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Late transition metal complexes derived from diphosphazane monosulfide ligands: X-ray crystal structures of $[Ru_3(\mu\text{-}CO)(CO)_7(\mu_3\text{-}S)\{Ph_2PN((S)\text{-}*CHMePh)PPh_2\text{-}\kappa^2P,P\}]$ and $[Rh(CO)Cl\{Ph_2PN((S)\text{-}*CHMePh)P(S)Ph_2\}\text{-}\kappa^2P,S]$ Part 16. Organometallic chemistry of diphosphazanes☆

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Abstract

The oxidative addition reactions of diphosphazane monosulfides, $Ph_2PN(R)P(S)Ph_2$ (R = (*S*)-*CHMePh (**1**), $CHMe_2$ (**2**)) with $[Ru_3(CO)_{12}]$ afford sulfur-monocapped triruthenium clusters of the type $[Ru_3(\mu\text{-}CO)(CO)_7(\mu_3\text{-}S)\{Ph_2PN(R)PPh_2\text{-}\kappa^2P,P\}]$ (R = (*S*)-*CHMePh (**3**), $CHMe_2$ (**4**)); the X-ray crystal structure of **3** reveals the chelating mode of coordination of the diphosphazane ligand, which is rarely observed for such type of complexes. The bridge-splitting reactions of **1** and **2** with $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ yield $[Rh(CO)Cl\{Ph_2PN(R)P(S)Ph_2\text{-}\kappa^2P,S\}]$ (R = (*S*)-*CHMePh (**5**), $CHMe_2$ (**6**)); the X-ray crystal structure of **5** confirms that the 'CO' ligand is *trans* to the P=S bond. The reactions of $[MCl_2(COD)]$ with **1** and **2** yield chelate complexes, $[MCl_2\{Ph_2PN(R)P(S)Ph_2\text{-}\kappa^2P,S\}]$ [M = Pd (**7** and **8**) or Pt (**9** and **10**)].

Keywords: Chiral phosphorus ligands; Cluster compounds; Organometallic compounds; P,S-donor ligands

1. Introduction

Heterofunctional ligands containing soft and hard donor sites have attracted considerable attention as they are expected to generate transition metal complexes, which are efficient for various catalytic transformations [1–4]. Transition metal complexes bearing P,S-donor ligands have been used as catalysts for hydroformylation [2,3] and hydrogenation [4] reactions. Heterofunctional diphosphazanes of the type $X_2PN(R)P(E)X_2$ containing phosphorus and other donor atoms such as sulfur, oxygen or nitrogen would display interesting coordination chemistry [5–8]. In continuation of our work on the organometallic chemistry of diphosphazane type ligands [9–11], herein we report the reactions of diphosphazane monosulfides, $Ph_2PN(R)P(S)Ph_2$ (R = (*S*)-*CHMePh (**1**) or $CHMe_2$ (**2**)) with $[Ru_3(CO)_{12}]$, $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ and $[MCl_2(1,5\text{-}COD)]$ (M = Pd, Pt) (1,5-COD = 1,5-cyclooctadiene). The molecular structures of the complexes $[Ru_3(\mu\text{-}CO)(CO)_7(\mu_3\text{-}S)\{Ph_2PN(R)PPh_2\text{-}\kappa^2P,P\}]$ (**3**) and $[Rh(CO)Cl\{Ph_2PN(R)P(S)Ph_2\text{-}\kappa^2P,S\}]$ (**5**) (R = (*S*)-*CHMePh) have been confirmed by single crystal X-ray diffraction. A part of this work has appeared in a Conference Proceedings [11]. The synthesis of chiral diphosphazane monosulfide (**1**) and its reactions with Rh(I), Rh(III) and Ir(III) complexes were reported while this manuscript was under preparation [12].

