Transition Metal Complexes with Sulfur Ligands, 138[+]

Synthesis, Structures, and Reactions of Sulfur-Rich Nickel and Platinum Complexes with [MS_3] and [MNS_2] Cores

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Dedicated to Professor Wolf Peter Fehlhammer on the occasion of his 60th birthday

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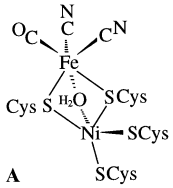
Nickel and platinum complexes with tridentate ligands, having [S_3] or [NS_2] donor sets were investigated in order to model active sites of enzymes such as hydrogenases or CO dehydrogenases. Starting from diphenyl sulfide, a preparative synthesis was developed for 'S_3'-H_2 ['S_3'-H_2 = bis(2-mercaptophenyl) sulfide]. Reactions of 'S_3'-H_2 or anionic '$S_3'^{2-}$ with nickel and platinum precursors resulted in the formation of binuclear [Ni('S_3')]$_2$ (**1**) and trinuclear [Pt('S_3')]$_3$ (**5**). Complex **1** was cleaved by PMe_3 or CN^- to give the mononuclear complexes [Ni('S_3')(PMe_3)] (**2**) and NMe_4[Ni('S_3')(CN)] (**3**). Attempts to coordinate hydride to the [Ni('S_3')] fragment led to C–S bond cleavage of the ligand and formation of $(NMe_4)_2$[{Ni(μ-SC_6H_5)($S_2C_6H_4$)}$_2$] (**4**). Oxidative addition of Li['S_3'-H] to [Pt(PPh_3)$_4$] afforded the platinum hydride complexes Li[Pt(H)('S_3')] and Li[Pt(H)(PPh_3)('S_3')] which, however, could not be separated from each other and yielded [Pt('S_3')(PPh_3)] (**6**) when treated with MeOH. In order to investigate electronic effects of the donor set, the 'S_3' ligand was modified by alkylation of one thiol group to give 'RS_3'-H derivatives (R = Me, Et, Cy) and by replacing a mercaptophenyl unit by an amine in 'Et_2NS_2'-H ['Et_2NS_2'-H = *N*,*N*-diethyl-2-(2-mercaptothiophenyl)ethylamine]. Reactions of Ni^{II} or Ni^0 compounds with these ligands in a 1:1 ratio yielded the 1:2 complexes [Ni('MeS_3')$_2$] (**7**), [Ni('EtS_3')$_2$] (**9**) and [Ni('CyS_3')$_2$] (**10**), with '$RS_3'^-$ acting as bidentate ligands only. Complex **7** reversibly reacted with PMe_3 to form *cis*-[Ni(PMe_3)$_2$('MeS_3')$_2$] (**8**), exhibiting monodentate 'MeS_3' ligands. [Ni('Et_2HNS_2')$_2$]Br_2 (**11**) reacted reversibly with bases to presumably give octahedral [Ni('Et_2NS_2')$_2$]. Complexes **7**, **9** and **10** also did not yield any [Ni('RS_3')(H)] hydride complex when treated with hydride sources. Oxidative addition of 'CyS_3'-H to [Pt(PPh_3)$_4$] yielded the hydride complexes [Pt(H)('CyS_3')] and [Pt(H)(PPh_3)('CyS_3')] which, however, formed an inseparable mixture and underwent C–S bond cleavage when heated, affording [Pt(*o*-$S_2C_6H_4$)(PPh_3)$_2$]. The molecular structures of **1**, **2**, **3**, **5**, **6**, **7**, and **11** were determined by X-ray crystallography, revealing butterfly-like shapes for the [MS_3L] cores of the complexes.

Introduction

The current interest in nickel thiolate and thioether complexes to a large extent results from the nickel–sulfur moieties that constitute the active centers of enzymes such as hydrogenases[1] or CO dehydrogenases.[2] For example, the X-ray structure analysis of hydrogenase from *D. gigas* has shown that the active site contains nickel surrounded by four cysteine thiolate donors, two of which form bridges to a [Fe(CO)(CN)$_2$] moiety (**A**).[3]



A

The search for hydrogenase model compounds has resulted in a considerable number of new ligands and complexes.[4] However, complexes which model structural *and* functional features of the enzyme centers have remained very rare. These features comprise sulfur coordination of the nickel center *and* catalysis of reactions according to Equations 1a and/or 1b.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \qquad (1a)$$

$$H_2 + D_2O \rightleftharpoons HD + HDO \qquad (1b)$$

Reaction according to Equation 1b requires the heterolytic cleavage of H_2 into H^+ and H^- ions. When this reaction takes place at the nickel–sulfur site of hydrogenases, nickel–sulfur hydride complexes are likely intermediates. Isolable complexes of this type are extremely rare in spite of the large number of nickel hydride complexes carrying phosphane or carbon coligands. Holm et al. reported five-coordinate complexes of the type [Ni(H)-{$N(C_2H_4SR)_3$}]$^+$,[5] and we have obtained four-coordinate [Ni(H)(PMe_3)($S_2C_6H_4$)]$^-$.[6] However, these complexes proved to be extremely moisture-sensitive and could not yet be shown to catalyze the H_2/D^+ exchange according to Equation 1b. Other nickel complexes, e.g., [Ni('S_5')][7] (**B**) or

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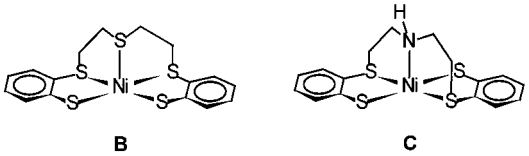
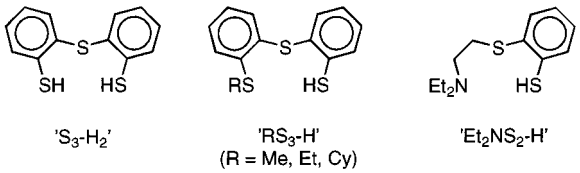
[Ni('N_HS_4')]$_2$[8] (**C**) readily underwent unwanted S−C(alkyl) cleavage reactions when investigated for the coordination of additional hydride ligands from hydride sources such as $LiAlH_4$, $LiBEt_3H$, or $NaBH_4$.[9]



These unwanted C−S cleavages, leading to destruction of the nickel−sulfur cores, drew our attention to the 'S_3'-H_2 ligand and its 'RS_3'-H and 'Et_2NS_2'-H derivatives.



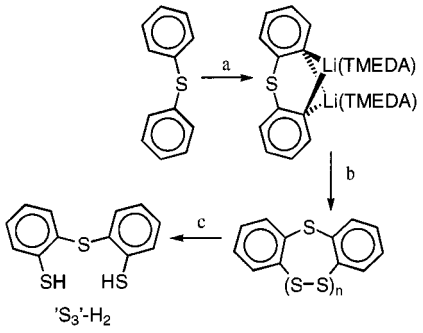
S−C(aryl) bonds are usually more stable than S−C(alkyl) bonds toward reductive S−C cleavage.[10] Furthermore, [Ni('S_3')] fragments formed from Ni^{II} salts and 'S_3'$^{2-}$ were anticipated to provide a readily accessible vacant site for hydride addition. Potential [Ni(H)('S_3')]$^-$ adducts directly compare with [Ni(H)(PMe_3)($S_2C_6H_4$)]$^-$ when the phosphane is exchanged for an isoelectronic thioether ligand. 'S_3'-H_2 is related to the recently described ligands MeN(*o*-$C_6H_4SH)_2$,[11] PhP(*o*-$C_6H_4SH)_2$,[12] PhP($C_2H_4SH)_2$,[13] and P(*o*-$C_6H_4SH)_3$,[14] which also give nickel complexes.

The first synthesis of 'S_3'-H_2, resulting in milligram yields after chromatography, has been reported by Block et al.[15] Therefore, the first goal of our investigations was to find a different approach to this ligand in order to make 'S_3'-H_2 available in preparative gram amounts. Attempts to coordinate 'S_3'$^{2-}$ and biologically relevant coligands such as H^-, H_2, S^{2-}, or CN^- to nickel(II) gave results that prompted us to extend our studies to platinum(II) complexes and the 'S_3' ligand derivatives 'RS_3'-H (R = Me, Et, Cy) and 'Et_2NS_2'-H.

Results and Discussion

Synthesis of 'S_3'-H_2

The target ligand 'S_3'-H_2 formed in a four-step one-pot reaction according to Scheme 1.



Scheme 1. Synthesis of 'S_3'-H_2

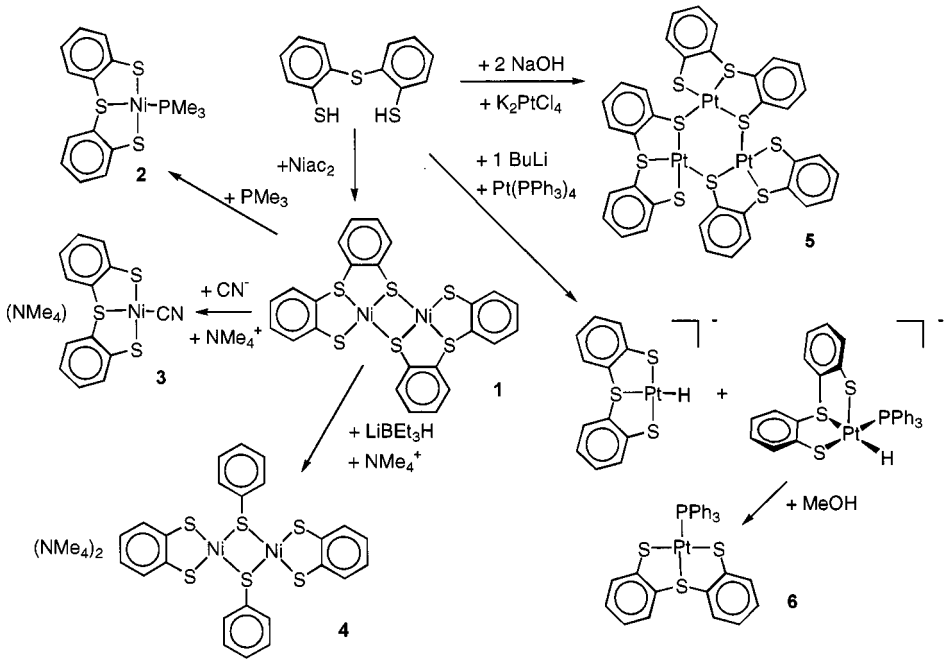
Twofold *ortho*-lithiation of diphenyl sulfide [$S(C_6H_5)_2$] with *n*BuLi in hexanes/TMEDA (tetramethylethylenediamine) at room temperature yielded [{Li(TMEDA)}$_2$S($C_6H_4)_2$] (step a), which has recently been characterized by Kranz et al.[16] Subsequent addition of 1.5 equivalents of elemental sulfur (3/8 S_8) gave a mixture of polysulfides in which the lithiated *ortho*-C atoms are bridged by S-chains (step b). Reduction of the S−S bonds was achieved with an excess of $LiAlH_4$ in THF at elevated temperature (70°C). Final acidification with concentrated hydrochloric acid, extraction and recrystallization from boiling THF/hexanes yielded 'S_3'-H_2 as white microcrystals (step c). By this method, 'S_3'-H_2 could be obtained in amounts of up to 10 g, which totaled ca. 20% yield from $S(C_6H_5)_2$.

