# Bis(bidentate) Complexes of Iminobis(diphenylphosphine chalcogenides) [M{N(XPPh$_2$)$_2$-*X*,*X'*}$_2$] (X = S or Se; M = Ni, Pd or Pt)†

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The compound NH(SePPh$_2$)$_2$ has been synthesised from NH(PPh$_2$)$_2$ and selenium in refluxing toluene. A range of complexes [M{N(XPPh$_2$)$_2$-*X*, *X'*}$_2$] (X = Se, M = Pt **1** or Pd **2**; X = S, M = Pt **3**, Pd **4** or Ni **5**) of the monoanions derived from NH(SePPh$_2$)$_2$ and its sulfur analogue have been prepared. The new compounds have been characterised by microanalysis, NMR and IR spectroscopy. The crystal structures of NH(SePPh$_2$)$_2$, **1**, **2** and **5** were determined. The neutral NH(SePPh$_2$)$_2$ crystallised as H-bonded dimer pairs with a noticeable difference in the hydrogen bonded and non-hydrogen bonded P=Se bond lengths. The P=Se groups are approximately *anti*. On complexation the anionic ligands are bidentate and in all cases the resulting MX$_2$P$_2$N rings are distinctly puckered.

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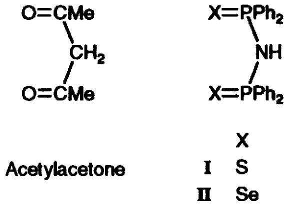
There is considerable interest in the co-ordination of metals by monoanionic, bidentate ligands. For example, acetylacetone and its derivatives form a large class of complexes which have been extensively studied.[1] The iminobis(diphenylphosphine chalcogenide) ligands **I** and **II** may be considered to be main group analogues of acetylacetone. They are readily prepared and offer the opportunity to vary both the donor atoms and the R group more easily than is the case for acetylacetone, and so should be amenable to fine-tuning for specific metal complexation. A number of complexes of the sulfide ligand **I**[2a] and its oxide analogue[2b] have been described. In contrast, the selenide compound **II** has been less well studied, with only a handful of rhenium(V)–oxo, –nitrido and –imido complexes having been reported.[3,4] One reason that compound **II** may not have been studied is the report[5] that it cannot be prepared by the simple oxidative-addition reaction of selenium with NH(PPh$_2$)$_2$. Contrary to this we have found that NH(SePPh$_2$)$_2$ is readily prepared by this route. Furthermore we describe the preparation of a range of iminobis(diphenylphosphine chalcogenide) complexes of nickel, palladium and platinum. The new compounds have been characterised by microanalysis, multielement NMR, IR and positive ion FAB mass spectroscopy. The crystal structures of **II** and of representative complexes are also reported. The molecular structure of [Pt{N(SePPh$_2$)$_2$-*Se*,*Se'*}$_2$]·CHCl$_3$ described here is, we believe, the first example and structural characterisation of a homoleptic *Se*,*Se'* complex containing the [N(SePPh$_2$)$_2$]$^-$ ligand.

## Experimental

Hexane and CH$_2$Cl$_2$ were dried and distilled under nitrogen before use, all other solvents and reagents were used as received. The compounds NH(PPh$_2$)$_2$, NH(SPPh$_2$)$_2$ and Na[N(SPPh$_2$)$_2$] were prepared by literature methods.[5,6] The $^{31}$P-{$^1$H} (109.4 MHz) and $^{195}$Pt-{$^1$H} (57.9 MHz) NMR spectra were recorded



in CD$_2$Cl$_2$ on a JEOL JNM EX270 spectrometer, infrared spectra (as KBr discs) on a Perkin-Elmer 1720X FTIR spectrometer. Microanalyses were performed by the Imperial College Microanalytical Service, positive ion FAB$^+$ mass spectra (3-nitrobenzyl alcohol matrix) were recorded on a Vacuum Generators Autospec Q instrument.

*Syntheses*.—NH(SePPh$_2$)$_2$ II. The compound NH(PPh$_2$)$_2$ (7.70 g, 20 mmol) and grey selenium (3.16 g, 40 mmol) were heated to reflux in sodium dried toluene (150 cm$^3$) under nitrogen for 4 h. After cooling the solution the white precipitate was filtered off, washed with toluene (3 × 15 cm$^3$) and diethyl ether (3 × 15 cm$^3$) and dried *in vacuo*. Yield: 9.1 g, 84% (Found: C, 52.75; H, 3.70; N, 2.50. Calc. for C$_{24}$H$_{21}$NP$_2$Se$_2$: C, 53.05; H, 3.90; N, 2.60%). $^{31}$P-{$^1$H} NMR: δ 53.0 [$^2J$($^{31}$P–$^{77}$Se) 793 Hz].

[Pt{N(SePPh$_2$)$_2$-*Se*,*Se'*}$_2$] **1**. The compounds [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene) (31 mg, 0.083 mmol) and NH(SePPh$_2$)$_2$ (91 mg, 0.167 mmol) were dissolved in dichloromethane (5 cm$^3$) under nitrogen to give an intense yellow solution. After 5 min hexane (10 cm$^3$) was added and the solution cooled to 0 °C to give **1** as orange-brown crystals. Yield 103 mg, 97% (Found: C, 44.65; H, 3.05; N, 2.10. Calc. for C$_{48}$H$_{40}$N$_2$P$_4$PtSe$_4$: C, 45.05: H, 3.15: N, 2.20%). NMR: $^{31}$P-{$^1$H}, δ 21.0 [$^2J$($^{31}$P–$^{195}$Pt) 105, $^1J$($^{31}$P–$^{77}$Se) 539 Hz]; $^{195}$Pt-{$^1$H}, δ −4242.

[Pd{N(SePPh$_2$)$_2$-*Se*,*Se'*}$_2$] **2**. The compounds Na$_2$[PdCl$_4$] (50 mg, 0.17 mmol), NH(SePPh$_2$)$_2$ (200 mg, 0.37 mmol) and KOBu$^t$ (41 mg, 0.37 mmol) were stirred together in acetone (5 cm$^3$) for 16 h. The solvent was removed *in vacuo* and the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

product extracted into $CH_2Cl_2$. Addition of hexane to this solution gave **2** as red crystals. Yield 145 mg, 73% (Found: C, 48.05; H, 3.05; N, 2.20. Calc. for $C_{48}H_{40}N_2P_4PdSe_4$: C, 48.40; H, 3.40; N, 2.35%). $^{31}P-\{^1H\}$ NMR: δ 26.3 [$^1J(^{31}P-^{77}Se)$ 543 Hz].

[Pt{N(SPPh$_2$)$_2$-*S,S′*}$_2$] **3**. The compounds [$PtCl_2$(cod)] (100 mg, 0.27 mmol) and Na[N(SPPh$_2$)$_2$] (252 mg, 0.54 mmol) were stirred in chloroform (10 cm$^3$) for 16 h. The product precipitated as a bright yellow solid and was recrystallised from $CH_2Cl_2$–$CCl_4$. Yield 225 mg, 77% (Found: C, 51.65; H, 3.15, N, 2.40. Calc. for $C_{48}H_{40}N_2P_4PtS_4$: C, 52.80; H, 3.70; N, 2.55%). $^{31}P-\{^1H\}$ NMR: δ 34.4 [s, $^2J(^{31}P-^{195}Pt)$ 95.4 Hz].

