Transition Metal Complexes with Sulfur Ligands, 139[+]

Synthesis and Exchange Reactions of Sulfur-Rich Nickel and Palladium [M(L)('S_3')] Complexes ['S_3'$^{2-}$ = Bis(2-mercaptophenyl)sulfide(2–)]

Dieter Sellmann,*[a] Franz Geipel,[a] and Frank W. Heinemann[a]

Dedicated to Professor Egon Uhlig on the occasion of his 70th birthday

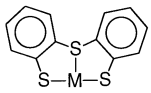
Keywords: Nickel complexes / Palladium complexes / S ligands / Exchange reactions / Azide / Sulfinylimide

In order to obtain suitable precursors for nickel and palladium complexes that model the reactivity of the active sites of hydrogenases and CO dehydrogenases, a series of [M(L)('S_3')] complexes has been synthesized [M = Ni^{II}, Pd^{II}; 'S_3'$^{2-}$ = bis(2-mercaptophenyl)sulfide(2–)]. X-ray structure determinations of [Ni('S_3')]$_3$ (**1**) and [Pd('S_3')]$_3$ (**2**) have revealed that the [M('S_3')] fragments trimerize to give six-membered [MS]$_3$ rings, which exhibit chair conformations with alternating M^{II} centers and thiolate bridging atoms. Reactions of the parent complex [Ni('S_3')]$_3$ (**1**) with nucleophiles L, such as thiolates SR^- (R = *t*Bu, Cy, Me, Ph), phosphanes PR_3 (R = Cy, Ph), chloride, or azide, have been found to yield the corresponding anionic or neutral [Ni(L)('S_3')] complexes, which were isolated as (NBu_4)[Ni(SR)('S_3')] [R = *t*Bu (**3**), Cy (**4**), Me (**5**), Ph (**6**)], [Ni(PR_3)('S_3')] [R = Cy (**7**), Ph (**8**)], (NBu_4)[Ni(Cl)('S_3')] (**9**), and (NBu_4)[Ni(N_3)('S_3')] (**10**). When treated with Me_3SiX, the S*t*Bu$^-$ ligand in (NBu_4)[Ni(S*t*Bu)('S_3')] (**3**) was exchanged to give (NBu_4)[Ni(X)('S_3')] [X = Cl^- (**9**), N_3^- (**10**), NCS^- (**11**), NSO^- (**12**)]. The palladium complex [Pd('S_3')]$_3$ (**2**) could also be cleaved with S*t*Bu$^-$, but the resulting (NBu_4)[Pd(S*t*Bu)('S_3')] (**13**) proved inert towards exchange reactions with Me_3SiX. All the mononuclear complexes have been characterized by standard spectroscopic techniques and by elemental analysis. The molecular structures of **3**, **4**, **6**, **7**, **8**, **9**, and **13** have been determined by X-ray crystallography. The [MS_3L] core geometries of all the complexes are non-planar, exhibiting a considerable tetrahedral distortion.

Introduction

Much of the current interest in nickel thiolate−thioether complexes stems from the discovery that nickel in sulfur-rich coordination spheres forms the active centers of enzymes such as hydrogenases[1] and CO dehydrogenases.[2] In the quest for model compounds of these enzymes, a considerable number of new nickel complexes with different donor sets and geometries has been synthesized.[3,4,5] However, complexes exhibiting structural (Ni−S coordination) and functional (catalysis of enzyme reactions) features of the enzymes have remained extremely rare. Our search for such compounds has recently yielded complexes containing [M('S_3')] fragments (M = Ni, Pt) with the tridentate ligand 'S_3'$^{2-}$ = bis(2-mercaptophenyl)sulfide(2−).[6]

The [M('S_3')] fragments with d^8 electron metal(II) centers were anticipated to have an accessible site for the coordination and activation of substrates. With regard to hydrogenases, dihydrogen and hydride are, of course, the substrates of primary interest. Unfortunately, however, all attempts to coordinate these species to [Ni('S_3')] fragments have to date been unsuccessful,[6] despite the fact that NMR spectroscopic investigations have yielded conclusive evidence for the formation of [Pt(H)('S_3')]$^-$.[6] Further experiments showed that a favored reaction of [M('S_3')] fragments is oligomerization to give either dinuclear [Ni('S_3')]$_2$ or trinuclear [Pt('S_3')]$_3$. These complexes contain thiolate bridges, which block the fourth coordination site at the metal centers. As a consequence, they are extremely sparingly soluble in all common solvents such that homogeneous phase reactions are prevented. The thiolate bridges in [Ni('S_3')]$_2$ or [Pt('S_3')]$_3$ may be cleaved by nucleophiles such as PMe_3 or cyanide. The resulting mononuclear [M(L)('S_3')] derivatives are much more soluble than the parent complexes, but the coligands L proved to be inert.[6] Thus, the aim of the work described herein was to obtain [M(L)('S_3')] species with exchangeable coligands L and thus a readily accessible coordination site.



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[a] Institut für Anorganische Chemie der Universität Erlangen-Nürnberg,
Egerlandstraße 1, D-91058 Erlangen, Germany
Fax: (internat.) + 49-(0)9131/852-7367
E-mail: sellmann@anorganik.chemie.uni-erlangen.de

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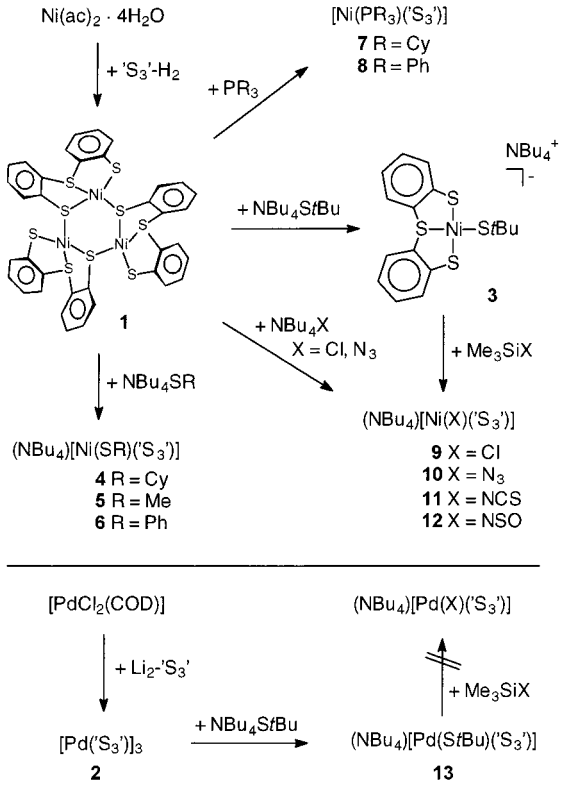
Results

Cleavage of [Ni('S_3')]$_3$ and Substitution Reactions of [Ni(L)('S_3')] Complexes (L = PR_3, SR^-)

The extremely insoluble [Ni('S_3')]$_2$ parent complex has previously been obtained from $Ni(ac)_2 \cdot 4\,H_2O$ and 'S_3'-H_2.[6] A solvothermal recrystallization from hot DMF (175°C) in a sealed ampoule yielded single crystals, X-ray structure analysis of which showed the product to contain dinuclear [Ni('S_3')]$_2$. On repeating the synthesis, we have now obtained single crystals from the mother liquor of the reaction solution at room temperature. An X-ray structure determination of these crystals revealed that they consisted of the trinuclear [Ni('S_3')]$_3$ (**1**). Complex **1** is structurally analogous to [Pt('S_3')]$_3$ and shows that the crystallization conditions can influence the trimerization vs. dimerization of [Ni('S_3')] fragments. These results prompted us to synthesize [Pd('S_3')]$_3$ (**2**) as well (for the sake of completeness). Complex **2** was obtained from 'S_3'-Li_2 and [$PdCl_2$(COD)] (Scheme 1).



