Reactions of $[R_2P(E)]_2NH$ (R = Ph or Pr^i, E = S or Se) with $[Ru_3(CO)_{12}]$: crystal structures of $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2NH\text{-}P,P'\}]$, $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(Pr^i{}_2P)_2NH\text{-}P,P'\}]$ and $[Ru_3(\mu_3\text{-}S)_2(CO)_7\{(Ph_2P)_2NH\text{-}P,P'\}]$

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

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

Oxidative addition of the chalcogenides $[R_2P(E)]_2NH$ (R = Ph or Pr^i, E = S or Se) to the metal carbonyl $[Ru_3(CO)_{12}]$ in the presence of Me_3NO (*ca.* 1 : 1 : 1 ratio) in toluene gave, after chromatographic separation (preparative TLC), new substituted tri- and tetra-nuclear capped sulfido (or selenido) ruthenium carbonyl complexes with $(Ph_2P)_2NH$ or $(Pr^i{}_2P)_2NH$ ligands. All compounds have been characterised by a combination of multinuclear NMR [$^{31}P\text{-}\{^1H\}$ and ^1H], IR spectroscopy and elemental analysis. Furthermore the solid-state structures of three representative examples, namely $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2NH\text{-}P,P'\}]$, $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(Pr^i{}_2P)_2NH\text{-}P,P'\}]$ and $[Ru_3(\mu_3\text{-}S)_2(CO)_7\{(Ph_2P)_2NH\text{-}P,P'\}]$ have been determined by single-crystal X-ray diffraction. In all these cases the integrity of the $[R_2P(E)]_2NH$ ligand, under the experimental conditions employed, is not retained.

Transition-metal chalcogenide compounds have received considerable attention as exemplified by the plethora of publications reported within the last few years.[1,2] One noticeable feature of many of these cluster compounds is the presence of both bridging chalcogenide anions and also tertiary phosphorus(III) ligands. The use of phosphorus(V) chalcogenide compounds, R_3PE, (E = chalcogen, R = alkyl or aryl group) as sources of R_3P and E has previously been documented. Recent work by Predieri and co-workers[2] demonstrated that $[Ph_2P(Se)]_2CH_2$ undergoes oxidative addition to the metal carbonyl $[Ru_3(CO)_{12}]$ affording a range of clusters (see later) including the novel cubane $[Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(dppm)]$ [dppm = $(Ph_2P)_2CH_2$].

We, and others, have been interested in the co-ordination chemistry of both $(Ph_2P)_2NH$ and $[\{Ph_2P(E)\}_2N]^-$ (E = O, S or Se), the latter derived upon deprotonation of $[Ph_2P(E)]_2NH$ with base.[3] Although numerous examples of bi- and tri-metallic complexes with the amine-backboned ligand $(Ph_2P)_2NH$ (dppa), closely related to $(Ph_2P)_2CH_2$, have been described, to our knowledge there are no reports of such compounds with ruthenium.[4] Diruthenium complexes with the diphosphazene bridges $(RO)_2PNEtP(OR)_2$ (R = Me or Pr^i) have previously been reported.[5] Here we describe our results on the reactivity of the tetraaryl-substituted $[Ph_2P(E)]_2NH$ (E = S and Se), closely related to $[Ph_2P(E)]_2CH_2$ (E = S or Se), and the tetraalkyl-substituted $[Pr^i{}_2P(S)]_2NH$, with $[Ru_3(CO)_{12}]$. The clusters $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2NH\text{-}P,P'\}]$, $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(Pr^i{}_2P)_2NH\text{-}P,P'\}]$ and $[Ru_3(\mu_3\text{-}S)_2(CO)_7\{(Ph_2P)_2NH\text{-}P,P'\}]$ have been fully characterised, including by X-ray crystallography. Interestingly the recently reported reaction of the mixed phosphorus(V) compound $Ph_2P(Se)NPPh_2PPh_2NP(Se)Ph_2$ with $[Ru_3(CO)_{12}]$ in the presence of Me_3NO afforded an unusual triruthenium cluster, namely $[Ru_3(CO)_6(\mu_3\text{-}Se)_2(\mu\text{-}PPh_2)(Ph_2PNPPh_2NPPh_2\text{-}N,P,P')]$, containing both the $[Ph_2PNPPh_2NPPh_2]^-$ ligand in a novel tridentate bonding mode and also capping diselenide ligands.[6]

Experimental

General

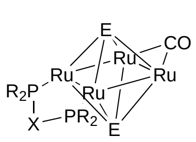
All reactions were performed under a nitrogen atmosphere using predried C_6H_5Me and standard Schlenk techniques. The compounds $[R_2P(E)]_2NH$ (R = Ph or Pr^i; E = S and Se, but not all permutations) were synthesized as reported previously.[7–9] The compounds $[Ru_3(CO)_{12}]$ and Me_3NO were used as supplied by Aldrich without further purification.