[Pd{N(SPPh$_2$)$_2$-*S,S′*}$_2$] **4**. The compounds $Na_2[PdCl_4]$ (50 mg, 0.17 mmol) and Na[N(SPPh$_2$)$_2$] (174 mg, 0.37 mmol) were stirred in acetone (5 cm$^3$) for 16 h. The solvent was removed *in vacuo* and the product extracted into $CH_2Cl_2$. Addition of hexane to this solution gave **4** as orange crystals. Yield 110 mg, 72% (Found: C, 57.00; H, 3.80; N 2.20. Calc. for $C_{48}H_{40}N_2P_4PdS_4$: C, 57.45; H, 4.00; N, 2.80%). $^{31}P-\{^1H\}$ NMR: δ 37.9.

[Ni{N(SPPh$_2$)$_2$-*S,S′*}$_2$] **5**. The compounds $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ (13 mg, 0.22 mmol) and NH(SPPh$_2$)$_2$ (100 mg, 0.22 mmol) were stirred in methanol (5 cm$^3$) for 72 h. The product formed as a brown precipitate which dissolved in $CH_2Cl_2$ to give a green solution. Addition of $Et_2O$ to this solution and cooling yielded brown crystals of **5**. Yield 130 mg, 62% (Found: C, 59.20; H, 3.65; N, 2.90. Calc. for $C_{48}H_{40}N_2NiP_4S_4$: C, 60.30; H, 4.20; N, 2.95%).

*X-Ray Crystallography.*—Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into chloroform solutions of the appropriate compound. Complexes **1** and **2** were obtained as chloroform solvates. Details of the data collections and refinements are summarised in Table 1. All four structures were solved by direct methods and refined by full-matrix least-squares methods using anisotropic thermal parameters for the non-hydrogen atoms. In complexes **1**, **2** and **5** the phenyl rings were refined as rigid bodies. In **II** the position of the N–H proton was determined from a Δ*F* map and refined isotropically subject to a refined N–H distance constraint. The positions of the remaining hydrogen atoms in compound **II** and those in **1**, **2** and **5** were idealised, assigned isotropic thermal parameters $U(H) = 1.8U_{eq}(C)$ and allowed to ride on their parent carbon atoms. In **1** and **2** the included solvent molecules were estimated to have occupancies of 0.5. In **2** the somewhat high final *R* value is a consequence of disorder in the included $CHCl_3$ solvent; this disorder could not be resolved into partial occupancy orientations. In all four structures absorption corrections (face indexed numerical corrections) were applied. Computations were performed using the SHELXTL PC system.[7]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

Although a number of complexes of [N(SPPh$_2$)$_2$]$^-$ have been described,[2] in contrast few selenium analogues are known. Wang *et al.*[5] have previously synthesised NH(SePPh$_2$)$_2$ **II** from the reaction between NH(PPh$_2$)$_2$ and KSeCN in 60% yield following acidic work-up. We have found that it can be more conveniently prepared in better yield by the direct reaction of 2 equivalents of grey selenium with NH(PPh$_2$)$_2$ in refluxing toluene [equation (1)].

$$NH(PPh_2)_2 + 2\,Se \longrightarrow Ph_2P(Se)NHP(Se)Ph_2 \quad (1)$$

We have studied the reactions of compounds **I** and **II** and their salts with Group 10 metal salts. The reaction of Na[N(SPPh$_2$)$_2$] with [$PtCl_2$(cod)] or $Na_2[PdCl_4]$ gives the complexes [M{N(SPPh$_2$)$_2$-*S,S′*}$_2$] (M = Pt **3** or Pd **4**). The nickel analogue **5** was obtained directly from the reaction of nickel carbonate with NH(SPPh$_2$)$_2$ [equation (2)].

**Table 1** Details of the crystal data collection and refinements

| Compound | **II** | **1**·CHCl$_3$ | **2**·CHCl$_3$ | **5** |
|---|---|---|---|---|
| Empirical formula | $C_{24}H_{21}NP_2Se_2$ | $C_{49}H_{41}Cl_3N_2P_4PtSe_4$ | $C_{49}H_{41}Cl_3N_2P_4PdSe_4$ | $C_{48}H_{40}N_2NiP_4S_4$ |
| Colour, habit | Clear, plate | Orange-brown prism | Yellow-orange, needle | Pale brown prism |
| *M* | 543.3 | 1399.0 | 1310.3 | 955.7 |
| Crystal size/mm | 0.20 × 0.40 × 0.40 | 0.11 × 0.16 × 0.17 | 0.20 × 0.26 × 0.50 | 0.10 × 0.16 × 0.20 |
| Diffractometer/radiation | Siemens P4, Mo-Kα | Siemens P4, Mo-Kα | Siemens P4, Mo-Kα | Siemens P4, Cu–Kα |
| *a*/Å | 10.787(4) | 9.558(3) | 9.512(6) | 13.353(2) |
| *b*/Å | 10.951(3) | 12.331(4) | 12.333(9) | 18.568(4) |
| *c*/Å | 11.297(4) | 13.040(5) | 13.079(8) | 18.651(4) |
| α/° | 63.81(2) | 110.94(3) | 110.79(5) | 90.11(2) |
| β/° | 75.23(2) | 96.45(3) | 96.45(5) | 93.00(2) |
| γ/° | 80.77(2) | 100.07(3) | 100.07(5) | 98.29(2) |
| *U*/Å$^3$ | 1156 | 1388 | 1387 | 4569 |
| *Z* | 2 | 1[a] | 1[a] | 4[b] |
| *D*/Mg m$^{-3}$ | 1.561 | 1.674 | 1.569 | 1.389 |
| μ/mm$^{-1}$ | 3.35 | 5.44 | 3.25 | 3.93 |
| *F*(000) | 540 | 674 | 642 | 1976 |
| 2θ Range/° | 4.0–50.0 | 3.0–50.0 | 3.0–55.0 | 0.0–116.0 |
| Min./max. transmission | 0.347/0.555 | 0.432/0.588 | 0.434/0.557 | 0.567/0.693 |
| Independent reflections | 4054 | 6363 | 4884 | 12 706 |
| Observed reflections | 3234 [$F > 3\sigma(F)$] | 3476[$F > 4\sigma(F)$] | 3418[$F > 4\sigma(F)$] | 9992[$F > 3\sigma(F)$] |
| Weighting scheme | $\sigma^2(F) + 0.0007F^2$ | $\sigma^2(F) + 0.0007F^2$ | $\sigma^2(F) + 0.0005F^2$ | $\sigma^2(F) + 0.0005F^2$ |
| No. of parameters refined | 266 | 304 | 259 | 872 |
| *R*,*R′*(%) | 4.08, 3.99 | 5.70, 5.59 | 7.31, 7.21 | 5.20, 5.66 |
| Maximum, mean Δ/σ ratio | 0.034, 0.003 | 2.834, 0.283 | 0.137, 0.009 | 0.076, 0.015 |
| Data/parameter ratio | 12.2 | 11.2 | 13.4 | 11.5 |
| Largest difference peak and hole/e Å$^{-3}$ | 0.70, −0.55 | 1.27, −1.08 | 1.26, −0.87 | 0.39, −0.41 |

Details in common: triclinic, space group $P\bar{1}$. [a] The complex has crystallographic $C_i$ symmetry. [b] Two crystallographically independent molecules.

$$2NH(SPPh_2)_2 + NiCO_3 \longrightarrow [Ni\{N(SPPh_2)_2\text{-}S,S'\}_2] + H_2O + CO_2 \qquad (2)$$

The selenium system behaves in a similar fashion to the sulfur compound for reactions with palladium, but for platinum no conversion of $NH(SePPh_2)_2$ to $[N(SePPh_2)_2]^-$ is necessary. The complex $[PtCl_2(cod)]$ reacts directly with $NH(SePPh_2)_2$ to give $[Pt\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ **1**. The complex $[Ni\{N(SePPh_2)\text{-}Se,Se'\}_2]$ could not be prepared from either $[N(SePPh_2)_2]^-$ with $NiCl_2$ or from $NH(SePPh_2)_2$ with the corresponding carbonate. With the exception of the platinum complex **1** all of these compounds appear to be air stable. Solutions of **1** are susceptible to aerial oxidation, freshly prepared solutions turning from yellow to red within 24 h. However no decomposition of the co-ordinated ligand, as seen for $[Re(O)Cl\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$,[2] is observed.