Scheme 1. Synthesis and reactions of [Ni('S_3')] and [Pd('S_3')] complexes

In order to achieve an all-sulfur coordination of the nickel center, we first examined reactions of [Ni('S_3')]$_3$ with thiolates. Both small and sterically demanding thiolates, such as SMe^- and SCy^-, gave essentially the same results. When black-brown THF suspensions of [Ni('S_3')]$_3$ (**1**) were treated with MeOH solutions of the respective NaSR salts at room temperature, dark-brown solutions resulted. Addition of NBu_4OH and subsequent workup yielded the dark-brown to black salts (NBu_4)[Ni(SR)('S_3')] with R = *t*Bu (**3**), Cy (**4**), Me (**5**), and Ph (**6**). These salts were found to be readily soluble in THF, acetone, MeOH, and CH_2Cl_2, but insoluble in Et_2O and *n*-hexane. The molecular structures of (NBu_4)[Ni(S*t*Bu)('S_3')] (**3**), (NBu_4)[Ni(SCy)('S_3')] (**4**), and (NBu_4)[Ni(SPh)('S_3')] (**6**) were determined by X-ray diffraction analysis.

Reactions with the bulky phosphanes PCy_3 and PPh_3 were then investigated in order to probe the lability of the phosphanes and the potential for formation of agostic C−H···Ni interactions in [Ni(PR_3)('S_3')] complexes. The [Ni(PR_3)('S_3')] complexes with R = Cy (**7**), Ph (**8**) were readily formed from THF suspensions of [Ni('S_3')]$_3$ and the respective phosphanes. They were fully characterized but proved as inert to substitution as [Ni(PMe_3)('S_3')]. No agostic C−H···Ni interactions could be detected, neither by X-ray structure determinations nor by ^{1}H-NMR spectra.

Halides and Pseudohalides as Nucleophiles

Initial attempts to cleave [Ni('S_3')]$_3$ with weak nucleophiles such as chloride from NMe_4Cl to give the [Ni(Cl)('S_3')]$^-$ anion invariably proved unsuccessful. However, this anion was readily formed when the S*t*Bu derivative (NBu_4)[Ni(S*t*Bu)('S_3')] (**3**) was treated with Me_3SiCl. The resulting (NBu_4)[Ni(Cl)('S_3')] (**9**) has been fully characterized and its molecular structure has been determined by X-ray diffraction analysis.

Since these results proved the viability of [Ni(Cl)('S_3')]$^-$, we repeated the attempts to cleave [Ni('S_3')]$_3$ directly with chloride, but employed NBu_4Cl instead of NMe_4Cl. Indeed, when suspensions of [Ni('S_3')]$_3$ in THF were treated with equimolar amounts of NBu_4Cl at room temperature, (NBu_4)-[Ni(Cl)('S_3')] (**9**) was formed in yields in excess of 70%. Analogously, (NBu_4)[Ni(N_3)('S_3')] (**10**) was obtained first from (NBu_4)[Ni(S*t*Bu)('S_3')] (**3**) and Me_3SiN_3 and subsequently from the direct reaction between [Ni('S_3')]$_3$ and NBu_4N_3. Syntheses of (NBu_4)[Ni(NCS)('S_3')] (**11**) and (NBu_4)[Ni(NSO)('S_3')] (**12**) required the "silylating" procedure. Thus, complexes **11** and **12** were obtained from (NBu_4)[Ni(S*t*Bu)('S_3')] (**3**) using Me_3SiNCS and Me_3Si-NSO, respectively. The driving force behind these syntheses is presumably the formation of Me_3SiS*t*Bu. Attempts to obtain (NBu_4)[Ni(NCO)('S_3')] using either of the aforementioned two methods proved unsuccessful.

The palladium complex [Pd('S_3')]$_3$ (**2**) could also be cleaved with S*t*Bu$^-$ to yield (NBu_4)[Pd(S*t*Bu)('S_3')] (**13**). Exploratory experiments showed the S*t*Bu$^-$ ligand in **13** to be inert. For example, treatment of **13** with Me_3SiX (X = Cl, N_3, NCS, or NSO) did not yield the corresponding [Pd(X)('S_3')]$^-$ ions.

Characterization of Complexes and Monitoring of Reactions

All the complexes are diamagnetic and have been characterized by standard spectroscopic techniques and elemental

analysis. Several of the complexes have also been characterized by X-ray structure analysis. In contrast to the extremely insoluble starting complexes [M('S_3')]$_3$, all [M(L)('S_3')] derivatives with phosphane or anionic coligands L proved sufficiently soluble in THF, acetone, or CH_2Cl_2 to allow recording of their NMR spectra. The solutions are black-brown (**3**−**6**), orange (**12**), red (**7**, **8**, **11**, **13**), or violet (**9**, **10**).

The ^{1}H-NMR splitting pattern of the aromatic protons is a typical feature of the [M('S_3')] fragment and can be used as a "fingerprint" of the individual complexes since

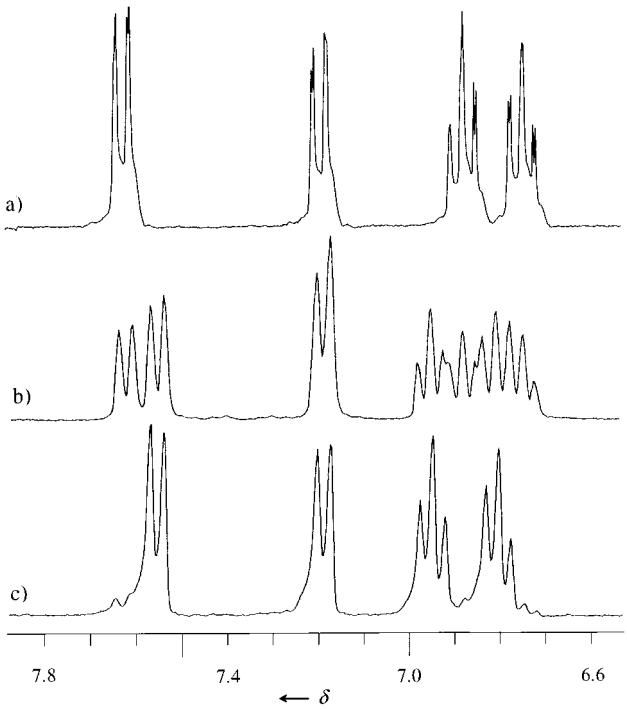


Figure 1. Aromatic region of the ^{1}H-NMR spectra of (a) (NBu_4)[Ni(S*t*Bu)('S_3')] in [D_8]THF, (b) 2 h after addition of Me_3SiN_3, and (c) after 12 h and almost complete formation of (NBu_4)[Ni(N_3)('S_3')]

the multiplet shifts specifically depend on the coligands L.

Figure 1 illustrates the ^{1}H-NMR spectroscopic monitoring of the reaction between (NBu_4)[Ni(S*t*Bu)('S_3')] (**3**) and Me_3SiN_3. The clean aromatic multiplets demonstrate that complex **3** is converted into the azido complex **10** without the formation of any other complexes as by-products. This is further corroborated by the IR spectrum and, in particular, the UV/Vis spectrum of the reaction solution, which shows two isosbestic points (Figure 2). In all cases, the ^{13}C{^{1}H}-NMR spectra of the mononuclear complexes exhibit six ^{13}C signals for the twelve aromatic C atoms of the 'S_3' ligand, in accordance with the twofold symmetry of the [M('S_3')] fragments. Strong and characteristic bands in the IR spectra are well suited for identifying the complexes **10** (2037 cm^{-1}), **11** (2105 cm^{-1}), and **12** (1230, 1030 cm^{-1}).

