Complexes of $[Ph_2P(O)NP(E)Ph_2]^-$ (E = S or Se): disparate ring conformations within a new palladacycle

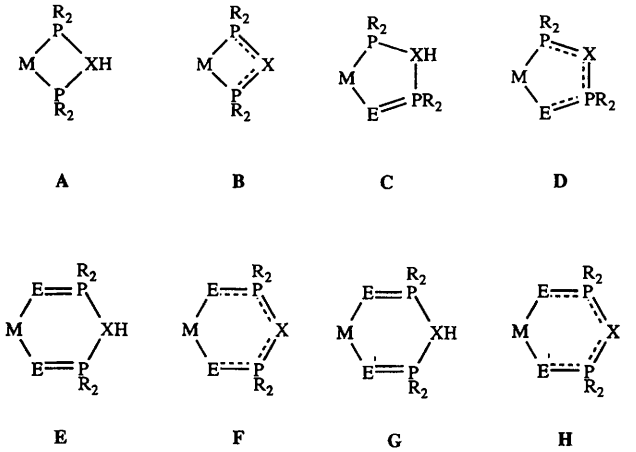
Alexandra M. Z. Slawin, Martin B. Smith and J. Derek Woollins *

Department of Chemistry, Loughborough University, Loughborough, Leics. LE11 3TU, UK

A new mixed oxygen–selenium ligand $Ph_2P(O)NHP(Se)Ph_2$, its potassium salt $K[Ph_2P(O)NP(Se)Ph_2]$ and the bis(chelate) palladium(II) complex *cis*-$[Pd\{Ph_2P(O)NP(Se)Ph_2\text{-}O,Se\}_2]$ have been prepared. In *cis*-$[Pd\{Ph_2P(O)NP(Se)Ph_2\text{-}O,Se\}_2]$ the two *cis* six-membered Pd–O–P–N–P–Se rings adopt different conformations: one is a pseudo-boat whilst the other is chair-like (X-ray evidence). Reaction of 2 equivalents of $K[Ph_2P(O)NP(Se)Ph_2]$ with $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) in MeOH, or more conveniently using the methoxo-bridged platinum(II) dimer $[\{Pt(\mu\text{-}OMe)(C_8H_{12}OMe)\}_2]$ ($C_8H_{12}OMe$ = 8-methoxycyclooct-4-en-1-yl), afforded $[Pt(C_8H_{12}OMe)\{Ph_2P(O)NP(Se)Ph_2\text{-}O,Se\}]$ as one isomer only. The mixed oxygen–sulfur salt $K[Ph_2P(O)NP(S)Ph_2]$ was used to prepare similar compounds, all of which have been characterised by a combination of multinuclear NMR ($^{31}P\text{-}\{^1H\}$, $^{195}Pt\text{-}\{^1H\}$ and ^1H), IR spectroscopy and microanalysis. The molecular structures of $Ph_2P(O)NHP(S)Ph_2$, *cis*-$[Pd\{Ph_2P(O)NP(Se)Ph_2\text{-}O,Se\}_2]$ and $[Pt(C_8H_{12}OMe)\{Ph_2P(O)NP(S)Ph_2\text{-}O,S\}]$ have been determined by single-crystal X-ray diffraction.

The ligating behaviour of the diphosphine $Ph_2PNHPPh_2$ (dppa), analogous to $Ph_2PCH_2PPh_2$ (dppm), has been investigated by several groups with a variety of different bonding modes observed and continues to remain an area of active research interest.[1] Of the numerous transition-metal complexes of dppa known the formation of four-membered M–P–NH–P metallacycles (**A**) in which the diphosphine ligand chelates is most prevalent. Moreover, since the amine proton of dppa is acidic, deprotonation with base (*e.g.* $LiBu^n$) affords the lithium salt $Li[Ph_2PNPPh_2]$ which is also closely related to $Li[Ph_2PCHPPh_2]$. Transmetallation provides a good entry to metal complexes of the bis(diphenylphosphino)amide anion $[Ph_2PNPPh_2]^-$ (**B**)[2] which alternatively are accessible by deprotonation of a chelated dppa metal complex with base.[3]

Metallacycle ring expansion can be achieved by the sequential introduction of chalcogen atoms (*e.g.* O, S or Se) at one or both phosphorus centres of dppa or its derivatives, prior to metal complexation, to afford five- or six-membered rings respectively. The variation in ring size and the contrasting hard/soft character of the donor atoms may have a significant influence on the co-ordination properties of these complexes. We recently found that monooxidation of dppa yields $Ph_2PNHP(E)Ph_2$ (E = O, S or Se) and demonstrated that these compounds readily form five-membered M–P–NH–P–E metallacycles containing a neutral chelating ligand (**C**).[4] Amine deprotonation of metal co-ordinated $Ph_2PNHP(E)Ph_2$ with, or in the absence of, base affords metallacycles containing the chelating anion $[Ph_2PNP(E)Ph_2]^-$ (**D**).[4,5] Moreover metal complexes of the carbon backbone analogues $Ph_2PCH_2P(E)Ph_2$ and $[Ph_2PCHP(E)Ph_2]^-$ are also known as exemplified in *cis*-$[M\{Ph_2PCH_2P(O)Ph_2\text{-}P,O\}_2]^{2+}$ (M = Pd or Pt)[6] and $[Rh\{Ph_2PCHP(S)Ph_2\text{-}P,S\}(cod)]$ (cod = cycloocta-1,5-diene).[7] In contrast, although very few compounds of $Ph_2P(E)NHP(E)Ph_2$ (E = O, S or Se) are documented[8–10] in which the neutral ligand chelates (**E**), the corresponding anions $[R_2P(E)NP(E)R_2]^-$ (R = Me, Ph, OPh but not all permutations) have been extensively studied and form stable M–E–P–N–P–E metallacycles (**F**).[11–22] These anions are excellent chelating agents for a wide range of metals and have found important use as metal extractant agents.[23] Dixon and co-workers[7,24,25] have studied the related methylene-bridged compounds $R_2P(E)CH_2P(E)R_2$ (E = O, S or Se) and their corresponding anions $[R_2P(E)CHP(E)R_2]^-$ with various late transition-metal elements.