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2. Experimental

2.1. General procedures

All the reactions and manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques. The solvents were purified and distilled under argon prior to use. Infrared spectra were recorded on a Bruker FTIR spectrometer using thin film samples in KBr disc. The ^{1}H- and ^{31}P-NMR spectra were recorded on a Bruker ACF-200 spectrometer in $CDCl_3$ solutions at 25 °C using Me_4Si or 85% H_3PO_4 (ext) as reference standards, respectively. The diphosphazane monosulfide (**2**) [5], [{Rh(μ-Cl)$(CO)_2$}$_2$] [13], [MCl_2(COD)] [M = Pd(II), Pt(II)] [14] were synthesized by published procedures. [$Ru_3(CO)_{12}$] (Strem) and $Me_3NO{\cdot}2H_2O$ (Aldrich) were used as received.

2.2. Synthesis of $Ph_2PN(R)P(S)Ph_2$ ($R = (S)$-*CHMePh (**1**))

Elemental sulfur (0.033 g, 1.02×10^{-3} mol) was added to a solution of the diphosphazane, $Ph_2PN((S)$-*CHMePh)PPh_2 [10] (0.50 g, 1.02×10^{-3} mol) in benzene (30 ml). The mixture was heated under reflux for 2 h, concentrated in vacuo to ~15 ml, and kept at 25 °C for 12 h to yield the diphosphazane monosulfide (**1**) as colorless crystals in 85–90% yield. If the concentrated solution did not give crystals of **1** after a day, a flash column chromatography on a silica gel column using petrol–ethylacetate (9:1 v/v) as eluant was performed to yield **1** in a pure form (yield 70%). M.p. 170–172 °C (lit. [12] 172–174 °C); Anal. Calc. for $C_{32}H_{29}NP_2S$: C, 73.7; H, 5.6; N, 2.7. Found: C, 73.9; H, 5.6; N, 2.4%. ^{1}H-NMR ($CDCl_3$, ppm): 7.77–7.06 (m, aryl protons), 5.17 (m, CH–*CHMePh), 1.82 (d, $^{3}J_{HH} = 7.0$ Hz, CH_3–*CHMePh).

2.3. Synthesis of [$Ru_3(\mu\text{-}CO)(CO)_7(\mu_3\text{-}S)\{Ph_2PN(R)PPh_2\text{-}\kappa^2P,P\}$] [$R = (S)$-*CHMePh (**3**) or $CHMe_2$ (**4**)]

A mixture of [$Ru_3(CO)_{12}$] (0.050 g, 7.82×10^{-5} mol), $Ph_2PN(R)P(S)Ph_2$ (0.041 g for R = (*S*)-*CHMePh, 0.036 g for R = $CHMe_2$, 7.82×10^{-5} mol) and $Me_3NO{\cdot}2H_2O$ (0.006 g, 8.60×10^{-5} mol) was dissolved in toluene (20 ml). The solution was heated under reflux for 1 h. The resulting dark red solution was evaporated to dryness and the residue dissolved in CH_2Cl_2 (2 ml). The title complexes were isolated by preparative TLC on silica, using CH_2Cl_2–petrol (1:1) as eluant (red band; R_f 0.9). (yield 25–30%).

Complex **3**: m.p. 186–188 °C. Anal. Calc. for $C_{40}H_{29}NO_8P_2Ru_3S$: C, 45.8; H, 2.8; N, 1.3. Found: C, 45.7; H, 2.8; N, 1.3%. IR (ν(C≡O), cm^{-1}): 2058s, 2015vs, 1984s, 1878m 1814w. ^{1}H-NMR ($CDCl_3$, ppm): 7.8–6.4 (m, aryl protons), 4.32 (m, CH–*CHMePh), 0.99 (d, $^{3}J_{HH} = 7.1$ Hz, CH_3–*CHMePh). ^{31}P-NMR ($CDCl_3$, ppm): 63.8 (s).