Further experiments showed that step b of Scheme 1 is crucial for the overall yield. In this step, species such as thianthrene $C_{12}H_8S_2$ whose reduction cannot yield 'S_3'-H_2, are also formed. Addition of EtBr to the mixture resulting from step a yielded bis(2-ethylphenyl) sulfide in 91% yield, demonstrating that the *ortho*-lithiation of diphenyl sulfide had occurred in nearly quantitative yield. Isolation of the extremely moisture-sensitive [{Li(TMEDA)}$_2$S($C_6H_4)_2$] and its subsequent reaction with elemental sulfur did not improve the overall yield. Treatment of the [{Li(TMEDA)}$_2$S($C_6H_4)_2$] solution with S_2Cl_2 resulted only in traces of 'S_3'-H_2.

Nickel(II) and Platinum(II) Complexes of 'S_3'$^{2-}$

Scheme 2 summarizes complexes and their reactions. The reaction of 'S_3'-H_2 with $Ni(ac)_2{\cdot}4H_2O$ yielded brown-black microcrystals of analytically pure [Ni('S_3')]$_2$ (**1**). Complex **1** is air stable, diamagnetic and so sparingly soluble even in hot DMF or DMSO that no meaningful NMR spectra could be recorded. Recrystallization from hot DMF (175°C) in a sealed ampoule yielded single crystals, whose X-ray crystal structure analysis revealed the dinuclear structure of **1**. The nickel centers exhibit a tetrahedrally distorted planar coordination by four sulfur donors. The fourth coordination site in each [Ni('S_3')] fragment is blocked by a thiolate bridge.

In order to investigate the accessibility of this fourth coordination site, suspensions of [Ni('S_3')]$_2$ (**1**) were treated with nucleophiles such as PMe_3, KCN, Li_2S, and N_2H_4 in mixtures of THF/MeOH, THF/MeOH/H_2O, or MeOH/H_2O, which warranted sufficient solubility of the nucleophiles. Although [Ni('S_3')]$_2$ (**1**) is practically insoluble in these solvent mixtures, in all cases rapid reactions occurred. The resulting PMe_3 and KCN reaction products could be fully characterized. Orange [Ni(PMe_3)('S_3')] (**2**), which was obtained in nearly quantitative yield, is diamagnetic, soluble in common organic solvents except pentane or MeOH, and air-stable for longer periods of time. NMR spectra and X-ray structure determination proved that [Ni(PMe_3)('S_3')] is mononuclear in solution and in solid state. The reaction of [Ni('S_3')]$_2$ (**1**) with KCN in MeOH/H_2O rapidly afforded a yellow solution from which, upon addition of NMe_4Cl,



Scheme 2. Synthesis and reactions of nickel(II) and platinum(II) 'S_3'$^{2-}$ complexes

brown NMe_4[Ni(CN)('S_3')] (**3**) precipitated. Complex **3** too, is diamagnetic and was shown to contain a four-coordinate Ni center by X-ray structure analysis.

The reactions of [Ni('S_3')]$_2$ (**1**) with N_2H_4 or Li_2S/NMe_4Cl yielded products whose elemental analyses, IR and NMR spectra indicated the formation of [Ni(N_2H_4)('S_3')] and $(NMe_4)_2$[μ-S{Ni('S_3')}$_2$], respectively. These species, however, could not be obtained in pure form.

Numerous attempts to cleave [Ni('S_3')]$_2$ (**1**) in an analogous way with hydrides, in order to obtain a [Ni(H)('S_3')]$^-$ species, remained unsuccessful. When [Ni('S_3')]$_2$ (**1**) was treated with $LiBEt_3H$ in THF at various temperatures (−90 to −30 °C) or with $NaBH_4$ in MeOH at room temperature, rapid reactions occurred yielding dark-yellow to brown solutions. Addition of NMe_4Cl in MeOH precipitated red-brown microcrystals whose elemental analyses and spectroscopic data were compatible with the dinuclear complex $(NMe_4)_2$[Ni(SC_6H_5)($S_2C_6H_4$)]$_2$ (**4**). Complex **4** is diamagnetic and soluble in DMF or DMSO. The ^{1}H- and ^{13}C-NMR spectra of **4** revealed that the 'S_3' ligand of **1** had been cleaved into thiophenolate and 1,2-benzenedithiolate ligands. The ESI mass spectrum of **4** showed a peak at *m*/*z* = 306.9 which was assigned to the dinuclear anion of **4** (calculated for $^{12}C_{24}{}^1H_{18}{}^{58}Ni_2{}^{32}S_6$: *m*/*z* = 306.922). The formation of **4** was corroborated by its independent synthesis from Ni^{2+}, $LiSC_6H_5$, $Li_2S_2C_6H_4$, and NMe_4Cl, yielding the identical compound. C−S bond cleavage in the 'S_3' ligand was also observed when mononuclear [Ni(PMe_3)('S_3')] (**2**) was treated with $LiBEt_3H$ or $NaBH_4$. [Ni('S_3')]$_2$ (**1**) did not react with molecular hydrogen at standard pressure or with equimolar amounts of hydrochloric acid. Excess hydrochloric acid hydrolyzed **1** to give $NiCl_2$ and free 'S_3'-H_2.

The synthesis of 'S_3'-H_2 demonstrates that 'S_3'$^{2-}$ is stable for longer periods of time in the presence of $LiAlH_4$ at elevated temperatures. Therefore the C−S bond cleavage by hydride reagents in nickel-coordinated 'S_3'$^{2-}$ is remarkable. It indicates a considerable activation of either the 'S_3' ligand or the hydrides by coordination to nickel(II). Following the tenet of coordination chemistry that the heavier homologues are frequently more stable, we also investigated reactions of 'S_3'-H_2 with platinum(II).

The reaction between K_2PtCl_4 and Na_2-'S_3' in H_2O yielded red [Pt('S_3')]$_3$ (**5**) besides other products. Its trinuclear structure was elucidated by X-ray diffraction. [Pt('S_3')]$_3$ (**5**) could also be obtained from [$PtCl_2$(COD)] and 'S_3'-H_2 in THF.[17] [Pt('S_3')]$_3$ (**5**) is air-stable and slightly more soluble than [Ni('S_3')]$_2$ (**1**), not only in DMF and DMSO, but also in THF and CH_2Cl_2. Treatment of [Pt'S_3']$_3$ (**5**) in THF with $LiBEt_3H$ at room temperature yielded yellow solutions. The ^{1}H-NMR spectra of these solutions indicated that the [Pt('S_3')] fragments had remained intact, but they showed no signals which could be assigned to a [Pt(H)('S_3')]$^-$ species. The viability of such a species, however, could be demonstrated when 'S_3'-H_2 was monodeprotonated with one equivalent of *n*BuLi and the resulting Li['S_3'-H] subsequently reacted with [Pt(PPh_3)$_4$]. By oxidative addition of the remaining SH moiety of Li['S_3'-H] to the Pt^0 center, a mixture of two hydride complexes resulted. They could be isolated in solid state, identified by their ^{1}H-NMR hydride resonances and coupling constants as Li[Pt(H)(PPh_3)('S_3')] [δ(PtH) = −10.65] and Li[Pt(H)('S_3')] [δ(PtH) = −15.72]. The Pt−H bonds were also indicated by the IR spectra showing ν(Pt−H) bands at 2109 cm^{-1} in KBr and 2127 cm^{-1} in dioxane. However these two complexes could not be separated because they exhibit practically identical solubilities. Attempts to separate the two complexes by fractional crystallization from THF/MeOH yielded only very few single orange crystals

of the hydride-free [Pt(PPh_3)('S_3')] (**6**), whose structure was determined by X-ray crystallography.

Synthesis of 'RS_3'-H Ligands (R = Me, Et, Cy) and 'RS_3' Nickel(II) and Platinum(II) Complexes

The 'RS_3'-H ligands were synthesized in order to investigate the influence of different donor sets (thioether vs. thiolate), charge (neutral vs. anionic), and sterical requirements (small vs. large R substituents) on the stability of potential nickel and platinum hydride complexes with S_3 donor sets. Selective monoalkylation of dithiols having equivalent thiol functions is not trivial,[18] and this also became apparent in the 'RS_3'-H synthesis. Alkylation of [Ni('S_3')] complexes was considered the most promising method, because previous alkylations of $[Ni(S_2C_6H_4)_2]^{2-}$ complexes had selectively yielded the monoalkylated 1,2-benzenedithiol derivatives, 1,2-C_6H_4(SH)(SR), in straightforward reactions.[19]

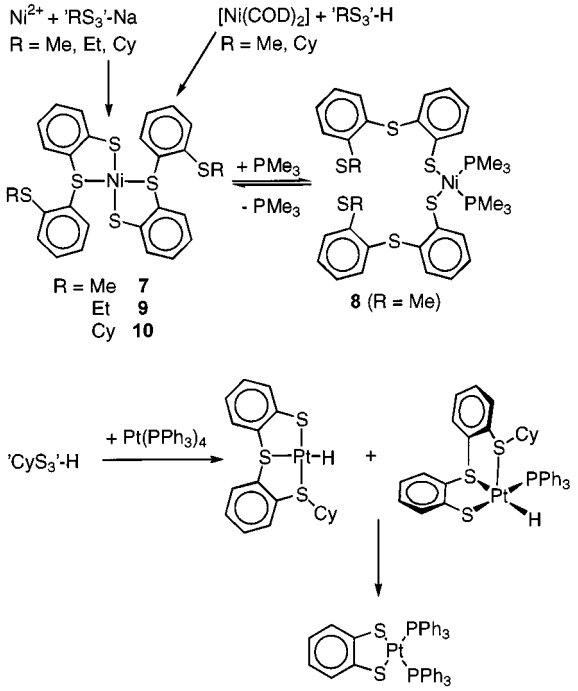
In contrast to these reactions, the alkylation of [Ni('S_3')]$_2$ (**1**) or [Ni(PMe_3)('S_3')] (**2**) with R_3OBF_4 (R = Me, Et) yielded mixtures of complexes that contained not only the monoalkylated target ligand 'RS_3'$^-$ but to a minor extent also dialkylated 'R_2S_3' species as well as the non-alkylated 'S_3'$^{2-}$ starting ligand. However, acidic hydrolysis of the complexes with aqueous HCl and subsequent purification of the resulting mixture of 'RS_3'-H, 'R_2S_3', and 'S_3'-H_2 species by repeated alkaline and acidic extractions yielded 'MeS_3'-H and 'EtS_3'-H in sufficient purity to be unambiguously identified by ^{1}H-NMR spectroscopy and used for the synthesis of complexes.