XH = CH_2 or NH; X = CH or N; E = O, S, Se

Although we are unaware of any examples of metal complexes with the neutral asymmetric ligands $R_2P(O)NHP(S)R_2$ (**G**), incorporating a 'hard' oxygen atom and a 'soft' sulfur atom, a few examples of metal complexes containing $[R_2P(O)NP(S)R_2]^-$ (R = Ph or OPh) (**H**) are documented.[22,26–28] Furthermore we are unaware of any reports of the corresponding selenium derivatives $[R_2P(O)NP(Se)R_2]^-$. A possible reason for this may in part be due to the absence of a simple synthetic procedure for such systems. The O,S and O,Se compounds are loosely related to both the monothio-β-diketonate[29] and the mixed phosphorus(V) compounds $Ph_2P(O)CH_2P(E)Ph_2$ (E = S or Se) reported by Grim and Walton.[30]

Of particular interest to us has been the ring conformations adopted by these inorganic (carbon-free) six-membered M–E–P–N–P–E ring systems. It is well established in metal acetylacetonate complexes that the ring adopts a planar conformation with extensive π delocalisation. In contrast, for a wide range of metal complexes containing a co-ordinated iminodiphosphonate ligand, π delocalisation is evident yet there is no propensity for planarity of the metallacycle rings. Various metal complexes with bidentate *S*,*S*′- or *Se*,*Se*′-chelating ligands exhibit puckered conformations and recent work by us[17] has established that modifying the exocyclic substituents bound to phosphorus in $[R_2P(S)NP(S)R_2]^-$ has a profound effect on the ring conformation. Furthermore, recent work has shown that in the manganese(I) complex $[Mn(CO)_4\{Ph_2P(S)NP(S)Ph_2\}]$ the unit cell contains two independent monomeric molecules in which both Mn–S–P–N–P–S rings adopt distinctly different co-ordination geometries.[18] It is also noteworthy that García-Montalvo *et al.*[27] have shown that in the lead complex $[Pb\{Ph_2P(O)NP(S)Ph_2\}_2]\cdot C_6H_6$ there are two dissimilar chelate rings. One has an intermolecular Pb ··· S contact between the Pb and the S atom within the chelate ring of an adjacent molecule leading to a dimeric structure.

We report here the synthesis of a new hybrid compound $Ph_2P(O)NHP(Se)Ph_2$, the potassium salt $K[Ph_2P(O)NP(Se)Ph_2]$ and the first crystal structure determination of a late transition-metal complex containing this anion. More interestingly, the structure shows that both Pd–O–P–N–P–Se rings in the homoleptic palladium(II) complex *cis*-$[Pd\{Ph_2P(O)NP(Se)Ph_2\text{-}O,Se\}_2]$ adopt distinctly different ring conformations.

Experimental

General

Unless otherwise stated, most manipulations were performed in air. Standard Schlenk techniques were used for experiments that were carried out under an oxygen-free nitrogen atmosphere using predried solvents. The compound $Ph_2P(O)NHPPh_2$ was prepared as previously reported[4] whilst the metal(II) complexes $[MCl_2(cod)]$ (M = Pd or Pt)[31] and $[\{Pt(\mu\text{-}OMe)(C_8H_{12}OMe)\}_2]$[32] were prepared according to literature methods. The compounds $KOBu^t$ (95% purity) and $HBF_4\cdot OEt_2$ (85% in diethyl ether) were obtained commercially from Aldrich Chemical Co. and used without further purification.

Infrared spectra were recorded as KBr pellets in the range 4000–220 cm^{-1} on a Perkin-Elmer System 2000 Fourier-transform spectrometer, ^1H NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with chemical shifts (δ) in ppm (±0.01) to high frequency of $SiMe_4$ and coupling constants (*J*) in Hz (±0.1), $^{31}P\text{-}\{^1H\}$ NMR spectra (36.2 MHz) on a JEOL FX90Q spectrometer with chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (*J*) in Hz (±3) and $^{195}Pt\text{-}\{^1H\}$ NMR spectra (53.7 MHz) on a Bruker AC250 Fourier-transform spectrometer with δ referenced to external H_2PtCl_6 (in D_2O–HCl). All NMR spectra were measured in $CDCl_3$ unless otherwise stated. Elemental analyses (Perkin-Elmer 2400 CHN elemental analyser) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

Sodium tetrachloropalladate and potassium tetrachloroplatinate were provided on loan by Johnson Matthey plc.

Preparations

$Ph_2P(O)NHP(Se)Ph_2$ I. A mixture of $Ph_2P(O)NHPPh_2$ (0.261 g, 0.650 mmol) and grey Se (0.074 g, 0.937 mmol) in tetrahydrofuran (thf) (7 cm^3) was stirred under a nitrogen atmosphere for 3 h. Unreacted Se was removed by filtration through a Celite pad and the volume concentrated *in vacuo* to *ca.* 1–2 cm^3. Addition of diethyl ether (40 cm^3) afforded a white solid. The mixture was cooled at −20 °C for 1 h and the solid filtered off. Yield 0.230 g, 74%. Selected IR data (KBr): 2714, 2659 [ν(NH)], 1200, 1182 [ν(PO)], 938 [ν_{asym}(PNHP)], 541 cm^{-1} [ν(PSe)]. ^1H NMR data: δ 7.99–7.93, 7.73–7.64 and 7.40–7.27 (aromatic H).

$Ph_2P(O)NHP(S)Ph_2$ II. A thf (20 cm^3) solution of $Ph_2P(O)NHPPh_2$ (0.512 g, 1.28 mmol) and elemental sulfur (0.043 g, 1.34 mmol) was stirred under a nitrogen atmosphere for 1 h. The volume was concentrated *in vacuo* to *ca.* 1–2 cm^3 and addition of diethyl ether (50 cm^3) afforded a white solid which was collected by suction filtration. Yield 0.464 g, 84%. Selected IR data (KBr): 2697 [ν(NH)], 1206, 1190 [ν(PO)], 937 [ν_{asym}(PNHP)], 628, 615 cm^{-1} [ν(PS)]. ^1H NMR data: δ 8.03–7.95, 7.74–7.66 and 7.37–7.27 (aromatic H). Slow diffusion of diethyl ether into a MeOH solution of compound **II** over several days gave crystals suitable for X-ray crystallography. An additional crop was obtained upon leaving the filtrate to stand for 2 d. Yield: 0.068 g, overall yield 96%.

$K[Ph_2P(O)NP(Se)Ph_2]$ 1. Under aerobic conditions, to a solution of $Ph_2P(O)NHP(Se)Ph_2$ (0.137 g, 0.285 mmol) in MeOH (7 cm^3) was added $KOBu^t$ (0.037 g, 0.330 mmol), as a solid in one portion. The solution was stirred for *ca.* 1 h, filtered and the solvent removed to dryness *in vacuo*. Yield 0.115 g, 78%. Selected IR data (KBr): 1197 [ν_{asym}(PNP)], 1132, 1089 [ν(PO)], 562 cm^{-1} [ν(PSe)]. ^1H NMR data [$(CD_3)_2SO$]: δ 8.02–7.93, 7.85–7.77 and 7.28–7.24 (aromatic H).