The $^{31}$P-{$^{1}$H} NMR spectra of **II** and **1**–**4** are straightforward. For compound **II** the spectrum consists of a singlet of 92% intensity together with an AA'X spectrum of 8% intensity associated with the $Ph_2P(Se)NHP(^{77}Se)Ph_2$ isotopomer (Fig. 1). In the complexes **1**–**4** the $^{31}$P-{$^{1}$H} NMR spectra are singlets with, in the case of the platinum-containing systems $^{2}J(^{31}P\text{–}^{195}Pt)$ satellites (105 and 95 Hz for **1** and **3** respectively). The spectra of **1** and **2** can only be satisfactorily interpreted if it is assumed that the $^{31}P\text{–}^{31}P$ coupling constant is approximately zero. The $^{1}J(^{31}P\text{–}^{77}Se)$ couplings in **1** and **2** are lower in magnitude than in the free ligand **II** suggesting a reduction in the P–Se bond order. In the IR spectra (Table 2), $\nu(P_2N)$ bands for $[Pt\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ appear at 1157s and 805s cm$^{-1}$ and the $\nu$(PSe) band appears at 536m cm$^{-1}$ reflecting the increased P–N bond order and decreased P=Se character in the deprotonated molecule compared to neutral $NH(SePPh_2)_2$ [$\nu(P_2N)$ at 937, 926, 918; $\nu$(PSe) at 595, 546 cm$^{-1}$]. The most prominent features of the positive ion FAB$^+$ mass spectra of **II** and **1**–**5** are due to the molecular ions $[M\{N(XPPh_2)_2\}_2]^+$ and $[N(SePPh_2)_2]^+$ which reveal the expected, characteristic, isotopic distribution patterns.

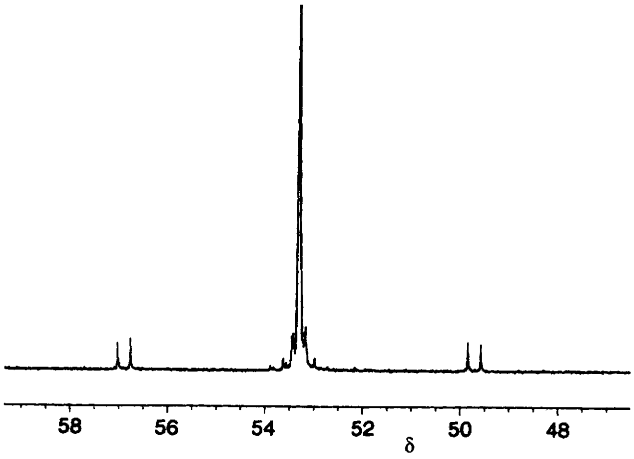

**Fig. 1** The $^{31}$P-{$^{1}$H} NMR spectrum of compound **II** expanded to illustrate details of the AA' portion of the AA'X spectrum of the $^{77}$Se-containing isotopomer

**Table 2** Selected IR data (cm$^{-1}$) for the compounds **I**, **II** and **1**–**5**

| Compound | $\nu(P_2N)$ | $\nu$(P=X) |
|---|---|---|
| **I** | 935m, 922s, 919vs | 645s, 622w |
| **II** | 937m, 926s, 918s | 595m, 546m |
| **1** | 1157m, 805s | 536m |
| **2** | 1172m, 800s | 537vs |
| **3** | 1220m, 1146m, 826s, 804m | 565vs |
| **4** | 1160m, 822s | 565vs |
| **5** | 1207m, 1174m, 804s | 565vs |

The crystal structure of compound **II** (Fig. 2, Tables 3 and 4) shows the compound to be isomorphous with its sulfur analogue.[8] The P=Se bond lengths [2.085(1) to P(2) and 2.101(1) Å to P(1)] are normal[9] and as expected longer than the analogous P=S distances in the sulfur compound [1.937(1) and 1.950(1) Å]. The P–N distances in **II** are 1.678(4) and 1.686(3) Å to P(1) and P(2) respectively whilst the P–N–P angle is noticeably enlarged at 132.3(2)° indicating a substantial amount of sp$^2$ character at the nitrogen. This is also reflected by the very small degree of pyramidalisation at the nitrogen centre; the nitrogen atom lies only 0.15 Å out of the plane of its substituents. The SePNPSe chain can, in principle, adopt a number of conformations, the geometry about the N–P(2) bond is *gauche* [P(1)–N–P(2)–Se(2) torsion angle 63°] and there is a further 111° torsional rotation in the same sense, about the N–P(1) bond. The cumulative effect is an approximately *anti* disposition of the two selenium atoms relative to each other with the Se(1)–P(1) ··· P(2)–Se(2) 'torsion angle' being 154°. The molecules in **II** are linked by N–H ··· Se hydrogen bonds to form dimer pairs positioned about a crystallographic centre of symmetry. The N–H, Se ··· H and N ··· Se distances are 0.94, 2.52 and 3.19 Å respectively and the N–H ··· Se(1a) angle