Alkylation of [Ni('S_3')] complexes by cyclohexyl bromide or tosylate proved impossible, probably due to steric hindrance. The "direct" alkylation of the monolithium salt Li['S_3'-H] with cyclohexyl bromide under drastic conditions (DMF, 125°C, 6 h) and acidic workup gave a mixture of 'CyS_3'-H, 'Cy_2S_3', and 'S_3'-H_2. Repeated extractions of this mixture, similar to those described above, yielded the 'CyS_3'-H target ligand in sufficient purity for identification and synthesis of complexes.

The ligating properties of the 'RS_3'$^-$ and 'S_3'$^{2-}$ ligands towards Ni^{II} differed more than expected. In all structurally characterized complexes, the 'RS_3' ligands acted as bidentate or even monodentate ligands only (Scheme 3).

The 1:1 reaction between Ni^{II} salts and Na['MeS_3'] gave the 1:2 complex [Ni('MeS_3')$_2$] (**7**). The identical complex was obtained in the attempt to coordinate 'MeS_3'-H to [Ni(1,5-cyclooctadiene)$_2$] in a 1:1 oxidative addition reaction. [Ni('MeS_3')$_2$] (**7**) is almost insoluble in all common solvents, but could be characterized by X-ray diffraction.

In an attempt to remove one 'MeS_3' ligand from [Ni('MeS_3')$_2$] (**7**) with PMe_3 in order to achieve a tridentate coordination of the remaining 'MeS_3', an excess of PMe_3 was required to achieve a reaction. However, this reaction did not yield the target complex [Ni(PMe_3)('MeS_3')] but [Ni(PMe_3)$_2$('MeS_3')$_2$] (**8**). The structure of **8** was concluded from elemental analysis and the ^{1}H-NMR spectrum showing one PMe_3 doublet and one set of eight aromatic signals for the



Scheme 3. Synthesis and reactions of nickel and platinum 'RS_3'$^-$ complexes

'MeS_3' ligand. One of the aromatic signals is split into a doublet of pseudotriplets by a long-range coupling to ^{31}P ($^5J_{H,P}$ = 2.6 Hz). This clearly indicates the postulated *cis* isomer of **8**, as strong coupling over five bonds can only take place along a W-shaped backbone, where the phosphane ligand is *trans* to the thiolate. The PMe_3 addition is reversible. Attempts to crystallize **8** from a $CDCl_3$ solution yielded PMe_3-free [Ni('MeS_3')$_2$] (**7**) in the course of three weeks.

'EtS_3'$^-$ was anticipated to give more soluble complexes. Indeed, [Ni('EtS_3')$_2$] (**9**), resulting from the 1:1 reaction between Ni^{II} salts and 'EtS_3'$^{2-}$, proved sufficiently soluble for recording ^{1}H-NMR spectra. They show only one set of 'EtS_3' signals indicating that [Ni('EtS_3')$_2$] (**9**) is structurally analogous to [Ni('MeS_3')$_2$] (**7**).

'CyS_3'$^-$ yielded complexes that were even more soluble. However, also with 'CyS_3'$^-$ only the 1:2 complex [Ni('CyS_3')$_2$] (**10**) could be obtained. It likewise resulted from Ni^{II} salts and 'CyS_3'-H, and oxidative addition reactions of 'CyS_3'-H with [Ni($CO)_4$], [Ni(phen)$_2$], or [Ni(PMe_3)$_4$]. Intermediate nickel hydride species such as [Ni(H)('CyS_3')] could not be detected.

Metal hydride species were observed with platinum, but again only as inseparable mixtures of at least two complexes. The oxidative addition of 'CyS_3'-H to [Pt(PPh_3)$_4$] gave a mixture of [Pt(H)('CyS_3')] and [Pt(H)(PPh_3)('CyS_3')], which were identified by their ^{1}H-NMR hydride signals at δ = −15.74 [$^1J(^{195}Pt-H)$ = 1155 Hz] and δ = −11.38 [$^1J(^{195}Pt-H)$ = 1260 Hz], respectively (Figure 1). The hy-

dride signals of [Pt(H)(PPh_3)('CyS_3')] are split into doublets by coupling to ^{31}P [^2J(H,P) = 20 Hz].

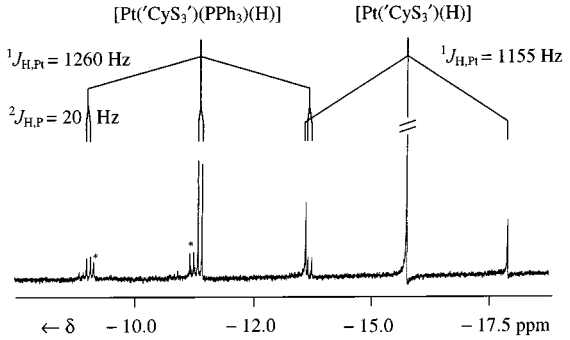
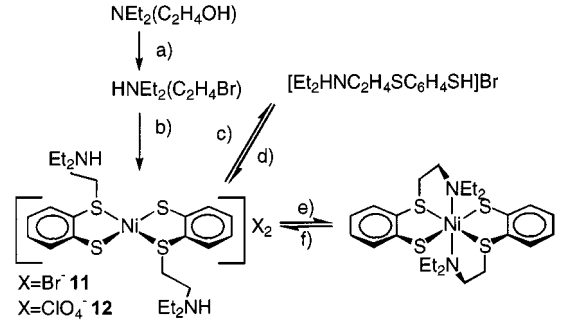


Figure 1. High-field region of the ^{1}H-NMR spectrum (270 MHz, [D_8]THF) of a mixture of [Pt('S_3')(PPh_3)(H)] and [Pt('S_3')(H)] (* denotes impurities)

Heating the mixtures in order to remove the PPh_3 ligand from [Pt(H)(PPh_3)('CyS_3')] resulted in C–S cleavage of the CyS_3 ligand, loss of the hydride ligands and formation of [$Pt(PPh_3)_2(S_2C_6H_4)$], which was characterized by elemental analysis and ^{1}H-NMR spectroscopy.

Synthesis and Reactions of [Ni('Et_2HNS_2')$_2$]$^{2+}$

In order to investigate the influence of amine vs. thioether donors, the tridentate amine–thioether–thiol ligand 'Et_2NS_2'-H was synthesized (Scheme 4).



Scheme 4. Synthesis and reactions of [Ni('Et_2HNS_2')$_2$]$^{2+}$: a) + PBr_3/HBr; b) + [$Ni(S_2C_6H_4)_2$]$^{2-}$; c) + HBr; d) + $Ni(ClO_4)_2 \cdot 6H_2O$; + *n*BuLi; f) + H_2O

Bromination of [$NEt_2(C_2H_4OH)$] with PBr_3 yielded $NEt_2(C_2H_4Br)$ as the ammonium salt [$NHEt_2(C_2H_4Br)$]Br. Subsequent treatment of the benzenedithiolate complex [$Ni(S_2C_6H_4)_2$]$^{2-}$ with [$NHEt_2(C_2H_4Br)$]Br gave [Ni('Et_2HNS_2')$_2$]Br_2 (**11**), which could be hydrolyzed with aqueous HBr to yield the ammonium bromide derivative ['Et_2HNS_2'-H]Br. Twofold deprotonation of ['Et_2HNS_2'-H]Br and reaction with either 0.5 or 1 equivalent of $Ni(ClO_4)_2 \cdot 6H_2O$ in both cases yielded the 1:2 complex [Ni('Et_2HNS_2')$_2$]$(ClO_4)_2$ (**12**). The reaction of [Ni('Et_2HNS_2')$_2$]$(ClO_4)_2$ suspensions in THF with 2 equivalents of strong bases such as BuLi or $LiBEt_3H$ reversibly gave dark-red solutions. They presumably contain [Ni('Et_2NS_2')$_2$] with six-coordinate Ni centers. However, a 1:1 complex containing [Ni('Et_2NS_2')] fragments could not be obtained.

X-ray Structure Determinations

X-ray structural characterizations allowed for the determination of the molecular structure of a considerable number of complexes and to confirm conclusions drawn from spectroscopic data. Figure 2 shows the molecular structures of [Ni('S_3')]$_2$ (**1**), [Ni(PMe_3)('S_3')] (**2**), NMe_4[Ni('S_3')CN)]·$0.5CH_2Cl_2$ (**3**·$0.5CH_2Cl_2$), [Ni('MeS_3')$_2$] (**7**), [Pt('S_3')(PPh_3)] (**6**), [Pt('S_3')]$_3$·2THF·MeOH, (**5**·2THF·MeOH), and [Ni('Et_2HNS_2')$_2$]Br_2 (**11**). Table 1 lists selected distances and angles.

All compounds consist of discrete molecules or ions. The solvate molecules do not interact with the metal complexes. [Ni('S_3')]$_2$ (**1**), [Ni('MeS_3')$_2$] (**7**), and [Ni('Et_2HNS_2')$_2$]Br_2 (**11**) exhibit crystallographically required inversion symmetry. In all complexes, the metal centers are four-coordinate, adopting distorted planar configurations. [Ni('S_3')]$_2$ (**1**), [Ni(PMe_3)('S_3')] (**2**), and [Ni(CN)('S_3')]$^-$ (**3**) exhibit a distinct tetrahedral distortion, whereas the platinum coordination of [Pt('S_3')]$_3$ (**5**) and [Pt(PPh_3)('S_3')] (**6**) is close to ideal square-planar.