$K[Ph_2P(O)NP(S)Ph_2]$ 2. Under aerobic conditions, to a solution of $Ph_2P(O)NHP(S)Ph_2$ (0.329 g, 0.759 mmol) in MeOH (10 cm^3) was added $KOBu^t$ (0.094 g, 0.838 mmol), as a solid in one portion. The solution was stirred for 45 min and the solvent removed to dryness *in vacuo*. Yield 0.336 g, 94%. Selected IR data (KBr): 1194 [ν_{asym}(PNP)], 1134, 1089 cm^{-1} [ν(PO)]. ^1H NMR data [$(CD_3)_2SO$]: δ 8.00–7.91, 7.84–7.75 and 7.26–7.21 (aromatic H).

***cis*-$[Pd\{Ph_2P(O)NP(Se)Ph_2\text{-}O,Se\}_2]$ 3.** A methanolic (2 cm^3) solution of $K[Ph_2P(O)NP(Se)Ph_2]$ (0.085 g, 0.164 mmol) was treated with solid $[PdCl_2(cod)]$ (0.024 g, 0.084 mmol) yielding a deep orange solution from which the solid product deposited after 1–2 min. The mixture was stirred for *ca.* 30 min and the product collected by suction filtration. Yield 0.067 g, 77%. Selected IR data (KBr): 1206 [ν_{asym}(PNP)], 1126, 1061 [ν(PO)], 566, 554 cm^{-1} [ν(PSe)]. ^1H NMR data: δ 7.91–7.80 and 7.38–7.25 (aromatic H). Slow diffusion of MeOH into a CH_2Cl_2 solution of compound **3** over several days gave crystals suitable for X-ray crystallography.

A similar procedure was used in the preparation of *cis*-$[Pd\{Ph_2P(O)NP(S)Ph_2\text{-}O,S\}_2]$ **4**. Yield 0.096 g, 94%. Selected IR data (KBr): 1223 [ν_{asym}(PNP)], 1125, 1055 [ν(PO)], 583, 567 cm^{-1} [ν(PS)]. ^1H NMR data: δ 7.92–7.80 and 7.41–7.26 (aromatic H). Alternatively the use of $Na_2[PdCl_4]$ instead of $[PdCl_2(cod)]$ gave good yields (75 and 77% respectively) for both **3** and **4**.

$[Pt(C_8H_{12}OMe)\{Ph_2P(O)NP(S)Ph_2\text{-}O,S\}]$ 5. (*a*) To the solids $[PtCl_2(cod)]$ (0.032 g, 0.086 mmol) and $K[Ph_2P(O)NP(S)Ph_2]$ (0.082 g, 0.174 mmol) was added MeOH (1.5 cm^3) to give a yellow solution. After stirring for a few minutes a white precipitate formed and the resulting mixture was stirred for 1 h. The solid was collected by suction filtration, washed with MeOH (1 cm^3) and dried. Yield 0.065 g. $^{31}P\text{-}\{^1H\}$ NMR spectroscopy confirmed the exclusive formation of **5**, however, the solid was found to be impure by elemental analysis. Examination of the filtrate residue by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy showed the presence of the protonated compound **II**. A $CDCl_3$–MeOH solution of **5** was left over the course of *ca.* 2 d to give crystals suitable for X-ray crystallography.

(*b*) To a suspension of $[\{Pt(\mu\text{-}OMe)(C_8H_{12}OMe)\}_2]$ (0.040 g, 0.0547 mmol) in MeOH (1 cm^3) was added $K[Ph_2P(O)NP(S)Ph_2]$ (0.053 g, 0.112 mmol). The white suspension dissolved and immediately a new white precipitate formed. This mixture was stirred for 5 min, filtered and the product washed with MeOH (0.2 cm^3) and dried. Yield 0.074 g, 88%. Selected

IR data (KBr): 1199 [ν_{asym}(PNP)], 1124, 1059 [ν(PO)], 573 cm^{-1} [ν(PS)]. ^{1}H NMR data: δ 7.93–7.72 and 7.41–7.32 (aromatic H) in addition to the expected $C_8H_{12}OMe$ resonances.

This procedure [method (*b*)] was used in the preparation of [Pt($C_8H_{12}OMe$){$Ph_2P(O)NP(Se)Ph_2$-*O*,*Se*}] **6**. Yield 0.075 g, 94%. Selected IR data (KBr): 1200 [ν_{asym}(PNP)], 1125, 1060 [ν(PO)], 573 cm^{-1} [ν(PSe)]. ^{1}H NMR data: δ 7.91–7.73 and 7.41–7.27 (aromatic H) in addition to the expected $C_8H_{12}OMe$ resonances.

Preliminary protonation studies

The metal complex (**3** or **4**, typically *ca.* 0.020 g) was dissolved in $CDCl_3$ (*ca.* 0.5 cm^3) and to this solution was added $HBF_4 \cdot OEt_2$ (85% in diethyl ether, about two drops) and the reaction monitored immediately by ^{31}P-{^{1}H} NMR spectroscopy. In both cases rapid and complete conversion into new species, tentatively assigned the dicationic compounds *cis*-[Pd{$Ph_2P(O)NHP(E)Ph_2$-*O*,*E*}$_2$][BF_4]$_2$ (E = Se **7** or S **8**).

Analytical data for all new compounds are compiled in Table 1.

X-Ray crystallography

The crystal structures of compounds **II**, **3** and **5** were obtained using a Rigaku AFC7S diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.541 78 Å) and ω scans. Details of the data collections and refinements are given in Table 3. Empirical absorption corrections (DIFABS)[33] were applied. The structures were solved by the heavy-atom method[34] and all of the non-hydrogen atoms refined anisotropically. The atoms of CH groups were idealised and fixed (C–H 0.95 Å). No additional constraints or restraints were applied. Refinement was by full-matrix least-squares methods based on *F*. Calculations were performed using TEXSAN.[35]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/175.

Calculations

Single-point calculations using the appropriate density function theory were carried out using the ADF program[36] which employs Slater type orbital (STO) basis sets and offers a choice of the low-density approximation (LDA) or the LDA with Becke's non-local exchange correction[37] (B) and the non-local correlation function due to Purdew[38] (BP). Triple-zeta basis sets were implemented with the calculations being performed on an IBM/RISC 6000 work station.

