Transition Metal Complexes with Sulfur Ligands, 140[+]

Mononuclear Ni, Pd and Pt Complexes with $'S_3'^{2-}$ Thioether Thiolate and HNP*n*Pr$_3$ Phosphorane Imine Ligands [$'S_3'^{2-}$ = Bis(2-mercaptophenyl)sulfide (2–)]

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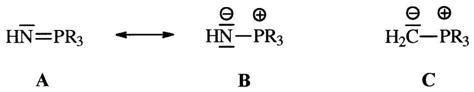
Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

Keywords: Phosphorane imine / Sulfur ligands / Nickel / Palladium / Platinum

Reaction of the trinuclear $[M('S_3')]_3$ complexes {M = Ni (**4**), Pd (**5**), Pt (**6**); $'S_3'^{2-}$ = bis(2-mercaptophenyl)sulfide (2–)} with HNP*n*Pr$_3$ yielded the new phosphorane imine complexes $[M(NHP\mathit{n}Pr_3)('S_3')]$ {M = Ni (**1**), Pd (**2**), Pt (**3**)}. The complexes **1**–**3** have been completely characterized and are rare examples of mononuclear phosphorane imine complexes with late transition metals. Spectroscopic and structural results indicate that the HNP*n*Pr$_3$ ligands favor the ylidic structure when binding to $[M('S_3')]$ fragments. X-ray structure determinations showed that $[M(NHP\mathit{n}Pr_3)('S_3')]$ complexes associate through N–H···S(thiolate) bridges to give centrosymmetric dimers.

Introduction

Phosphorane imines HNPR$_3$ (R = alkyl, aryl), their *N*-organosubstituted RNPR$_3$ analogues and deprotonated phosphorane imide derivatives $[NPR_3]^-$ have proved to be versatile ligands. For example, HNPR$_3$ ligands can bind to metal centers in high, medium or low oxidation states, e.g. $[TiF_3(NPPh_3)(NHPPh_3)]_2$,[1] $[Zr_2Cl_4(NPMe_3)_4(NHPMe_3)]$,[2] $[Cp^*TaF_4(NHPPh_3)]$,[3] $[CoCl_2(NHPMe_3)_2]$,[4] $[PdCl(\eta^3\text{-}C_3H_5)(NHPPh_3)]$, $[Rh(CO)_2Cl(NHPPh_3)]$[5] and $[Mo_2(CO)_6(\mu\text{-}NHPPh_3)_3]$.[6] Phosphorane imides $[NPR_3]^-$, which are unstable in the free state and which can act as building blocks in numerous metal clusters, form as PR$_3$ adducts of nitrido or intermediary nitrene ligands, or can result from deoxygenation of nitrosylligands by phosphanes as demonstrated by complexes of the type $[MX(NPR_3)]_4$ (M = Mn, Co, Ni, Zn; X = Cl, Br, I),[7] $[NiCl(\mu^3\text{-}NH)(\mu^3\text{-}NPMe_3)(PMe_3)]$[8] and $[Mo(NPR_3)(NO)('S_4')]$[9] {R = alkyl, aryl, $'S_4'^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane (2−)}. The coordination chemistry of phosphorane imides has recently been reviewed.[10] Phosphorane imido metal complexes with terminal $[M-NPR_3]$ groups exhibit an interesting peculiarity which is still poorly understood. The M−N−P angle of such complexes can vary over a wide range from nearly 180° to almost 120°[10] as demonstrated by $[MoCl_4(NPPh_3)(pyridine)]$ {176.6(6)°}[11] and $[Mo(NPMePh_2)(NO)('S_4')]$ {129.7(4)°}.[12] As yet, it has not been possible to correlate unambiguously these angles with properties such as coordination number or oxidation state of the metal centers. Nevertheless, the structural variability of M−N−PR$_3$ groups suggests that NPR_3^- ligands are electronically flexible in the sense that they can act as two- or four-electron donors.[10] Electronic flexibility or ambiguity is also suggested for free HNPR$_3$ compounds by the valence bond formulae **A** and **B**.