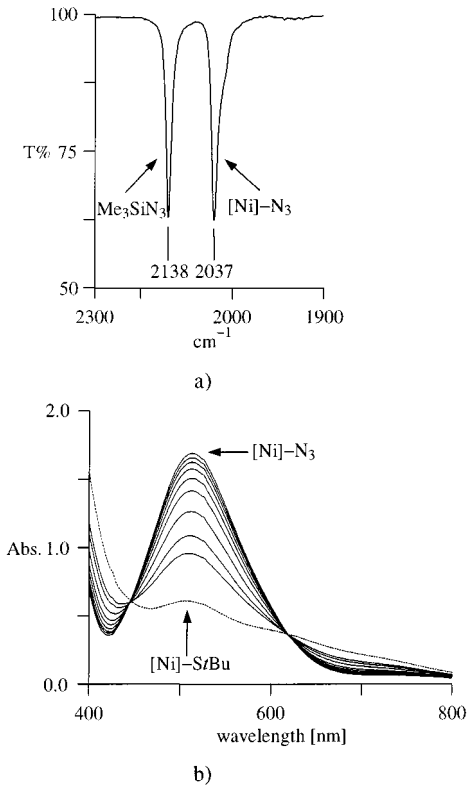


Figure 2. (a) IR spectrum of the reaction solution containing (NBu_4)[Ni(S*t*Bu)('S_3')], Me_3SiN_3, and the resulting (NBu_4)[Ni(N_3)('S_3')], (b) UV/Vis monitoring of the reaction between (NBu_4)[Ni(S*t*Bu)('S_3')] and Me_3SiN_3 in THF

X-ray Structure Determinations

Several of the complexes were obtained in the form of single crystals suitable for X-ray structure analysis. Figure 3 depicts the mononuclear structures, showing different views of the individual species. Table 1 lists selected distances and angles.

All the complexes were found to consist of discrete molecules or ions. The [M('S_3')] fragments invariably exhibit the characteristic butterfly-shape, which arises from the rigid 'S_3' topology and sp^3 hybridization of the central S(thicether) donor.[6] The 'S_3' topology is also responsible for the tetrahedral distortion of the [MS_3L] cores, which are not planar as might have been expected for low-spin four-coordinate d^8 electron metal(II) centers. Figure 4 illustrates this tetrahedral distortion in [Ni(Cl)('S_3')]$^-$.

Distances and angles show no anomalies. It has been pointed out previously that the M−S(thiother) distances are invariably shorter than the corresponding M−S(thiolate) distances and are practically unaffected by the *trans* ligands L. Because the ligands used here range from "hard" chloride, through "soft" σ-π donating thiolates, to σ-donor/π-acceptors such as phosphanes, the [M('S_3')] fragments evidently also exhibit the structural invariance that has previously been noted as a typical feature of [MS_x] centers.[7] The molecular structure of the PCy_3 complex [Ni(PCy_3)('S_3')] (**7**) differs from those of all the other complexes in that it has crystallographic C_S symmetry.

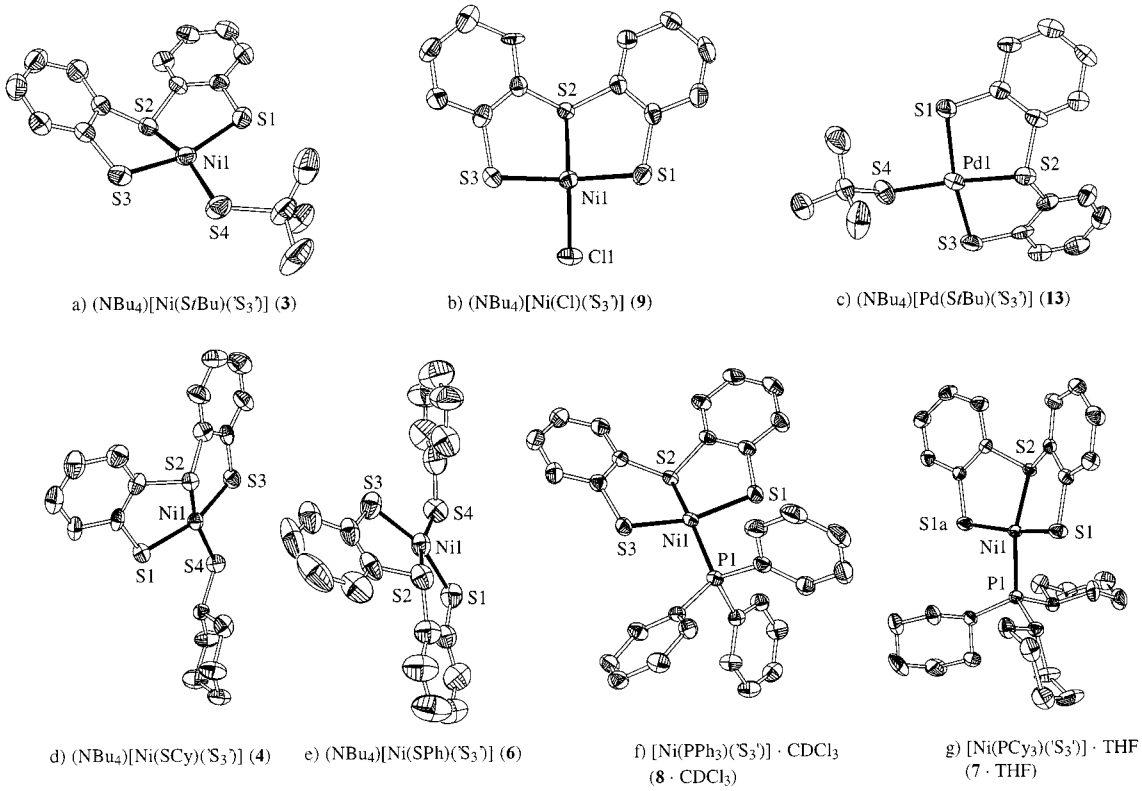


Figure 3. ORTEP plots of (a) $(NBu_4)[Ni(StBu)('S_3')]$ (**3**), (b) $(NBu_4)[Ni(Cl)('S_3')]$ (**9**), (c) $(NBu_4)[Pd(StBu)('S_3')]$ (**13**), (d) $(NBu_4)[Ni(SCy)('S_3')]$ (**4**), (e) $(NBu_4)[Ni(SPh)('S_3')]$ (**6**), (f) $[Ni(PPh_3)('S_3')] \cdot CDCl_3$ (**8** · $CDCl_3$), and (g) $[Ni(PCy_3)('S_3')] \cdot THF$ (**7** · THF); 50% probability ellipsoids; hydrogen atoms, solvent molecules and counterions omitted for the sake of clarity; different projections were chosen to illustrate the tetrahedral distortion of the $[M('S_3')]$ fragments

Table 1. Selected distances [pm] and angles [°] in $(NBu_4)[Ni(StBu)('S_3')]$ (**3**), $(NBu_4)[Ni(SCy)('S_3')]$ (**4**), $(NBu_4)[Ni(SPh)('S_3')]$ (**6**), $[Ni(PCy_3)('S_3')] \cdot THF$ (**7** · THF), $[Ni(PPh_3)('S_3')] \cdot CDCl_3$ (**8** · $CDCl_3$), $(NBu_4)[Ni(Cl)('S_3')]$ (**9**), and $(NBu_4)[Pd(StBu)('S_3')]$ (**13**)