Infrared spectra were recorded either as KBr pellets or in CH_2Cl_2 on a Perkin-Elmer System 2000 Fourier-transform spectrometer, ^1H NMR spectra (250 MHz) on a Bruker AC250 Fourier-transform spectrometer with chemical shifts (δ) in ppm (±0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz (±0.1 Hz), $^{31}P\text{-}\{^1H\}$ NMR spectra (36.2 or 101.3 MHz) either on a JEOL FX90Q or Bruker AC250 Fourier-transform spectrometer with chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz (±3). 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 Service within the Department of Chemistry.

Preparations

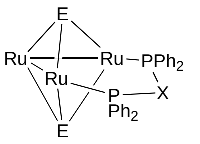
Reaction of $[Ru_3(CO)_{12}]$ with $[Ph_2P(Se)]_2NH$. The reagents $[Ru_3(CO)_{12}]$ (0.100 g, 0.156 mmol), $[Ph_2P(Se)]_2NH$ (0.086 g, 0.158 mmol) and Me_3NO (0.013 g, 0.173 mmol) were refluxed in C_6H_5Me (90 cm^3) for 1.5 h under N_2. The resulting dark red solution was evaporated to dryness and the residue dissolved in CH_2Cl_2 (2 cm^3). One product $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2NH\text{-}P,P'\}]$ **1** (distinct deep orange band) was separated by preparative thin-layer chromatography [SiO_2; eluent, CH_2Cl_2–light petroleum (b.p. 40–60 °C) (2 : 1, v/v)]. In addition several other bands were collected from which only minor amounts of uncharacterised material were obtained. Cluster **1** was recrystallised from CH_2Cl_2 (1.5 cm^3) and light petroleum (15 cm^3), the solid washed with portions of light petroleum (2 × 2 cm^3) and dried *in vacuo*. Yield: 0.074 g, 39% [Found (Calc. for $C_{33}H_{22}NO_{9.5}P_2Ru_4Se_2$): C, 32.9 (32.8); H, 1.0 (1.85); N, 0.95 (1.15)%]. IR: (KBr) 3263 (ν_{NH}); (CH_2Cl_2) 2046m, 2013vs, 1967m and 1808w cm^{-1} (ν_{CO}). NMR: $^{31}P\text{-}\{^1H\}$, δ 67.3; ^1H, δ 7.53–7.41 (aromatic H) and 4.86 (NH) [$^2J(P\text{-}NH)$ 10 Hz]. Slow diffusion of light petroleum into a CH_2Cl_2 solution of complex **1** over the course of *ca.* 3 d gave crystals suitable for X-ray crystallography.

In a similar manner the cluster $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(Pr^i{}_2P)_2NH\text{-}P,P'\}]$ **2** was isolated in low yield (9%) from



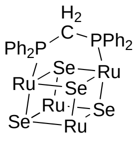
[$Ru_4(\mu_4\text{-}E)_2(\mu\text{-}CO)(CO)_8\{(R_2P)_2X\}$]

I E = Se, R = Ph, X = CH_2
1 E = Se, R = Ph, X = NH
2 E = S, R = Pr^i, X = NH
4 E = S, R = Ph, X = NH



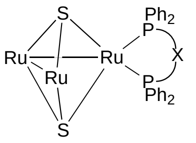
[$Ru_3(\mu_3\text{-}E)_2(CO)_7\{(R_2P)_2X\}$]

II E = Se, R = Ph, X = CH_2
3a E = S, R = Ph, X = NH



[$Ru_4(\mu_3\text{-}Se)_4(CO)_{10}\{(Ph_2P)_2CH_2\}$]

III



[$Ru_3(\mu_3\text{-}S)_2(CO)_7\{(Ph_2P)_2X\}$]

IV X = $C_5H_2O_2$
3b X = NH

[$Ru_3(CO)_{12}$] and [$Pr^i_2P(S)]_2NH$ [Found (Calc. for $C_{21}H_{29}NO_9P_2Ru_4S_2$): C, 26.05 (26.0); H, 2.65 (3.0); N, 1.5 (1.45)%]. IR: (KBr) 3291 (ν_{NH}); (CH_2Cl_2) 2048m, 2014vs, 2005m (sh), 1984w, 1969m, 1939w and 1811w cm^{-1} (ν_{CO}). NMR: $^{31}P\text{-}\{^1H\}$, δ 96.0; ^1H, δ 3.11 (NH) [^2J(P–N*H*) 10 Hz] in addition to the expected isopropyl resonances. Slow diffusion of light petroleum into a CH_2Cl_2 solution of complex **2** over the course of several months gave crystals suitable for X-ray crystallography.