$$\mathrm{H\bar{N}{=}PR_3} \longleftrightarrow \mathrm{H\overset{\ominus}{\underline{\bar{N}}}{-}\overset{\oplus}{P}R_3} \qquad \mathrm{H_2\overset{\ominus}{\underline{C}}{-}\overset{\oplus}{P}R_3}$$

A **B** **C**

While formula **A** indicates a double bond character for the PN bond, the dipolar formula **B** exhibits a PN single bond and emphasizes the isoelectronic nature of phosphorane imines and the phosphorane ylides **C**. A high-precision low-temperature neutron and X-ray diffraction study of HNPPh$_3$[13] did not yield structural evidence for the preference of either formula **A** or formula **B**. Our interest in phosphorane imine or imido complexes originates from reactions that transform small nitrogen-containing molecules into other compounds in the coordination sphere of sulfur rich molecules.[14] In this context, we noted that phosphorane imine complexes of the late transition metals are rare. The few examples known usually contain *N*-substituted RNPR$_3$ ligands such as in $[CuCl_2(Me_3SiNPMe_3)]_2$,[15] where removal of the nitrogen substituent leads to phosphorane imido clusters, for example, $[Cu_6Cl_6(NPMe_3)_4]^+$.[16] $[NiCl(PMe_3)(Ph_2P(\mathit{o}\text{-}C_6H_4)-N{=}PMe_3)]^+$ appears to be the first mononuclear nickel phosphorane imine complex described in the literature.[17] It was obtained only recently and contains an N=PMe$_3$ entity as part of a chelate ligand. $[NiBr_2\{HNP(NMe_2)_3\}_2]$ is the second example of mononuclear nickel phosphorane imine complexes

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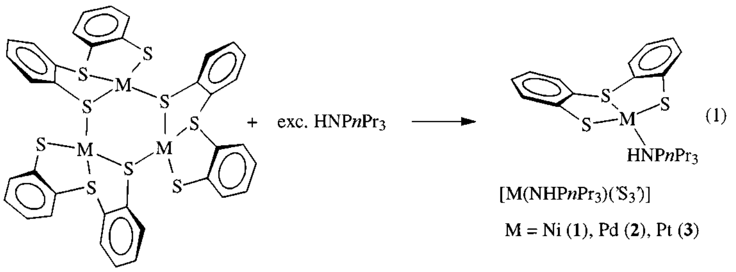

and was mentioned in the review article cited above.[10] Other mononuclear complexes of nickel, palladium and platinum with parent $HNPR_3$ imine ligands are unknown. We have now obtained such complexes from reactions of the trinuclear $[M('S_3')]_3$ complexes[18] {M = Ni, Pd, Pt, $'S_3'^{2-}$ = bis(2-mercaptophenyl)sulfide(2−)} with $HNP\textit{n}Pr_3$. The resulting $[M(NHP\textit{n}Pr_3)('S_3')]$ complexes were fully characterized and are described here.

Results and Discussion

Treatment of the trinuclear $[M('S_3')]_3$ (M = Ni, Pd, Pt) complexes with a slight excess of $HNP\textit{n}Pr_3$ yielded the mononuclear $[M(NHP\textit{n}Pr_3)('S_3')]$ complexes {M = Ni (**1**), Pd (**2**), Pt (**3**)} according to Equation 1.