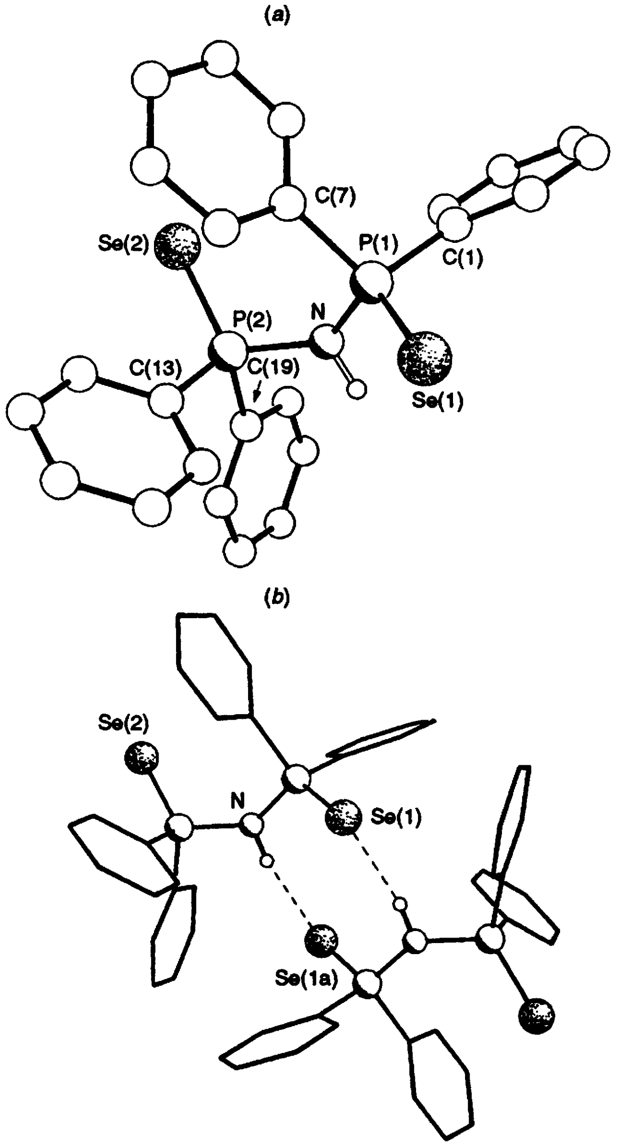

**Fig. 2** The crystal structure of compound **II** showing (*a*) a single molecule with the numbering scheme and (*b*) a hydrogen-bonded dimer pair

**Table 3** Atomic coordinates ( × 10$^4$) for compound **II**, with estimated standard deviations (e.s.d.s) in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Se(1) | 4864(1) | 4131(1) | 3506(1) |
| P(1) | 6785(1) | 4337(1) | 3446(1) |
| Se(2) | 9929(1) | 2526(1) | 5125(1) |
| P(2) | 7974(1) | 2673(1) | 5939(1) |
| N | 7107(3) | 3966(3) | 4949(3) |
| C(1) | 7263(4) | 6071(4) | 2423(4) |
| C(2) | 8197(5) | 6585(4) | 2693(5) |
| C(3) | 8546(5) | 7910(5) | 1904(5) |
| C(4) | 7957(5) | 8738(5) | 856(5) |
| C(5) | 7037(5) | 8238(5) | 562(5) |
| C(6) | 6695(4) | 6912(5) | 1338(4) |
| C(7) | 7867(4) | 3238(4) | 2781(4) |
| C(8) | 9007(4) | 3684(5) | 1878(4) |
| C(9) | 9799(5) | 2810(5) | 1381(5) |
| C(10) | 9469(5) | 1494(5) | 1815(5) |
| C(11) | 8328(5) | 1055(5) | 2720(5) |
| C(12) | 7519(4) | 1929(4) | 3188(4) |
| C(13) | 7151(4) | 1157(4) | 6436(4) |
| C(14) | 7837(5) | −47(4) | 6492(4) |
| C(15) | 7179(6) | −1169(5) | 6788(5) |
| C(16) | 5867(6) | −1111(5) | 7067(6) |
| C(17) | 5189(5) | 75(6) | 7017(6) |
| C(18) | 5817(4) | 1202(4) | 6709(5) |
| C(19) | 7651(4) | 3078(4) | 7381(4) |
| C(20) | 6880(5) | 2332(5) | 8590(4) |
| C(21) | 6628(6) | 2741(6) | 9635(5) |
| C(22) | 7159(5) | 3861(6) | 9470(5) |
| C(23) | 7949(5) | 4608(5) | 8267(6) |
| C(24) | 8197(4) | 4221(4) | 7225(5) |

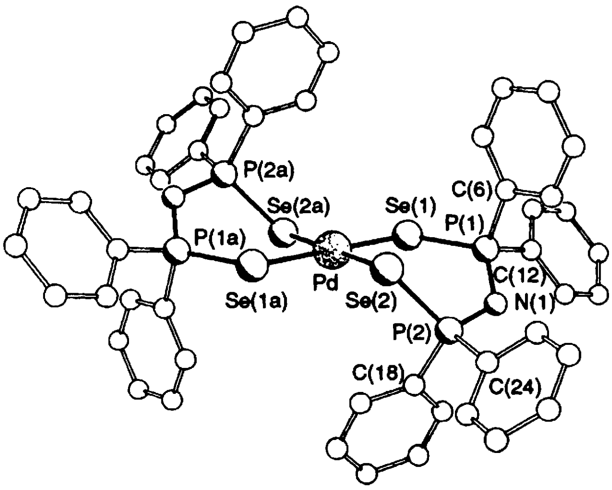

**Fig. 3** The crystal structure of **2**; the platinum analogue **1** is isomorphous

**Table 4** Bond lengths (Å) and angles (°) for **II**

| | | | |
|---|---|---|---|
| Se(1)–P(1) | 2.101(1) | P(1)–N | 1.678(4) |
| P(1)–C(1) | 1.811(4) | P(1)–C(7) | 1.809(5) |
| Se(2)–P(2) | 2.085(1) | P(2)–N | 1.686(3) |
| P(2)–C(13) | 1.804(5) | P(2)–C(19) | 1.809(5) |
| C(1)–C(2) | 1.384(8) | C(1)–C(6) | 1.389(6) |
| C(2)–C(3) | 1.379(6) | C(3)–C(4) | 1.371(7) |
| C(4)–C(5) | 1.378(10) | C(5)–C(6) | 1.378(7) |
| C(7)–C(8) | 1.380(5) | C(7)–C(12) | 1.382(6) |
| C(8)–C(9) | 1.388(8) | C(9)–C(10) | 1.377(8) |
| C(10)–C(11) | 1.380(6) | C(11)–C(12) | 1.379(7) |
| C(13)–C(14) | 1.389(6) | C(13)–C(18) | 1.390(6) |
| C(14)–C(15) | 1.386(8) | C(15)–C(16) | 1.367(9) |
| C(16)–C(17) | 1.370(8) | C(17)–C(18) | 1.369(8) |
| C(19)–C(20) | 1.370(5) | C(19)–C(24) | 1.391(7) |
| C(20)–C(21) | 1.390(9) | C(21)–C(22) | 1.355(10) |
| C(22)–C(23) | 1.376(7) | C(23)–C(24) | 1.371(9) |
| | | | |
| Se(1)–P(1)–N | 114.5(1) | Se(1)–P(1)–C(1) | 112.1(1) |
| N–P(1)–C(1) | 103.9(2) | Se(1)–P(1)–C(7) | 111.4(2) |
| N–P(1)–C(7) | 106.3(2) | C(1)–P(1)–C(7) | 108.1(2) |
| Se(2)–P(2)–N | 116.1(1) | Se(2)–P(2)–C(13) | 113.8(1) |
| N–P(2)–C(13) | 105.5(2) | Se(2)–P(2)–C(19) | 113.1(1) |
| N–P(2)–C(19) | 99.5(2) | C(13)–P(2)–C(19) | 107.6(2) |
| P(1)–N–P(2) | 132.3(2) | P(1)–C(1)–C(2) | 121.3(3) |
| P(1)–C(1)–C(6) | 120.1(4) | C(2)–C(1)–C(6) | 118.7(4) |
| C(1)–C(2)–C(3) | 120.5(4) | C(2)–C(3)–C(4) | 120.3(6) |
| C(3)–C(4)–C(5) | 120.0(5) | C(4)–C(5)–C(6) | 119.8(5) |
| C(1)–C(6)–C(5) | 120.7(5) | P(1)–C(7)–C(8) | 121.6(4) |
| P(1)–C(7)–C(12) | 118.3(3) | C(8)–C(7)–C(12) | 120.1(4) |
| C(7)–C(8)–C(9) | 119.6(5) | C(8)–C(9)–C(10) | 120.3(4) |
| C(9)–C(10)–C(11) | 119.8(5) | C(10)–C(11)–C(12) | 120.2(5) |
| C(7)–C(12)–C(11) | 120.0(4) | P(2)–C(13)–C(14) | 120.6(3) |
| P(2)–C(13)–C(18) | 120.0(3) | C(14)–C(13)–C(18) | 119.3(4) |
| C(13)–C(14)–C(15) | 119.3(5) | C(14)–C(15)–C(16) | 120.6(5) |
| C(15)–C(16)–C(17) | 120.1(6) | C(16)–C(17)–C(18) | 120.4(5) |
| C(13)–C(18)–C(17) | 120.3(4) | P(2)–C(19)–C(20) | 123.1(4) |
| P(2)–C(19)–C(24) | 117.5(3) | C(20)–C(19)–C(24) | 119.4(5) |
| C(19)–C(20)–C(21) | 119.8(5) | C(20)–C(21)–C(22) | 120.2(4) |
| C(21)–C(22)–C(23) | 120.5(6) | C(22)–C(23)–C(24) | 119.9(6) |
| C(19)–C(24)–C(23) | 120.1(4) | | |