Table 1 Microanalytical data for the new compounds (calculated values in parentheses)

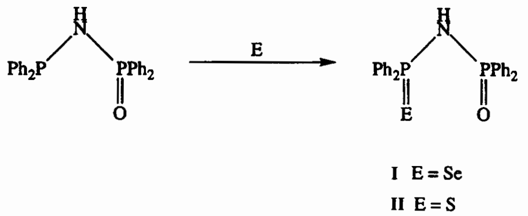
Compound	Analysis (%)		
	C	H	N
I	59.65 (60.0)	4.20 (4.40)	3.05 (2.90)
II	66.25 (66.5)	4.85 (4.65)	3.40 (3.25)
1	55.6 (55.6)	3.80 (3.90)	2.75 (2.70)
2	60.65 (61.1)	4.05 (4.30)	3.10 (2.95)
3*	53.35 (53.9)	3.50 (3.80)	2.70 (2.60)
4	59.15 (59.35)	4.15 (4.15)	2.95 (2.90)
5	52.35 (51.7)	4.80 (4.60)	2.15 (1.85)
6	48.35 (48.7)	4.05 (4.35)	2.05 (1.70)

* Theoretical value includes $0.25H_2O$ as observed in the crystal structure.

Table 2 The ^{31}P-{^{1}H} and ^{195}Pt-{^{1}H} NMR data (*J*/Hz) for the new compounds

Compound	$\delta(P_E)$[a]	$\delta(P_O)$	$^2J(P_EP_O)$	Additional data
I	52.4	21.0	24	^1J(PSe) 779
II	57.0	21.1	17	
	56.1[b]	23.1	17.5	
	54.2[c]	22.1	*d*	
1[e]	23.6	12.9	2.2	^1J(PSe) 664
2[f]	35.3	13.9	3.3	
	37.9[b]	16.1	*d*	
	34.7[c]	12.4	*d*	
3	16.5	30.6	2.2	^1J(PSe) 492
4	33.0	31.6	3.3	
5	30.3	27.1	4.4	δ(Pt) −3529
	(109.9)[g]	(33.0)[h]		
6	15.0	26.9	3.3	δ(Pt) −3510
	(116.5)[g]	(30.8)[h]		^1J(PSe) 486
7	43.5[i]	44.7	5.5	^1J(PSe) 585
8	57.6[i,j]	45.9	7.0	

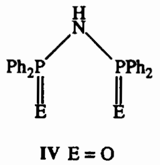
[a] E = S or Se. [b] Taken from ref. 26. [c] Taken from ref. 39. [d] $^2J(P_SP_O)$ value not given. [e] Recorded in C_4H_8O–C_6D_6 insert. [f] Recorded in MeOH–C_6D_6 insert. [g] Value in parentheses denotes $^2J(PtP_E)$. [h] Value in parentheses denotes $^2J(PtP_O)$. [i] *In situ* reaction ($CDCl_3$–$HBF_4 \cdot OEt_2$). [j] Tentative assignment only.



I E = Se

II E = S

Scheme 1



IV E = O

V E = S

VI E = Se

Results and Discussion

Previous work has shown that phosphorus(V) compounds of the type $Ph_2P(O)CH_2P(E)Ph_2$ are synthesised by H_2O_2 oxidation of $Ph_2PCH_2P(E)Ph_2$ (E = S or Se).[30] We have prepared the mixed oxygen–selenium compound $Ph_2P(O)NHP(Se)Ph_2$ **I** from the monooxidised[4] $Ph_2P(O)NHPPh_2$ and grey selenium in thf (Scheme 1). Reaction of $Ph_2P(O)NHPPh_2$ and S_8 in thf (Scheme 1) gives the known acid $Ph_2P(O)NHP(S)Ph_2$ **II** prepared here by a more convenient method than previously reported[39] starting from $Ph_2P(S)NHP(S)Ph_2$. The mixed sulfur–selenium compound $Ph_2P(S)NHP(Se)Ph_2$ **III** can be synthesised from $Ph_2P(S)NHPPh_2$ and elemental Se; the synthetic and spectroscopic details will be described elsewhere.[40]

Both neutral compounds **I** and **II** gave the expected AX ^{31}P-{^{1}H} NMR spectra (Table 2) and we confidently assign the ^{31}P resonances by comparison with known values for the symmetric $Ph_2P(E)NHP(E)Ph_2$ [δ(P) 20.7, E = O **IV**; 55.8, E = S **V**; 52.7, E = Se **VI**]. In addition, the ^{31}P spectral data for **II** agree well with previous reported values.[26,39] The ^1J(PSe) coupling constant of 779 Hz for **I** is in good agreement with that reported for **VI** (793 Hz) and $Ph_2PNHP(Se)Ph_2$ (757 Hz).[4,15]

Suitable crystals of compound **II**·$0.3H_2O$ were grown by slow diffusion of diethyl ether into a MeOH solution of **II** over several days. The water solvate is derived from the methanol

Table 3 Details of the X-ray data collections and refinements for compounds **II**, **3** and **5**

Compound	**II**·0.3H$_2$O	**3**·0.25H$_2$O	**5**
Empirical formula	$C_{24}H_{21.60}NO_{1.30}P_2S$	$C_{48}H_{40.50}N_2O_{2.25}P_4PdSe_2$	$C_{33}H_{35}NO_2P_2PtS$
Crystal colour, habit	Clear, plate	Red, needle	Clear, plate
Crystal dimensions/mm	0.17 × 0.19 × 0.12	0.35 × 0.11 × 0.12	0.20 × 0.20 × 0.03
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a/Å	10.560(4)	10.680(4)	14.922(3)
b/Å	8.929(3)	24.154(5)	9.727(1)
c/Å	23.972(3)	10.085(4)	22.563(5)
α/°		92.22(3)	
β/°	98.13(2)	115.49(2)	106.43(2)
γ/°		94.22(3)	
U/Å^3	2237	2334	3140
Z	4	2	4
M	438.85	1069.58	766.74
D_c/g cm^{-3}	1.30	1.52	1.62
μ(Cu-Kα)/mm^{-1}	2.78	6.60	10.3
$2\theta_{max}$/°	120.2	120.2	120.3
F(000)	916	1069	1520
Measured reflections	3803	7384	5213
Independent reflections (R_{int})	3585 (0.058)	6949 (0.074)	5001 (0.038)
Observed reflections [$I > 3.0\sigma(I)$]	2323	5307	3090
Reflection/parameter ratio	8.2:1	9.9:1	8.5:1
Minimum, maximum transmission	0.76, 1.00	0.86, 1.00	0.65, 1.00
p in weighting scheme *	0.003	0.003	0.007
No. of variables	285	537	362
Final R,R'	0.073, 0.058	0.032, 0.027	0.041, 0.041
Maximum Δ/σ	0.61	0.08	0.05
Largest difference peak, hole/e Å^{-3}	0.94, −0.35	0.33, −0.63	1.14, −0.78

* $\Sigma w = (|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o)]^{-1}$, $\sigma^2(F_o{}^2) = s^2(C + R^2B) + (pF_o{}^2)^2/Lp^2$.