In the course of the reactions, the black $[Ni('S_3')]_3$ or dark-red $[Pt('S_3')]_3$ complexes slowly dissolved and red-purple (Ni) or yellow (Pt) solutions formed, from which the corresponding $[M(NHP\textit{n}Pr_3)('S_3')]$ complexes were isolated in an analytically pure form. The complexes **1−3** readily dissolve in THF, acetone or CH_2Cl_2, but are only sparingly soluble in Et_2O, *n*-hexane, or CH_3CN. The IR spectra of **1−3** (KBr discs) exhibit the typical absorption patterns for the $[M('S_3')]$ fragments and, in addition, sharp ν(NH) bands of the $HNP\textit{n}Pr_3$ ligands in the region of 3273−3292 cm^{-1}. In comparison to the ν(NH) of free $HNP\textit{n}Pr_3$ (3367 cm^{-1}), the ν(NH) bands are slightly red-shifted. The complexes **1−3** are diamagnetic and yielded high-resolution NMR spectra. Figure 1 shows the ^1H NMR spectrum of **1**. The splitting pattern in the aromatic region is characteristic for $[M('S_3')]$ fragments and can be used as a diagnostic probe for monitoring these reactions.

The chemical shifts of the NH protons depend on the metal center binding the $HNP\textit{n}Pr_3$ ligand. In comparison to uncoordinated $HNP\textit{n}Pr_3$ with an NH signal at $\delta = -0.59$ (CD_2Cl_2), the NH signals of the complexes (CD_2Cl_2) are either high-field shifted (**1**: $\delta = -1.85$) or low-field shifted (**2**: $\delta = -0.03$; **3**: $\delta = +0.54$). Thus, within the series of complexes **1−3**, the NH protons are increasingly deshielded, possibly indicating an increasing NH acidity of the $HNP\textit{n}Pr_3$ ligands. The NH signals are slightly broadened and not split by $^2J_{H-P}$ coupling (down to temperatures of −60 °C), although the NH signal of complex **3** exhibits a $^2J_{H-Pt}$ coupling constant of 41.5 Hz. The $^{13}C\{^1H\}$ NMR spectra exhibit only six signals for the twelve aromatic C atoms of the 'S3' ligand, indicating a twofold symmetry of the $[M('S_3')]$ fragments. The NH chemical shifts are of interest with regard to the ylene structure **A** or ylide structure **B**. Protons at sp^2 hybridized N atoms in HN=X compounds (X = NH, CH_2, CR_2) such as diazenes, methylene imines or ketimines, are usually strongly low-field shifted ($\delta = 10-15$), regardless of whether the HN=X species are in the free state or are coordinated to metal centers.[19] The NH signals of **1−3**, and of other diamagnetic $HNPR_3$ com-

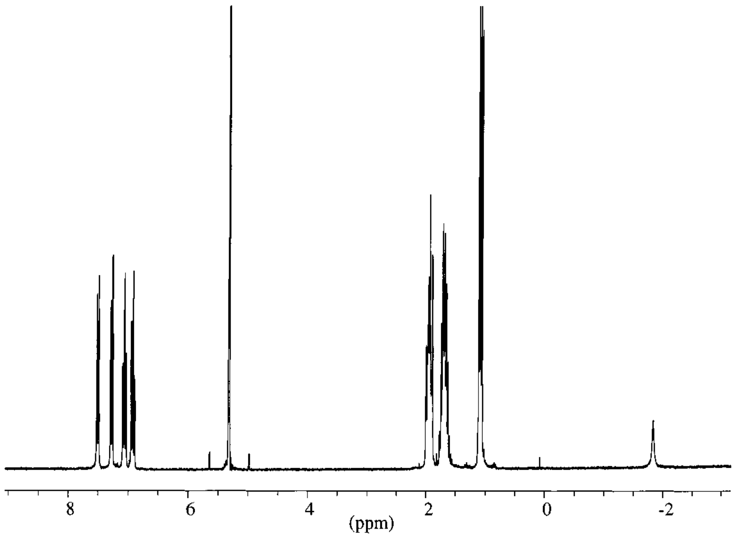

Figure 1. ^1H NMR spectrum of $[Ni(NHP\textit{n}Pr_3)('S_3')]$ (**1**) in CD_2Cl_2

plexes,[3,5,6] however, appear in the shift range typical of ammonia, amines, hydrazines etc. Thus the NH shifts of **1−3** seem to suggest the single bond formula **B** rather than the double bond structure **A** for complexed $HNPnPr_3$.

