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Synthesis and characterisation of the first E-unidentate $[Ph_2P(O)NP(E)Ph_2]^-$ metal complexes $[Au\{Ph_2P(O)NP(E)Ph_2\text{-}E\}\{Ph_2P(O)NHPPh_2\}]$ and $[Pd\{Ph_2P(O)NP(E)Ph_2\text{-}E\}_2(H_2NCH_2CH_2NH_2)]$ (E = S or Se)

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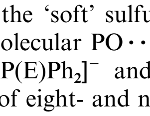
Chloride metathesis of [AuCl(HL)] [HL = $Ph_2P(O)NHPPh_2$] or $[PdCl_2(en)]$ (en = ethane-1,2-diamine) in CH_3OH with either 1 (or 2) equivalents of $[Ph_2P(O)NP(E)Ph_2]^-$ (E = S or Se) gave the neutral compounds $[Au\{Ph_2P(O)NP(E)Ph_2\text{-}E\}(HL)]$ or $[Pd\{Ph_2P(O)NP(E)Ph_2\text{-}E\}_2(en)]$ respectively; the anionic ligands in these complexes adopt a new bonding mode and furthermore are involved in intramolecular N–H · · · OP hydrogen bonding with HL or en.

The co-ordination chemistry of $[R_2P(E)NP(E)R_2]^-$ (E = lone pair, O, S or Se) and related systems has received much interest of late.[1,2] In particular the bis(chalcogenide) ligands $[R_2P(E)NP(E)R_2]^-$, closely associated with the ubiquitous acetylacetonate (acac) and its derivatives, have found relevance in diverse areas such as selective metal extractants, NMR shift reagents and more recently in catalysis.[1,3] Asymmetric analogues of acac such as $[R_2P(O)NP(E)R_2]^-$ (E = S or Se) incorporating dissimilar Group 16 atoms have, until recently, been poorly studied.[4] However the facile synthesis of $[R_2P(O)NP(E)R_2]^-$ now means that this type of chemistry is likely to prove much more fruitful than in the related mixed acac area.

Whereas $[R_2P(E)NP(E)R_2]^-$, $[R_2P(O)NP(E)R_2]^-$ and acac bind metal ions predominantly *via* chelation we reasoned that $[R_2P(O)NP(E)R_2]^-$ could also function as ambidentate ligands, ligating through either the O or E donor atom. Here we report the first examples of metal complexes with the unsymmetrical ligands $[R_2P(O)NP(E)R_2]^-$ (E = S **1**; E = Se **2**; R = Ph) in a novel co-ordination mode. X-Ray crystallography reveals that $[Ph_2P(O)NP(E)Ph_2]^-$ binds in a unidentate manner through exclusively the 'soft' sulfur (or selenium) donor centre. Moreover intramolecular PO · · · H–N hydrogen bonding between $[Ph_2P(O)NP(E)Ph_2]^-$ and the ancillary ligands results in the formation of eight- and nine-membered metallacycles.



E = S **1**
E = Se **2**

Reaction of **1** (or **2**), as their potassium salts, with a suspension of [AuCl(HL)] [HL = $Ph_2P(O)NHPPh_2$][5] in CH_3OH gave the 1 : 1 complexes $[Au\{Ph_2P(O)NP(E)Ph_2\text{-}E\}(HL)]$ (E = S **3**; E = Se **4**) in high yields (typically >90%) [equation (1)] and which display the expected spectroscopic properties.‡ The structures of **3** and **4** were supported by IR [absence of ν(AuCl) vibrations] and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. Notably $\delta(P_O)$ for the co-ordinated ligand $[Ph_2P(O)NP(E)Ph_2]^-$ in **3** and **4** were similar to values previously reported for $K[Ph_2P(O)NP(E)Ph_2]$ [$\delta(P_O)$ 13.9 **1**; 12.9 **2**] but appreciably shifted to lower frequency (typically *ca.* 15 ppm) with respect to values documented for complexes bearing these ligands in a O,E-chelating fashion.[4] Hence the ^{31}P NMR resonances appear sensitive to the ligation mode adopted by the ligand and serve as a convenient probe. Further confirmation that the phosphoryl group of HL remains 'dangling' is reflected in the similarity of the $^{31}P\text{-}\{^1H\}$ data [$\delta(P_O)$ 25.3 **3**; 25.4 **4**] with that of [AuCl(HL)] [$\delta(P_O)$ 26.4].[5] The molecular structure§ of $\mathbf{3}\cdot 0.5H_2O\cdot 0.5CH_3OH$ [Fig. 1(a)] shows the gold(I) centre to be co-ordinated by the P^{III} donor atom of HL and the S atom of $[Ph_2P(O)NP(S)Ph_2]^-$ in a slightly distorted linear geometry [P(3)–Au(1)–S(1) 174.42(12)°]. The two ligands are locked into a nine-membered AuN_2OP_3S auracycle [Fig. 1(b)] by an intramolecular N–H · · · OP hydrogen bond [N · · · O 2.67, H · · · O 1.91 Å, N–H · · · O 147°] and which