The distances and angles are in the usual range found in diamagnetic nickel(II) and platinum(II) thioether–thiolate complexes. It is worth noting, however, that the Ni–S(thioether) distances of [Ni('S_3')]$_2$ (**1**) [210.3(3) pm], [Ni(PMe_3)('S_3')] (**2**) [213.8(2) pm], and [Ni(CN)('S_3')]$^-$ (**3**) [212.4(1) pm] are short and smaller than the respective Ni–S(thiolate) distances. Ni–S(thioether) distances in comparable complexes are usually in the range of ca. 217–218 pm,[20] and Ni–S distances in nickel thioether–thiolate complexes frequently do not differ at all.[21] If they differ, the Ni–S(thioether) distances are longer than the Ni–S(thiolate) distances.[22] It is remarkable that even in [Ni(PMe_3)('S_3')] (**2**) and [Ni(CN)('S_3')]$^-$ (**3**), the Ni–S(thioether) distances are short despite of the coordination *trans* to PMe_3 or CN^-, respectively, which are ligands known to have a strong *trans* influence.[23] The same holds true for the platinum complex [Pt('S_3')(PPh_3)] (**6**).[24] The short M–S(thioether) distances can be rationalized by the topology and rigidity of the 'S_3' ligand leading to rigid annellated five-membered [MSCCS] rings that force the thioether donors close to the metal centers. The rigidity of the 'S_3' ligand and sp^3 hybridization of the thioether donor further lead to the particular geometry of the [M('S_3')] fragments. They all exhibit a butterfly-like shape as illustrated by Figure 3.

In [Ni('S_3')]$_2$ (**1**), two such fragments are bridged by thiolate donors. The resulting four-membered [Ni_2S_2] ring is folded along the [S–S] axis such that the Ni(1)–Ni(1a) distance is 273.2(4) pm, and the molecule adopts a bowl-like shape (Figure 4).

A comparable Ni–Ni distance is found in [$Ni(SC_2H_4SC_2H_4S)]_2$ (273.9 pm).[25] These distances are significantly longer than Ni–Ni distances in nickel metal (249.2 pm)[26] and complexes such as [$Ni_8S(t$BuS$)_9$] (244.4 and 247.1 pm),[27] [$Ni(PhC(O)S)_2]_2$ (249 pm)[28] or [Ni(1,3-diphenyltriazenido)$_4]_2$ (238 pm),[29] for which Ni–Ni bonds

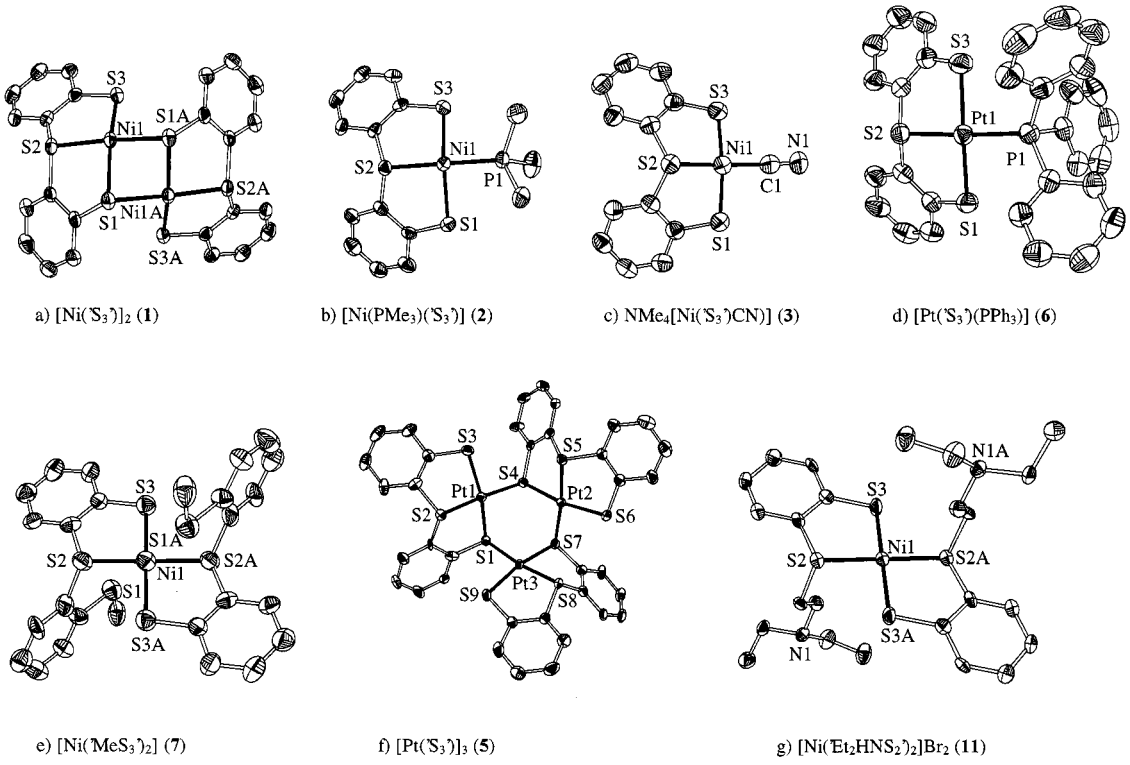


Figure 2. ORTEP Diagrams of a) [Ni('S_3')]$_2$ (**1**), b) [Ni(PMe_3)('S_3')] (**2**), c) NMe_4[Ni('S_3')CN)]·0.5CH_2Cl_2 (**3**·0.5CH_2Cl_2), d) [Pt('S_3')(PPh_3)] (**6**), e) [Ni('MeS_3')$_2$] (**7**), f) [Pt('S_3')]3·2THF·MeOH, (**5**·2THF·MeOH), g) [Ni('Et_2HNS_2')$_2$]Br_2 (**11**) (50% probability ellipsoids; hydrogen atoms, solvent molecules and counter ions omitted)

Table 1. Selected distances [pm] and angles [°] of [Ni('S_3')]$_2$ (**1**), [Ni('S_3')(PMe_3)] (**2**), NMe_4[Ni('S_3')(CN)]·0.5CH_2Cl_2 (**3**·0.5CH_2Cl_2), [Ni('MeS_3')$_2$] (**7**), [Ni('Et_2HNS_2')$_2$]Br_2 (**11**), [Pt('S_3')]3·2THF·MeOH (**5**·2THF·MeOH) and [Pt('S_3')(PPh_3)] (**6**)

Compound	[Ni('S_3')]$_2$	[Ni('S_3')(PMe_3)]	[Ni('S_3')(CN)]$^-$	[Ni('MeS_3')$_2$]	[Ni('Et_2NS_2')$_2$]Br_2		[Pt('S_3')]$_3$[c]		[Pt('S_3')(PPh_3)]
	1	**2**	**3**	**7**	**11**		**5**		**6**
M(1)−S(1)	218.3(1)	216.2(2)	216.2(1)	333.8(3)	477.1(9)[b]	231.2(3)	231.6(3)[d]	232.7(3)[e]	231.2(1)
M(1)−S(2)	210.4(3)	213.8(2)	212.4(1)	215.6(3)	216.1(2)	225.8(4)	225.4(3)	225.1(3)	228.7(1)
M(1)−S(3)	213.7(1)	214.8(2)	215.8(1)	219.0(3)	217.3(2)	230.3(3)	228.5(3)	228.2(4)	231.2(1)
M(1)−L	216.9(3)[a]	215.8(2)	185.7(4)			232.1(4)[f]	232.0(3)[g]	231.1(3)[h]	226.1(1)
M−M	273.2(4)	−	−	−	−	362.0(1)[i]	338.6(1)[k]	351.2(1)[l]	−
S(1)−M(1)−S(2)	87.89(9)	89.81(7)	90.10(4)			89.09(12)	87.28(11)	86.07(12)	87.69(4)
S(1)−M(1)−S(3)	161.80(3)	158.50(7)	160.03(5)			167.31(12)	167.33(13)	168.13(11)	163.92(5)
S(2)−M(1)−S(3)	92.02(7)	91.71(7)	90.80(4)	90.56(11)	91.11(9)	86.47(13)	88.89(12)	89.36(12)	87.08(4)
S(1)−M(1)−L	83.15(8)[a]	90.73(7)	92.76(11)			88.83(12)[f]	88.30(11)[g]	88.27(12)[h]	94.40(4)
S(2)−M(1)−L	165.73(3)[a]	168.08(7)	166.91(12)			175.91(12)[f]	173.52(12)[g]	172.38(11)[h]	177.85(4)
S(3)−M(1)−L	99.95(7)[a]	92.13(8)	90.86(11)			96.27(12)[f]	96.41(12)[g]	97.15(12)[h]	90.76(4)

[a] L = S(1a). − [b] Ni(1)−N(1). − [c] Three independent [PtS_3] units. − [d] Pt(2)−S(4). − [e] Pt(3)−S(7). − [f] L = S(4). − [g] L = S(7). − [h] L = S(1). − [I] Pt(1)−Pt(2). − [k] Pt(2)−Pt(3). − [l] Pt(3)−Pt(1).

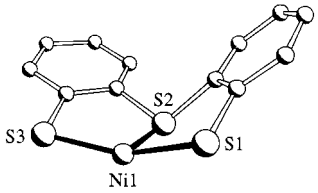


Figure 3. [Ni('S_3')] fragment in [Ni(PMe_3)('S_3')] (**2**)

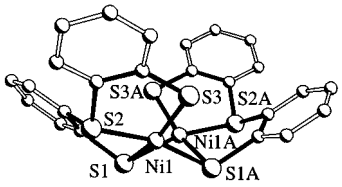


Figure 4. Lateral view of [Ni('S_3')]$_2$ (**1**)

are discussed. However, even Ni−Ni distances of 276.3(3) pm[30] and 279.5(3) pm[31] have been assumed to indicate weak Ni−Ni interactions. The trinuclear [Pt('S_3')]$_3$ (**5**) exhibits a cyclohexane-like [PtS_3]$_3$ six-membered ring with chair conformation. The Pt−S−Pt thiolate bridges are nearly symmetrical. Related structures are found in [$Pd(SC_2H_4SC_2H_4S)$]$_3$,[25b] [Ni('μ-$S_2C_3Me_2$')$_3$],[32] and [Ni('tBuS$_4$')]$_3$.[33]

The structures of [Ni('MeS_3')$_2$] (**7**) and [Ni('Et_2HNS_2')$_2$]Br_2 (**11**) unambiguously show that the potentially tridentate ligands only serve as bidentate ligands. The S(1) and S(1a) thioether donors of [Ni('MeS_3')$_2$] (**7**) occupy approximately apical positions in a distorted octahedron, but the Ni−S(1) and Ni−S(1a) distances [333.8(3) pm] are significantly larger than the sum of the van der Waals radii (310 pm)[26] and exclude Ni−S bonding interactions.

Conclusion

The objective of this work was to find nickel−sulfur ligand complexes that are stable towards reductive C−S cleavage and offer vacant sites for the coordination of hydrogenase-relevant small molecules. To achieve this goal, syntheses of 'S_3'-H_2, 'RS_3'-H (R=Me, Et, Cy), and 'Et_2NS_2'-H have been developed. X-ray structure analyses of the resulting nickel(II) and platinum(II) complexes have established the structural basis for reactivity studies.