is 166°. There are no interactions involving the other selenium atom. It is interesting that the P=Se bond lengths differ significantly with the H-bonded selenium, Se(1) having a longer P=Se bond length than Se(2) as a consequence of the hydrogen bond to Se(1).

Upon deprotonation and co-ordination compound **II** acts as a bidentate ligand in complexes **1**–**5**. The crystal structures of **1** and **2** (both of which crystallise as chloroform solvates, Fig. 3, Tables 5–7) are isomorphous* and reveal a square-planar geometry for the metal centre which is positioned upon a crystallographic centre of symmetry. The $MSe_2P_2N$ rings adopt a folded geometry with P(1) lying essentially within the co-ordination plane [Pt–Se(1)–Se(2)–P(1) coplanar to within 0.04 Å] and with the P(1)–N(1)–P(2)–Se(2) plane (coplanar to within 0.13 Å) folded by 58° out of the co-ordination plane. In both **1** and **2** the M–Se(1) bond is shorter than the M–Se(2) bond by *ca.* 0.02 Å, *i.e.* 10σ. There is also a large difference in the M–Se(1)–P(1) and M–Se(2)–P(2) angles [in **1**, **2** the angles are 108.0(1), 108.3(1) and 100.8(1), 100.6(1)° respectively]. Clearly, there is substantially increased bonding between the metal centre and Se(1) in both structures and the bonding is consistent with a pronounced influence of one of the valence canonical forms *i.e.* with some localisation of the bonding. In comparison with the geometry of the free ligand **II**, the P–Se distances in **1** and **2** are, as expected, substantially increased whilst the P–N bond lengths are shortened. The angle at nitrogen is contracted in **1** and **2** as a consequence of the co-ordination of the two selenium atoms. There is only a marginal increase in the Se–P–N angles upon co-ordination.

There is noticeable distortion in the co-ordination geometry at Pt(Pd) with the ligand bite angles being 99.5 (99.3)° and the remaining angles being 80.5 (80.7)°. As a consequence of the contraction of the Se(1)–M–Se(2) angle there is a short intramolecular Se(1) ··· Se(2a) contact of 3.15 Å [*cf.* Se(1) ··· Se(2) 3.72 Å]. There are no significant intermolecular contacts between the metallacyclic components of the structures.

The crystal structure of complex **5** (Fig. 4, Tables 8 and 9) contains two crystallographically independent molecules which

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* The analogous platinum–sulfur compound, **3** is isomorphous with **1** and **2** [*a* = 9.550(6), *b* = 12.256(16), *c* = 13.017(12) Å, α = 110.70(8), β = 96.69(6), γ = 99.93(8) °, *U* = 1378 Å$^3$] but crystals suitable for a full structure analysis could not be obtained.

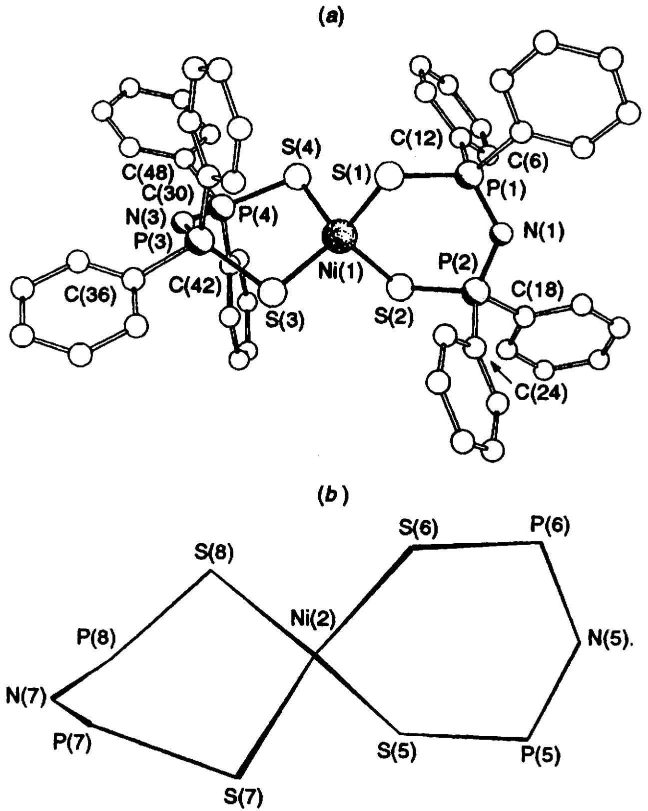

**Fig. 4** The crystal structure of **5** showing (*a*) a ball and stick representation of one of the crystallographically independent molecules and (*b*) a line drawing with the numbering scheme in the second molecule

**Table 5** Atomic coordinates ( × $10^4$) for complex **2**, with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pd | 5 000 | 5 000 | 5 000 |
| Se(1) | 6 161(2) | 7 111(1) | 5 668(1) |
| P(1) | 6 719(3) | 7 804(3) | 7 488(2) |
| C(1) | 3 920(9) | 8 195(9) | 7 498(6) |
| C(2) | 2 758 | 8 466 | 8 025 |
| C(3) | 2 833 | 8 612 | 9 138 |
| C(4) | 4 070 | 8 485 | 9 725 |
| C(5) | 5 233 | 8 213 | 9 199 |
| C(6) | 5 158 | 8 068 | 8 085 |
| C(7) | 9 206(12) | 9 513(12) | 8 532(10) |
| C(8) | 10 117 | 10 638 | 8 833 |
| C(9) | 9 657 | 11 476 | 8 469 |
| C(10) | 8 287 | 11 189 | 7 804 |
| C(11) | 7 376 | 10 064 | 7 503 |
| C(12) | 7 836 | 9 226 | 7 867 |
| N(1) | 7 563(9) | 7 128(9) | 8 058(7) |
| P(2) | 7 160(3) | 5 690(3) | 7 662(2) |
| Se(2) | 4 931(1) | 4 799(1) | 6 798(1) |
| C(13) | 8 088(8) | 3 878(8) | 6 162(8) |
| C(14) | 9 142 | 3 388 | 5 616 |
| C(15) | 10 535 | 4 091 | 5 798 |
| C(16) | 10 874 | 5 284 | 6 526 |
| C(17) | 9 821 | 5 774 | 7 071 |
| C(18) | 8 427 | 5 071 | 6 890 |
| C(19) | 6 885(18) | 6 025(9) | 9 822(10) |
| C(20) | 6 912 | 5 710 | 10 748 |
| C(21) | 7 420 | 4 712 | 10 738 |
| C(22) | 7 900 | 4 029 | 9 802 |
| C(23) | 7 873 | 4 343 | 8 876 |
| C(24) | 7 365 | 5 341 | 8 886 |
| C(30) | 2 837(84) | 1 066(43) | 6 032(44) |
| Cl(1) | 4 181(16) | 1 604(13) | 7 454(12) |
| Cl(2) | 1 660(13) | 1 441(20) | 6 206(14) |
| Cl(3) | 3 386(27) | −140(16) | 5 420(11) |