Complex **4**: m.p. 195–200 °C. Anal. Calc. for $C_{35}H_{27}NO_8P_2Ru_3S$: C, 42.6; H, 2.8; N, 1.4. Found: 43.1; H, 2.8; N, 1.3%. IR (ν(C≡O), cm^{-1}): 2047m, 2009s, 1962m, 1940sh, 1813m. ^{1}H-NMR ($CDCl_3$, ppm): 7.6–6.5 (m, aryl protons), 3.90 (m, CH–$CHMe_2$), 0.87 (d, $^{3}J_{HH} = 7.1$ Hz, CH_3–$CHMe_2$). ^{31}P-NMR ($CDCl_3$, ppm): 72.4 (s).

2.4. Synthesis of cis-[$Rh(CO)Cl\{Ph_2PN(R)P(S)Ph_2\text{-}\kappa^2P,S\}$] [$R = (S)$-*CHMePh (**5**), $CHMe_2$ (**6**)]

A mixture of [{Rh(μ-Cl)$(CO)_2$}$_2$] (0.050 g, 1.28×10^{-4} mol) and $Ph_2PN(R)P(S)Ph_2$ (0.133g for R = (*S*)-*CHMePh, 0.117g for R = $CHMe_2$, 2.56×10^{-4} mol) was dissolved in 20 ml of benzene. The mixture was stirred for 2 h and concentrated in vacuo to 5 ml. Petrol (5 ml) was added and the solution kept at 25 °C for 12 h to obtain the title complexes as yellow crystals (yield 80–85%).

Complex **5**: m.p. 186 °C. Anal. Calc. for $C_{33}ClH_{29}NOP_2RhS$: C 57.6, H 4.2, N 2.0% Found: C 57.5, H 4.3, N 2.2%. IR (cm^{-1}): 1985s, 1432m, 1099s, 1014m, 937m, 870s, 749s, 695s, 591m, 522m, 495m. ^{1}H-NMR ($CDCl_3$, ppm): 8.4 –6.3 (m, aryl protons), 5.10 (m, CH–*CHMePh), 1.20 (d, $^{3}J_{HH} = 7.1$ Hz, CH_3–*CHMePh).

Complex **6**: m.p. 194 °C. Anal. Calc. for $C_{28}ClH_{27}NOP_2RhS$: C 53.7, H 4.4, N 2.2% Found: C 53.6, H 4.4, N 2.3%. IR (cm^{-1}): 1981s, 1435m, 1170w, 1100s, 1026w, 979s, 898s, 840s, 747m, 693m, 578m, 560m, 518m, 498m, 444m ^{1}H-NMR ($CDCl_3$, ppm): 8.0–7.3 (m, aryl protons), 4.00 (m, CH–$CHMe_2$), 0.60 (d, $^{3}J_{HH} = 7.1$ Hz, CH_3–$CHMe_2$).

2.5. Synthesis of [$MCl_2\{Ph_2PN(R)P(S)Ph_2\text{-}\kappa^2P,S\}$] ($M = Pd, Pt$) (**7**–**10**)

A mixture of [MCl_2(COD)] (M = Pd or Pt) (0.057 g for M = Pd, 0.075 g for M = Pt, 2.00×10^{-4} mol) and $Ph_2PN(R)P(S)Ph_2$ (0.104 g for R = (*S*)-*CHMePh, 0.091 g for R = $CHMe_2$, 2.00×10^{-4} mol) was dissolved in CH_2Cl_2 (10 ml) and the solution stirred at 25 °C for 1 h. Evaporation of the solvent in vacuo yielded an oily residue which was washed twice with hot petrol to remove cyclooctadiene and crystallised from CH_2Cl_2–petrol (1:3) mixture to yield the title complexes (yield 80–85%).