X-ray Structure Determinations of 1−3

The molecular structures of all three complexes were determined by X-ray structure analyses. The crystals contain discrete molecules which, however, form dimers through N−H···S(thiolate) contacts. Figure 2 depicts their molecular structures and Table 1 lists selected distances and angles.

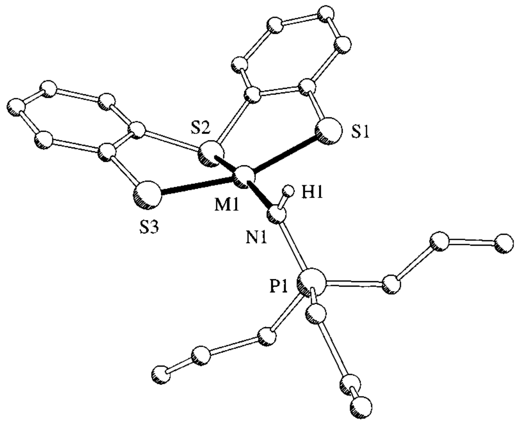

Figure 2. Molecular structure of $[M(NHPnPr_3)('S_3')]$ {M = Ni (**1**), Pd (**2**), Pt (**3**)}, (C bonded H atoms omitted)

Table 1. Selected distances (pm) and angles (°) of $[Ni(NHPnPr_3)('S_3')]$ (**1**), $[Pd(NHPnPr_3)('S_3')]$ (**2**) and $[Pt(NHPnPr_3)('S_3')]$ (**3**)

Complex (M)	**1** (Ni)	**2** (Pd)	**3** (Pt)
M1−N1	191.7(5)	206.3(3)	205.0(1)
M1−S1	217.4(2)	229.47(10)	229.5(5)
M1−S2	211.6(2)	221.75(9)	220.8(4)
M1−S3	218.4(2)	230.52(10)	230.2(5)
N1−P1	159.5(5)	159.6(3)	163(2)
N1−H1	78(5)	79(5)	86
N1−M1−S2	170.9(2)	175.26(9)	176.2(5)
S1−M1−S3	161.77(6)	163.46(4)	164.4(2)
M1−N1−P1	127.1(3)	123.5(2)	122.0(9)
M1−N1−H1	118(5)	116(4)	119
P1−N1−H1	110(4)	115(4)	119
N1···S3a[a]	366.0(5)	368.7(3)	367(2)
H1···S3a[a]	289(6)	296(5)	296
N1−H1···S3a[a]	169(5)	165(5)	141

[a] Symmetry code: −x + 1, −y + 2, −z + 1

Complexes **1−3** are isostructural. The $HNPnPr_3$ ligands coordinate through their N donors to the $[M('S_3')]$ fragments. The resulting $[MNS_3]$ core geometries are considerably tetrahedrally distorted and not strictly planar as would be expected for four-coordinate low-spin d^8 M^{II} centers. A comparison of the [N1−M1−S2] and [S1−M1−S3] angles in complexes **1−3** demonstrates that this distortion is most pronounced in the nickel complex **1**, which exhibits angles of 170.9(2)° and 161.77(6)°, respectively. This distortion is to a major extent caused by the topology of the $'S_3'$ ligand. The sp^3 hybridization of the central thioether S donor (S2) forces the $[M('S_3')]$ fragments to adopt a butterfly-like conformation, in which the two $'S_3'$ benzene ring planes exhibit an average dihedral angle of 109°.