Compound	[Ni]−S*t*Bu (**3**)	[Ni]−SCy (**4**)	[Ni]−SPh (**6**)	[Ni]−PCy_3 (**7**)	[Ni]−PPh_3 (**8**)	[Ni]−Cl (**9**)	[Pd]−S*t*Bu (**13**)
M1−S1	217.2(2)	218.3(2)	217.5(1)	217.6(1)	217.5(1)	217.0(1)	229.1(1)
M1−S2	214.2(1)	211.9(2)	211.5(1)	213.3(1)	213.1(1)	211.4(2)	226.0(2)
M1−S3	221.2(2)	216.8(2)	218.0(1)	217.6(1)[a]	215.8(1)	219.5(2)	231.0(1)
M1−L	219.2(2)	219.2(2)	220.0(1)	220.9(1)	219.7(1)	220.6(2)	233.3(2)
S1−M1−S2	90.86(6)	89.47(6)	90.00(5)	88.72(3)	89.14(3)	91.05(7)	88.44(5)
S1−M1−S3	160.88(7)	160.09(6)	159.78(5)	163.66(5)[a]	159.73(4)	161.31(6)	164.04(6)
S2−M1−S3	86.66(6)	89.73(6)	89.46(5)	88.72(3)[a]	89.85(3)	87.86(7)	86.96(5)
S1−M1−L	100.68(6)	97.40(7)	96.89(6)	94.01(3)	91.64(3)	92.32(7)	95.72(6)
S2−M1−L	164.04(7)	163.70(6)	164.95(5)	159.55(5)	164.11(3)	166.90(6)	175.72(5)
S3−M1−L	85.91(6)	88.75(6)	88.64(5)	94.01(3)[a]	94.81(3)	92.93(7)	89.30(6)

[a] S3 = S1a (symmetry code: x, $-y - {}^1/_2$, z).

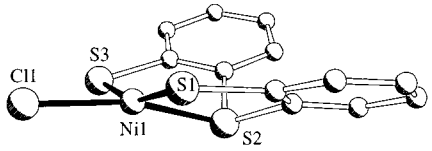


Figure 4. View showing the tetrahedral $[NiClS_3]$ core distortion in $[Ni(Cl)('S_3')]^-$

Figure 5 depicts views of the two trinuclear $[M('S_3')]_3$ complexes **1** and **2** from different angles, while Table 2 lists selected distances and angles. Like the previously described $[Pt('S_3')]_3$ complex,[6] the trinuclear $[Ni('S_3')]_3$ (**1**) and $[Pd('S_3')]_3$ (**2**) exhibit a cyclohexane-like $[M^{II}S]_3$ six-membered ring with a chair conformation that leads to a characteristic propeller-like twist of the three $[M('S_3')]$ units (Figure 5b). Related structures have been found for $[Ni('\mu\text{-}S_2C_3Me_2')]_3$,[5e] $[Ni('tBuS_4')]_3$,[8] and $[Pd(SC_2H_4SC_2H_4S)]_3$.[9]

Concluding Discussion

The trinuclear complex $[Ni('S_3')]_3$ (**1**) has been characterized. Complex **1** and the similarly new $[Pd('S_3')]_3$ (**2**) now complete the series of $[M('S_3')]_3$ complexes with Ni^{II}, Pd^{II}, and Pt^{II}. The extremely sparingly soluble $[Ni('S_3')]_3$ (**1**) gave

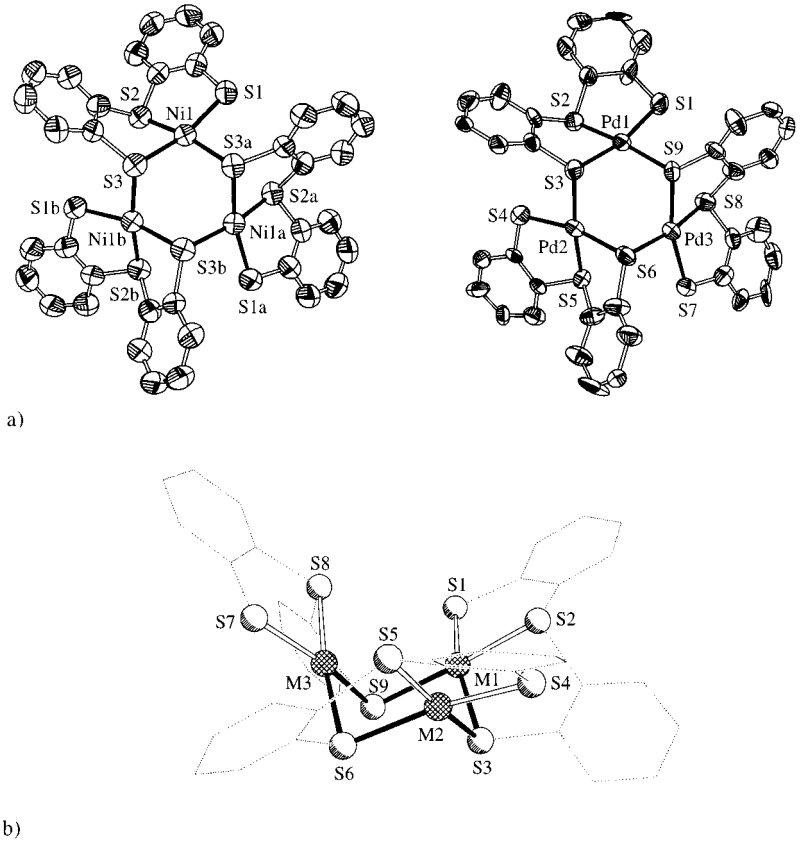


Figure 5. (a) Molecular structures of the $[M('S_3')]_3$ complexes (**1**·3 THF·6 MeOH) (M = Ni), and (**2**·2 CH_2Cl_2) (M = Pd); 50% probability ellipsoids; hydrogen atoms and solvent molecules omitted for the sake of clarity; (b) view showing the chair conformation of the $[MS]_3$ rings

Table 2. Selected distances [pm] and angles [°] in $[Ni('S_3')]_3 \cdot 3$ THF · 6 MeOH (**1** · 3 THF · 6 MeOH), and $[Pd('S_3')]_3 \cdot 2\ CH_2Cl_2$ (**2** · 2 CH_2Cl_2)

Compound	$[Ni('S_3')]_3$ (**1**)		$[Pd('S_3')]_3$[c] (**2**)	
M1−S1	214.2(2)	229.0(7)	226.3(7)[d]	226.6(7)[e]
M1−S2	213.4(2)	226.6(7)	225.7(7)	226.4(7)
M1−S3	221.4(2)	236.1(7)	232.6(7)	234.3(7)
M1−L	218.4(2)[a]	233.8(7)[f]	229.7(7)[g]	229.8(7)[h]
M1···M2	333.6(2)[b]	337.9(4)	355.3(4)[i]	340.9(4)[j]
S3···L	311.0(4)[a]	337.8(9)[f]	325.6(9)[h]	333.3(9)[k]
S1−M1−S2	90.7(1)	88.2(3)	89.2(3)	87.5(3)
S1−M1−S3	163.5(1)	166.7(2)	164.8(3)	166.2(3)
S2−M1−S3	87.7(1)	86.1(2)	86.7(2)	87.4(2)
S1−M1−L	94.4(1)[a]	95.2(3)[f]	96.4(3)[g]	94.7(3)[h]
S2−M1−L	169.6(1)[a]	172.6(2)[f]	170.8(3)[g]	172.9(3)[h]
S3−M1−L	90.0(1)[a]	91.9(3)[f]	89.6(2)[g]	91.9(2)[h]
M1−S3−M2	98.7(1)[b]	93.0(3)	100.4(3)[l]	93.5(2)[m]