Reaction of [$Ru_3(CO)_{12}$] with [$Ph_2P(S)]_2NH$. The reagents [$Ru_3(CO)_{12}$] (0.102 g, 0.160 mmol), [$Ph_2P(S)]_2NH$ (0.072 g, 0.160 mmol) and Me_3NO (0.014 g, 0.186 mmol) were refluxed in C_6H_5Me (90 cm^3) for 1.5 h under N_2. The resulting dark orange solution was evaporated to dryness and the residue dissolved in CH_2Cl_2 (2 cm^3). Two major products **3** (deep orange band) and then **4** (deep red band) were separated by preparative thin-layer chromatography [SiO_2; eluent, dichloromethane–light petroleum (1:1, v/v)] in addition to several other bands. Cluster **3** was isolated as an orange solid. Yield: 0.048 g, 32% [Found (Calc. for $C_{31.50}H_{22}ClNO_7P_2Ru_3S_2$): C, 37.1 (38.15); H, 2.1 (2.25); N, 1.45 (1.4)%]. IR: (KBr) 3313, 3302, 3281 (ν_{NH}); (CH_2Cl_2) 2068m, 2056s, 2013vs, 1989m (sh) and 1964m cm^{-1} (ν_{CO}). NMR: $^{31}P\text{-}\{^1H\}$, δ 106.8 and 75.0, 70.9 [^2J(PP) 38 Hz] (*ca.* 1:1 ratio of two species **3a** and **3b** from integration); ^1H, δ 7.71–7.38 (aromatic H), 4.75 and 3.07 (both NH) [^2J(P–N*H*) 7.5 Hz]. Slow diffusion of light petroleum into a CH_2Cl_2 solution of complex **3** over the course of *ca.* 4 d gave crystals of [$Ru_3(\mu_3\text{-}S)_2(CO)_7\{(Ph_2P)_2NH\text{-}P,P'\}$] **3a** suitable for X-ray crystallography. The cluster [$Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2NH\text{-}P,P'\}$] **4** was recrystallised from CH_2Cl_2 (1 cm^3) and light petroleum (15 cm^3), the solid washed with portions of light petroleum (2 × 3 cm^3) and dried *in vacuo*. Yield: 0.051 g, 29% [Found (Calc. for $C_{33}H_{21}NO_9P_2Ru_4S_2$): C, 36.1 (35.85); H, 1.65 (1.9); N, 1.1 (1.25)%]. IR: (KBr) 3266 (ν_{NH}); (CH_2Cl_2) 2050m, 2016vs, 1971m and 1814m cm^{-1} (ν_{CO}). NMR: $^{31}P\text{-}\{^1H\}$, δ 71.6; ^1H, δ 7.49–7.41 (aromatic H) and 4.39 (NH) [^2J(P–N*H*) 10 Hz].

X-Ray crystallography

The crystal structures of complexes **1**–**3a** were obtained using a Rigaku AFC7S diffractometer with graphite-monochromated (Cu-Kα, λ = 1.541 78 Å) radiation and ω scans at room temperature. Details of the data collections and refinements are given in Table 1. Empirical absorption corrections (DIFABS)[10] were applied. The structures were solved by the heavy-atom method.[11] Compound **1** contained 0.5 H_2O as a solvent of crystallisation. The O atom was refined isotropically and the H atoms were not located. In **3a** a 0.5 CH_2Cl_2 solvate was refined with one 50% Cl atom anisotropic and the 50% C and two 25% Cl sites isotropic; the partial weight H atoms were not located. All of the other non-hydrogen atoms were refined anisotropically. The CH atoms were idealised and fixed (C–H 0.95 Å). No additional constraints or restraints were applied. Refinements (based on *F*) were by full-matrix least-squares methods. Calculations were performed using TEXSAN.[12]

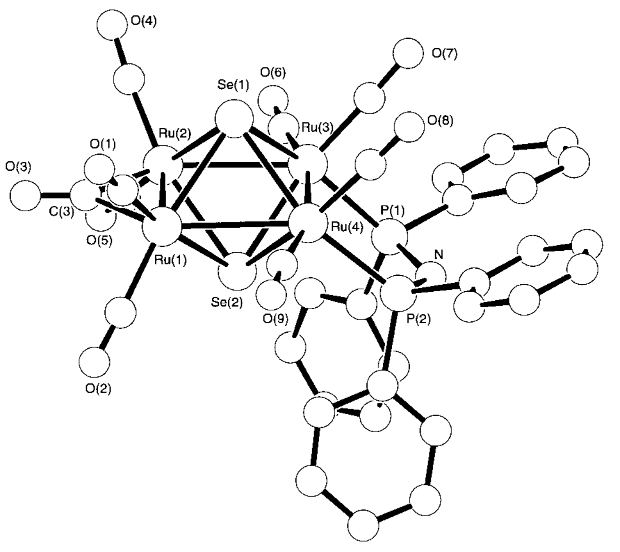


Fig. 1 Molecular structure of [$Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2NH\text{-}P,P'\}]\cdot0.5H_2O$ **1** (CH, NH protons and solvent molecules omitted for clarity)

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.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/489.