**Table 6** Atomic coordinates ( × $10^4$) for complex **1**, with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pt | 0 | 0 | 0 |
| Se(1) | −1155(2) | −2105(1) | −662(1) |
| P(1) | −1722(3) | −2794(3) | −2484(2) |
| C(1) | 1081(9) | −3175(9) | −2494(6) |
| C(2) | 2240 | −3458 | −3016 |
| C(3) | 2174 | −3616 | −4136 |
| C(4) | 949 | −3492 | −4734 |
| C(5) | −210 | −3210 | −4213 |
| C(6) | −144 | −3051 | −3093 |
| C(7) | −4245(10) | −4528(11) | −3533(10) |
| C(8) | −5153 | −5652 | −3823 |
| C(9) | −4683 | −6490 | −3467 |
| C(10) | −3305 | −6206 | −2820 |
| C(11) | −2398 | −5082 | −2530 |
| C(12) | −2868 | −4244 | −2886 |
| N(1) | −2578(9) | −2090(9) | −3052(8) |
| P(2) | −2175(3) | −684(3) | −2664(2) |
| Se(2) | 61(1) | 197(1) | −1796(1) |
| C(13) | −3106(8) | 1150(8) | −1154(8) |
| C(14) | −4145 | 1647 | −597 |
| C(15) | −5530 | 946 | −764 |
| C(16) | −5875 | −252 | −1489 |
| C(17) | −4835 | −749 | −2046 |
| C(18) | −3451 | −48 | −1879 |
| C(19) | −1525(19) | −784(16) | −4687(12) |
| C(20) | −1655(26) | −567(24) | −5672(14) |
| C(21) | −2543(22) | 177(18) | −5814(11) |
| C(22) | −3503(26) | 512(30) | −5088(19) |
| C(23) | −3491(23) | 164(28) | −4175(18) |
| C(24) | −2401(11) | −367(10) | −3915(7) |
| C(19′) | −2847(37) | 656(18) | −3899(12) |
| C(20′) | −2862(35) | 956(22) | −4838(16) |
| C(22′) | −2321(41) | −933(17) | −5879(10) |
| C(23′) | −2188(30) | −1186(11) | −4914(10) |
| C(30) | 1934(68) | 3846(43) | 8827(44) |
| Cl(1) | 3327(12) | 3520(19) | 8789(14) |
| Cl(2) | 847(15) | 3429(13) | 7537(12) |
| Cl(3) | 1538(26) | 5183(17) | 9552(11) |

Primes denote disordered components.

**Table 7** Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

| | M = Pt **1** | M = Pd **2** |
|---|---|---|
| M–Se(1) | 2.425(2) | 2.434(2) |
| M–Se(2) | 2.445(2) | 2.457(2) |
| P(1)–Se(1) | 2.183(3) | 2.189(3) |
| P(1)–N(1) | 1.596(13) | 1.561(12) |
| P(2)–N(1) | 1.583(11) | 1.621(11) |
| P(2)–Se(2) | 2.191(3) | 2.178(3) |
| P(1)–C(6) | 1.806(9) | 1.780(10) |
| P(1)–C(12) | 1.784(12) | 1.750(13) |
| P(2)–C(18) | 1.786(9) | 1.762(9) |
| P(2)–C(24) | 1.807(12) | 1.799(14) |
| Se(1)–M–Se(2) | 99.5(1) | 99.3(1) |
| Se(1)–M–Se(2a) | 80.5(1) | 80.7(1) |
| M–Se(1)–P(1) | 108.0(1) | 108.3(1) |
| Se(1)–P(1)–N(1) | 118.7(4) | 119.1(4) |
| P(1)–N(1)–P(2) | 123.3(5) | 122.9(5) |
| N(1)–P(2)–Se(2) | 115.4(4) | 115.7(4) |
| P(2)–Se(2)–M | 100.8(1) | 100.6(1) |

have essentially identical conformations. In both molecules the $NiS_4P_4N_2$ core has approximate $C_2$ symmetry about the Ni···N axis with the $NiS_2P_2N$ rings adopting puckered conformations within which no four adjacent atoms are coplanar. The puckering of each ring is similar to that observed in **1** and **2** but is more pronounced in **5**. Although the sequence of torsion angles within each metallacyclic ring in **5** follows the