The M−S distances in the $[M('S_3')]$ fragments lie in the ranges observed also for other Ni^{II}, Pd^{II} and Pt^{II} thioether thiolate complexes.[20] However, it should be noted that the M−S2(thioether) distances of **1** {211.6(2) pm}, **2** {221.75(9) pm} and **3** {220.8(4) pm} are relatively short and are smaller than the corresponding M−S(thiolate) distances. This is a significant feature of $[M('S_3')]$ fragments and is probably caused by the steric constraints of the $'S_3'$ ligand.[18] The M−N distances of **1** {191.7(5) pm}, **2** {206.3(3) pm} and **3** {205.0(14) pm} indicate M−N single bonds, but are also relatively short. This is shown by comparing, for example, the Ni−N distances in **1** {191.7(5) pm}, the phosphorane imine complex $[NiCl(PMe_3)(Ph_2P(o\text{-}C_6H_4)-N{=}PMe_3)]^+$ {201.1(7) pm}[17] and the oligonuclear phosphorane imido complex $[NiBr(NPMe_3)]_4$ (av. 202.1 pm).[7c] The P−N distances of **1** {159.5(5) pm}, **2** {159.6(3) pm} and **3** {163(2) pm} are identical within the 3 σ criterion. Calculations on $HNPMe_3$[21] and the above mentioned diffraction study of $HNPPh_3$[13] indicate that such distances are compatible with formulae **A** and **B**. The M−N−P and the (less accurate) M−N−H angles of **1** {127.1(3)°, 118(5)°}, **2** {123.5(2)°, 116(4)°} and **3** {122.0(9)°} suggest, at first glance, sp^2 hybridization of the N donors. However, the angle sums around the N atoms of **1** (355.1°) and **2** (354.5°) show that the coordination geometry of the three-coordinate N donors is not strictly planar but slightly distorted to trigonal pyramidal.

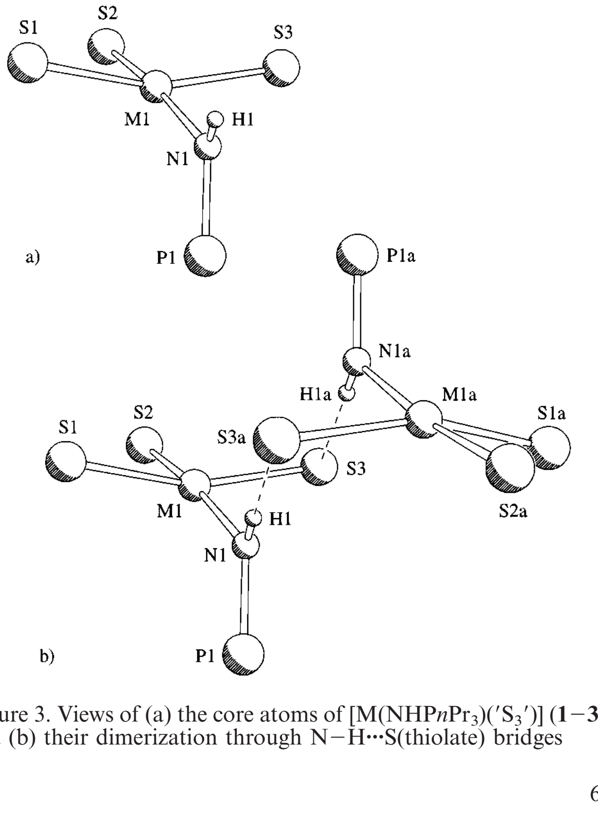

Figure 3. Views of (a) the core atoms of $[M(NHPnPr_3)('S_3')]$ (**1−3**), and (b) their dimerization through N−H···S(thiolate) bridges

Figure 3 illustrates the dimerization of [M(NHP*n*Pr$_3$)('S$_3$')] complexes through N−H···S(thiolate) bridges. The resulting dimers possess crystallographically imposed centers of inversion. The HNP*n*Pr$_3$ ligands coordinate to the [M('S$_3$')] fragments in such a way that the NH bonds are approximately orthogonal to the [MNS$_3$] cores giving rise to N···S(thiolate) distances between two adjacent molecules of 366.0(5) pm in **1**, 368.7(3) pm in **2** and 367(2) pm in **3**. The corresponding H···S(thiolate) distances, which are shorter than the sum of the van der Waals radii (N = 155 pm, H = 120 pm, S = 180 pm),[22] and the N−H···S directionality (see Table 1), indicate hydrogen bonding. Inter- and intramolecular hydrogen bonds between HNPR$_3$ and chloride or iodide co-ligands have previously been suggested in [CdI$_2$(NHPPh$_3$)$_2$]$_2$[23] and [Cp*$_2$UCl$_2$(NHPPh$_3$)].[24]