Nickel(II) coordination by 'S_3'$^{2-}$ gave binuclear [Ni('S_3')]$_2$ (**1**) and platinum(II) formed trinuclear [Pt('S_3')]$_3$ (**5**). The [Ni('S_3')] fragment is robust and yielded stable [Ni(L)('S_3')] adducts with coligands such as PMe_3 and CN^-. In this respect, the [Ni('S_3')] fragment contrasts with other nickel thioether−thiolate complexes in which the ligands are decoordinated by cyanide.[34] The [Ni('S_3')] fragment probably also adds hydride. However, nickel-coordinated 'S_3'$^{2-}$ is unstable towards hydride reagents such as $LiAlH_4$ or $LiBEt_3H$. They cleaved the 'S_3'$^{2-}$ ligand into thiophenolate and 1,2-benzenedithiolate that formed [{Ni(SC_6H_5)($S_2C_6H_4$)}$_2$]$^{2-}$. This putatively indicates that in the reaction between [Ni('S_3')] fragments and hydride sources, highly reactive [Ni(H)('S_3')]$^-$ species form because 'S_3'$^{2-}$ in the free state is stable towards $LiAlH_4$, even under vigorous reaction conditions. While no [M(H)('S_3')]$^-$ species with M = Ni could be identified, a [Pt(H)('S_3')]$^-$ complex was detected by ^{1}H-NMR spectroscopy and isolated in the solid state. However, it could not be separated from [Pt(H)(PPh_3)('S_3')]$^-$ complexes which were formed concomitantly. Modification of 'S_3'$^{2-}$ by alkylating one thiolate donor gave the new ligands 'RS_3'-H with R = Me, Et, Cy. When coordinated to nickel(II), these ligands act as bidentate ligands only. Under all applied conditions, exclusively 1:2 complexes of the general formula [Ni('RS_3')$_2$] resulted, in which the RS-thioether donors do not coordinate.

[Ni('RS_3')] hydride complexes could not be detected. In contrast, when [Pt(PPh_3)$_4$] was treated with 'CyS_3'-H, ^{1}H-NMR spectroscopy revealed the formation of [Pt(H)('CyS_3')]. The concomitant formation of the equally highly soluble [Pt(H)(PPh_3)('CyS_3')] prevented the isolation in pure form. Additionally, the platinum-bonded hydride appears to be still highly reactive, because at elevated temperatures 'CyS_3' cleavage and formation of [Pt(PPh_3)$_2$($S_2C_6H_4$)] took place.

Modification of the 'RS_3'-H ligands by exchanging the RSC_6H_4 entity for $NEt_2(C_2H_4)$ gave the new ligand 'Et_2NS_2'$^-$. It formed the 1:2 nickel complex [Ni('Et_2HNS_2')$_2$]Br_2 (**11**) in which the two amine N atoms are protonated.

In conclusion, the tridentate sulfur ligand 'S_3'$^{2-}$ forms nickel(II) and platinum(II) complexes whose [M('S_3')] fragments coordinate coligands such as PR_3, CN^-, and H^-. The resulting [M(H)('S_3')]$^-$ species were detectable with platinum(II). The alkylated derivatives 'RS_3' preferably act as bidentate ligands and give the 1:2 complexes [Ni('RS_3')$_2$]. Current studies are probing the interaction of molecular hydrogen with the new complexes.

Experimental Section

General Methods: Unless otherwise noted, all reactions and operations were carried out under nitrogen at room temperature using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR or NMR spectroscopy. − Spectra were recorded with the following instruments: IR (KBr pellets or CaF_2 cuvettes, solvent bands were compensated): Zeiss IMR 25 and Perkin−Elmer 983. − NMR: Jeol JNM-GX 270 and Jeol JNM-EX 270; with the residual protiosolvent signal used as reference for ^{1}H-NMR spectra. $^{13}C\{^1H\}$-NMR spectra were referenced using the solvent peaks, $^{31}P\{^1H\}$-NMR spectra were referenced externally. Chemical shifts are quoted on the δ scale (downfield shifts are positive) related to tetramethylsilane (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Spectra were recorded at room temperature unless stated otherwise. ^{1}H: 270.0 MHz, $^{13}C\{^1H\}$; 67.8 MHz, $^{31}P\{^1H\}$: 109.4 MHz. − Mass spectra: Varian MAT 212 spectrometer and Jeol M.Station 700. − Elemental analyses: Carlo Erba EA 1106 or 1108 analyzer. − $S(C_6H_5)_2$ and *n*BuLi (2.5 M in hexanes) were purchased from Aldrich. 'S_2'-H_2,[35] [Pt(PPh_3)$_4$],[36] [Pt(PEt_3)$_4$],[37] and [$PtCl_2$(COD)][38] were prepared by literature methods.

'S_3'-H_2: At room temperature, TMEDA (38 mL, 253 mmol), a solution of *n*BuLi in hexanes (2.5 M, 100 mL, 250 mmol) and diphenyl sulfide (20 mL, 118 mmol) were successively added to 200 mL of hexanes. The solution was stirred for 24 h, in the course of which a beige solid precipitated. Under vigorous stirring elemental sulfur (10.8 g, 337 mmol) was added, the resulting yellow suspension was stirred for another 48 h, and concentrated to dryness. The yellow residue was dissolved in THF (200 mL) and $LiAlH_4$ (10.0 g, 264 mmol) was added in small portions. ***Caution:*** *A vigorous reaction takes place and the reaction suspension starts foaming up.* Subsequently, the reddish suspension was heated at reflux for 5 h, in the course of which the color turned to light yellow green. The resulting mixture was cautiously added in small portions to a mixture of crushed ice (400 g) and concentrated hydrochloric acid (200 mL). ***Caution:*** *A vigorous evolution of* H_2 and H_2S occurs, and this reaction must be carried out in a well-ventilated hood. After the vigorous reaction had ceased, a further 50 mL of concentrated HCl was added, and the resulting suspension was extracted with of CH_2Cl_2 (3 × 200 mL). The combined organic phases were washed with dilute aqueous HCl, dried with Na_2SO_4, and concentrated to dryness. The reddish yellow waxy residue was digested with Et_2O (ca. 200 mL) until an ivory solid resulted. It was separated, recrystallized from hot THF/hexanes to give brilliant white 'S_3'-H_2. Yield: 6.5 g [22% from $S(C_6H_5)_2$]. − $C_{12}H_{10}S_3$ (250.41): calcd. C 57.56, H 4.03, S 38.42; found C 57.74, H 4.06, S 38.72. − MS (FD, CCl_4); *m/z*: 250 [M$^+$]. − ^{1}H NMR ($CDCl_3$): δ = 7.45−7.35 (m, 2 H, C_6H_4), 7.25−7.0 (m, 6 H, C_6H_4), 4.10 (s, 2 H, SH). − ^{1}H NMR (C_6D_6): δ = 7.01 (m, 2 H, H6-C_6H_4), 6.96 (m, 2 H, H3-C_6H_4), 6.68 (m, 2 H, H4-C_6H_4), 6.63 (m, 2 H, H5-C_6H_4), 3.81 (m, 2 H, SH).

– $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 135.6, 132.9, 130.8, 128.9, 127.2 (C_6H_4). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 135.7 (C2-C_6H_4), 132.8 (C1-C_6H_4), 132.5 (C6-C_6H_4), 130.2 (C3-C_6H_4), 128.2 (C4-C_6H_4), 126.5 (C5-C_6H_4). – IR (KBr): $\tilde{\nu}$ = 3052, 2555, 1565, 1445, 1426, 1259, 1035, 745 cm^{-1}.

[Ni('S_3')]$_2$ (1): 'S_3'-H_2 (2.450 g, 9.78 mmol) in THF (30 mL) was added dropwise to a solution of $Ni(ac)_2{\cdot}4H_2O$ (2.435 g, 9.78 mmol) in MeOH (50 mL). A brown precipitate formed which was separated, washed with MeOH (50 mL) and recrystallized from boiling DMF to give black microcrystals of **1**. Yield: 2.73 g (91%). – $C_{24}H_{16}Ni_2S_6$ (614.17): calcd. C 46.94, H 2.63, S 31.33; found C 46.81, H 2.56, S 30.83. – IR (KBr): $\tilde{\nu}$ = 3050, 1561, 1443, 1425, 1093, 759, 747, 740, 729 cm^{-1}.

[Ni('S_3')(PMe_3)] (2): PMe_3 (370 mg, 4.86 mmol) was added to a brown suspension of [Ni('S_3')]$_2$ (**1**) (1.065 g, 1.73 mmol) in THF (5 mL) and a dark brown solution formed. Addition of MeOH (40 mL) precipitated orange microcrystals that were separated, washed with MeOH (40 mL) and dried. Yield: 1.25 g (94%). – $C_{15}H_{17}NiPS_3$ (383.16): calcd. C 47.02, H 4.47, S 25.11; found C 47.11, H 4.46, S 24.57. – ^1H NMR (C_6D_6): δ = 7.55 (d, 2 H, H6-C_6H_4), 7.28 (d, 2 H, H3-C_6H_4), 6.82 (m 2 H, H5-C_6H_4), 6.65 (m, 2 H, H4-C_6H_4), 0.93 [d, $^2J_{H,P}$ = 10.9 Hz, 9 H, $P(CH_3)_3$]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 152.5 (d, $^3J_{P,C}$ = 14.0 Hz, C_6H_4) 133.3, 130.5, 129.4, 128.3, 123.5 (C_6H_4), 14.9 [d, $^1J_{P,C}$ = 30.6 Hz, $P(CH_3)_3$]. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 153.6 (d, *trans*-$^3J_{P,C}$ = 14.1 Hz, C1-C_6H_4), 133.3 (d, *cis*-$^3J_{P,C}$ = 2.0 Hz, C2-C_6H_4), 130.1 (d, $^4J_{P,C}$ = 1.7 Hz, C6-C_6H_4), 128.7 (s, C5-C_6H_4), 128.1 (d, $^4J_{P,C}$ = 1.2 Hz, C3-C_6H_4), 122.6 (s, C4-C_6H_4), 13.5 [d, $^1J_{P,C}$ = 30.6 Hz, $P(CH_3)_3$]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = –9.2 [$P(CH_3)_3$]. – IR (KBr): $\tilde{\nu}$ = 3040, 2960, 1564, 1444, 1425, 1096, 950, 735 cm^{-1}.