**Table 8** Atomic coordinates ( × 10$^4$) for complex **5**, with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Ni(1) | 3 823(1) | 198(1) | 2 622(1) | Ni(2) | 10 937(1) | −5 128(1) | 2 377(1) |
| S(1) | 2 797(1) | −781(1) | 3 058(1) | S(5) | 11 961(1) | −4 198(1) | 1 855(1) |
| P(1) | 1 446(1) | −682(1) | 2 557(1) | P(5) | 13 299(1) | −4 245(1) | 2 398(1) |
| N(1) | 1 004(3) | 60(2) | 2 646(2) | N(5) | 13 769(3) | −4 983(2) | 2 369(2) |
| C(1) | −466(3) | −1 222(2) | 2 988(2) | C(51) | 15 187(2) | −3 724(1) | 1 905(2) |
| C(2) | −1 198 | −1 754 | 3 252 | C(52) | 15 906 | −3 199 | 1 618 |
| C(3) | −947 | −2 435 | 3 438 | C(53) | 15 658 | −2 512 | 1 449 |
| C(4) | 36 | −2 585 | 3 361 | C(54) | 14 691 | −2 351 | 1 566 |
| C(5) | 768 | −2 054 | 3 097 | C(55) | 13 972 | −2 877 | 1 853 |
| C(6) | 517 | −1 372 | 2 910 | C(56) | 14 219 | −3 563 | 2 022 |
| C(7) | 2 041(3) | −1 461(2) | 1 427(2) | C(57) | 13 659(3) | −4 306(2) | 3 876(2) |
| C(8) | 2 091 | −1 639 | 703 | C(58) | 13 550 | −4 104 | 4 586 |
| C(9) | 1 608 | −1 260 | 176 | C(59) | 12 968 | −3 561 | 4 734 |
| C(10) | 1 076 | −703 | 372 | C(60) | 12 495 | −3 219 | 4 173 |
| C(11) | 1 026 | −525 | 1 095 | C(61) | 12 604 | −3 420 | 3 463 |
| C(12) | 1 509 | −904 | 1 622 | C(62) | 13 186 | −3 964 | 3 315 |
| P(2) | 1 551(1) | 878(1) | 2 603(1) | P(6) | 13 234(1) | −5 804(1) | 2 429(1) |
| C(13) | 1 071(2) | 2 032(2) | 1 755(2) | C(63) | 13 691(2) | −6 978(2) | 3 236(2) |
| C(14) | 395 | 2 458 | 1 436 | C(64) | 14 348 | −7 373 | 3 622 |
| C(15) | −647 | 2 243 | 1 466 | C(65) | 15 360 | −7 074 | 3 760 |
| C(16) | −1 013 | 1 602 | 1 814 | C(66) | 15 715 | −6 381 | 3 511 |
| C(17) | −337 | 1 175 | 2 133 | C(67) | 15 058 | −5 986 | 3 125 |
| C(18) | 705 | 1 391 | 2 103 | C(68) | 14 046 | −6 285 | 2 987 |
| C(19) | 2 159(3) | 896(2) | 4 036(2) | C(69) | 13 558(3) | −6 884(2) | 1 449(2) |
| C(20) | 2 344 | 1 199 | 4 724 | C(70) | 13 473 | −7 208 | 768 |
| C(21) | 2 057 | 1 875 | 4 872 | C(71) | 13 012 | −6 878 | 193 |
| C(22) | 1 585 | 2 247 | 4 333 | C(72) | 12 636 | −6 225 | 298 |
| C(23) | 1 400 | 1 943 | 3 646 | C(73) | 12 721 | −5 901 | 978 |
| C(24) | 1 688 | 1 268 | 3 497 | C(74) | 13 182 | −6 231 | 1 553 |
| S(2) | 2 901(1) | 1 046(1) | 2 143(1) | S(6) | 11 855(1) | −5 978(1) | 2 848(1) |
| S(3) | 5 011(1) | 654(1) | 3 519(1) | S(7) | 10 221(1) | −4 582(1) | 3 289(1) |
| P(3) | 6 155(1) | 86(1) | 3 331(1) | P(7) | 8 774(1) | −5 070(1) | 3 197(1) |
| N(3) | 6 583(3) | 127(2) | 2 554(2) | N(7) | 8 180(3) | −5 038(2) | 2 439(2) |
| C(25) | 5 241(3) | −988(2) | 4 213(2) | C(75) | 8 185(3) | −6 563(2) | 3 068(2) |
| C(26) | 4 965 | −1 705 | 4 431 | C(76) | 8 165 | −7 283 | 3 283 |
| C(27) | 5 213 | −2 279 | 4 026 | C(77) | 8 715 | −7 443 | 3 904 |
| C(28) | 5 737 | −2 138 | 3 402 | C(78) | 9 285 | −6 882 | 4 311 |
| C(29) | 6 013 | −1 422 | 3 183 | C(79) | 9 304 | −6 161 | 4 095 |
| C(30) | 5 765 | −847 | 3 589 | C(80) | 8 754 | −6 001 | 3 474 |
| C(31) | 8 187(2) | 287(2) | 3 738(2) | C(81) | 7 167(2) | −4 380(2) | 3 588(2) |
| C(32) | 9 033 | 487 | 4 204 | C(82) | 6 615 | −4 040 | 4 068 |
| C(33) | 8 924 | 809 | 4 866 | C(83) | 6 955 | −3 951 | 4 787 |
| C(34) | 7 968 | 931 | 5 062 | C(84) | 7 848 | −4 203 | 5 026 |
| C(35) | 7 121 | 730 | 4 596 | C(85) | 8 401 | −4 544 | 4 546 |
| C(36) | 7 231 | 408 | 3 934 | C(86) | 8 060 | −4 632 | 3 827 |
| P(4) | 6 016(1) | 154(1) | 1 783(1) | P(8) | 8 622(1) | −5 058(1) | 1 668(1) |
| C(37) | 6 059(3) | 1 277(2) | 771(2) | C(87) | 9 666(3) | −4 031(2) | 788(2) |
| C(38) | 6 065 | 2 002 | 572 | C(88) | 9 956 | −3 327 | 542 |
| C(39) | 6 111 | 2 542 | 1 099 | C(89) | 9 635 | −2 737 | 882 |
| C(40) | 6 150 | 2 358 | 1 823 | C(90) | 9 023 | −2 852 | 1 467 |
| C(41) | 6 144 | 1 633 | 2 022 | C(91) | 8 734 | −3 556 | 1 712 |
| C(42) | 6 099 | 1 093 | 1 496 | C(92) | 9 055 | −4 146 | 1 373 |
| C(43) | 6 287(2) | −494(2) | 472(2) | C(93) | 7 673(2) | −5 670(2) | 389(2) |
| C(44) | 6 816 | −863 | 0 | C(94) | 6 833 | −5 871 | −83 |
| C(45) | 7 751 | −1 061 | 222 | C(95) | 5 867 | −5 782 | 119 |
| C(46) | 8 157 | −891 | 917 | C(96) | 5 741 | −5 491 | 793 |
| C(47) | 7 628 | −522 | 1 389 | C(97) | 6 581 | −5 290 | 1 265 |
| C(48) | 6 693 | −324 | 1 166 | C(98) | 7 547 | −5 379 | 1 063 |
| S(4) | 4 546(1) | −290(1) | 1 677(1) | S(8) | 9 728(1) | −5 672(1) | 1 544(1) |

same pattern there are differences in their magnitude of up to 20° for equivalent angles. These differences reflect the stereochemical freedom of the NiS$_2$P$_2$N ring. The Ni–S bond lengths and the S–Ni–S angles are in the ranges 2.284(2)–2.316(2) Å and 104.8(1)–113.8(1)° respectively. As was the case in **1** and **2** the P–S and P–N bond lengths are increased and decreased respectively as a consequence of deprotonation and co-ordination. In contrast to **1** and **2** the P–N–P angles in **5** are little changed from that seen in **I** [range in **5** 127.6(2)–130.6(3)° *cf.* 132.7(1)° in **I** and 132.3(2)° in **II**]. It is interesting that despite the electronic relationship of acetylacetone and **II** (which although not isoelectronic are closely related), although Group 10 complexes of acetylacetone all contain planar six-membered rings, here the rings are all puckered. The difference between acetylacetone **I** and **II** may reflect the ability of the heavier main group ligand to form delocalised rings without any requirement for planarity since in the case of complexes of **I** and **II** low-lying d orbitals are available. The ability of main group rings to use d orbitals in pseudo-aromatic systems has been extensively discussed.[10] A similar effect has recently been noted[2] for