Results and Discussion

The synthesis and spectroscopic characterisation of [$Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2CH_2\text{-}P,P'\}$] **I**, [$Ru_3(\mu_3\text{-}Se)_2(CO)_7\{(Ph_2P)_2CH_2\text{-}P,P'\}$] **II** and [$Ru_4(\mu_3\text{-}Se)_4(CO)_{10}\{(Ph_2P)_2CH_2\text{-}P,P'\}$] **III** containing the carbon-spaced diphosphine ligand $(Ph_2P)_2CH_2$, was recently reported by Predieri and co-workers.[2] Adopting a similar procedure, we now find that analogues of **I** and **II** can be prepared in reasonable yields using the corresponding compounds [$Ph_2P(E)]_2NH$ (E = Se or S). Hence refluxing [$Ru_3(CO)_{12}$], [$Ph_2P(Se)]_2NH$ and the oxidative decarbonylation reagent Me_3NO (*ca.* 1:1:1.1 ratio) in C_6H_5Me under N_2 affords [$Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2NH\text{-}P,P'\}$] **1** in 39% yield after chromatography (preperative TLC) compared to only 5% yield reported for **I**.[2] We also observe the formation of a variety of other minor products from this reaction; the exact identity of these remains currently unknown. Complex **1** was initially characterised by $^{31}P\text{-}\{^1H\}$ and ^1H NMR, IR spectroscopy and elemental analysis. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet at δ 67.3 shifted to high frequency with respect to free dppa (δ 43.2) by *ca.* 24 ppm. In the ^1H NMR spectrum ($CDCl_3$) the expected triplet at δ 4.86 for the NH proton [^2J(P–N*H*) 10 Hz] was observed, suggesting the equivalence of the two phosphorus nuclei. In contrast, for free $(Ph_2P)_2NH$ δ(NH) 3.15 [^2J(P–N*H*) 5 Hz]. In the IR spectrum (KBr disc) of **1** a sharp band at 3263 cm^{-1} was observed and assigned as ν_{NH}, whilst in solution (CH_2Cl_2) bands at 2046, 2013, 1967 and 1808 cm^{-1} indicate that **1** contains both terminal and bridging carbonyl ligands. Under similar conditions reaction of the tetraalkyl-substituted disulfide [$Pr^i_2P(S)]_2NH$ gave [$Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(Pr^i_2P)_2NH\}$] **2** albeit in low yield (9%) along with several other uncharacterised products. The

^{31}P-{^{1}H} NMR spectrum showed a singlet at δ 96.0 {*cf.* 91.2 ppm for [$\mathrm{Pr^i_2P(S)]_2NH}$}[9] and in the ^{1}H NMR spectrum ($\mathrm{CDCl_3}$) the expected triplet at δ 3.11 for the NH proton [^{2}J(P–N*H*) 10 Hz] was observed, suggesting again the equivalence of the two phosphorus nuclei. Solutions of the nonacarbonyls **1** and **2** (or **4**, see later) are stable in air for extended periods (*ca.* 20 d) without decomposition. Alternatively when compound **1** (or 4) was refluxed in $\mathrm{C_6H_5Me}$ (under $\mathrm{N_2}$) for 24 h no significant decomposition was noted. In the IR spectrum (KBr disc) of **2** a sharp band at 3291 cm^{-1} assigned to ν_{NH} was also observed whilst in solution ($\mathrm{CH_2Cl_2}$) bands at 2048, 2014, 2005, 1984, 1969, 1939 and 1811 cm^{-1} indicate that **2** contains both terminal and bridging carbonyl ligands.

The structures of **1** and **2** have been established by X-ray crystallography (Figs. 1, 2 and Table 2 respectively). Compounds **1** and **2** are essentially isostructural. The clusters adopt octahedral geometries with the four ruthenium atoms in a square plane [maximum deviation from the Ru(1)–Ru(2)–Ru(3)–Ru(4) mean plane is 0.013 and 0.04 Å for **1** and **2** respectively] and the chalcogenide dianions lying above and below the $\mathrm{Ru_4}$ plane [in **1** atoms Se(1) and Se(2) lie 1.64 and 1.65 Å above and below the $\mathrm{Ru_4}$ plane whilst in **2** atoms S(1) and S(2) lie 1.51 and 1.55 Å from the plane]. The carbonyl group which bridges Ru(1) and Ru(2) is almost coplanar with the $\mathrm{Ru_4}$ plane [the C(3) atom lies 0.03 and 0.09 Å out of the $\mathrm{Ru_4}$ plane for **1** and **2** respectively]. The Ru–Ru bond lengths are in the range 2.737(2) [Ru(3)–Ru(4)]–2.851(2) [Ru(1)–Ru(4)] Å for **1** and 2.729(1) [Ru(1)–Ru(2)]–2.797(1) [Ru(2)–Ru(3)] Å for **2**. The P–N–P ligand is inclined to the $\mathrm{Ru_4}$ plane (43 and 41° for **1** and **2** respectively) and furthermore in these ligands the P–N bonds are normal single bonds and the N atom is almost perfectly trigonal. We are unaware of any metal complexes of $\mathrm{(Pr^i_2P)_2NH}$ although there are a few reports on $\mathrm{[\{Pr^i_2P(S)\}_2N]^-}$.[9,13]

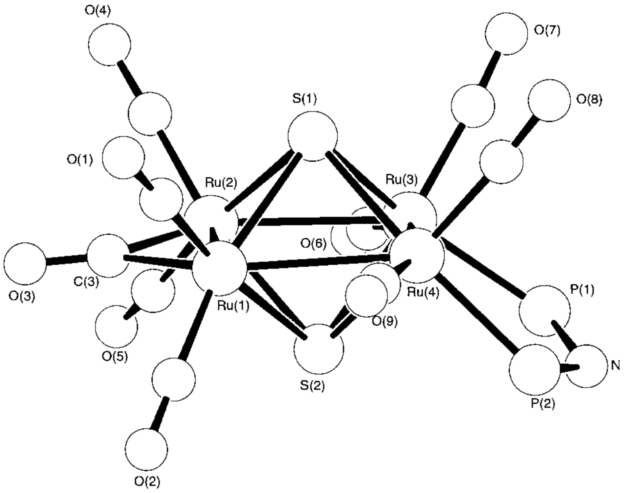


Fig. 2 Molecular structure of $\mathrm{[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(Pr^i_2P)_2NH\text{-}}$*P,P′*}] **2** showing the core geometry only (isopropyl groups and the NH proton omitted for clarity)