[$PdCl_2\{Ph_2PN$(*CHMePh)$P(S)Ph_2\text{-}\kappa^2P,S\}$] (**7**): m.p. 205 °C. Anal. Calc. for $C_{32}Cl_2H_{29}NP_2PdS$: C, 54.9; H, 4.2; N 2.0. Found: C, 54.2; H, 4.2; N, 2.1%. IR (cm^{-1}): 1437s, 1102s, 1013m, 935m, 875m, 769m, 746s, 691s. ^{1}H-NMR ($CDCl_3$, ppm): 8.1–6.1 (m, aryl protons), 4.94 (m,

CH–*CHMePh), 1.17 (d, $^3J_{HH} = 7.1$ Hz, CH_3–*CHMePh).

[$PdCl_2$\{$Ph_2PN(CHMe_2)P(S)Ph_2$-κ^2P,S\}] (**8**): m.p. 212 °C. Anal. Calc. for $C_{27}Cl_2H_{27}NP_2PdS$: C, 50.9; H, 4.3; N, 2.2. Found: C, 49.7; H, 4.2; N, 2.1%. IR (cm^{-1}): 1436s, 1100s, 1012s, 933m, 874m, 769m, 746s, 689s. ^{1}H-NMR ($CDCl_3$, ppm): 8.2–6.8 (m, aryl protons), 4.42 (m, CH–$CHMe_2$), 1.24 (d, $^3J_{HH} = 7.0$ Hz, CH_3–$CHMe_2$).

[$PtCl_2$\{Ph_2PN(*CHMePh)$P(S)Ph_2$-κ^2P,S\}] (**9**): m.p. 218 °C. Anal. Calc. for $C_{32}Cl_2H_{29}NP_2PtS$: C, 48.8; H, 3.7; N, 1.8. Found: C, 48.6; H, 3.8; N, 1.6%. IR (cm^{-1}): 1437s, 1103s, 1031m, 1013w, 935m, 875m, 811m, 772m, 745s, 689s. ^{1}H-NMR ($CDCl_3$, ppm): 8.4–6.1 (m, aryl protons), 5.30 (m, CH–*CHMePh), 1.17 (d,$^3J_{HH} = 7.0$ Hz, CH_3–*CHMePh).

[$PtCl_2$\{$Ph_2PN(CHMe_2)P(S)Ph_2$-κ^2P,S\}] (**10**): m.p. 193 °C. Anal. Calc. for $C_{27}Cl_2H_{27}NP_2PtS$: C, 44.7; H, 3.8; N, 1.9. Found: C, 44.3; H, 3.7; N, 1.9%. ^{1}H-NMR ($CDCl_3$, ppm): 8.1–6.8 (m, aryl protons), 4.38 (m, CH–$CHMe_2$), 1.17 (d, $^3J_{HH} = 7.0$ Hz, CH_3–$CHMe_2$).

2.6. X-ray diffraction study of 3 and 5

Crystals of **3** and **5** suitable for X-ray analysis were grown by slow evaporation of a toluene solution and dichloromethane–petrol (1:1) solutions, respectively. A suitable crystal for X-ray analysis was glued to a glass fiber and coated with paraffin oil to protect it from atmospheric air and moisture during data collection. Cell constants were obtained by least-squares refinement of the setting angles of 25 reflections in the range $16 < 2\theta < 30°$. The intensity data collection was monitored for any variations by three repeatedly measured control reflections. Lorentz and polarization corrections were applied to the intensity data. The structure was solved by Patterson methods using SHELXS-86 (G.M. Sheldrick, Universität Göttingen, 1990) and refined by full-matrix methods against the F_o^2 data employing SHELXL-93 (G.M. Sheldrick, Universität Göttingen, 1993) program; the hydrogen atoms were allowed to ride on the attached atoms during refinements.