[a] L = S3a (symmetry code: $-y-1, x-y-1, z$). − [b] M2 = Ni1b (symmetry code: $-x+y, -x-1, z$). − [c] Three independent $[Pd('S_3')]$ units. − [d] Pd2−S4. − [e] Pd3−S7. − [f] L = S9. − [g] L = S3. − [h] L = S6. − [i] Pd2−Pd3. − [j] Pd3−Pd1. − [k] S6−S9. − [l] Pd2−S6−Pd3. − [m] Pd3−S9−Pd1.

mononuclear $[Ni(L)('S_3')]$ complexes with L = thiolates, phosphanes, halides, and pseudohalides, which proved to be much more soluble than **1**. The chloro ligand in $(NBu_4)[Ni(Cl)('S_3')]$ (**9**) and the S*t*Bu$^-$ ligand in $(NBu_4)[Ni(S\mathit{t}Bu)('S_3')]$ (**3**) were found to be labile, making **3** and **9** suitable starting materials for the synthesis of other $[Ni(L)('S_3')]$ complexes that had previously been found to be inaccessible by direct reaction of $[Ni('S_3')]_3$ and the respective L. It is noteworthy that $(NBu_4)[Ni(N_3)('S_3')]$ (**10**) represents one of the few azido complexes in which a hard azide ligand is bound to a sulfur-rich metal complex fragment.[10] Very few such NSO complexes have been reported[11] and, to the best of our knowledge, $(NBu_4)[Ni(NSO)('S_3')]$ (**12**) represents the first NSO complex with an $[MS_x]$ center.

Experimental Section

General Methods: Unless noted otherwise, all reactions and operations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use. − As far as possible, reactions were monitored by IR or NMR spectroscopy. Spectra were recorded on the following instruments: IR (KBr discs or CaF_2 cuvettes, solvent bands were compensated): Perkin−Elmer 983, 1620 FT-IR, and 16PC FT-IR. − NMR: Jeol JNM-GX 270, EX 270, and Lambda LA 400 with the residual protio-solvent signal used as an internal reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane (^1H, $^{13}C\{^1H\}$ NMR) or 85% H_3PO_4 ($^{31}P\{^1H\}$ NMR); spectra were recorded at 25°C. − UV/Vis: Shimadzu UV3101 PC spectrophotometer. − Mass spectra: Jeol MSTATION 700 spectrometer. − Elemental analyses: Carlo Erba EA 1106 or 1108 analyzer. − Me_3SiCl, Me_3SiN_3, Me_3SiNCS, NBu_4Cl, and PR_3 were purchased from either Aldrich or Fluka;

'S_3'-H_2,[6] [$PdCl_2$(COD)],[12] and Me_3SiNSO[13] were prepared according to literature methods.

[Ni('S_3')]$_3$ (1): A solution of 'S_3'$-H_2$ (4.327 g, 17.28 mmol) in THF (70 mL) was added dropwise to $Ni(ac)_2 \cdot 4\ H_2O$ (4.300 g, 17.28 mmol) in MeOH (10 mL) and the resulting brown suspension was refluxed for 4 h. The black-brown precipitate was then separated by filtration, washed with THF (50 mL), and dried in vacuo. A second batch of the product was obtained in the form of single crystals on slow evaporation of the solvent from the filtrate at room temperature. Yield: 5.093 g of **1**·THF (89%). − $C_{40}H_{32}Ni_3OS_9$ (993.41): calcd. C 48.36, H 3.25, S 29.05; found C 48.01, H 3.03, S 30.58.

[Pd('S_3')]$_3$ (2): A solution of 'S_3'$-H_2$ (1.327 g, 5.3 mmol) in THF (30 mL) was combined with *n*BuLi (4.24 mL, 10.6 mmol) at −50°C and the mixture was subsequently allowed to warm to room temperature. Addition of [$PdCl_2$(COD)] led to a dark-red reaction mixture, which was stirred at room temperature overnight and then stored at −30°C for 24 h. A brown solid precipitated, which was separated, washed with MeOH/THF, and dried in vacuo. Yield: 1.536 g of **2** · THF (77%). − $C_{40}H_{32}OPd_3S_9$ (1136.48): calcd. C 42.28, H 2.84, S 25.39; found C 42.29, H 2.71, S 24.79.

(NBu$_4$)[Ni(SR)('S_3')], where R = *t*Bu (3), Cy (4), Me (5), Ph (6) − General Procedure: The appropriate thiol was first deprotonated in MeOH by the addition of one equivalent of NaOMe or LiOMe. The resulting solution was then combined with a black-brown suspension of [Ni('S_3')]$_3$ (**1**) in THF and the mixture was stirred until all the solid material had dissolved (ca. 30 min). One equivalent of NBu_4OH in MeOH was then added and all volatile components were removed in vacuo. The residue obtained was taken up in THF (ca. 20 mL), undissolved material was removed by filtration, and the filtrate was concentrated to one-third of its original volume. On layering with Et_2O or *n*-hexane, black crystals precipitated, which were separated after 4 d, washed with Et_2O (60 mL), and dried in vacuo.

(NBu$_4$)[Ni(S*t*Bu)('S_3')] (3): 1.685 g (1.83 mmol) of **1**; 5.1 mL (5.61 mmol) of a 1.1 M solution of NaS*t*Bu in MeOH; 6.9 mL (5.52 mmol) of a 0.8 M solution of NBu_4OH in MeOH; 30 mL of THF. Yield: 1.858 mg (53%). − $C_{32}H_{53}NNiS_4$ (638.71): calcd. C 60.18, H 8.36, N 2.19, S 20.08; found C 60.14, H 8.81, N 2.29, S 19.47. − ^{1}H NMR (269.6 MHz, [D_6]acetone): δ = 7.67 (d, 2 H, C_6H_4), 7.22 (d, 2 H, C_6H_4), 6.94 (m, 2 H, C_6H_4), 6.82 (m, 2 H, C_6H_4), 3.48 (t, 8 H, NCH_2), 1.77 (m, 8 H, NCH_2CH_2), 1.50 (s, 9 H, $SCCH_3$), 1.37 [m, 8 H, $N(CH_2)_2CH_2$], 0.90 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR (100.4 MHz, [D_6]acetone): δ = 158.0, 134.3, 129.8, 128.2, 128.0, 121.0 (C_6H_4), 59.4 (NCH_2), 40.1 ($SCCH_3$), 37.5 ($SCCH_3$), 24.6, 20.3 [$NCH_2(CH_2)_2$], 13.9 [$N(CH_2)_3CH_3$].

(NBu$_4$)[Ni(SCy)('S_3')] (4): 1.365 g (1.48 mmol) of **1**; 8.84 mL (4.42 mmol) of a 0.5 M solution of NaSCy in MeOH; 4.44 mL (4.44 mmol) of a 1.0 M solution of NBu_4OH in MeOH; 50 mL of THF. Yield: 2.508 g (85%). − $C_{34}H_{55}NNiS_4$ (664.78): calcd. C 61.43, H 8.34, N 2.11, S 19.29; found C 61.35, H 8.45, N 2.19, S 18.68. − ^{1}H NMR (269.6 MHz, [D_6]acetone): δ = 7.65 (d, 2 H, C_6H_4), 7.20 (d, 2 H, C_6H_4), 6.94 (m, 2 H, C_6H_4), 6.82 (m, 2 H, C_6H_4), 3.49 (t, 8 H, NCH_2), 2.43−1.10 [m, 27 H, $NCH_2(CH_2)_2$, SC_6H_{11}], 0.90 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR (67.8 MHz, [D_6]acetone): δ = 157.2, 134.7, 129.8, 128.4, 128.1, 121.2 (C_6H_4), 69.3, 59.5, 39.9, 29.6, 29.4, 24.7, 20.4, 14.1 (SC_6H_{11}, $NC_{16}H_{36}$).