Conclusions

Three new phosphorane imine complexes have been synthesized and characterized. The complexes **1−3** are rare examples of mononuclear phosphorane imine complexes containing late transition metals. In addition, **1−3** contrast with previously reported complexes as their metal coordination spheres contain only sulfur donors, apart from the HNPR$_3$ ligand. Coordination of HNP*n*Pr$_3$ to the [M('S$_3$')] fragments causes a considerable stabilization of HNP*n*Pr$_3$ towards hydrolysis. ^{1}H NMR spectroscopic data and the X-ray crystal structures indicate that HNP*n*Pr$_3$ favors the ylidic structure **B** when binding to [M('S$_3$')] fragments. Studies are underway to evaluate the synthetic potential of the NH group and the influence of the electron-rich sulfur donors upon the reactivity of the HNP*n*Pr$_3$ ligands

Experimental Section

General: Unless stated otherwise, all reactions and manipulations were carried out under nitrogen 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 on the following instruments: IR (KBr discs or CaF$_2$ cuvettes, solvent bands were compensated) Perkin−Elmer 983, 1620 FT IR or 16PC FT-IR. NMR: Jeol-JNM-GX 270, EX 270 or Lambda LA 400 with the protio-solvent signal used as an internal reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane (^{1}H, ^{13}C{^{1}H} NMR) or 85% H$_3$PO$_4$ (^{31}P{^{1}H} NMR). Spectra were recorded at 25°C. Mass spectra: Jeol MSTATION 700 spectrometer. Elemental analyses: Carlo Erba EA 1106 or 1108 analyzer. The starting [M('S$_3$')]$_3$ complexes {M = Ni (**4**), Pd (**5**), Pt (**6**)}[18] and HNP*n*Pr$_3$ (**7**)[25] were prepared by literature methods.

[M(NHP*n*Pr$_3$)('S$_3$')] (M = Ni, Pd, Pt). − General Procedure: HNP*n*Pr$_3$ (**7**) was added to suspensions of **4−6** in 10 mL of THF. The reaction mixtures were stirred for 12 h at room temperature yielding red-purple, red-brown, or yellow solutions. Undissolved traces of white material were removed by centrifugation. The solutions were reduced in volume to about 2 mL, layered with 10 mL of acetonitrile and cooled to −30°C. Precipitated microcrystals were separated after one week, washed with 10 mL of acetonitrile and dried in vacuo.

[Ni(NHP*n*Pr$_3$)('S$_3$')] (1): Synthesised from **4** (510 mg, 0.55 mmol) and **7** (0.48 mL, 2.20 mmol) to give **1** as red-purple microcrystals. Yield: 424 mg (53%). − $C_{21}H_{30}NNiPS_3$ (482.32): calcd. C 52.30, H 6.27, N 2.90, S 19.94; found C 52.69, H 6.36, N 3.08, S 18.34. −

Table 2. Selected crystallographic data of [Ni(NHP*n*Pr$_3$)('S$_3$')] (**1**), [Pd(NHP*n*Pr$_3$)('S$_3$')] (**2**) and [Pt(NHP*n*Pr$_3$)('S$_3$')] (**3**)