$$HL{-}Au{-}Cl \xrightarrow[CH_3OH]{\mathbf{1}\text{ (or }\mathbf{2})} HL{-}Au{-}EPPh_2NP(O)Ph_2 \quad (1)$$

E = S **3**
E = Se **4**

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‡ Compounds **1** (and **2**) were prepared as described in ref. 4. A typical synthesis is illustrated here for compound **3**. To a CH_3OH suspension (1 cm^3) of [AuCl(HL)] (0.053 g, 0.0836 mmol) was added solid **1** (0.043 g, 0.0912 mmol) in one portion. The suspension dissolved and the product **3** precipitated almost immediately. After stirring the mixture for *ca.* 15 min the solid was collected by suction filtration and dried *in vacuo*. Yield 0.078 g, 90%. Selected spectroscopic data for complexes **3**–**6**. For **3**: NMR ($CDCl_3$) $^{31}P\text{-}\{^1H\}$ (referenced to 85% H_3PO_4): δ 61.9 (P) and 25.3 (P_O) [HL ligand, *J*(PP) 28.6 Hz]; 28.5 (P_S) and 14.0 (P_O) [*J*(PP) not resolved]. ^1H: δ 10.75 (NH), 8.25–7.18 (aromatic H). IR (KBr) ν(PO) 1240, 1219, 1150 and ν(PS) 561 cm^{-1} (Found: C, 55.00; H, 3.75; N, 2.35. $C_{48}H_{41}AuN_2O_2P_4S\cdot 0.5H_2O\cdot 0.5CH_3OH$ requires C, 55.15; H, 4.20; N, 2.65%). For **4**: NMR ($CDCl_3$) $^{31}P\text{-}\{^1H\}$: δ 63.2 (P) and 25.4 (P_O) [HL ligand, *J*(PP) 33.0 and 8.8]; 15.3 (P_{Se}) [*J*(PSe) 470 Hz] and 14.5 (P_O) [*J*(PP) not resolved]. ^1H: δ 10.63 (NH), 8.13–7.10 (aromatic H). IR (KBr) ν(PO) 1235, 1217, 1151 and ν(PSe) 553 cm^{-1} (Found: C, 52.40; H, 4.00; N, 2.40. $C_{48}H_{41}AuN_2O_2P_4Se\cdot 0.5H_2O\cdot 0.5CH_3OH$ requires C, 52.80; H, 4.05; N, 2.55%). For **5**: NMR ($CDCl_3$) $^{31}P\text{-}\{^1H\}$: δ 28.8 (P_S) and 14.9 (P_O) [*J*(PP) 2.2 Hz]. ^1H: δ 7.91–7.81, 7.38–7.28 (aromatic H), 4.56 (NH) and 2.25 (CH_2). IR (KBr) ν(PS) 567 cm^{-1}. FAB MS: *m*/*z* 970 $(M - en)^+$ (Found: C, 58.10; H, 4.60; N, 5.40. $C_{50}H_{48}N_4O_2P_4PdS_2$ requires C, 58.20; H, 4.70; N, 5.45%). For **6**: NMR ($CDCl_3$) $^{31}P\text{-}\{^1H\}$: δ 15.6 (P_O) and 14.2 (P_{Se}) [*J*(PSe) 515 Hz] [*J*(PP) not resolved]. ^1H: δ 7.94–7.84, 7.38–7.30 (aromatic H), 4.38 (NH) and 2.27 (CH_2). IR (KBr) ν(PSe) 553 and 544 cm^{-1}. FAB MS: *m*/*z* 1065 $(M - en)^+$ (Found: C, 52.80; H, 4.10; N, 5.10. $C_{50}H_{48}N_4O_2P_4PdSe_2$ requires C, 53.35; H, 4.30; N, 5.00%).