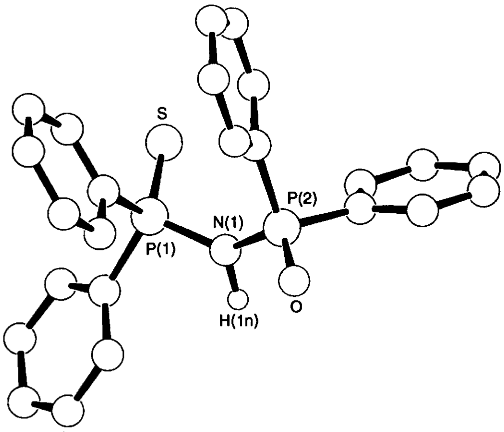
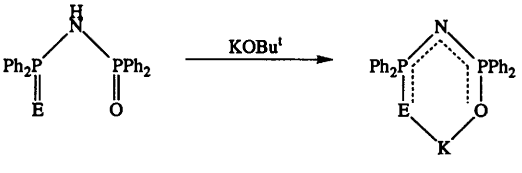


Fig. 1 Crystal structure of compound **II**. The molecule is disordered, each E site at each phosphorus contains contributions from both S and O. At P(1) the proportions of sulfur: oxygen are 70:30 with this being reversed at P(2). The major form is illustrated

Table 4 Selected bond lengths (Å) and angles (°) for compound II

S–P(1)	1.881(4)	P(1)–N(1)	1.681(5)
N(1)–P(2)	1.669(5)	P(2)–O	1.54(3)
S–P(1)–N(1)	111.1(2)	P(1)–N(1)–P(2)	133.5(3)
N(1)–P(2)–O	116.8(9)		



1 E = Se

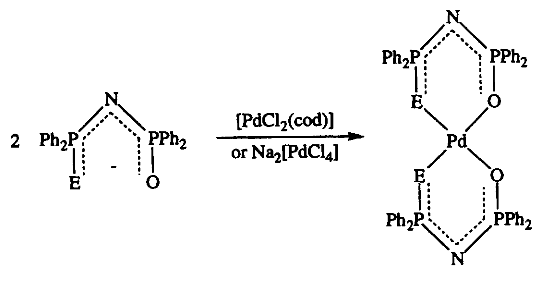
2 E = S

Scheme 2

which was not predried. The crystal structure (Fig. 1, Table 4) shows that the P(1)–S(1), P(1)–N(1), N(1)–P(2) and P(2)–O(2) bond lengths and angles are comparable to the equivalent parameters found in **IV** and **V** though a detailed discussion is not possible because of disorder in the structure of **II**.[41,42] The molecules are hydrogen bonded into infinite chains by use of N–H ··· E [E = 70% O, 30% S, N ··· E 3.0(1) Å] in the screw direction. The other E atom forms a hydrogen bond to the disordered (30% occupancy) H_2O molecule. In comparison in the solid state **V** and **VI** form dimer pairs as a consequence of N–H ··· E (E = S or Se) hydrogen bonds between the P=E and NH groups of an adjacent molecule[15,41,42] whilst **IV** exists as the tautomer $Ph_2P(O)NP(OH)Ph_2$ and OH ··· O hydrogen bonding links these molecules into infinite zigzag chains.[42]

Since the mixed compounds **I** and **II** each contain an acidic NH proton, reaction with KOBu^t in methanol gave K[$Ph_2P(O)NP(Se)Ph_2$] **1** and the known salt K[$Ph_2P(O)NP(S)Ph_2$] **2** (Scheme 2). Deprotonation is readily inferred by ^{31}P-{^{1}H} and IR spectroscopy (Table 2 and Experimental section). The ^{31}P assignments are based upon comparison with values for K[$Ph_2P(E)NP(E)Ph_2$] [δ(P) 12.5, E = O; 37.7, E = S; 28.5, E = Se].

Transmetallation of compounds **1** or **2** with the metal(II) compounds [$PdCl_2$(cod)] or $Na_2[PdCl_4]$ in methanol gave the corresponding complexes [Pd{$Ph_2P(O)NP(E)Ph_2$-*O*,*E*}$_2$] (E = Se **3** or S **4**) (Scheme 3) which have been characterised by a combination of ^{1}H and ^{31}P-{^{1}H} NMR, IR spectroscopy and elemental analyses (Tables 1 and 2, Experimental section). The ^{31}P-{^{1}H} NMR spectra of **3** and **4** indicated only one isomer present in solution although we were unable to assign the exact geometry (*i.e. cis* or *trans*). In the crystallographically characterised octahedral compounds [SnR_2{$Ph_2P(O)NP(S)Ph_2$}$_2$] (R = Me or Ph) the two sulfur chalcogen atoms are *trans* to each other.[26] However the square-planar homoleptic palladium(II) complexes [Pd{RC(O)CHC(S)R}$_2$]



3 E = Se
4 E = S

Scheme 3

Table 5 Selected bond lengths (Å) and angles (°) for compound **3**

Pd–Se(1)	2.381(7)	Pd–Se(2)	2.383(8)
Se(1)–P(1)	2.201(1)	Se(2)–P(3)	2.198(2)
P(1)–N(1)	1.586(4)	P(3)–N(2)	1.577(4)
N(1)–P(2)	1.603(4)	N(2)–P(4)	1.584(4)
P(2)–O(1)	1.519(3)	P(4)–O(2)	1.524(3)
O(1)–Pd	2.085(3)	O(2)–Pd	2.075(3)
Pd–Se(1)–P(1)	101.5(4)	Pd–Se(2)–P(3)	96.6(1)
Se(1)–P(1)–N(1)	115.8(1)	Se(2)–P(3)–N(2)	116.8(2)
P(1)–N(1)–P(2)	123.7(2)	P(3)–N(2)–P(4)	132.1(3)
N(1)–P(2)–O(1)	117.4(2)	N(2)–P(4)–O(2)	118.2(2)
P(2)–O(1)–Pd	124.3(2)	P(4)–O(2)–Pd	123.6(2)
O(1)–Pd–Se(1)	99.8(1)	O(2)–Pd–Se(2)	91.6(1)
O(1)–Pd–O(2)	85.8(1)	Se(1)–Pd–Se(2)	82.8(1)