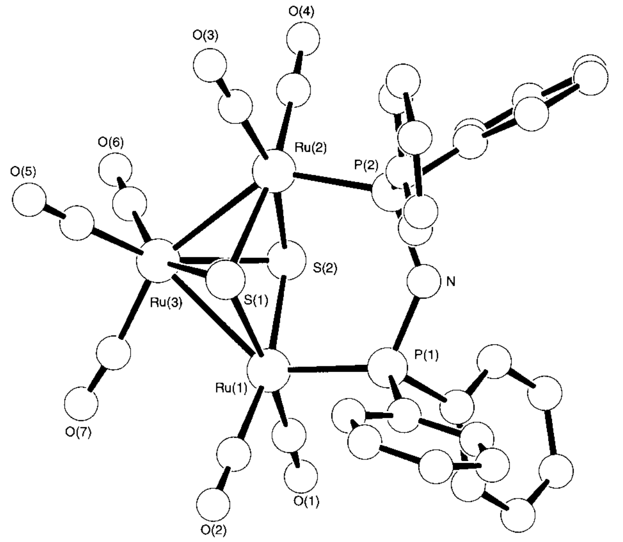


Fig. 3 Molecular structure of $\mathrm{[Ru_3(\mu_3\text{-}S)_2(CO)_7\{(Ph_2P)_2NH\text{-}}$*P,P′*}]·$\mathrm{0.5CH_2Cl_2}$ **3a** (CH, NH protons and solvent molecules omitted for clarity)

Table 1 Details of the X-ray data collections and refinements for compounds **1**–**3a**

	1	**2**	**3a**
Empirical formula	$\mathrm{C_{33}H_{22}NO_{9.5}P_2Ru_4Se_2}$	$\mathrm{C_{21}H_{29}NO_9P_2Ru_4S_2}$	$\mathrm{C_{31.50}H_{22}ClNO_7P_2Ru_3S_2}$
M	1208.69	969.81	991.25
Crystal colour, habit	Red, needle	Orange-red, needle	Red, block
Crystal dimensions/mm	0.01 × 0.06 × 0.28	0.10 × 0.13 × 0.30	0.20 × 0.30 × 0.30
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	15.656(3)	13.363(2)	12.276(2)
b/Å	16.971(4)	13.680(2)	13.897(1)
c/Å	16.488(3)	17.294(2)	11.660(2)
α/°			104.32(1)
β/°	92.87(1)	90.78(1)	99.15(1)
γ/°			92.71(1)
U/Å^3	4375	3161	1895
Z	4	4	2
D_c/g cm^3	1.84	2.04	1.74
μ/mm^{-1}	13.98	17.80	12.42
$2\theta_{\mathrm{max}}$/°	120.3	120.2	120.2
F(000)	2308	1888	970
Measured reflections	7051	5185	5963
Independent reflections (R_{int})	6773 (0.098)	4947 (0.043)	5658 (0.072)
Observed reflections [I>3.00σ(I)]	3485	3548	4910
Reflection/parameter ratio	7.5:1	10.1:1	11.4:1
Minimum, maximum transmission	0.67, 1.00	0.59, 1.00	0.90, 1.00
P in weighting scheme*	0.005	0.002	0.004
No. variables	465	353	437
Final *R*, *R′**	0.044, 0.050	0.032, 0.031	0.038, 0.041
Maximum Δ/σ	0.52	0.01	0.52
Largest difference peak, hole/e Å^{-3}	0.98, −0.48	0.50, −0.53	1.05, −0.79

* All *R* indices and weighting scheme defined in ref. 12.