Compound	**1**	**2**	**3**
Formula	$C_{21}H_{30}NNiPS_3$	$C_{21}H_{30}NPPdS_3$	$C_{21}H_{30}NPPtS_3$
M_r [g/mol]	482.32	530.01	618.70
Crystal size [mm]	0.50 × 0.50 × 0.30	0.42 × 0.35 × 0.25	0.40 × 0.30 × 0.14
$F(000)$	2032	2176	2432
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*
a [pm]	1290.3(2)	1311.4(1)	1310.1(4)
b [pm]	1824.1(2)	1813.5(1)	1819.3(6)
c [pm]	1959.8(3)	1965.0(2)	1960.7(5)
V [nm^3]	4.6127(11)	4.6732(6)	4.673(2)
Z	8	8	8
$D_{calcd.}$ [g/cm^3]	1.389	1.507	1.759
μ [mm^{-1}]	1.189	1.138	6.349
Diffractometer	Siemens P4	Siemens P4	Siemens P4
Radiation [pm]	Mo-*K*α (λ = 71.073)	Mo-*K*α (λ = 71.073)	Mo-*K*α (λ = 71.073)
Temperature [K]	200	200	200
Scan technique	ωscan	ωscan	ωscan
2Θ range [°]	4.1−54.0	4.1−54.0	4.1−52.1
Scan speed [°/min]	6.0−60.0	5.0−50.0	4.0−40.0
Meas. reflections	4260	6224	4689
Indep. reflections	3374	5103	3750
R_{int} [%]	4.93	2.73	10.55
Obs. reflections	2330	3653	2177
σ criterion	$F_0 > 4\sigma(F_0)$	$F_0 > 4\sigma(F_0)$	$F_0 > 4\sigma(F_0)$
$R1$; wR2 [%]	4.92; 11.83	3.64; 9.39	7.31; 20.85
Ref. parameters	364	334	247
Abs. correct. T_{min}/T_{max}	−	0.3611, 0.4017	0.0045, 0.0210

IR (KBr): $\tilde{\nu}$ = 3273 cm^{-1} (NH). − ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.50 (d, 2 H, C_6H_4), 7.28 (d, 2 H, C_6H_4), 7.06 (m, 2 H, C_6H_4), 6.92 (m, 2 H, C_6H_4), 1.94 (m, 6 H, PCH_2), 1.69 (m, 6 H, PCH_2CH_2), 1.05 (t, 9 H, $P(CH_2)_2CH_3$), −1.85 (s, br, 1 H, NH). − $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): δ = 152.2, 133.5, 129.4, 128.7, 127.5, 122.2 [C(aryl)], 29.5 (d, $^1J_{P-C}$ = 60.3 Hz), 16.0 (d, J_{P-C} = 3.3 Hz), 15.8 (d, J_{P-C} = 16.6 Hz) [$P(C_3H_7)_3$]. − $^{31}P\{^1H\}$ NMR (161.7 MHz, CD_2Cl_2): δ = 51.38 [s, $P(C_3H_7)_3$]. − MS (FD, THF); *m*/*z*: 482 [Ni(NHP*n*Pr$_3$)('S$_3$')]$^+$.

[Pd(NHP*n*Pr$_3$)('S$_3$')] (2): Synthesised from **5** (355 mg, 0.33 mmol) and **7** (0.33 mL, 1.50 mmol) to give **2** as red-brown microcrystals. Yield: 216 mg (41%). − $C_{21}H_{30}NPPdS_3$ (530.01): calcd. C 47.59, H 5.70, N 2.64, S 18.15; found C 47.90, H 5.95, N 2.73, S 17.08 − IR (KBr): $\tilde{\nu}$ = 3292 cm^{-1} (NH). − ^{1}H NMR (399.7 MHz, CD_2Cl_2): δ = 7.52 (d, 2 H, C_6H_4), 7.29 (d, 2 H, C_6H_4), 7.11 (m, 2 H, C_6H_4), 6.98 (m, 2 H, C_6H_4), 1.93 (m, 6 H, PCH_2), 1.66 (m, 6 H, PCH_2CH_2), 1.10 (t, 9 H, $P(CH_2)_2CH_3$), −0.03 (s, br, 1 H, NH). − $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): δ = 152.6, 133.4, 130.6, 129.2, 128.6, 122.5 [C(aryl)], 29.4 (d, $^1J_{P-C}$ = 60.3 Hz), 16.0 (d, J_{P-C} = 4.2 Hz), 15.8 (d, J_{P-C} = 15.7 Hz) [$P(C_3H_7)_3$]. − $^{31}P\{^1H\}$ NMR (161.7 MHz, CD_2Cl_2): δ = 51.27 [s, $P(C_3H_7)_3$]. − MS (FD, THF); *m*/*z*: 530 [Pd(NHP*n*Pr$_3$)('S$_3$')]$^+$.