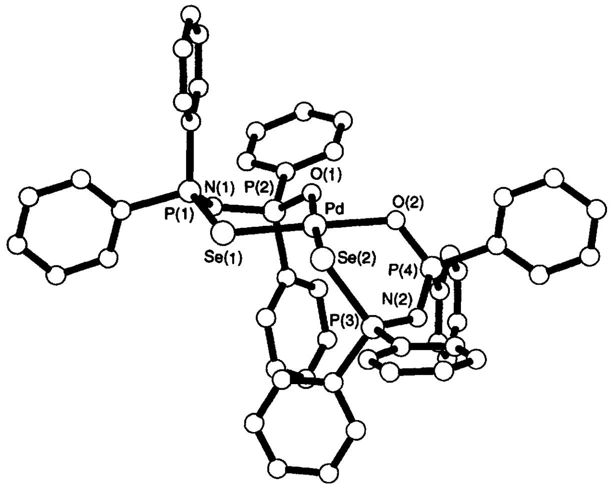


Fig. 2 Crystal structure of compound **3**

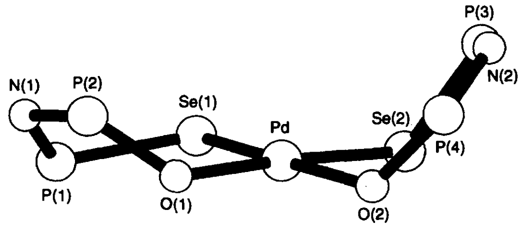


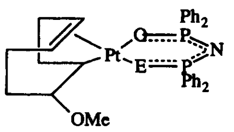
Fig. 3 Core geometry in compound **3**

(R = C_4H_3S, Bu^t or Ph)[43–45] and [Pd{PhC(O)NHC(S)-NEt_2}$_2$][46] have a *cis* arrangement of donor atoms and the chelate rings are planar as determined from X-ray crystallography. It is noteworthy that in the palladium(II) compound [Pd{$(PhO)_2P(O)NP(S)(OPh)_2$-*N*,*S*}$_2$] *N*,*S* is favoured over *O*,*S* co-ordination and that the *trans* isomer is formed.[28]

To confirm the structure of compound **3** we carried out a single-crystal X-ray diffraction study (Fig. 2, Table 5). This reveals that both anionic ligands are co-ordinated in a bidentate mode with a *cis* arrangement of the donor atoms around the palladium centre [maximum deviation from the Pd–Se(1)–Se(2)–O(1)–O(2) mean plane is 0.08 Å for O(1)] as expected from a consideration of the *trans* influence (oxygen *trans* to selenium). The most striking feature of the structure is the remarkable difference in geometry of the two, chemically equivalent, Pd–O–P–N–P–Se rings (Fig. 3). The Pd–Se(1)–P(1)–N(1)–P(2)–O(1) ring has a boat-like geometry. In this ring the Pd–Se(1)–P(1)–O(1) atoms are approximately coplanar [maximum deviation from the mean plane 0.22 Å for O(1)] with the plane inclined by 49° to the O(1)–P(2)–N(1)–P(1) mean plane [maximum deviation 0.062 Å for N(1)]. In contrast in the other ring the O(2)–P(4)–N(2)–P(3)–Se(2) fragment is approximately planar [maximum deviation 0.18 Å for O(2)] and is hinged with respect to the co-ordination plane [*i.e.* along the O(2) ··· Se(2) vector] by *ca.* 58°. The two rings have equivalent bond lengths with the P–N bonds being, as expected, somewhat shorter than a formal single bond. There are some differences in bond angles at nitrogen [P(1)–N(1)–P(2) 123.7(2), P(3)–N(2)–P(4) 132.1(3)°] and selenium [Pd–Se(1)–P(1) 101.5(4), Pd–Se(2)–P(3) 96.6(1)°] but the angles at phosphorus and oxygen are equivalent for the two different ring conformations. Careful examination of the packing in the structure of **3** does not reveal any major intramolecular interactions. The oxygen of the partial occupancy (25%) water molecule is located 3.17 and 3.38 Å from O(2) and O(1) respectively. Careful inspection of the packing indicates that one of the phenyl groups is involved in secondary interactions with an adjacent phenyl group of another molecule [C(4) ··· C(24′) 3.59, C(2) ··· C(3′) 3.59 Å]. It is interesting to speculate that this may explain the difference between the structure of **3** and that of homoleptic metal(II) complexes in which both of the rings adopt similar puckered conformations using *S*,*S*′- or Se,Se′-chelating ligands.[15]

We have previously noted differences in ring conformation in [$R_2P(S)NP(S)R_2$]$^-$ complexes as a consequence of changing the R group from Ph to OPh.[17] The only other reported example of the hinged conformation seen here for M–E–P–N–P–E rings of this type is the observation of two crystallographically independent molecules in the structure of [Mn(CO)$_4${$Ph_2P(S)NP(S)Ph_2$}] where the two molecules in the asymmetric unit adopt different conformations with respect to each other.[18] We have carried out density function calculations upon the two rings in compound **3**. Calculations incorporating the phenyl rings proved impractical but those in which the phosphorus centres carried hydrogen atoms did converge. They revealed only a very minor energy difference between the two conformations with the hinged Pd–O(2)–P(4)–N(2)–P(3)–Se(2) ring being *ca.* 10 kJ mol^{-1} more stable than the boat-like ring. This energy difference is less than the errors in the calculation and the similarity in overall energy supports the commonly made assertion that delocalisation in heavier main-group systems does not have to be accompanied by planarity.

By analogy with the procedure used for the synthesis of compounds **3** and **4** we have also studied the reactions of **1** and **2** with [$PtCl_2$(cod)]. Previous work by us[15] has shown that the compounds [Pt{$Ph_2P(E)NP(E)Ph_2$-*E*,*E*′}$_2$] (E = S or Se) are readily accessible from [$PtCl_2$(cod)] and 2 equivalents of either K[$Ph_2P(S)NP(S)Ph_2$] or $Ph_2P(Se)NHP(Se)Ph_2$. Instead of the anticipated [Pt{$Ph_2P(O)NP(E)Ph_2$-*O*,*E*}$_2$] (E = S or Se) complexes, the reaction of 2 equivalents of **2** and [$PtCl_2$(cod)] in MeOH rapidly develops a yellow solution followed by (within 5 min) the formation of a white solid **5**. The ^{31}P-{^1H} NMR spectrum (in $CDCl_3$) shows the exclusive formation of one phosphorus-containing species and was identified (X-ray, see below) as the platinum(II) complex