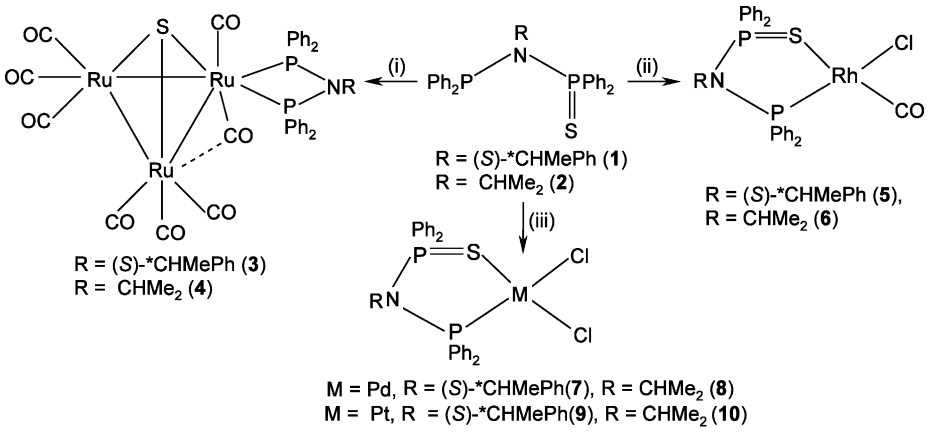
3. Results and discussion

The synthesis of the diphosphazane monosulfide, $Ph_2PN(R)P(S)Ph_2$ (R = $CHMe_2$) (**2**) was reported from our laboratory previously [5]. We now report the preparation of the chiral analogue, $Ph_2PN(R)P(S)Ph_2$ (R = (*S*)-*CHMePh) (**1**) by a similar procedure using benzene as the solvent. The yield of **1** is higher than that reported very recently by Simon-Manso et al. [12], who used diethyl ether as the solvent for the reaction.

3.1. Reactions of $Ph_2PN(R)P(S)Ph_2$ with $[Ru_3(CO)_{12}]$

The oxidative addition reactions of diphosphazane monosulfides $Ph_2PN(R)P(S)Ph_2$ {R = (*S*)-*CHMePh (**1**), $CHMe_2$ (**2**)} with $[Ru_3(CO)_{12}]$ in toluene at 105 °C in the presence of Me_3NO afford sulfur-mono capped triruthenium clusters, $[Ru_3(\mu\text{-}CO)(CO)_7(\mu_3\text{-}S)$\{$Ph_2PN$-$(R)PPh_2$-$\kappa^2P,P$\}] {R = (*S*)-*CHMePh (**3**), or $CHMe_2$ (**4**)} (Scheme 1). These complexes could be isolated in a pure form by preparative TLC, but their yields are low owing to the formation of several other products, which could not be characterized. The structures of **3** and **4** have been elucidated by IR and NMR spectroscopic techniques. The IR spectra indicate the presence of both terminal and bridging carbonyl ligands. The molecular structure of **3** has been established by single crystal X-ray diffraction. Complex **4** is assigned an analogous structure because its spectroscopic features are very similar to those of **3** (see Section 2 for IR and NMR data). It may be noted that the phosphorus-31 chemical shifts for **4** and **5** lie downfield from those of the respective free ligands, $Ph_2PN(R)PPh_2$ (R = (*S*)-*CHMePh, $CHMe_2$) (Table 1). On the other hand, there is a significant upfield shift of the methyl proton resonances in the metal clusters relative to those for the free ligands. The values of [$\Delta\delta(CH_3) = \delta$ (complex) $- \delta$ (ligand)] for complexes **3** and **4** are 0.79 and 0.23, respectively [10c]. It is also worth noting that the downfield shifts of the ^{31}P resonance observed for the chelate complexes **3** and **4** are much less than the similar downfield shifts observed for the dichalcogenide capped triruthenium clusters, $[Ru_3(\mu_3\text{-}S)_2(CO)_7(\mu\text{-}(Ph_2P)_2NH)]$ in which the diphosphazane acts as a bridging ligand [15]. The reaction of $Ru_3(CO)_{12}$ with the chiral ligand **1** using the benzophenone-ketyl induced CO substitution method also gives the chelate cluster **3** as the only product as shown by ^{31}P-NMR spectrum of the reaction mixture. Oxidative sulfur transfer occurs even under these conditions.