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

	1 (E = Se)	**2** (E = S)		**1** (E = Se)	**2** (E = S)
Ru(1)–Ru(2)	2.758(2)	2.729(1)	Ru(3)–E(2)	2.555(2)	2.469(2)
Ru(1)–Ru(4)	2.851(2)	2.787(1)	Ru(3)–P(1)	2.287(4)	2.322(2)
Ru(1)–E(1)	2.578(2)	2.516(2)	Ru(4)–E(1)	2.552(2)	2.439(2)
Ru(1)–E(2)	2.576(2)	2.470(2)	Ru(4)–E(2)	2.579(2)	2.494(2)
Ru(1)–C(3)	2.04(2)	2.031(7)	Ru(4)–P(2)	2.298(4)	2.304(2)
Ru(2)–Ru(3)	2.828(2)	2.797(1)	Ru–C range (terminal)	1.80(2)–1.91(2)	1.846(8)–1.899(8)
Ru(2)–E(1)	2.571(2)	2.450(2)	P(1)–N	1.675(11)	1.694(5)
Ru(2)–E(2)	2.589(2)	2.525(2)	P(2)–N	1.694(11)	1.687(6)
Ru(2)–C(3)	2.03(2)	2.032(7)	C(3)–O(3) (bridging)	1.16(2)	1.167(8)
Ru(3)–Ru(4)	2.737(2)	2.730(1)	C–O range (terminal)	1.09(2)–1.19(2)	1.13(1)–1.16(1)
Ru(3)–E(1)	2.567(2)	2.457(2)			
Ru(2)–Ru(1)–Ru(4)	89.7(1)	90.0(1)	Ru(4)–Ru(3)–P(1)	93.8(1)	91.3(1)
Ru(2)–Ru(1)–E(1)	57.5(1)	55.5(1)	E(1)–Ru(3)–E(2)	79.9(1)	76.6(1)
Ru(2)–Ru(1)–E(2)	58.0(1)	57.9(1)	E(1)–Ru(3)–P(1)	151.1(1)	145.6(1)
Ru(4)–Ru(1)–E(1)	55.8(1)	54.5(1)	E(2)–Ru(3)–P(1)	87.0(1)	94.8(1)
Ru(4)–Ru(1)–E(2)	56.5(1)	56.2(1)	Ru(1)–Ru(4)–Ru(3)	89.8(1)	90.1(1)
E(1)–Ru(1)–E(2)	79.3(1)	75.5(1)	Ru(1)–Ru(4)–E(1)	56.7(1)	57.1(1)
Ru(1)–Ru(2)–Ru(3)	89.9(1)	89.9(1)	Ru(1)–Ru(4)–E(2)	56.4(1)	55.4(1)
Ru(1)–Ru(2)–E(1)	57.7(1)	57.8(1)	Ru(1)–Ru(4)–P(2)	138.7(1)	132.2(1)
Ru(1)–Ru(2)–E(2)	57.5(1)	55.9(1)	Ru(3)–Ru(4)–E(1)	58.0(1)	56.4(1)
Ru(3)–Ru(2)–E(1)	56.5(1)	55.4(1)	Ru(3)–Ru(4)–E(2)	57.4(1)	56.2(1)
Ru(3)–Ru(2)–E(2)	56.1(1)	55.0(1)	Ru(3)–Ru(4)–P(2)	92.6(1)	95.7(1)
E(1)–Ru(2)–E(2)	79.2(1)	75.6(1)	E(1)–Ru(4)–E(2)	79.8(1)	76.4(1)
Ru(2)–Ru(3)–Ru(4)	90.6(1)	89.8(1)	E(1)–Ru(4)–P(2)	149.5(1)	152.0(1)
Ru(2)–Ru(3)–E(1)	56.7(1)	55.1(1)	E(2)–Ru(4)–P(2)	91.2(1)	89.5(6)
Ru(2)–Ru(3)–E(2)	57.2(1)	56.9(1)	Ru–E–Ru range	64.4(1)–101.1(1)	66.2(1)–105.9(1)
Ru(2)–Ru(3)–P(1)	133.9(1)	144.4(1)	Ru(3)–P(1)–N(1)	110.9(4)	113.6(2)
Ru(4)–Ru(3)–E(1)	57.4(1)	55.8(1)	Ru(4)–P(2)–N(1)	112.2(4)	109.8(2)
Ru(4)–Ru(3)–E(2)	58.2(1)	57.1(1)	P(1)–N(1)–P(2)	126.1(6)	127.6(3)

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

Ru(1)–Ru(3)	2.811(1)	Ru(3)–S(1)	2.406(2)
Ru(1)–S(1)	2.367(2)	Ru(3)–S(2)	2.411(2)
Ru(1)–S(2)	2.369(2)	Ru–C range	1.870(8)–1.905(8)
Ru(1)–P(1)	2.267(2)		
Ru(2)–Ru(3)	2.771(1)	P(1)–N	1.691(5)
Ru(2)–S(1)	2.373(2)	P(2)–N	1.697(5)
Ru(2)–S(2)	2.372(2)	C–O range	1.132(8)–1.149(9)
Ru(2)–P(2)	2.281(2)		
Ru(3)–Ru(1)–S(1)	54.6(1)	Ru(1)–Ru(3)–S(2)	53.3(1)
Ru(3)–Ru(1)–S(2)	54.7(1)	Ru(2)–Ru(3)–S(1)	54.0(1)
Ru(3)–Ru(1)–P(1)	134.6(1)	Ru(2)–Ru(3)–S(2)	54.0(1)
S(1)–Ru(1)–S(2)	80.9(1)	S(1)–Ru(3)–S(2)	79.3(1)
S(1)–Ru(1)–P(1)	92.9(1)	Ru(1)–S(1)–Ru(2)	97.4(1)
S(2)–Ru(1)–P(1)	93.3(1)	Ru(1)–S(1)–Ru(3)	72.1(1)
Ru(3)–Ru(2)–S(1)	55.1(1)	Ru(2)–S(1)–Ru(3)	70.9(1)
Ru(3)–Ru(2)–S(2)	55.3(1)	Ru(1)–S(2)–Ru(3)	97.3(1)
Ru(3)–Ru(2)–P(2)	136.0(1)	Ru(1)–S(2)–Ru(3)	72.0(1)
S(1)–Ru(2)–S(2)	80.8(1)	Ru(2)–S(2)–Ru(3)	70.8(1)
S(1)–Ru(2)–P(2)	92.2(1)	Ru(1)–P(1)–N	115.8(2)
S(2)–Ru(2)–P(2)	94.7(1)	Ru(2)–P(2)–N	114.5(2)
Ru(1)–Ru(3)–Ru(2)	79.3(1)	P(1)–N–P(2)	137.7(3)
Ru(1)–Ru(3)–S(1)	53.3(1)		