[Pt(NHP*n*Pr$_3$)('S$_3$')] (3): Synthesised from **6** (1.01 g, 0.77 mmol) and **7** (0.76 mL, 3.47 mmol) to give **3** as yellow microcrystals. Yield: 590 mg (41%). − $C_{21}H_{30}NPPtS_3$ (618.70): calcd. C 40.77, H 4.89, N 2.26, S 15.55; found C 40.91, H 5.04, N 2.46, S 15.42 − IR (KBr): $\tilde{\nu}$ = 3287 cm^{-1} (NH). − ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.64 (d, 2 H, C_6H_4), 7.41 (d, 2 H, C_6H_4), 7.05 (m, 2 H, C_6H_4), 6.91 (m, 2 H, C_6H_4), 1.94 (m, 6 H, PCH_2), 1.64 (m, 6 H, PCH_2CH_2), 1.07 (t, 9 H, $P(CH_2)_2CH_3$), 0.54 (s + d, $^2J_{H-Pt}$ = 41.5 Hz, br, 1 H, NH). − $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): δ = 152.2, 133.9, 130.8 (s + d, $^3J_{C-Pt}$ = 63.2 Hz), 128.8, 128.4 (s + d, $^3J_{C-Pt}$ = 57.4 Hz), 122.2 [C(aryl)], 28.4 (d, $^1J_{P-C}$ = 59.8 Hz), 15.6 (d, J_{P-C} = 4.1 Hz), 15.4 (d, J_{P-C} = 16.2 Hz) [$P(C_3H_7)_3$]. − $^{31}P\{^1H\}$ NMR (161.7 MHz, CD_2Cl_2): δ = 51.27 (s + d, $^2J_{Pt-P}$ = 36.7 Hz, $P(C_3H_7)_3$). − MS (FD, THF); *m*/*z*: 619 [Pt(NHP*n*Pr$_3$)('S$_3$')]$^+$.

X-ray Structure Analyses of [Ni(NHP*n*Pr$_3$)('S$_3$')] (1), [Pd(NHP*n*Pr$_3$)('S$_3$')] (2) and [Pt(NHP*n*Pr$_3$)('S$_3$')] (3): Dark red rhombohedra were obtained by slowly evaporating a concentrated acetone solution of **1**. Red single crystals were formed by layering a CD_2Cl_2 solution of **2** with *n*-hexane. Yellow single crystals were grown by slowly evaporating a concentrated THF solution of **3**. Suitable single crystals were sealed under N_2 in glass capillaries. Data were corrected for Lorentz and polarization effects. For **2** and **3** absorption effects have been corrected using Psi-scans (see Table 2), while for **1** absorption effects have been neglected. The structures were solved by direct methods (SHELXTL 5.03[26]). Full-matrix least-squares refinement was carried out on F^2 (SHELXTL 5.03). All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms of **1** and **2** were taken from the difference Fourier map and were either refined isotropically **1** or kept fixed with a common isotropic displacement parameter **2**. In the case of **3** the hydrogen atoms were geometrically positioned with isotropic displacement parameters fixed at 1.5 times *U*(eq) of the preceding carbon atom. Selected crystallographic data are summarized in Table 2.[27]

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[26] SHELXTL 5.03 for Siemens Crystallographic Research Systems, Copyright **1995** by Siemens Analytical X-Ray Instruments Inc., Madison, WI, U.S.A.

[27] 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-130662 (**1**), -130663 (**2**), -130664 (**3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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