Predieri and coworkers have demonstrated that the reactions of $[Ru_3(CO)_{12}]$ with diphosphinoalkane diselenides, $Ph_2P(Se)(CH_2)_nP(Se)Ph_2$ ($n = 1$ or 2) give diselenido bicapped trinuclear clusters of the type $[Ru_3(\mu_3\text{-}Se)_2(CO)_7$\{$\mu$-$(Ph_2P)_2(CH_2)_n$\}] as the main products. A tetranuclear cluster $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)$-$(CO)_8$\{$\mu$-$(Ph_2P)_2CH_2$\}] and the cubane-like cluster $[Ru_4(\mu_4\text{-}Se)_4(CO)_{10}$\{$\mu$-$(Ph_2P)_2CH_2$\}] have also been isolated from the reaction of $[Ru_3(CO)_{12}]$ with $Ph_2P(Se)$-$(CH_2)P(Se)Ph_2$. In all these cases, the diphosphane functions as a bridging ligand [16–18]. Only in the case of 1,1 bis(diphenylphosphino)ferrocene diselenide ($dppfSe_2$), have two isomeric *nido*-clusters $[Ru_3(\mu_3$-$Se)_2(dppf)(CO)_7]$ which contain dppf as a chelating or a bridging ligand been isolated and structurally characterized [18,19].



Scheme 1. Reactions of $Ph_2PN(R)P(S)Ph_2$ with $[Ru_3(CO)_{12}]$, $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ and $[MCl_2(COD)]$ (M = Pd or Pt).

The reactions of $Ru_3(CO)_{12}$ with diphosphazane dichalcogenides, $Ph_2P(E)NHP(E)Ph_2$ (E = S or Se) ($dppaE_2$) in the presence of Me_3NO afford diselenido bicapped tetranuclear clusters, $[Ru_4(\mu_4\text{-}E)_2(\mu\text{-}CO)(CO)_8\{\mu\text{-}(Ph_2P)_2NH\}]$ and a trinuclear cluster, $[Ru_3(\mu_3\text{-}S)_2(CO)_7\{\mu\text{-}(Ph_2P)_2NH\}]$, in which the dppa ligand bridges two ruthenium centers. The formation of a bicapped sulfido triruthenium cluster, $[Ru_3(\mu_3\text{-}S)_2(CO)_7\{(Ph_2P)_2NH\}]$ bearing a chelated dppa has been inferred from spectroscopic data [15]. Complexes **3** and **4** represent a new type of structural motif (see below) in mono chalcogenido capped triruthenium carbonyl clusters in that they contain a chelating diphosphazane ligand. They belong to the family of clusters of the type, $[M_3(\mu_3\text{-}E)(L)_{10}]$ (E = S or Se; L = two-electron donor ligand) [20].

3.2. Reactions of $Ph_2PN(R)P(S)Ph_2$ with $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ and $[MCl_2(COD)]$ [M = Pd or Pt]

The reactions of two equivalents of diphosphazane monosulfides, $Ph_2PN(R)P(S)Ph_2$ [R = (*S*)-*CHMePh (**1**), $CHMe_2$ (**2**)] with one equivalent of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ give $[Rh(CO)Cl\{Ph_2PN(R)P(S)Ph_2\text{-}\kappa^2P,S\}]$ [R = (*S*)-*CHMePh (**5**), $CHMe_2$ (**6**)] in good yields (Scheme 1). These yellow-colored complexes (**5** and **6**) are stable in a wide range of organic solvents and are characterized by spectroscopic and analytical techniques (see Section 2 and Table 1). The molecular structure of complex **5** is confirmed by a single crystal X-ray diffraction study.