The corresponding reaction of the disulfide $[Ph_2P(S)]_2NH$ with $[Ru_3(CO)_{12}]$ yields, after chromatography, two major products identified as $[Ru_3(\mu_3\text{-}S)_2(CO)_7\{(Ph_2P)_2NH\text{-}P,P'\}]$ **3** (32%) (two isomers) and $[Ru_4(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_8\{(Ph_2P)_2NH\text{-}P,P'\}]$ **4** (29%). Compound **4** is ostensibly similar to both **1** and **2** described above and shows the expected spectroscopic properties. In contrast the $^{31}P\text{-}\{^1H\}$ NMR spectrum ($CDCl_3$) of **3** at ambient temperature reveals the presence of two species **3a** and **3b** (*ca.* 1:1 ratio by integration): **3a** has δ 106.8 (*cf.* 43.2 for dppa) indicating equivalent phosphorus nuclei and **3b** exhibits an AB spectrum [δ 75.0 and 70.9, ^2J(PP) 38 Hz] consistent with a compound containing unsymmetrical phosphorus nuclei. When an NMR sample was cooled in 10 °C increments from 0 to −50 °C no change in either the spectra nor the ratio of species was observed. Deuteriochloroform solutions of **3** decompose over *ca.* 2 d in air which contrasts with the stability of **1**, **2** and **4**. The presence of both **3a** and **3b** in solution is also mirrored in the ^1H NMR spectrum which shows two NH resonances (see Experimental section). The structure of **3b** is not entirely apparent but we tentatively suggest it may be analogous to that of $[Ru_3(\mu_3\text{-}S)_2(CO)_7(bpcd)]$ **IV** [bpcd = 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione],[14] in which both P nuclei are bound to one ruthenium centre. In our hands we have so far been unable to separate these compounds by chromatography (TLC). However layering a CH_2Cl_2 solution of **3** with light petroleum (b.p. 40–60 °C) gave crystals of **3a** suitable for X-ray crystallography. The structure of **3a** is shown in Fig. 3 with selected bond lengths and angles collected in Table 3. In **3a** the S(1) and S(2) atoms lie ±1.54 Å from the Ru_3 plane with the P–N–P ligand being inclined by only 16° to the Ru_3 plane. The Ru(1)–Ru(3) and Ru(2)–Ru(3) distances [2.811(1) and 2.771(1) Å] are similar to those in **1** and **2** but the Ru(1)···Ru(2) distance (3.56 Å) is essentially non-bonding. This distance is shorter than that observed in related Ru_3 clusters.[14–18] This leads to an increase in the P–N–P angle to accommodate the larger bite in **3a** *versus* **1** and **2** [the P–N–P angles are 137.7(3), 126.1(6) and 127.6(3)° respectively]. In contrast, experimental[19] and calculated[20] P–N–P angles for free $(Ph_2P)_2NH$ are 118.9(2) (from X-ray crystallography) and 122.62° respectively. Furthermore, the P–N–P angle in **3a** is considerably larger than previously observed in other bi- and tri-metallic compounds of dppa [112.7(3)–125.2(6)° range] with M–M bonds.[4] The P–N bond lengths in **3a** [1.691(5) Å for P(1)–N(1) and 1.697(5) Å for P(2)–N(1)] are similar to those in $(Ph_2P)_2NH$ [1.692(3) Å][19] and **1** [1.675(11) Å for P(1)–N(1) and 1.694(11) Å for P(2)–N(1)]. The Ru(1) and Ru(2) centres are each bound to two terminal carbonyl ligands and Ru(3) is co-ordinated to three, whilst the Ru–P bond lengths in **3a** [2.267(2) and 2.281(2) Å] are as expected.

Further work currently in progress is aimed at seeking to extend the methodology to other bidentate phosphines with nitrogen-containing backbones.

Acknowledgements

We are grateful to the EPSRC for support.