5 E = S
6 E = Se

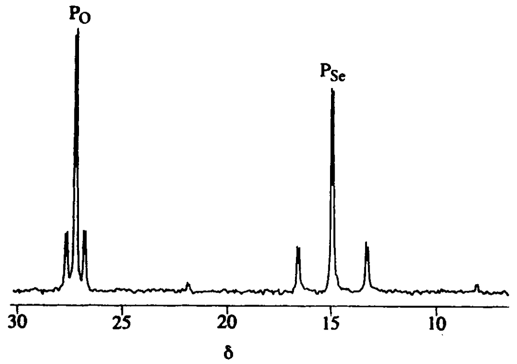


Fig. 4 $^{31}P\text{-}\{^1H\}$ NMR spectrum (36.2 MHz) of compound **6**

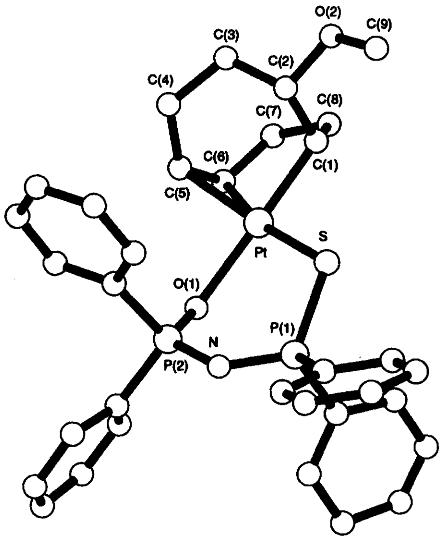
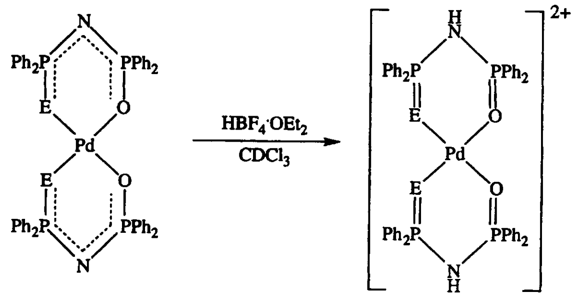


Fig. 5 Crystal structure of compound **5**

Table 6 Selected bond lengths (Å) and angles (°) for compound **5**

Pt–S	2.310(3)	S–P(1)	2.039(4)
Pt–O(1)	2.189(6)	P(1)–N	1.566(8)
Pt–C(1)	2.07(1)	P(2)–O(1)	1.506(7)
Pt–C(5)	2.12(1)	P(2)–N	1.600(7)
Pt–C(6)	2.16(1)		
S–Pt–O(1)	97.9(2)	C(1)–Pt–C(5)	89.8(4)
S–Pt–C(1)	87.5(3)	C(1)–Pt–C(6)	81.1(4)
S–Pt–C(5)	154.7(3)	Pt–S–P(1)	106.8(1)
S–Pt–C(6)	162.5(4)	S–P(1)–N	117.6(3)
O(1)–Pt–C(1)	173.2(4)	O(1)–P(2)–N	115.9(4)
O(1)–Pt–C(5)	87.1(3)	Pt–O(1)–P(2)	119.1(3)
O(1)–Pt–C(6)	92.7(4)	P(1)–N–P(2)	126.8(5)



7 E = Se
8 E = S

Scheme 4

$[Pt(C_8H_{12}OMe)\{Ph_2P(O)NP(S)Ph_2\text{-}O,S\}]$ **5**. In the corresponding reaction of **1** and $[PtCl_2(cod)]$ under similar conditions the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the solution showed, in addition to two major broad resonances [δ(P) 13.0 and 11.0], the presence of small amounts of $[Pt(C_8H_{12}OMe)\{Ph_2P(O)NP(Se)Ph_2\text{-}O,Se\}]$ **6**. A more convenient route to **5** and **6** (in 88 and 94% yields respectively) is the methoxy bridge-cleavage reaction of the platinum(II) dimer $[\{Pt(\mu\text{-}OMe)(C_8H_{12}OMe)\}_2]$[32] with **2** (or **1**) in MeOH. The exact assignments of P$_O$ and P$_E$ in the $^{31}P\text{-}\{^1H\}$ NMR spectra of **5** and **6** (Fig. 4) coincide with similar δ(P) chemical shifts and $^2J(PtP_O)/^2J(PtP_E)$ values found for $[Pt\{Ph_2P(E)NP(E)Ph_2\text{-}E,E\}_2]$ [E = S, δ(P) 34.4, $^2J(PtP_S)$ 95; E = Se, δ(P) 21.0, $^2J(PtP_{Se})$ 105, $^1J(PSe)$ 539 Hz]. The observed $^2J(PtP_O)$ coupling constants of 33.0 (**5**) and 30.8 Hz (**6**) for these six-membered metallacycles are smaller than for the five-membered complex $[Pt\{Ph_2PNP(O)Ph_2\text{-}P,O\}_2]$ [$^2J(PtP_O)$ 167 Hz].[4] No further attempts at synthesizing analogues of **3** and **4** have been made.

Since we were unable to verify exactly what isomer had been synthesized a crystal structure determination was carried out. Crystals of compound **5** suitable for X-ray crystallography were grown from $CDCl_3$–MeOH. The structure (Fig. 5, Table 6) shows that the complex is approximately square planar with Pt–S and Pt–O distances of 2.310(3) and 2.189(6) Å respectively. The $PtOSP_2N$ ring adopts a pseudo-boat conformation. As anticipated the P–N bonds are both shorter than in the proligand though comparison of geometric parameters could not be fruitful here because of the disorder in the structure of **I**. A comparison of selected bond lengths in our structure with that of related compounds is noteworthy. The P–O and P–S distances are 1.506(7) and 2.039(4) Å respectively and comparable to those observed in $[SnMe_2\{Ph_2P(O)NP(S)Ph_2\text{-}O,S\}_2]$ [P–O 1.524(2), P–S 2.023(1) Å], $[SnPh_2\{Ph_2P(O)NP(S)Ph_2\text{-}O,S\}_2]$ [P–O 1.530(5), P–S 2.018(3) Å] and $[Pb\{Ph_2P(O)NP(S)Ph_2\text{-}O,S\}_2]\cdot C_6H_6$ [P–O 1.519(7) and 1.510(7), P–S 2.000(4) and 1.996(4) Å].[26,27] Cavell *et al.*[29] found that in the compounds $[MR(sacac)(PPh_3)]$ (M = Pd or Pt, R = Me or Et, sacac = dithioacetylacetonate) the M–C bond is *trans* to oxygen and this arrangement is similar to what we observe in **5**.

