °C): δ 81 (s). *Anal.* Calc. (Found) for C₁₆H₃₈NiP₂S₂: C, 46.28 (46.27); H, 9.22 (9.21)%.

4.13. $[Ni_2(dippe)_2(\mu-S)(\mu-SH)][BF_4]$

Eighty-five percent of HBF_4 in Et_2O (0.024 g, 0.148 mmol) was added to an acetone solution of $[Ni(dippe)(\mu-S)]_2$ (0.105 g, 0.148 mmol). The reaction

was stirred for 15 min and the solution concentrated and cooled to -30 °C, producing $[Ni_2(dippe)_2(\mu-S)(\mu-SH)][BF_4]$ in 50% yield. The resulting solid was washed with cold hexanes and then dried under vacuum. ¹H NMR (acetone-d₆, 25 °C): δ 2.39 (br s, 8H), 1.97 (d, J = 20.9 Hz, 8H), 1.49–1.27 (m, 48H), -0.16 (br t, observed at -50 °C, 1H). ³¹P{¹H} NMR (acetone-d₆, -30 °C): δ 86.97 (m), 82.62 (m). *Anal.* Calc. (Found) for C₂₈H₆₅Ni₂P₄S₂F₄B: C, 42.35 (41.73); H, 8.25 (8.16)%.

4.14. Structure determinations of 2a-2c, 4a and 4b

Single crystals of each compound were mounted under Paratone-8277 on glass fibers and immediately placed in a cold nitrogen stream at -80 or -90 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 10-30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.54°). Frames were integrated with the Siemens SAINT program to 0.75 Å for all of the data sets. The unit cell parameters for all of the crystals were based upon the least-squares refinement of three-dimensional centroids of > 5000 reflections.¹ Data were corrected for absorption using the program SADABS [20]. Space group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program (Siemens, SHELXTL 5.04). The structures were solved by using direct methods and refined by full-matrix least-squares on $F^{2,2}$ For all of the structures, the non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions giving data:parameter ratios greater than 10:1.

There was nothing unusual about the solution or refinement of any of the structures, with the exceptions of compound **2c**, which crystallized with a molecule of THF solvent in the unit cell. Compound **4a** crystallizes with 4 independent molecules within the asymmetric unit. Further experimental details of the X-ray diffraction studies are provided in Section 5. Positional parameters for all atoms, anisotropic thermal parame-

 $^{^1}$ It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10 \times the listed value.

² Using the SHELX-95 package, $R_1 = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$, $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f.(\text{maximum of } 0 \text{ or } F_o^2) + (1 - f)F_c^2]$.

ters, all bond lengths and angles, as well as fixed hydrogen positional parameters are given in Section 5 for all of the structures.

5. Supplementary material

Tables of crystallographic data, atomic coordinates bond distances and angles, and anisotropic thermal parameters for 2a-2c, 4a, 4b, and a kinetic plot for the reaction of 1 with chloroethane are available from the author upon request.

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