(NMe_4)[Ni('S_3')(CN)] (3): A solution of KCN (141.5 mg, 2.17 mmol) in a mixture of MeOH (10 mL) and H_2O (1 mL) was added dropwise to a brown suspension of [Ni('S_3')]$_2$ (**1**) (650 mg, 1.06 mmol) in THF (10 mL). The resulting yellow green solution was concentrated to dryness, and the remaining solid was redissolved in MeOH (20 mL) and H_2O (1 mL). The solution was filtered, combined with NMe_4Cl (220 mg, 2.0 mmol) in MeOH (2 mL), and layered with Et_2O (20 mL). Brown crystals precipitated, which were separated after 7 d, washed with Et_2O and dried in vacuo. Yield: 520 mg (60%).– $C_{17}H_{20}N_2NiS_3$ (407.26) calcd. C 50.14, H 4.95, N 6.88; found C 45.58, H 4.36, N 5.98. – ^1H NMR ([D_6]acetone/$CDCl_3$): δ = 7.36 (d, 2 H, C_6H_4), 7.03 (d, 2 H, C_6H_4), 6.78 (m, 2 H, C_6H_4), 6.68 (m, 2 H, C_6H_4), 2.92 [12 H, s, $N(CH_3)_4$]. – IR (KBr): $\tilde{\nu}$ = 3050, 3026, 2110, 1569, 1482, 1441, 1431, 948, 733 cm^{-1}.

(NMe_4)$_2$[{Ni(SC_6H_5)($S_2C_6H_4$)}$_2$] (4). – a) From [Ni('S_3')]$_2$ and $LiBEt_3H$: At –90°C, $LiBEt_3H$ (3 mL of a 1 M THF solution, 3 mmol) was added to a brown suspension of [Ni('S_3')]$_2$ (**1**) (615 mg, 1.0 mmol) in THF (15 mL). When the temperature was slowly raised to –30°C, a yellow–green solution formed. It was layered with a cold solution of NMe_4Cl (0.329 g, 3.0 mmol) in MeOH (15 mL) and kept at –30°C for 3 d. Red-brown microcrystals precipitated which were separated, washed with MeOH, and dried in vacuo. Yield: 340 mg (45%). – **b) From Ni(ac)$_2$·4H$_2$O, $SC_6H_5^-$, and *o*-$S_2C_6H_4^{2-}$:** A solution of thiophenol (1.10 g, 10 mmol) and LiOMe (380 mg, 10 mmol) in MeOH (10 mL) was added to $Ni(ac)_2{\cdot}4H_2O$ (2.48 g, 10 mmol) in MeOH (40 mL). A red-brown suspension resulted, which was combined with a solution of *o*-$C_6H_4(SH)_2$ (1.42 g, 10 mmol) and LiOMe (760 mg, 20 mmol) in MeOH (20 mL), stirred for 2 h and concentrated to dryness. Addition of DMF (40 mL) to the residue and heating the suspension to 100°C for 2 h gave a clear brown solution, which was reduced in volume to 10 mL. Addition of Me_4NCl (1.095 g, 10 mmol) in MeOH (50 mL) at room temperature precipitated red-brown microcrystals which were separated, washed with MeOH (45 mL) and Et_2O (20 mL), and dried in vacuo. Yield: 3.06 g (80%). – $C_{32}H_{42}N_2Ni_2S_6$ (764.51): calcd. C 50.28, H 5.54, N 3.66, S 25.16; found C 47.16, H 5.38, N 3.23, S 23.42. – MS (ESI, MeOH) ([$^{12}C_{24}{}^1H_{18}{}^{58}Ni_2{}^{32}S_6$]$^{2-}$); *m/z*: calcd. 306.922; found 306.9. – ^1H NMR ([D_6]DMSO): δ = 8.22 (m, 4 H, C_6H_5), 7.05 (m, 6 H, C_6H_5), 6.80 (m, 4 H, C_6H_4), 6.40 (m, 4 H, C_6H_4), 3.07 [s, 24 H, $N(CH_3)_4$]. – $^{13}C\{^1H\}$ NMR ([D_6]DMSO): δ = 150.0, 139.8, 134.8, 126.8, 125.5, 124.3, 118.7 (C_6H_5, C_6H_4), 54.35 [t, $^1J_{C,N}$ = 4.2 Hz, $N(CH_3)_4$]. – IR (KBr): $\tilde{\nu}$ = 3045, 3007, 1571, 1542, 1479, 1433, 1282, 1233, 1101, 1021, 948, 743, 692, 665 cm^{-1}.

[Pt('S_3')]$_3$ (5). – a) From K_2PtCl_4 and 'S_3'-H_2: A solution of K_2PtCl_4 (1.06 g, 2.55 mmol) in H_2O (20 mL) was combined with a solution of 'S_3'-H_2 (640 mg, 2.55 mmol) in aqueous NaOH (51 mL of a 0.1 M solution, 5.1 mmol). A yellow suspension resulted which was stirred at 50°C for 2 h. The yellow solid was separated, washed with H_2O (40 mL), dried at 50°C, and extracted with THF (20 mL). The red THF extracts were filtered and layered with MeOH to give yellow-red crystals of [Pt('S_3')]3·2THF·MeOH. – ^1H NMR ([D_8]THF): δ = 7.95–6.40 (m, C_6H_4). – **b) From [$PtCl_2$(COD)] and 'S_3'-H_2:**[17] Solid 'S_3'-H_2 (865 mg, 3.46 mmol) was added to a solution of [$PtCl_2$(COD)] (1.293 g, 3.46 mmol) in THF (20 mL) and the resulting solution was stirred for 12 h. A yellow precipitate formed which was isolated, washed with THF (10 mL) and dried in vacuo. Yield: 1.24 g (81%). – $C_{36}H_{24}S_9Pt_3$ (1330.44): calcd. C 32.50, H 1.82; found C 32.54, H 1.95.

Li[Pt('S_3')(H)], Li[Pt('S_3')(H)(PPh_3)], and [Pt('S_3')(PPh_3)] (6): *n*BuLi (0.4 mL of a 2.5 M solution in hexanes, 1.0 mmol) was added to a solution of 'S_3'-H_2 (250 mg, 1.0 mmol) in THF (10 mL), and a pale yellow solution resulted, which was added dropwise to a suspension of [$Pt(PPh_3)_4$] (1.24 g, 1.0 mmol) in THF (30 mL). A yellow-orange solution resulted and was stirred for 1 h at 70°C and concentrated to dryness. The orange residue was extracted with warm hexanes (120 mL) in several portions and the remaining pale yellow powder was isolated and dried in vacuo. It was characterized by ^1H-NMR spectroscopy to be a mixture of Li[Pt('S_3')(H)], Li[Pt('S_3')(H)(PPh_3)] and some remaining PPh_3. – ^1H NMR ([D_8]THF): δ = 7.93–6.62 (m, C_6H_4/C_6H_5), –10.65 {d + dd, $^1J_{H,Pt}$ = 1274 Hz, $^2J_{H,P}$ = 21 Hz, Pt*H* in Li[Pt('S_3')(*H*)(PPh_3)]}, –15.72 {s + d, $^1J_{H,Pt}$ = 1242 Hz, Pt*H* in Li[Pt('S_3')(*H*)]}. – IR (KBr): $\tilde{\nu}$ = 2109 cm^{-1} (ν_{PtH}); (*p*-dioxane): $\tilde{\nu}$ = 2127 cm^{-1} (ν_{PtH}).

'MeS_3'-H: At –90°C, solid [Ni('S_3')(PMe_3)] (270 mg, 0.71 mmol) was added to a suspension of Me_3OBF_4 (105 mg, 0.71 mmol) in CH_2Cl_2 (15 mL). The suspension was warmed to room temperature and stirred for 4 h to give a yellow-brown solution. Addition of Et_2O (20 mL) precipitated a yellow-green powder that was separated, washed with little Et_2O and redissolved in CH_2Cl_2 (15 mL) to give a yellow-green solution. Addition of half-concentrated hydrochloric acid (20 mL) resulted in decoloration of the CH_2Cl_2 phase. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (15 mL). The combined CH_2Cl_2 extracts were dried with Na_2SO_4 and concentrated to give an oily pale yellow residue. It was dissolved in Et_2O (20 mL) and the resulting solution was extracted with aqueous NaOH (10%, 20 mL). The aqueous phase was separated, washed with Et_2O (10 mL), acidified with aqueous HCl, and extracted with CH_2Cl_2 (30 mL) in several portions. The combined CH_2Cl_2 layers were dried with Na_2SO_4 and concentrated to give 'MeS_3'-H as a colorless oil, which was identified by NMR spectroscopy. Yield: 60 mg (32%). – ^1H NMR ($CDCl_3$): δ = 7.50–6.95 (m, 8 H, C_6H_4), 4.26 (s, 1 H, SH), 2.54

(s, 3 H, CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 140.2, 136.9, 134.1, 134.0, 132.6, 131.3, 130.3, 129.1, 128.4, 127.2, 126.9, 126.5 (C_6H_4), 16.8 (CH_3).

NBu_4'EtS_3': $Et_3O{\cdot}BF_4$ (743 mg, 3.91 mmol) in CH_2Cl_2 (5 mL) was added to a stirred brown suspension of [Ni('S_3')]$_2$ (1.20 g, 1.96 mmol) in CH_2Cl_2 (50 mL). In the course of 16 h, a brown solution resulted to which concentrated aqueous HCl (40 mL) was added. After stirring for another 2 h, the CH_2Cl_2 phase had turned colorless. The CH_2Cl_2 phase was separated and the remaining aqueous phase was extracted with CH_2Cl_2 (20 mL). The combined CH_2Cl_2 extracts were concentrated to give a colorless oil, which was dissolved in MeOH (20 mL) and combined with 5 mL of a 1 M MeOH solution of Bu_4NOH (5 mmol). Et_2O (100 mL) was added and the resulting solution cooled to −78°C. Colorless microcrystals precipitated, which were separated at −78°C after 1 d, washed with Et_2O (−78°C) and dried. Yield: 1.20 g (59%).− ^1H NMR ([D$_4$]MeOH): δ = 7.47−7.26 (m, 4 H, C_6H_4), 7.11 (m, 1H, C_6H_4), 6.70 (m, 1H, C_6H_4), 6.56 (m, 1H, C_6H_4), 6.32 (m, 1H, C_6H_4), 3.22 (t, 8 H, NCH_2), 2.92 (q, 2 H, SCH_2), 1.64 (m, 8 H, NCH_2CH_2), 1.39 (m, 8 H, $NCH_2CH_2CH_2$), 1.28 (t, 3 H, SCH_2CH_3), 0.99 (t, 12 H, $NCH_2CH_2CH_2CH_3$). − $^{13}C\{^1H\}$ NMR ([D$_4$]MeOH): δ = 148.5, 144.0, 140.3, 136.9, 135.8, 135.1, 129.5, 127.8, 126.5, 126.2, 125.0, 121.9 (C_6H_4), 59.5 (t, $^1J_{C,N}$ = 5.3 Hz, NCH_2), 27.1 (SCH_2), 24.9 (NCH_2CH_2), 20.8 ($NCH_2CH_2CH_2$), 14.2 (SCH_2CH_3), 14.0 ($NCH_2CH_2CH_2CH_3$).