(NBu$_4$)[Ni(SMe)('S_3')] (5): 369 mg (0.41 mmol) of **1**; 12.32 mL (1.23 mmol) of a 0.1 M solution of LiSMe in MeOH; 1.50 mL (1.20 mmol) of a 0.8 M solution of NBu_4OH in MeOH; 20 mL of THF. Yield: 494 mg (69%). − $C_{29}H_{47}NNiS_4$ (596.63): calcd. C 58.38, H 7.94, N 2.35, S 21.49; found C 58.11, H 8.27, N 2.39, S 21.39. − ^{1}H NMR (269.6 MHz, [D_6]acetone): δ = 7.66 (d, 2 H, C_6H_4), 7.21 (d, 2 H, C_6H_4), 6.96 (m, 2 H, C_6H_4), 6.84 (m, 2 H, C_6H_4), 3.50 (t, 8 H, NCH_2), 1.78 (m, 8 H, NCH_2CH_2), 1.59 (s, 3 H, SCH_3), 1.38 [m, 8 H, $N(CH_2)_2CH_2$], 0.90 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR (67.7 MHz, [D_6]acetone): δ = 156.9, 134.9, 129.8, 128.4, 128.2, 121.2 (C_6H_4), 59.5, 24.6, 20.4, 13.9, 11.1 (SCH_3, $NC_{16}H_{36}$).

(NBu$_4$)[Ni(SPh)('S_3')] (6): 845 mg (0.92 mmol) of **1**; 5.52 mL (2.76 mmol) of a 0.5 M solution of NaSPh in MeOH; 3.50 mL (2.80 mmol) of a 0.8 M solution of NBu_4OH in MeOH; 20 mL of THF. Yield: 1.400 g (77%). − $C_{34}H_{49}NNiS_4$ (658.70): calcd. C 61.99, H 7.50, N 2.13, S 19.47; found C 62.03, H 7.47, N 2.14, S 19.57. − ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.70 (d, 2 H, C_6H_5), 7.55 (d, 2 H, C_6H_4), 7.21 (d, 2 H, C_6H_4), 7.02−6.84 (m, 7 H, C_6H_5, C_6H_4), 3.18 (t, 8 H, NCH_2), 1.50 (m, 8 H, NCH_2CH_2), 1.29 [m, 8 H, $N(CH_2)_2CH_2$], 0.87 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR (67.7 MHz, CD_2Cl_2): δ = 155.0, 140.3, 133.8, 134.4, 129.4, 128.1, 127.7, 127.2, 122.6, 121.4 (C_6H_5, C_6H_4), 59.4, 24.6, 20.3, 13.9 ($NC_{16}H_{36}$).

[Ni(PR$_3$)('S_3')], where R = Cy (7), Ph (8) − General Procedure: The appropriate PR_3 was added as a solid to a stirred black-brown THF suspension of [Ni('S_3')]$_3$ (**1**). In the course of few seconds, a deep-red solution formed, which was filtered. Upon dropwise addition of MeOH (ca. 20 mL), a dark-red solid precipitated, which was separated, washed with MeOH (ca. 50 mL), and dried in vacuo.

[Ni(PCy$_3$)('S_3')] (7): 665 mg (0.72 mmol) of **1**; 841 mg (3.00 mmol) of PCy_3; 10 mL of THF. Yield: 1.16 g (91%). − $C_{30}H_{41}NiPS_3$ (587.50): calcd. C 61.33, H 7.03, S 16.37; found C 61.47, H 7.29, S 16.23. − IR (KBr): $\tilde{\nu}$ = 1099 cm^{-1}, δ(PCH). − ^{1}H NMR (270.6 MHz, $CDCl_3$): δ = 7.70 (d, 2 H, C_6H_4), 7.40 (d, 2 H, C_6H_4), 7.10 (m, 2 H, C_6H_4), 7.00 (m, 2 H, C_6H_4), 2.20−1.20 [m, 33 H, $P(C_6H_{11})_3$]. − ^{13}C{^{1}H} NMR (67.7 MHz, $CDCl_3$): δ = 152.4 (d, $^3J_{P,C}$ = 10.2 Hz), 132.2, 129.7, 128.2, 127.0, 122.2 (C_6H_4), 34.0 (d, $^1J_{P,C}$ = 20.2 Hz), 30.0, 27.6 (d, $J_{P,C}$ = 10.1 Hz), 26.4 [$P(C_6H_{11})_3$]. − ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 28.3 [s, $P(C_6H_{11})_3$]. − MS (FD, THF); *m/z*: 587 [Ni(PCy_3)('S_3')]$^+$.

[Ni(PPh$_3$)('S_3')] (8): 500 mg (0.54 mmol) of **1**; 525 mg (2.00 mmol) of PPh_3; 5 mL of THF. Yield: 894 mg (97%). − $C_{30}H_{23}NiPS_3$ (569.36): calcd. C 63.29, H 4.07, S 16.89; found C 63.47, H 4.17, S 16.51. − IR (KBr): $\tilde{\nu}$ = 1094 cm^{-1}, δ(PCH). − ^{1}H NMR (269.6 MHz, $CDCl_3$): δ = 7.82 (m, C_6H_5), 7.72 (d, 2 H, C_6H_4), 7.46 (m, C_6H_5), 7.28 (d, 2 H, C_6H_4), 7.07 (m, 2 H, C_6H_4), 7.01 (m, 2 H, C_6H_4). − ^{13}C{^{1}H} NMR (67.7 MHz, CD_2Cl_2): δ = 152.8 (d, $^3J_{P,C}$ = 5.7 Hz), 134.9 (d, $J_{P,C}$ = 12.2 Hz), 132.6, 131.3, 130.0 (d, $^1J_{P,C}$ = 48.0 Hz), 129.7, 129.0, 128.6 (d, $J_{P,C}$ = 10.8 Hz), 127.8, 123.0 [C_6H_4, $P(C_6H_5)_3$]. − ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 30.4 [s, $P(C_6H_5)_3$].

(NBu$_4$)[Ni(Cl)('S_3')] (9): [Ni('S_3')]$_3$ (**1**) (1.660 g, 1.80 mmol) and NBu_4Cl (1.550 g, 5.41 mmol) were combined in THF (20 mL) and the mixture was stirred at room temperature for 24 h to give a violet suspension. This suspension was then cooled to −30°C, and the precipitate was filtered off, washed with THF, and dried in vacuo. Yield: 2.311 g (73%). − $C_{28}H_{44}ClNNiS_3$ (584.99): calcd. C 57.49, H 7.58, N 2.39, S 16.44; found C 56.98, H 7.68, N 2.36, S 16.54. − ^{1}H NMR (269.7 MHz, [D_8]THF): δ = 7.63 (d, 2 H, C_6H_4), 7.18 (d, 2 H, C_6H_4), 6.94 (m, 2 H, C_6H_4), 6.77 (m, 2 H, C_6H_4), 3.53 (t, 8 H, NCH_2), 1.75 (m, 8 H, NCH_2CH_2), 1.38 [m, 8 H, $N(CH_2)_2CH_2$], 0.90 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR

(67.7 MHz, [D$_6$]acetone): δ = 153.9, 138.2, 131.7, 129.4, 129.0, 122.3 (C_6H_4), 59.4, 24.8, 20.7, 14.1 ($NC_{16}H_{36}$).