Reactions of $[MCl_2(COD)]$ (M = Pd, Pt) with 1:1 molar proportions of $Ph_2PN(R)P(S)Ph_2$ {R = (*S*)-

Table 1
$^{31}P\{^1H\}$-NMR spectral data of transition metal complexes of diphosphazane monosulfides [a]

Compound	Chemical shift (ppm)				$^2J_{PP}$ (Hz)
	δPPh_2	ΔPPh_2 [b]	$\delta P(S)Ph_2$	$\Delta P(S)Ph_2$ [b]	
1 (L^1)	51.5 (br, s)	–	71.3 (d)	–	14.6
2 (L^2) [c]	54.4 (d)	–	67.5 (d)	–	63.0
$[Rh(CO)\{\kappa^2\text{-}L^1\}Cl]$ (**5**)	112.3 (dd)	60.8	68.5 (d)	−2.8	63.0 [d]
$[Rh(CO)\{\kappa^2\text{-}L^2\}Cl]$ (**6**)	114.9 (dd)	60.0	69.2 (d)	1.7	65.0 [e]
$[PdCl_2\{\kappa^2\text{-}L^1\}]$ (**7**)	94.8 (d)	43.3	72.6 (d)	1.3	49.0
$[PdCl_2\{\kappa^2\text{-}L^2\}]$ (**8**)	97.3 (d)	42.9	75.2 (d)	7.7	51.0
$[PtCl_2\{\kappa^2\text{-}L^1\}]$ (**9**)	69.0 (d)	17.5	71.5 (d)	0.3	46.8 [f]
$[PtCl_2\{\kappa^2\text{-}L^2\}]$ (**10**)	69.6 (d)	15.2	71.6 (d)	4.1	47.7 [g]

[a] Recorded at 81 or 162 MHz in $CDCl_3$.
[b] $\Delta = \delta$ (complex) $- \delta$ (ligand).
[c] Data from Ref. [5].
[d] $^1J_{Rh-P}$ 167.0 Hz.
[e] $^1J_{Rh-P}$ 164 Hz.
[f] $^1J_{Pt-P}$ 3794, $^2J_{Pt-P(s)}$ 105.8 Hz.
[g] $^1J_{Pt-P}$ 3787 Hz, $^2J_{Pt-P(S)}$ 99.5 Hz.

*CHMePh **1**, $CHMe_2$ **2**} in dichloromethane at ambient temperature give the chelate complexes [MCl_2{Ph_2PN-(R)P(S)Ph_2-κ^2P,S}] [M = Pd, R = (*S*)-*CHMePh (**7**), R = $CHMe_2$ (**8**); M = Pt, R = (*S*)-*CHMePh (**9**), R = $CHMe_2$ (**10**)]. The structure of complexes **7**–**10** have been assigned on the basis of NMR data (see Section 2 and Table 1).

3.3. Phosphorus-31-NMR data

The ^{31}P-NMR data for the ligands **1** and **2** and their complexes are listed in Table 1. The chemical shifts of the PPh_2 phosphorus (P^{III} centers) are substantially shifted to a lower field compared to those of the free ligands. The pronounced deshielding of P^{III} is probably due to the chelate ring stabilizing effect and is in agreement with a similar trend observed for metal complexes of diphosphazane monosulfide ligands [7]. The coordination shift of the $P(S)Ph_2$ phosphorus is generally very small (−2.8 to +4.1 ppm); evidently, the coordination of the chalcogen atom in these complexes does not confer any extraordinary chelate ring effect for the chalcogen- bearing phosphorus as compared to the trivalent phosphorus directly bound to the metal center. The $^2J_{PP}$ value for *N*-isopropyl diphosphazane monosulfide (**2**) is much larger than that for the *N*-(*S*)-*CHMePh diphosphazane monosulfide (**1**) but irrespective of the substituent on the nitrogen, the $^2J_{P-P}$ values for the complexes of a particular metal show only small variations (1–2 Hz) presumably because of the freezing of the ligand conformation upon complex formation [7].