§ Crystal data for complex **3**: $C_{48}H_{41}AuN_2O_2P_4S\cdot 0.5H_2O\cdot 0.5CH_3OH$, $M = 1055.76$, monoclinic, space group $C2/c$, $a = 39.344(1)$, $b = 13.227(1)$, $c = 18.491(1)$ Å, $\beta = 91.47(1)°$, $U = 9619.5(4)$ Å^3, $Z = 8$, $\mu(Mo\text{-}K\alpha) = 3.28$ mm^{-1}, $T = 293$ K, $R1 = 0.0496$ for 6926 unique reflections.

Crystal data for complex **6**: $C_{50}H_{48}N_4O_2P_4PdSe_2\cdot 0.5OEt_2$, $M = 1162.23$, triclinic, space group $P\bar{1}$, $a = 15.403(8)$, $b = 19.198(8)$, $c = 10.318(4)$ Å, $\alpha = 97.07(3)$, $\beta = 94.37(4)$, $\gamma = 67.02(4)°$, $U = 2786(2)$ Å^3, $Z = 2$, $\mu(Cu\text{-}K\alpha)$ 5.59 mm^{-1}, $T = 293$ K, $R1 = 0.044$ for 8300 unique reflections. CCDC reference number 186/970. See http://www.rsc.org/suppdata/dt/1998/1537/ for crystallographic files in .cif format.

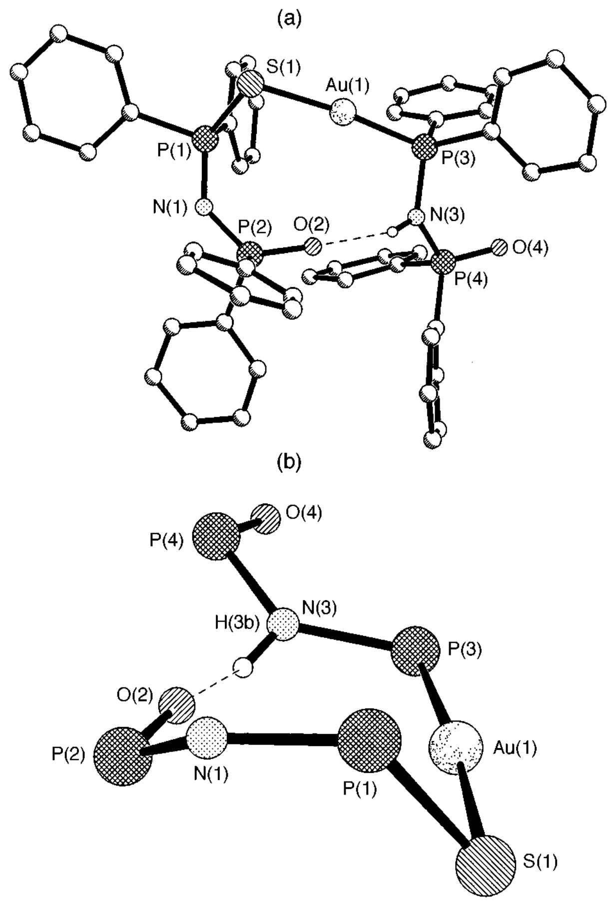
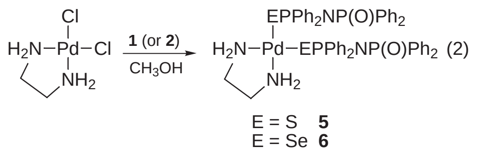


Fig. 1 (a) The crystal structure of **3** (solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (°): Au(1)–P(3) 2.262(4), Au(1)–S(1) 2.335(3), S(1)–P(1) 2.042(4), P(1)–N(1) 1.569(10), N(1)–P(2) 1.601(10), P(2)–O(2) 1.510(8), P(3)–N(3) 1.657(9), N(3)–P(4) 1.645(9), P(4)–O(4) 1.460(8); S(1)–Au(1)–P(3) 174.42(12), Au(1)–S(1)–P(1) 96.1(2), S(1)–P(1)–N(1) 120.7(4), P(1)–N(1)–P(2) 134.8(6), N(1)–P(2)–O(2) 119.2(5), Au(1)–P(3)–N(3) 106.0(4), P(3)–N(3)–P(4) 132.4(6), N(3)–P(4)–O(4) 111.8(5). (b) Core geometry in **3** (all C atoms removed for clarity)