(NBu_4)[Ni(N_3)('S_3')] (10): A 1.0 M THF solution of NBu_4N_3 (3.0 mL, 3.00 mmol) was added to a black-brown suspension of [Ni('S_3')]$_3$ (**1**) (900 mg, 0.97 mmol) in THF (10 mL). The reaction mixture was stirred overnight at room temperature to give a violet solution, which was then filtered. Layering of the filtrate with (iPr)$_2$O (10 mL) led to the precipitation of black-violet microcrystals, which were separated, washed with (iPr)$_2$O, and dried in vacuo. Yield: 1.364 g (79%). − $C_{28}H_{44}N_4NiS_3$ (591.55): calcd. C 56.85, H 7.50, N 9.47, S 16.26; found C 56.87, H 8.47, N 9.17, S 16.36. − IR (KBr): $\tilde{\nu}$ = 2035 cm^{-1}, ν(N_3). − ^{1}H NMR (269.7 MHz, [D$_8$]THF): δ = 7.56 (d, 2 H, C_6H_4), 7.19 (d, 2 H, C_6H_4), 6.96 (m, 2 H, C_6H_4), 6.81 (m, 2 H, C_6H_4), 3.49 (t, 8 H, NCH_2), 1.75 (m, 8 H, NCH_2CH_2), 1.39 [m, 8 H, $N(CH_2)_2CH_2$], 0.89 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR (67.8 MHz, [D$_8$]THF): δ = 154.9, 134.7, 129.7, 128.5, 128.3, 121.6 (C_6H_4), 59.6, 25.0, 20.7, 14.2 ($NC_{16}H_{36}$).

(NBu_4)[Ni(X)('S_3')] from 3 and Me_3SiX, where X = Cl^- (9), N_3^- (10), NCS^- (11), NSO^- (12) − General Procedure: The appropriate Me_3SiX was added to a black-brown THF solution of (NBu_4)[Ni(StBu)('S_3')] (**3**). A color change was observed within a period of time ranging from 5 min up to 48 h depending on the Me_3SiX compound. All volatile components were then removed in vacuo, and the residue obtained was extracted with Et_2O (ca. 10 mL), separated, washed with Et_2O, and dried in vacuo.

(NBu_4)[Ni(Cl)('S_3')] (9): 250 mg (0.39 mmol) of **3**; 0.10 mL (1.07 mmol) of Me_3SiCl; 3 mL of THF; volatile components were removed after 30 min.; violet powder.

(NBu_4)[Ni(N_3)('S_3')] (10): 275 mg (0.43 mmol) of **3**; 0.15 mL (1.47 mmol) of Me_3SiN_3; 15 mL of THF; volatile components were removed after 24 h; violet powder.

(NBu_4)[Ni(NCS)('S_3')] (11): 125 mg (0.20 mmol) of **3**; 0.07 mL (0.47 mmol) of Me_3SiNCS; 3 mL of THF; volatile components were removed after 5 min; dark-red powder. Yield: 114 mg (94%). − $C_{29}H_{44}N_2NiS_4$ (607.61): calcd. C 57.33, H 7.30, N 4.61, S 21.11; found C 56.82, H 7.33, N 4.78, S 20.12. − IR (KBr): $\tilde{\nu}$ = 2105 cm^{-1}, ν(NCS). − ^{1}H NMR (269.6 MHz, [D$_6$]acetone): δ = 7.66 (d, 2 H, C_6H_4), 7.21 (d, 2 H, C_6H_4), 7.06 (m, 2 H, C_6H_4), 6.92 (m, 2 H, C_6H_4), 3.47 (t, 8 H, NCH_2), 1.81 (m, 8 H, NCH_2CH_2), 1.45 [m, 8 H, $N(CH_2)_2CH_2$], 0.95 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR (67.7 MHz, [D$_6$]acetone): δ = 153.3 (C_6H_4), 140.6 (NCS), 133.2, 129.3, 129.0, 128.0, 122.4 (C_6H_4), 59.2, 24.4, 20.2, 13.8 ($NC_{16}H_{36}$).

(NBu_4)[Ni(NSO)('S_3')] (12): 1.00 g (1.57 mmol) of **3**; 500 mg (3.70 mmol) of Me_3SiNSO; 20 mL of THF; volatile components were removed after 2 d; orange powder. Yield: 824 mg (86%). − $C_{28}H_{44}N_2NiOS_4$ (611.60): calcd. C 54.99, H 7.25, N 4.58, S 20.97; found C 54.75, H 7.22, N 4.21, S 20.28. − IR (KBr): $\tilde{\nu}$ = 1230 cm^{-1}, ν_{asym}(NSO), 1030 cm^{-1}, ν_{sym}(NSO). − ^{1}H NMR (269.6 MHz, [D$_8$]THF): δ = 7.59 (d, 2 H, C_6H_4), 7.19 (d, 2 H, C_6H_4), 6.95 (m, 2 H, C_6H_4), 6.81 (m, 2 H, C_6H_4), 3.41 (t, 8 H, NCH_2), 1.65 (m, 8 H, NCH_2CH_2), 1.35 [m, 8 H, $N(CH_2)_2CH_2$], 0.85 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR (67.8 MHz, [D$_8$]THF): δ = 155.8, 134.1, 129.9, 128.4, 128.2, 121.5 (C_6H_4), 59.6, 25.0, 20.7, 14.2 ($NC_{16}H_{36}$).

(NBu_4)[Pd(StBu)('S_3')] (13): A 1.1 M MeOH solution of NaStBu (0.74 mL, 0.81 mmol), NBu_4Cl (220 mg, 0.80 mmol), and [Pd('S_3')]$_3$ (**2**) (290 mg, 0.27 mmol) were combined in THF (10 mL). The resulting mixture was stirred at room temperature for 24 h to give a red solution. Undissolved material was removed by filtration, and the red filtrate was concentrated to one-third of its original volume. Layering with Et_2O led to the precipitation of red crystals, which were separated after 4 d, washed with Et_2O (10 mL), and dried in vacuo. Yield: 452 mg (81%). − $C_{32}H_{53}NPdS_4$ (686.44): calcd. C 55.99, H 7.78, N 2.04, S 18.68; found C 53.37, H 8.36, N 1.98, S 18.05. − ^{1}H NMR (269.7 MHz, [D$_6$]acetone): δ = 7.64 (d, 2 H, C_6H_4), 7.25 (d, 2 H, C_6H_4), 6.97 (m, 2 H, C_6H_4), 6.85 (m, 2 H, C_6H_4), 3.41 (t, 8 H, NCH_2), 1.73 (m, 8 H, NCH_2CH_2), 1.46 (s, 9 H, $SCCH_3$) 1.38 [m, 8 H, $N(CH_2)_2CH_2$], 0.90 [t, 12 H, $N(CH_2)_3CH_3$]. − ^{13}C{^{1}H} NMR (100.4 MHz, [D$_6$]acetone): δ =

Table 3. Selected crystallographic data for [Ni('S_3')]$_3$ · 3 THF · 6 MeOH (**1** · 3 THF · 6 MeOH), [Pd('S_3')]$_3$ · 2 CH_2Cl_2 (**2** · 2 CH_2Cl_2), (NBu_4)[Ni(StBu)('S_3')] (**3**), (NBu_4)[Ni(SCy)('S_3')] (**4**), and (NBu_4)[Ni(SPh)('S_3')] (**6**)