'EtS_3'-H: [Ni('EtS_3')$_2$] (**9**) (280 mg, 0.46 mmol) was suspended in CH_2Cl_2 (20 mL), concentrated HCl (20 mL) was added and the mixture was stirred for 2 h. The CH_2Cl_2 phase was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and concentrated to yield 'EtS_3'-H as a colorless oil. Yield: 230 mg (90%). − MS (FD, CH_2Cl_2); *m*/*z*: 278 [M^+]. − ^1H NMR (CD_2Cl_2): δ = 7.47−7.03 (m, 7 H, C_6H_4), 6.88 (d, 1 H, C_6H_4), 4.28 (s, 1 H, SH), 3.02 (q, 2 H, SCH_2), 1.35 (t, 3 H, SCH_2CH_3).

'CyS_3'-H: At −30°C, 'S_3'-H_2 (5.90 g, 23.6 mmol) in THF (25 mL) was combined with *n*BuLi (10 mL of 2.5 M in hexanes, 25 mmol), and the resulting solution was concentrated to dryness at room temperature. The light yellow residue was dissolved in DMF (50 mL), combined with cyclohexyl bromide (8.00 g, 49.1 mmol) and heated to 125°C for 6 h. All volatile materials were removed at 110°C in vacuo (1 mbar), the remaining oil was dissolved in CH_2Cl_2 (30 mL) and half-concentrated HCl (50 mL) was added. The CH_2Cl_2 phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (60 mL). The combined CH_2Cl_2 phases were washed with dilute aqueous HCl (5 mL), dried with Na_2SO_4, and concentrated. The remaining oil was redissolved in Et_2O (40 mL) and hexanes (10 mL) and filtered. Aqueous NaOH (50 mL, 10%) was added to the filtrate, the mixture was agitated vigorously in a separating funnel and subsequently allowed to separate. In the course of ca. 30 min three phases formed of which the thin middle one displayed a pale red color. This phase was carefully separated, acidified with half-concentrated HCl and extracted with CH_2Cl_2 (60 mL). The CH_2Cl_2 extracts were washed with dilute aqueous HCl (10 mL), dried with Na_2SO_4, and concentrated at 60°C (0.1 mbar). The remaining oil of 'CyS_3'-H was identified by NMR spectroscopy. Yield: 3.27 g (42%). − ^1H NMR ($CDCl_3$): δ = 7.55−7.01 (m, 7 H, C_6H_4), 6.67 (d, 1 H, C_6H_4), 4.33 (s, 1 H, SH), 3.27 [m, 1 H, $SCH(CH_2)_5$], 2.13 [1.15 (m, 10 H, $SCH(CH_2)_5$]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 140.0, 139.2, 136.3, 133.7, 133.0, 130.1, 129.5, 129.2, 127.8, 127.1, 126.1, 126.0 (C_6H_4), 46.7 [$SCH(CH_2)_5$], 33.2, 26.0, 25.7 [$SCH(CH_2)_5$].

[Ni('MeS_3')$_2$] (7): 'MeS_3'-H (210 mg, 0.80 mmol) in THF (10 mL) was treated with NaOMe (0.8 mL of a 1 M solution in MeOH, 0.80 mmol) and combined with $NiBr_2{\cdot}3H_2O$ (270 mg, 1.0 mmol) in MeOH (10 mL). A red solution resulted from which an orange to ochreous solid precipitated that was separated after 1 d, washed with MeOH (30 mL), and dried. Yield: 210 mg (90%). − $C_{26}H_{22}NiS_6$ (585.56): calcd. C 53.33, H 3.79; found C 52.18, H 3.86. − IR (KBr): $\tilde{\nu}$ = 3047, 2963, 2924, 1564, 1442, 1423, 1097, 750 cm^{-1}.

[Ni('MeS_3')$_2$(PMe_3)$_2$] (8): PMe_3 (70 mg, 0.92 mmol) was added to a suspension of Ni('MeS_3')$_2$] (**7**) (60 mg, 0.10 mmol) in THF (5 mL), and a deep red solution resulted. Addition of MeOH (8 mL) precipitated an orange solid that was separated, washed with MeOH (5 mL) and Et_2O (15 mL), and dried. Yield: 55 mg (75%). − $C_{32}H_{40}NiP_2S_6$ (737.72): calcd. C 52.10, H 5.47, S 26.08; found C 51.99, H 5.41, S 25.64. − ^1H NMR ($CDCl_3$): δ = 7.80 (d, 2 H, C_6H_4), 7.39 (d, 2 H, C_6H_4), 7.28 (pseudo-t, 2 H, C_6H_4), 7.18 (d, 2 H, C_6H_4), 7.04 (pseudo-t, 2 H, C_6H_4), 6.88 (d pseudo-t, 2 H, $^5J_{H,P}$ = 2.6 Hz, C_6H_4), 6.82−6,69 (m, 4 H, C_6H_4), 2.38 (s, 6 H, CH_3), 1.27 [d, 18 H, $^2J_{H,P}$ = 5 Hz, $P(CH_3)_3$].

[Ni('EtS_3')$_2$] (9): $NiCl_2{\cdot}6H_2O$ (200 mg, 0.85 mmol) in MeOH (5 mL) was added to a stirred solution of NBu_4'EtS_3' (440 mg, 0.85 mmol) in MeOH (10 mL). An orange-brown precipitate formed that was separated after 2 h, washed with MeOH (15 mL) and recrystallized from hot DMF. Yield: 460 mg (88%). − $C_{28}H_{26}NiS_6$ (613.61): calcd. C 54.81, H 4.27, S 31.35; found C 54.51, H 4.29, S 30.18. − ^1H NMR (C_6D_6): δ = 7.92 (m, 2 H, C_6H_4), 7.41 (m, 2 H, C_6H_4), 6.94−6.78 (m, 6 H, C_6H_4), 6.68−6.57 (m, 4 H, C_6H_4), 6.38 (m, 2 H, C_6H_4), 2.57 (q, 4 H, CH_2), 0.99 (t, 6 H, CH_3). − IR (KBr): $\tilde{\nu}$ = 3049, 2965, 2924, 1566, 1444, 1424, 1261, 1246, 1100, 756, 738 cm^{-1}.

[Ni('CyS_3')$_2$] (10): Ni(ac)$_2{\cdot}4H_2O$ (250 mg, 1.0 mmol) in MeOH (10 mL) was added to 'CyS_3'-H (175 mg, 0.53 mmol) in THF (10 mL), yielding a red solution. This solution was reduced in volume to 5 mL, and MeOH (20 mL) was added. An orange-brown solid precipitated which was separated, washed with MeOH (30 mL) and dried. Yield: 170 mg (90%). − $C_{36}H_{38}NiS_6$ (721.80): calcd. C 59.91, H 5.31, S 26.65; found C 60.00, H 5.22, S 26.38. − MS (FD, CH_2Cl_2); *m*/*z*: 720 [M^+]. − ^1H NMR ($CDCl_3$): δ = 7.99−6.69 (m, 8 H, C_6H_4), 3.35 [m, 1 H,$SCH(CH_2)_5$], 2.16−1.08 [m, 10 H, $SCH(CH_2)_5$]. − IR (KBr): $\tilde{\nu}$ = 3048, 2927, 2850, 1565, 1443, 1424, 1099, 745 cm^{-1}.

[Pt(H)('CyS_3')] and [Pt(H)('CyS_3')(PPh_3)]: A solution of 'CyS_3'-H (335 mg, 1.0 mmol) in THF (10 mL) was added to a suspension of [Pt(PPh_3)$_4$] (1.25 g, 1.0 mmol) in THF (30 mL). The yellow suspension was stirred for 20 min upon which an orange solution resulted, which was heated to reflux for 1 h. After allowing to come to room temperature, MeOH (20 mL) was added to precipitate a pale yellow solid. This product was separated and extracted several times with hot hexanes (120 mL). The remaining pale yellow powder was dried in vacuo and was characterized by means of NMR spectroscopy to consist of a mixture of [Pt('CyS_3')(H)], [Pt('CyS_3')(H)(PPh_3)] and PPh_3. − ^1H NMR ([D$_8$]THF): δ = 7.98−6.43 (m, C_6H_4/C_6H_5), 3.15−3.09 [m, $SCH(CH_2)_5$], 2.05−0.97 [m, $SCH(CH_2)_5$], −11.38 {d + dd, $^1J_{H,Pt}$ = 1260 Hz, $^2J_{H,P}$ = 20 Hz, PtH in [Pt('CyS_3')(H)(PPh_3)]}, −15.74 {s + d, $^1J_{H,Pt}$ = 1155 Hz, Pt*H* in [Pt('CyS_3')(H)]}. − $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 23.5 {s + d, $^1J_{P,Pt}$ = 3260 Hz, *P*Ph_3 in [Pt('CyS_3')(H)(PPh_3)]}. − IR (KBr): $\tilde{\nu}$ = 2110 cm^{-1} (ν_{PtH}); (THF): $\tilde{\nu}$ = 2117 cm^{-1} (ν_{PtH}).

[Pt(PPh_3)$_2$($S_2C_6H_4$)]: A solution of 'CyS_3'-H (330 mg, 1.0 mmol) in toluene (5 mL) was combined with a suspension of [Pt(PPh_3)$_4$] (1.240 g, 1.0 mmol) in toluene (25 mL). The resulting orange suspension was heated to 80°C (10 min) and then to 100°C to give a clear yellow-orange solution. After 30 min at 100°C, yellow microc-

rystals of $[Pt(PPh_3)_2(S_2C_6H_4)]$ precipitated, which were isolated at room temperature, washed with toluene (15 mL) and pentanes (15 mL), and dried in vacuo. − $C_{42}H_{34}P_2PtS_2$ (859.90): calcd. C 58.67, H 3.99, S 7.46; found C 58.77, H 4.04, S 7.38. − ^{1}H NMR (CD_2Cl_2): δ = 7.70−7.10 (m, 32 H, C_6H_4, C_6H_5), 6.68 (m, 2 H, C_6H_4).