accounts for the *anti* conformation of the NH and P=O oxygen. In addition the S(1)–Au(1)–P(3)–N(3)–O(2)–P(2) portion of the ring is planar with a maximum deviation of 0.05 Å [for O(2)]. Both P(1) and N(1) lie above [1.36 and 1.00 Å respectively] and H(3b) below [−0.34 Å] the mean plane. The Au(1)–P(3) and Au(1)–S(1) distances [2.262(4) and 2.335(3) Å respectively] are normal whilst the bond lengths and angles within the S–P–N–P–O backbone are consistent with some degree of delocalisation. The P(1)–N(1)–P(2) angle in **3** is somewhat enlarged [134.8(6)°] as would be anticipated for a terminal bound ligand. In the crystal structure of **3**$\cdot$0.5$H_2O$$\cdot$0.5$CH_3OH$ the half weight H_2O and CH_3OH solvate molecules are H-bonded together.

Transmetallation of **1** (or **2**) with [$PdCl_2$(en)] (en = ethane-1,2-diamine) in a 2:1 molar ratio in CH_3OH gave [Pd{$Ph_2P(O)NP(E)Ph_2$-*E*}$_2$(en)] (E = S **5**; E = Se **6**) and which could be recrystallised from CH_2Cl_2–OEt_2 [or light petroleum (b.p. 60–80 °C)] [equation (2)]. Compounds **5** and **6** were characterised spectroscopically‡ and δ(P_O) for the co-ordinated [$Ph_2P(O)NP(E)Ph_2$]$^-$ ligand observed at δ 14.9 (for **5**) and 15.6



$$\text{H}_2\text{N–}\overset{\text{Cl}}{\text{Pd}}\text{–Cl}\ (\text{en}) \xrightarrow[\text{CH}_3\text{OH}]{\mathbf{1}\ (\text{or}\ \mathbf{2})} \text{H}_2\text{N–}\overset{\text{EPPh}_2\text{NP(O)Ph}_2}{\text{Pd}}\text{–EPPh}_2\text{NP(O)Ph}_2\ (\text{en}) \quad (2)$$