Compound	**1** · 3 THF · 6 MeOH	**2** · 2 CH_2Cl_2	**3**	**4**	**6**
Formula	$C_{54}H_{72}Ni_3O_9S_9$	$C_{38}H_{28}Cl_4Pd_3S_9$	$C_{32}H_{53}NNiS_4$	$C_{34}H_{55}NNiS_4$	$C_{34}H_{49}NNiS_4$
M_r [g/mol]	1329.79	1234.14	638.70	664.74	658.69
Crystal system	trigonal	triclinic	monoclinic	orthorhombic	monoclinic
Space group	*P*3(bar)	*P*1(bar)	$P2_1/n$	*Pbca*	*C*2/*c*
a [pm]	1851.0(7)	951.6(6)	1059.1(3)	1005.4(2)	4474.6(9)
b [pm]	1851.0(7)	1462.7(10)	1931.8(3)	1608.9(9)	1024.3(2)
c [pm]	983.2(8)	1593.7(12)	1717.8(5)	4352.5(9)	1590.4(3)
α [°]	90	88.47(6)	90	90	90
β [°]	90	77.90(5)	103.20(3)	90	107.70(3)
γ [°]	120	82.01(5)	90	90	90
V [nm^3]	2.917(3)	2.148(3)	3.422(2)	7.041(4)	6.944(2)
Z	2	2	4	8	8
$d_{calcd.}$ [g/cm^3]	1.514	1.908	1.240	1.254	1.260
μ [cm^{-1}]	13.34	19.59	8.32	8.12	8.22
Cryst. size [mm^3]	0.5 × 0.4 × 0.4	0.3 × 0.2 × 0.1	0.7 × 0.5 × 0.4	0.4 × 0.4 × 0.1	0.8 × 0.4 × 0.2
ω-scan [°/min]	8.0	10.0	10.0	3.0−30.0	3.0−30.0
2θ range [°]	4.0−54.0	3.8−52.0	4.1−52.0	6.1−54.0	4.0−50.1
Measured refl.	5423	9400	8330	5453	8680
Independent refl.	4145	8436	6710	5453	6136
Observed refl.	1083	1487	3625	1024	2776
ref. parameters	228	487	344	361	361
$R1$[a]; $wR2$ [%]	6.4; 17.5	7.4; 20.0	6.5; 19.5	2.9; 7.5	4.7; 10.7

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

Table 4. Selected crystallographic data for [Ni(PCy_3)('S_3')] · THF (**7** · THF), [Ni(PPh_3)('S_3')] · $CDCl_3$ (**8** · $CDCl_3$), (NBu_4)[Ni(Cl)('S_3')] (**9**), and (NBu_4)[Pd(S*t*Bu)('S_3')] (**13**)

Compound	**7** · THF	**8** · $CDCl_3$	**9**	**13**
Formula	$C_{34}H_{49}NiOPS_3$	$C_{31}H_{23}Cl_3DNiPS_3$	$C_{28}H_{44}ClNNiS_3$	$C_{32}H_{53}NPdS_4$
M_r [g/mol]	659.59	689.72	584.98	686.39
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	*Pnma*	$P2_1/c$	$P2_1/n$	*Pbca*
a [pm]	2275.1(7)	1731.1(2)	953.8(4)	1952.2(2)
b [pm]	1713.1(4)	922.5(1)	1660.4(7)	1666.1(3)
c [pm]	859.8(3)	1883.4(3)	1891.2(6)	2116.0(2)
α [°]	90	90	90	90
β [°]	90	95.4(1)	90.01(4)	90
γ [°]	90	90	90	90
V [nm^3]	3.351(2)	2.994(1)	2.995(2)	6.882(2)
Z	4	4	4	8
$d_{calcd.}$ [g/cm^3]	1.307	1.530	1.297	1.325
μ [$^{-1}$]	8.39	12.00	9.63	8.03
Cryst. size [mm^3]	0.5 × 0.5 × 0.3	0.6 × 0.6 × 0.6	0.5 × 0.3 × 0.1	0.4 × 0.3 × 0.1
ω-scan [°/min]	3.0−30.0	3.0−30.0	3.0−30.0	3.0−30.0
2θ range [°]	4.0−54.0	4.0−54.0	4.2−55.2	4.2−52.0
Measured refl.	6237	6810	9724	8097
Independent refl.	3787	6593	6922	6766
Observed refl.	1882	4317	3644	2310
ref. parameters	190	352	309	350
$R1$[a]; $wR2$ [%]	3.4; 7.4	3.6; 8.9	4.1; 11.0	4.0; 7.9

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

158.0, 134.2, 131.2, 129.6, 128.5, 121.4 (C_6H_4), 59.4 (NCH_2), 41.7 ($SCCH_3$), 37.6 ($SCCH_3$), 24.6, 20.4 [$NCH_2(CH_2)_2$], 13.9 [$N(CH_2)_3CH_3$].

X-ray Structure Analyses of [Ni('S_3')]$_3$ · 3 THF · 6 MeOH (1 · 3 THF · 6 MeOH), [Pd('S_3')]$_3$ · 2 CH_2Cl_2 (2 · 2 CH_2Cl_2), (NBu_4)[Ni(S*t*Bu)('S_3')] (3), (NBu_4)[Ni(SCy)('S_3')] (4), (NBu_4)[Ni(SPh)('S_3')] (6), [Ni(PCy_3)('S_3')] · THF (7 · THF), [Ni(PPh_3)('S_3')] · $CDCl_3$ (8 · $CDCl_3$), (NBu_4)[Ni(Cl)('S_3')] (9), and (NBu_4)[Pd(S*t*Bu)('S_3')] (13): Black hexagons of **1** · 3 THF · 6 MeOH were grown by slow evaporation of the solvent at room temperature from the THF/MeOH mother liquor resulting from the synthesis of [Ni('S_3')]$_2$.[6] Black single crystals of **2** · 2 CH_2Cl_2 were formed upon layering a CH_2Cl_2 solution of **2** with Et_2O. Black-red plates of **3**, **4**, **6**, and **13** were obtained directly from the respective reaction solutions. Orange plates of **7** · THF were grown by layering a THF solution of **7** with MeOH. Red-brown blocks of **8** · $CDCl_3$ were similarly grown by layering the $CDCl_3$ solution of **8** that had been used for NMR measurements with MeOH. Black plates of **9** were grown by layering a THF solution of **9** with Et_2O. In all cases, suitable single crystals were sealed in glass capillaries under N_2. Data were collected at 200 K (**1** · 3 THF · 6 MeOH, **3**, **4**, **6**, **7** · THF, **8** · $CDCl_3$, **9**, **13**) or 298 K (**2** · 2 CH_2Cl_2) on a Siemens P4 or a Nicolet R3 m/V (**2** · 2 CH_2Cl_2) diffractometer using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) by the ω-scan technique. In the case of **2** · 2 CH_2Cl_2 and **3**, an absorption correction was applied on the basis of ψ-scans. The structures were solved by direct methods (SHELXTL-PLUS[14a] or SHELXTL 5.03[14b]). Full-matrix least-squares refinement was carried out on F^2 (SHELXL-93[14c] or SHELXTL 5.03[14b]). All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms in **3**, **4**, **6**, **7** · THF, **8** · $CDCl_3$, and **9** were taken from the difference Fourier map and were kept fixed with a common isotropic displacement parameter. In the case of **1** · 3 THF · 6 MeOH, **2** · 2 CH_2Cl_2, and **13**, the hydrogen atoms were geometrically positioned with isotropic displacement parameters fixed at 1.5 times the U(eq) of the adjacent carbon atom. One *n*-butyl group (C40−C43) in the cation of **3** is evidently disordered, but no well-separated sites could be refined. In the case of complex **9**, the crystal under study proved to be a pseudomerohedral twin. The twin component ratio was refined to give 0.694(1) and 0.306(1), respectively. Selected crystallographic data are listed in Tables 3 and 4.[15]

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[15] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-128896 (**1** · 3 THF · 6 MeOH), -128897 (**2** · CH_2Cl_2), -128898 (**3**), -128899 (**4**), -128900 (**6**), -128901 (**7** · THF), -128902 (**8** · $CDCl_3$), -128903 (**9**), -128904 (**13**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: (internat.) +44 (0)1223/336033, E-mail: deposit@ccdc.cam.ac.uk].

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