**Table 9** Selected bond lengths (Å) and angles (°) for complex **5**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni(1)–S(1) | 2.291(2) | Ni(1)–S(2) | 2.289(2) | Ni(2)–S(5) | 2.294(2) | Ni(2)–S(6) | 2.284(2) |
| Ni(1)–S(3) | 2.316(2) | Ni(1)–S(4) | 2.298(2) | Ni(2)–S(7) | 2.299(2) | Ni(2)–S(8) | 2.302(2) |
| S(1)–P(1) | 2.021(2) | P(1)–N(1) | 1.587(4) | S(5)–P(5) | 2.020(2) | P(5)–N(5) | 1.589(4) |
| P(1)–C(6) | 1.801(3) | P(1)–C(12) | 1.800(5) | P(5)–C(56) | 1.803(3) | P(5)–C(62) | 1.807(4) |
| N(1)–P(2) | 1.591(4) | P(2)–C(18) | 1.804(4) | N(5)–P(6) | 1.594(4) | P(6)–C(68) | 1.796(3) |
| P(2)–C(24) | 1.807(4) | P(2)–S(2) | 2.021(2) | P(6)–C(74) | 1.807(3) | P(6)–S(6) | 2.021(2) |
| S(3)–P(3) | 2.023(2) | P(3)–N(3) | 1.583(4) | S(7)–P(7) | 2.010(2) | P(7)–N(7) | 1.590(4) |
| P(3)–C(30) | 1.809(3) | P(3)–C(36) | 1.808(3) | P(7)–C(80) | 1.804(4) | P(7)–C(86) | 1.814(4) |
| N(3)–P(4) | 1.594(4) | P(4)–C(42) | 1.815(4) | N(7)–P(8) | 1.586(4) | P(8)–C(92) | 1.805(4) |
| P(4)–C(48) | 1.807(4) | P(4)–S(4) | 2.015(2) | P(8)–C(98) | 1.809(3) | P(8)–S(8) | 2.014(2) |
| S(1)–Ni(1)–S(2) | 111.6(1) | S(1)–Ni(1)–S(3) | 108.8(1) | S(5)–Ni(2)–S(6) | 111.3(1) | S(5)–Ni(2)–S(7) | 104.8(1) |
| S(2)–Ni(1)–S(3) | 113.8(1) | S(1)–Ni(1)–S(4) | 103.2(1) | S(6)–Ni(2)–S(7) | 109.3(1) | S(5)–Ni(2)–S(8) | 110.0(1) |
| S(2)–Ni(1)–S(4) | 106.4(1) | S(3)–Ni(1)–S(4) | 112.4(1) | S(6)–Ni(2)–S(8) | 109.6(1) | S(7)–Ni(2)–S(8) | 111.7(1) |
| Ni(1)–S(1)–P(1) | 101.8(1) | S(1)–P(1)–N(1) | 118.5(2) | Ni(2)–S(5)–P(5) | 101.1(1) | S(5)–P(5)–N(5) | 118.3(1) |
| S(1)–P(1)–C(6) | 107.3(1) | N(1)–P(1)–C(6) | 105.4(2) | S(5)–P(5)–C(56) | 106.9(1) | N(5)–P(5)–C(56) | 105.6(2) |
| S(1)–P(1)–C(12) | 108.1(2) | N(1)–P(1)–C(12) | 110.7(2) | S(5)–P(5)–C(62) | 108.0(1) | N(5)–P(5)–C(62) | 111.1(2) |
| C(6)–P(1)–C(12) | 106.1(2) | P(1)–N(1)–P(2) | 130.0(3) | C(56)–P(5)–C(62) | 106.2(2) | P(5)–N(5)–P(6) | 129.9(2) |
| P(1)–C(6)–C(1) | 119.2(1) | P(1)–C(6)–C(5) | 120.8(1) | P(5)–C(56)–C(51) | 119.6(1) | P(5)–C(56)–C(55) | 120.4(1) |
| P(1)–C(12)–C(7) | 119.6(1) | P(1)–C(12)–C(11) | 120.4(1) | P(5)–C(62)–C(57) | 119.8(1) | P(5)–C(62)–C(61) | 120.2(1) |
| N(1)–P(2)–C(18) | 107.8(2) | N(1)–P(2)–C(24) | 108.5(2) | N(5)–P(6)–C(68) | 108.0(2) | N(5)–P(6)–C(74) | 108.5(2) |
| C(18)–P(2)–C(24) | 105.5(2) | N(1)–P(2)–S(2) | 117.3(2) | C(68)–P(6)–C(74) | 105.3(2) | N(5)–P(6)–S(6) | 117.8(2) |
| C(18)–P(2)–S(2) | 107.5(1) | C(24)–P(2)–S(2) | 109.5(1) | C(68)–P(6)–S(6) | 106.4(1) | C(74)–P(6)–S(6) | 110.2(1) |
| P(2)–C(18)–C(13) | 121.2(1) | P(2)–C(18)–C(17) | 118.5(1) | P(6)–C(68)–C(63) | 120.3(1) | P(6)–C(68)–C(67) | 119.5(1) |
| P(2)–C(24)–C(19) | 117.9(1) | P(2)–C(24)–C(23) | 122.0(1) | P(6)–C(74)–C(69) | 121.8(1) | P(6)–C(74)–C(73) | 118.1(1) |
| Ni(1)–S(2)–P(2) | 106.2(1) | Ni(1)–S(3)–P(3) | 101.0(1) | Ni(2)–S(6)–P(6) | 107.4(1) | Ni(2)–S(7)–P(7) | 102.0(1) |
| S(3)–P(3)–N(3) | 117.9(2) | S(3)–P(3)–C(30) | 107.8(1) | S(7)–P(7)–N(7) | 117.7(1) | S(7)–P(7)–C(80) | 107.6(1) |
| N(3)–P(3)–C(30) | 111.2(2) | S(3)–P(3)–C(36) | 109.0(1) | N(7)–P(7)–C(80) | 110.3(2) | S(7)–P(7)–C(86) | 107.9(1) |
| N(3)–P(3)–C(36) | 105.2(2) | C(30)–P(3)–C(36) | 104.9(2) | N(7)–P(7)–C(86) | 105.6(2) | C(80)–P(7)–C(86) | 107.3(2) |
| P(3)–N(3)–P(4) | 130.6(3) | P(3)–C(30)–C(25) | 119.4(1) | P(7)–N(7)–P(8) | 127.6(2) | P(7)–C(80)–C(75) | 120.0(1) |
| P(3)–C(30)–C(29) | 120.6(1) | P(3)–C(36)–C(31) | 117.9(1) | P(7)–C(80)–C(79) | 120.0(1) | P(7)–C(86)–C(81) | 119.6(1) |
| P(3)–C(36)–C(35) | 122.0(1) | N(3)–P(4)–C(42) | 109.3(2) | P(7)–C(86)–C(85) | 120.4(1) | N(7)–P(8)–C(92) | 110.3(2) |
| N(3)–P(4)–C(48) | 107.0(2) | C(42)–P(4)–C(48) | 107.9(2) | N(7)–P(8)–C(98) | 105.5(2) | C(92)–P(8)–C(98) | 104.6(2) |
| N(3)–P(4)–S(4) | 117.8(2) | C(42)–P(4)–S(4) | 107.4(1) | N(7)–P(8)–S(8) | 117.3(2) | C(92)–P(8)–S(8) | 108.7(1) |
| C(48)–P(4)–S(4) | 107.1(1) | P(4)–C(42)–C(37) | 121.8(1) | C(98)–P(8)–S(8) | 109.6(1) | P(8)–C(92)–C(87) | 120.4(1) |
| P(4)–C(42)–C(41) | 118.1(1) | P(4)–C(48)–C(43) | 120.5(1) | P(8)–C(92)–C(91) | 119.5(1) | P(8)–C(98)–C(93) | 121.4(1) |
| P(4)–C(48)–C(47) | 119.5(1) | Ni(1)–S(4)–P(4) | 103.9(1) | P(8)–C(98)–C(97) | 118.5(1) | Ni(2)–S(8)–P(8) | 100.3(1) |

[Pb{N(SPPh$_2$)$_2$-*S*,*S*′}$_2$]. Further studies into substituent effects on the geometries of M[N(XPPh$_2$)$_2$] rings are in progress.

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