E = S **5**
E = Se **6**

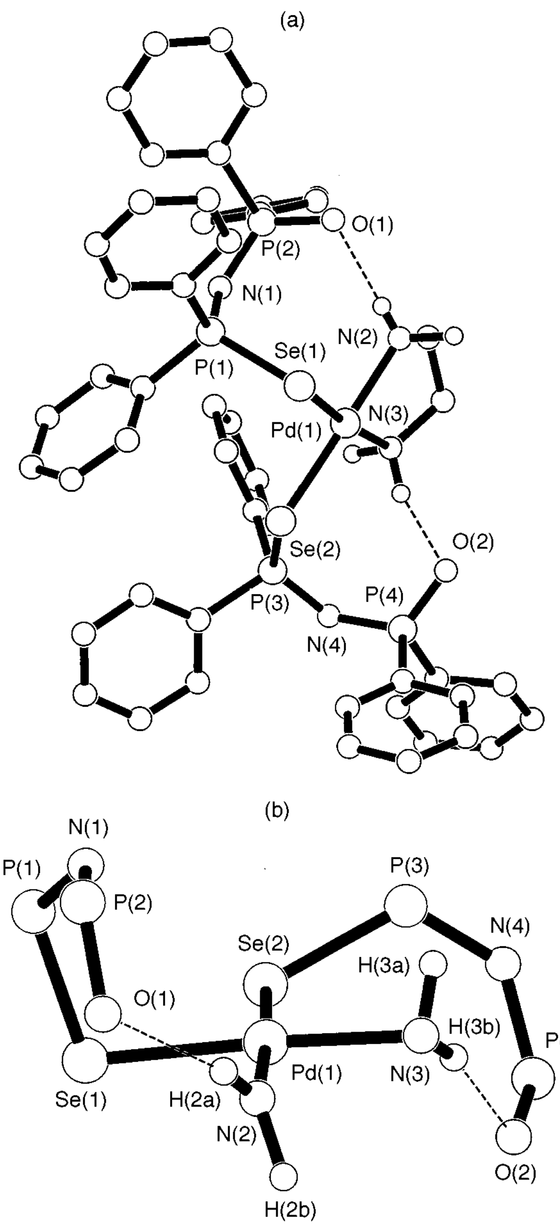


Fig. 2 (a) The crystal structure of **6** (solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (°): Pd(1)–Se(1) 2.413(1), Pd(1)–Se(2) 2.410(2), Pd(1)–N(2) 2.043(6), Pd(1)–N(3) 2.081(6), Se(1)–P(1) 2.199(2), P(1)–N(1) 1.580(6), N(1)–P(2) 1.605(6), P(2)–O(1) 1.493(6), Se(2)–P(3) 2.198(2), P(3)–N(4) 1.560(6), N(4)–P(4) 1.603(6), P(4)–O(2) 1.507(5); Se(1)–Pd(1)–Se(2) 85.16(4), Se(1)–Pd(1)–N(2) 91.2(2), Se(1)–Pd(1)–N(3) 174.7(2), Se(2)–Pd(1)–N(2) 175.9(2), Se(2)–Pd(1)–N(3) 99.9(2), N(2)–Pd(1)–N(3) 83.7(3), Pd(1)–Se(1)–P(1) 99.64(6), Se(1)–P(1)–N(1) 117.7(3), P(1)–N(1)–P(2) 131.2(4), N(1)–P(2)–O(1) 118.8(3), Pd(1)–Se(2)–P(3) 107.06(7), Se(2)–P(3)–N(4) 120.8(3), P(3)–N(4)–P(4) 133.3(4), N(4)–P(4)–O(2) 117.7(3). (b) Core geometry in **6** (all C atoms removed for clarity)

(for **6**) are similar to those values discussed for **3** and **4**. Furthermore the absence of ν(PdCl) vibrations is also consistent with the formation of **5** and **6**. A crystal structure§ [Fig. 2(a)] of **6**$\cdot$0.5OEt_2 shows the palladium centre to be bound by two terminal [$Ph_2P(O)NP(Se)Ph_2$-*Se*]$^-$ ligands and a bidentate $H_2NCH_2CH_2NH_2$ ligand in a slightly distorted square planar geometry with co-ordination angles in the range 83.7(3)–99.9(2) and 174.7(2)–175.9(2)°. The Pd–Se distances in **6** [2.413(1) and 2.410(2) Å] are slightly longer than those seen in *cis*-[Pd{$Ph_2P(O)NP(Se)Ph_2$-*O*,*Se*}$_2$] [2.381(7) and 2.383(8) Å].[4] The P–N bond lengths and angles in **6** are similar to those in **3**. Both [$Ph_2P(O)NP(Se)Ph_2$]$^-$ ligands are involved in intramolecular N–H···OP hydrogen bonding with $H_2NCH_2CH_2NH_2$ [N(2)···O(1) 2.79, H(2a)···O(1) 2.06 Å, N(2)–H(2a)···O(1) 168°; N(3)···O(2) 2.78, H(3b)···O(2) 1.85 Å, N(3)–H(3b)···O(2) 162°]. This leads to a spirocyclic arrangement composed of two eight-membered rings [Fig. 2(b)] about a central palladium(II) metal centre. The two PdN_2OP_2Se puckered rings are not identical [transannular separations Pd(1)···O(1) 4.13, Pd(1)···N(1) 3.71 Å; Pd(1)···O(2) 3.90, Pd(1)···N(4) 4.48 Å]. An intermolecular N–H···OP hydrogen bond is observed between H(2b) and O(2*) of an adjacent molecule [N(2)···O(2*) 2.87, H(2b)···O(2*) 2.05 Å, N(2)–H(2b)···O(2*) 128°].

Interestingly under similar conditions, reaction of the symmetrical ligands $[Ph_2P(E)NP(E)Ph_2]^-$ (E = S or Se) gave either the three-co-ordinate complexes [Au{$Ph_2P(E)NP(E)Ph_2$-*E*,*E′*}-(HL)] or the known[6] homoleptic complexes [Pd{$Ph_2P(E)NP(E)Ph_2$-*E*,*E′*}$_2$] in which substitution of all ligands has resulted. Surprisingly there are very few examples of related metal-β-diketonates (including monothio derivatives) that exhibit a unidentate mode of co-ordination akin to that observed here.[7,8] The ambidentate nature of **1** and **2** may lead to new complexes that could be of importance in catalytic systems. Further studies are currently in progress.

Acknowledgements

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