References

1 W.-Y. Yeh, C. Stern and D. F. Shriver, *Inorg. Chem.*, 1996, **35**, 7857; C. Goh, B. M. Segal, J. Huang, J. R. Long and R. H. Holm, *J. Am. Chem. Soc.*, 1996, **118**, 11 844; S. Dehnen and D. Fenske, *Chem. Eur. J.*, 1996, **2**, 1407; P. Baistrocchi, M. Careri, D. Cauzzi, C. Graiff, M. Lanfranchi, P. Manini, G. Predieri and A. Tiripicchio, *Inorg. Chim. Acta*, 1996, **252**, 367; F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini and A. Bencini, *J. Chem. Soc., Dalton Trans.*, 1996, 3991; S. Behrens, M. Bettenhausen, A. C. Deveson, A. Eichhöfer, D. Fenske, A. Lohde and U. Woggon, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2215; V. W.-W. Yam, K. K.-W. Lo and K.-K. Cheung, *Inorg. Chem.*, 1996, **35**, 3459; V. W.-W. Yam, K. K.-W. Lo, C.-R. Wang and K.-K. Cheung, *Inorg. Chem.*, 1996, **35**, 5116; S. Kamiguchi, H. Imoto and T. Saito, *Chem. Lett.*, 1996, 555; G. M. Ferrence, P. E. Fanwick and C. P. Kubiak, *Chem. Commun.*, 1996, 1575; A. Bencini, F. Fabrizi de Biani and M. G. Uytterhoeven, *Inorg. Chim. Acta*, 1996, **244**, 231; J. Mizutani, S. Yamada, H. Imoto and T. Saito, *Inorg. Chem.*, 1996, **35**, 244; F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini, P. Zanello, A. Cinquantini, A. Bencini, M. G. Uytterhoeven and G. Giorgi, *J. Chem. Soc., Dalton Trans.*, 1995, 3881; L. C. Roof and J. W. Kolis, *Chem. Rev.*, 1993, **93**, 1037.

2 D. Cauzzi, C. Graiff, M. Lanfranchi, G. Predieri and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1995, 2321.

3 P. Bhattacharyya and J. D. Woollins, *Polyhedron*, 1995, **14**, 3367; J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 2893 and refs. therein.

4 C. S. Browning, D. H. Farrar, D. C. Frankel and J. J. Vittal, *Inorg. Chim. Acta*, 1997, **254**, 329; F. A. Cotton and F. E. Kühn, *Inorg. Chim. Acta*, 1996, **252**, 257; D. L. Arnold, F. A. Cotton and F. E. Kühn, *Inorg. Chem.*, 1996, **35**, 4733, 5764; D. Pohl, J. Ellermann, M. Moll, F. A. Knoch and W. Bauer, *Z. Anorg. Allg. Chem.*, 1996, **622**, 283; D. Pohl, J. Ellermann, F. A. Knoch, M. Moll and W. Bauer, *Chem. Ber.*, 1994, **127**, 2167; *J. Organomet. Chem.*, 1994, **481**, 259; J. Ellermann and K. J. Meier, *Z. Anorg. Allg. Chem.*, 1991, **603**, 77; J. Ellermann, F. A. Knoch and K. J. Meier, *Z. Naturforsch., Teil B*, 1990, **45**, 1657; M. T. Costello, D. R. Derringer, P. E. Fanwick, A. C. Price, M. I. Rivera, E. Scheiber, E. W. Siurek III and R. A. Walton, *Polyhedron*, 1990, **9**, 573; D. E. Derringer, P. E. Fanwick, J. Moran and R. A. Walton, *Inorg. Chem.*, 1989, **28**, 1384; R. Usón, J. Fornies, R. Navarro, M. Tomas, C. Fortuno, J. I. Cebollada and A. J. Welch, *Polyhedron*, 1989, **8**, 1045; R. Usón, A. Laguna, M. Laguna, M. N. Fraile, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1986, 291; G. Liehr, G. Szucsányi and J. Ellermann, *J. Organomet. Chem.*, 1984, **265**, 95.

5 K. J. Edwards, J. S. Field, R. J. Haines, B. D. Homann, M. W. Stewart, J. Sundermeyer and S. F. Wollam, *J. Chem. Soc., Dalton Trans.*, 1996, 4171; J. S. Field, R. J. Haines, M. W. Stewart and S. F. Woollam, *J. Chem. Soc., Dalton Trans.*, 1996, 1031.

6 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Chem. Commun.*, 1996, 2095.

7 I. Haiduc, in *Inorganic Experiments*, ed. J. D. Woollins, VCH, Weinheim, 1994.

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

9 D. Cupertino, R. Keyte, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 2695.

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

11 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.

12 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Woodlands, TX, 1985, 1992.

13 D. Cupertino, R. Keyte, A. M. Z. Slawin, J. D. Woollins and D. J. Williams, *Polyhedron*, 1996, **15**, 4441.

14 H. Shen, S. G. Bott and M. G. Richmond, *Inorg. Chim. Acta*, 1996, **241**, 71.

15 P. Baistrocchi, D. Cauzzi, M. Lanfranchi, G. Predieri, A. Tiripicchio and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1995, **235**, 173.

16 T. M. Layer, J. Lewis, A. Martín, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1992, 3411.

17 B. F. G. Johnson, T. M. Layer, J. Lewis, A. Martín and P. R. Raithby, *J. Organomet. Chem.*, 1992, **429**, C41.

18 B. F. G. Johnson, J. Lewis, P. G. Lodge and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1979, 719.

19 H. Nöth and E. Fluck, *Z. Naturforsch., Teil B*, 1984, **39**, 744.

20 C. S. Browning, D. H. Farrar and M. R. Peterson, *J. Mol. Struct.*, 1991, **251**, 153.

Received 15*th January* 1997; *Paper* 7/00383H