[$Et_2HNC_2H_4Br$]Br: At 0°C, $Et_2NC_2H_4OH$ (45.1 g, 385 mmol) was cautiously combined with aqueous HBr (100 mL, 47%, 884 mmol) and PBr_3 (86.4 g, 320 mmol). The mixture was sealed in a thick-walled glass ampoule and heated to 140°C for 11 h. From the resulting brown product, all volatile components were removed in vacuo, the residue was redissolved in boiling EtOH (150 mL) and allowed to cool to room temperature. Upon addition of Et_2O (200 mL), colorless microcrystals precipitated, which were separated, washed with Et_2O (100 mL), and dried. Yield: 79.9 g (80%). − $C_6H_{15}Br_2N$ (261.01): calcd. C 27.61, H 5.79, N 5.37; found C 27.20, H 5.99, N 4.88.− ^{1}H NMR ([D$_4$]MeOH): δ = 4.78 (s, 1 H, NH), 3.72 (m, 2 H, NC_2H_4Br), 3.56 (m, 2 H, NC_2H_4Br), 3.25 [q, 4 H, $N(CH_2CH_3)_2$], 1.28 [t, 6 H, $N(CH_2CH_3)_2$]. − ^{13}C{^{1}H} NMR ([D$_4$]MeOH): δ = 54.0 (NCH_2CH_2Br), 48.9 [$N(CH_2CH_3)_2$], 24.4 [$N(CH_2CH_2)Br$], 9.1 [$N(CH_2CH_3)_2$].

[Ni(‘Et_2HNS_2’)$_2$](ClO$_4$)$_2$ (12): ***Caution:*** *Although we did not face any difficulties, the use of perchlorates in the presence of organic material may cause explosions and perchlorates must be treated accordingly (protective shields).* A stirred solution of *o*-$C_6H_4(SH)_2$ (3.685 g, 25.9 mmol) in MeOH (30 mL) was deprotonated with NaOMe (2.81 g, 51.8 mmol) and added to a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (4.74 g, 13.0 mmol) in MeOH (65 mL). To the resulting brown-yellow solution of $[Ni(S_2C_6H_4)_2]^{2-}$, a solution of $[Et_2HNC_2H_4Br]Br$ (6.76 g, 25.9 mmol) in MeOH (50 mL) was added dropwise within 20 min. The resulting solution was stirred for 24 h at room temperature, subsequently heated at reflux for 4 h, and then allowed to cool to room temperature again. A yellow-red precipitate formed which was separated, washed with MeOH (40 mL) and dried in vacuo for 3 d. Yield: 6.7 g (70%). − $C_{24}H_{38}Cl_2N_2NiO_8S_4$ (740.45): calcd. C 38.93, H 5.17, N 3.78, S 17.32; found C 39.58, H 5.41, N 3.83, S 17.26. − ^{1}H NMR ([D$_4$]MeOH): δ = 7.62 (m, 1 H, C_6H_4), 7.44 (m, 1 H, C_6H_4), 7.26 (m, 1 H, C_6H_4), 7.13 (m, 1 H, C_6H_4), 4.88 (s, NH), 3.71 (br., 2 H, NC_2H_4S), 3.57 (br., 2 H, NC_2H_4S), 3.24 (q, 4 H, NCH_2CH_3), 1.19 (t, 6 H, NCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 3053, 2971, 2933, 2656, 2470, 1566, 1447, 1419, 1261, 1244, 1097, 741, 624 cm^{-1}.

[‘Et_2HNS_2’-H]Br: [Ni(‘Et_2HNS_2’)$_2$](ClO$_4$)$_2$ (**12**) (500 mg, 0.675 mmol) in $CHCl_3$ (20 mL) was treated with concentrated aqueous HBr (20 mL, 47%, 175 mmol) and stirred vigorously for 2 h. The resulting light-yellow $CHCl_3$ phase was separated, dried with Na_2SO_4 and concentrated to dryness, yielding a white solid of [‘Et_2HNS_2’-H]Br that was identified by NMR spectroscopy. Yield: 270 mg (62%). − ^{1}H NMR ($CDCl_3$): δ = 10.90 (s, 1 H, br., NH), 8.02−6.21 (m, 4 H, C_6H_4), 4.59 (s, 1 H, SH), 4.00−3.19 (m, 8 H, NC_2H_4S, NCH_2CH_3), 1.63 (t, 6 H, NCH_2CH_3).

X-ray Structure Analysis of [Ni(‘S_3’)]$_2$ (1), [Ni(‘S_3’)(PMe$_3$)] (2), NMe$_4$[Ni(‘S_3’)(CN)]·0.5CH_2Cl_2 (3·0.5CH_2Cl_2), [Ni(‘MeS_3’)$_2$] (7), [Ni(‘Et_2HNS_2’)$_2$]Br_2 (11), [Pt(‘S_3’)]$_3$·2THF·MeOH (5·2THF·MeOH) and [Pt(‘S_3’)(PPh$_3$)] (6): Black cubes of [Ni(‘S_3’)]$_2$ (**1**) were obtained by solvothermal crystallization. A suspension of **1** (80 mg) in DMF (2 mL) was sealed in a thick-walled glass ampoule, heated to 175°C for 10 h by means of an electric furnace and slowly cooled to room temperature at a rate of 1°C·h^{-1}. Black prisms of [Ni(‘S_3’)(PMe$_3$)] (**2**) crystallized from a saturated THF solution that was layered with MeOH. Red-black columns of NMe$_4$[Ni(‘S_3’)(CN)]·0.5CH_2Cl_2 (**3**·0.5CH_2Cl_2) were grown from a saturated 1:1 THF/MeOH solution that was layered with Et_2O. In the course of 20 d, red prisms of [Ni(‘MeS_3’)$_2$] (**7**) grew from a $CDCl_3$ solution of [Ni(‘MeS_3’)$_2$(PMe$_3$)$_2$] which had been used for NMR measurements. [Ni(‘Et_2HNS_2’)$_2$]Br_2 (**11**) crystallized as yellow platelets upon cooling of a hot MeOH solution of [Ni(‘Et_2HNS_2’)$_2$](ClO$_4$)$_2$ (**12**) and LiBr to room temperature. Yellow-red plates of [Pt(‘S_3’)]3·2THF·MeOH (**5**·2THF·MeOH) were grown from a THF solution that was layered with MeOH. Orange columns of [Pt(‘S_3’)(PPh$_3$)] (**6**) resulted from a mixture of Li[Pt(‘S_3’)(H)] and Li[Pt(‘S_3’)(H)(PPh$_3$)] in THF that had been layered with MeOH. Suitable single crystals were sealed in glass capillaries under N_2. Data was collected at 293 K (**1**, **3**·0.5CH_2Cl_2, **6**) or 200 K (**2**, **5**·2THF·MeOH, **7**, **11**) with a Siemens P4 diffractometer using Mo-K_α radiation (λ = 71.073 pm), a graphite

Table 2. Selected crystallographic data of [Ni(‘S_3’)]$_2$ (**1**), [Ni(‘S_3’)(PMe$_3$)] (**2**), NMe$_4$[Ni(‘S_3’)(CN)]·0.5CH_2Cl_2 (**3**·0.5CH_2Cl_2), [Ni(‘MeS_3’)$_2$] (**7**), [Ni(‘Et_2HNS_2’)$_2$]Br_2 (**11**), [Pt(‘S_3’)]3·2THF·MeOH (**5**·2THF·MeOH) and [Pt(‘S_3’)(PPh$_3$)] (**6**)

Compound	**1**	**2**	**3**·0.5CH_2Cl_2	**7**	**11**	**5**·2THF·MeOH	**6**
Formula	$C_{24}H_{16}Ni_2S_6$	$C_{15}H_{17}NiPS_3$	$C_{17.5}H_{21}ClN_2NiS_3$	$C_{26}H_{22}NiS_6$	$C_{24}H_{38}Br_2N_2NiS_4$	$C_{45}H_{44}O_3Pt_3S_9$	$C_{30}H_{23}PPtS_3$
M_r [g/mol]	614.1	383.1	449.7	585.5	701.3	1506.6	705.7
Cryst. system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	*C*2/*c*	*Cc*	*P*2/*c*	$P2_1/n$	$P2_1/c$	*P*1bar	$P2_1/n$
a [pm]	2131.9(11)	900.4(3)	1686.5(2)	977.1(9)	1374.7(8)	788.5(1)	899.0(1)
b [pm]	876.2(6)	1832.9(7)	994.3(2)	1151.0(14)	1102.8(3)	1721.8(3)	1139.3(3)
c [pm]	1392.8(15)	1051.1(3)	1276.1(2)	1087.3(7)	1012.5(4)	1742.1(3)	2558.7(4)
α [°]						96.94(1)	
β [°]	123.56(8)	106.28(3)	105.04(1)	91.16(6)	108.46(4)	92.61(1)	90.93(1)
γ [°]						100.60(1)	
V [nm^3]	2.168(3)	1.665(1)	2.066(1)	1.223(2)	1.456(1)	2.302(1)	2.620(1)
Z	4	4	4	2	2	2	4
$d_{calcd.}$ [gcm^{-3}]	1.88	1.53	1.45	1.59	1.60	2.17	1.79
μ [cm^{-1}]	23.28	16.24	13.74	13.21	37.14	95.41	56.73
Cryst. size [mm]	0.4 × 0.4 × 0.3	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.4 × 0.3 × 0.2	0.4 × 0.4 × 0.2	0.4 × 0.2 × 0.1	1.0 × 0.2 × 0.2
2θ range [°]	4−54	4−54	4−54	5−50	5−52	3−54	3−54
Measd. refl.	4446	3390	6837	2582	3123	11637	10224
Indep. refl.	2397	3272	4550	2152	2724	10077	5771
Obsd. refl.	1857	2717	2452	1024	1356	6110	4295
Ref. parameters	145	179	222	151	151	543	316
*R*1[a]; *wR*2 [%]	2.4; 5.7	4.4; 12.5	3.9; 10.3	7.9; 23.2	6.6; 18.6	5.3; 13.6	2.2; 5.4

[a] [$I > 2\sigma(I)$].

monochromator and ω-scan technique (scan speed 3.0−30° min^{-1}). Due to the experimental setup, ψ-scan absorption correction was not possible, therefore absorption effects have been corrected using ΔF^2 methods (XABS2)[39] in the case of **2**, **5**·2THF·MeOH, **6**, **7**, and **11**. Structures were solved by direct methods (SHELXTL). Full-matrix least-squares refinements on F^2 were carried out with SHELXTL 5.03.[40] Non-hydrogen atoms were refined isotropically. The hydrogen atoms of **1**, **2**, **3**·0.5CH_2Cl_2, **6**, **7**, and **11** were located in Fourier synthesis difference maps. The hydrogen atoms in [Pt('S_3')]3·2THF·MeOH (**5**·2THF·MeOH) were geometrically positioned. For all hydrogen atoms both the positional parameters and a common isotropic displacement parameter were restricted during refinement. In the case of **2**, the absolute structure has been established by refinement of the Flack parameter[41] [$x = -0.02(2)$]. Table 2 contains selected crystallographic data.[42]

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[42] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118908 (**1**), -118909 (**2**), -118910 (**3**), -118911 (**5**), -118912 (**6**), -118913 (**7**), -118914 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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