We recently reported that *cis*-$[M\{Ph_2PNP(O)Ph_2\text{-}P,O\}_2]$ (M = Pd or Pt)[4] undergoes rapid protonation with $HBF_4\cdot OEt_2$ at both of the nitrogen atoms to give the dicationic complexes *cis*-$[M\{Ph_2P(O)NHPPh_2\text{-}P,O\}_2][BF_4]_2$. Since there are few examples of metal complexes of neutral $Ph_2P(E)NHP(E)Ph_2$[8–10] we decided to investigate the reaction of *cis*-$[Pd\{Ph_2P(O)NP(E)Ph_2\text{-}O,E\}_2]$ (E = Se **3** or S **4**) with $HBF_4\cdot OEt_2$ in $CDCl_3$ by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy (Table 2). The new dicationic complexes $[Pd\{Ph_2P(O)NHP(E)Ph_2\text{-}O,E\}_2][BF_4]_2$ (E = Se **7** or S **8**) (Scheme 4) are formed instantaneously and we tentatively suggest that the *cis* arrangement of donor atoms is retained.

Further studies on the ligating properties of these compounds with metals are in progress.

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References

1 P. Bhattacharyya and J. D. Woollins, *Polyhedron*, 1995, **14**, 3367; M. Paul and H. Schmidbaur, *Chem. Ber.*, 1996, **129**, 77; D. Pohl, J. Ellermann, M. Moll, F. A. Knoch and W. Bauer, *Z. Anorg. Allg. Chem.*, 1996, **622**, 283; R. Graziani and U. Casellato, *Acta Crystallogr., Sect. C*, 1996, **52**, 852; D. Pohl, J. Ellermann, F. A. Knoch and M. Moll, *J. Organomet. Chem.*, 1995, **495**, C6.

2 M. Gómez, G. Muller, J. Sales and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1993, 221; H. Schmidbaur, S. Lauteschläger and B. Milewski-Mahrla, *J. Organomet. Chem.*, 1983, **254**, 59.

3 C. S. Browning and D. H. Farrar, *J. Chem. Soc., Dalton Trans.*, 1995, 521.

4 P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 3675; P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 3189.

5 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 1283.

6 S. J. Higgins, R. Taylor and B. L. Shaw, *J. Organomet. Chem.*, 1987, **325**, 285.

7 J. Browning, K. R. Dixon and R. W. Hilts, *Organometallics*, 1989, **8**, 552.

8 G. P. McQuillan and I. A. Oxton, *Inorg. Chim. Acta*, 1978, **29**, 69.

9 I. Cuadrado and M. Moran, *Transition Met. Chem.*, 1984, **9**, 96.

10 R. O. Day, R. R. Holmes, A. Schmidpeter, K. Stoll and L. Howe, *Chem. Ber.*, 1991, **124**, 2443.

11 R. Rösler, C. Silvestru, G. Espinosa-Pérez, I. Haiduc and R. Cea-Olivares, *Inorg. Chim. Acta*, 1996, **241**, 47.

12 C. S. Browning, D. H. Farrar and D. C. Frankel, *Inorg. Chim. Acta*, 1996, **241**, 111.

13 H. Bock, H. Schödel, Z. Havlas and E. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1355.

14 C. Silvestru, R. Rösler, I. Haiduc, R. Cea-Olivares and G. Espinosa-Pérez, *Inorg. Chem.*, 1995, **34**, 3352.

15 P. Bhattacharyya, J. Novosad, J. R. Phillips, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 1607.

16 P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 2489.

17 J. R. Phillips, A. M. Z. Slawin, A. J. P. White, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 2467.

18 N. Zúniga-Villarreal, C. Silvestru, M. Reyes Lezama, S. Hernández-Ortega and C. Alvarez Toledano, *J. Organomet. Chem.*, 1995, **496**, 169.

19 C. Silvestru, I. Haiduc, R. Cea-Olivares and A. Zimbron, *Polyhedron*, 1994, **13**, 3159.

20 I. Haiduc, C. Silvestru, H. W. Roesky, H.-G. Schmidt and M. Noltemeyer, *Polyhedron*, 1993, **12**, 69.

21 R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1993, 723.

22 O. Siiman and J. Vetuskey, *Inorg. Chem.*, 1980, **19**, 1672.

23 O. Novrátil, E. Herrmann, G. Grossmann and J. Teply, *Collect. Czech. Chem. Commun.*, 1990, **55**, 364.

24 D. E. Berry, J. Browning, K. R. Dixon, R. W. Hilts and A. Pidcock, *Inorg. Chem.*, 1992, **31**, 1479.

25 J. Browning, G. W. Bushnell and K. R. Dixon, *Inorg. Chem.*, 1981, **20**, 3912.

26 R. Rösler, J. E. Drake, C. Silvestru, J. Yang and I. Haiduc, *J. Chem. Soc., Dalton Trans.*, 1996, 391.

27 V. García-Montalvo, R. Cea-Olivares and G. Espinosa-Pérez, *Polyhedron*, 1996, **15**, 829.

28 P. Z. Zák, M. Fofana, J. Kamenícek and T. Glowiak, *Acta Crystallogr., Sect. C*, 1989, **45**, 1686.

29 K. J. Cavell, H. Jin, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 1973.

30 S. O. Grim and E. D. Walton, *Inorg. Chem.*, 1980, **19**, 1982.

31 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 47; J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

32 A. B. Goel, S. Goel and D. G. Vanderveer, *Inorg. Chim. Acta*, 1981, **54**, L169.

33 DIFABS, N. G. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

34 DIRDIF 92, PATTY, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.

35 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985 and 1992.

36 G. te Velde and E. J. Baerands, *J. Comput. Phys.*, 1992, **99**, 84.

37 A. D. Velde, *Int. J. Quantum Chem.*, 1983, **23**, 1915; *J. Chem. Phys.*, 1986, **84**, 4524; *Phys. Rev. A*, 1988, **38**, 3098.

38 J. P. Purdew, *Phys. Rev. A*, 1986, **33**, 8822.

39 A. Schmidpeter and H. Groeger, *Chem. Ber.*, 1967, **100**, 3979.

40 P. Bhattacharyya, M. B. Smith and J. D. Woollins, unpublished work.

41 P. B. Hitchcock, J. F. Nixon, I. Silaghi-Dumitrescu and I. Haiduc, *Inorg. Chim. Acta*, 1985, **96**, 77; S. Husebye and K. Maartman-Moe, *Acta Chem. Scand., Ser. A*, 1983, **37**, 439.

42 H. Nöth, *Z. Naturforsch., Teil B*, 1982, **37**, 1491.

43 L. A. M. Baxter, A. J. Blake, F. J. J. Dijksma, R. O. Gould and G. A. Heath, *Acta Crystallogr., Sect. C*, 1994, **50**, 1225.

44 L. E. Pope and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, 1976, **32**, 1599.

45 L. M. Shkol'nikova, M. Yu. Yutal, E. A. Shugam and A. N. Knyazeva, *Zh. Strukt. Khim.*, 1973, **14**, 92.

46 V. G. Fitzl, L. Beyer, J. Sieler, R. Richter, J. Kaiser and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1977, **433**, 237.

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