3.4. Molecular structure of 3

The molecular structure of **3**, determined by a single crystal X-ray diffraction study, is shown in Fig. 1. The structure represents a 48-electron triruthenium cluster framework that contains a chelated chiral diphosphazane ligand. The space group has been identified as $P2_1$; there are two crystallographically independent molecules in the unit cell. Crystallographic information and salient bond lengths and bond angles are given in Tables 2 and 3. There are no significant differences between the bonding parameters of the two molecules. The torsion angles around the chiral carbon atom in both the molecules (molecules 1 and 2) do, however, differ. The two molecules can be regarded as rotamers arising from rotation around the N–C bond. The structure of **3**

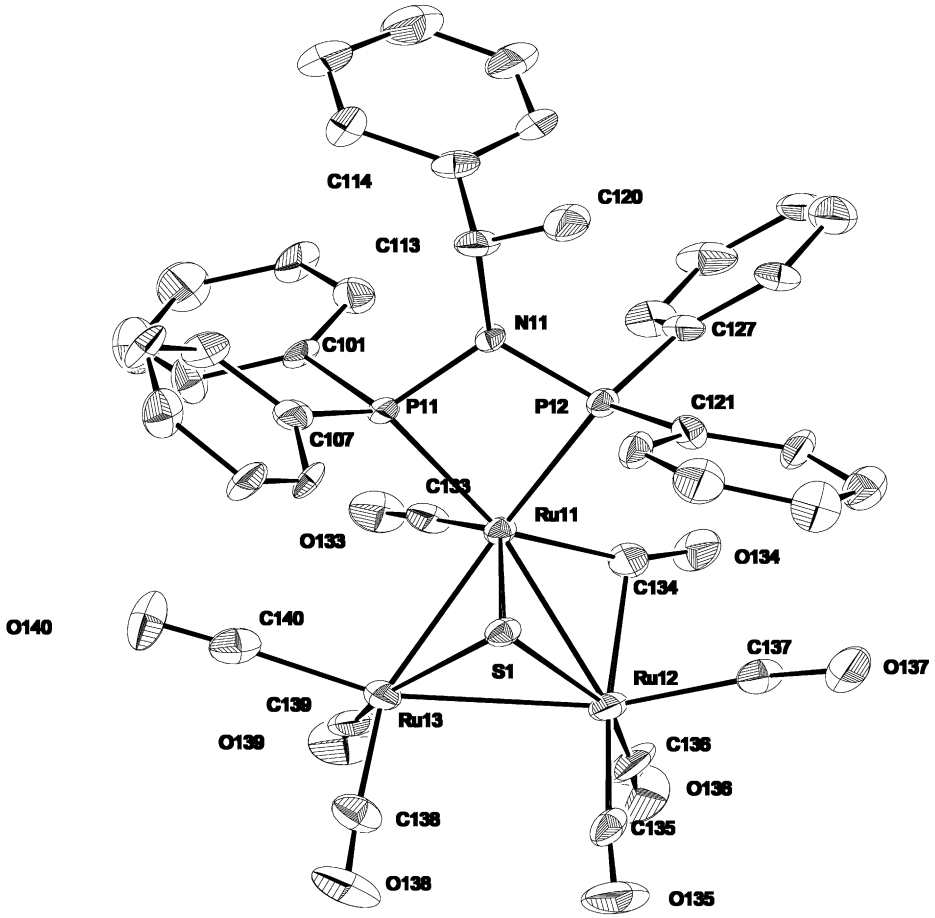


Fig. 1. A view of the molecular structure of [Ru_3(μ_3–S)(μ-CO)(CO)$_7${Ph_2PN((*S*)-*CHMePh)PPh_2-κ^2P,P}] (**3**) (molecule 1 only shown) with the atomic labeling scheme.

Table 2
X-ray crystallographic data and structure refinements for **3** and **5**

	3	**5**
Empirical formula	$C_{40}H_{29}NO_8P_2Ru_3S$	$C_{33}H_{29}ClNOP_2RhS$
Formula weight	1048.85	687.02
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71070	0.71070
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Unit cell dimensions		
a (Å)	12.183(4)	13.421(4)
b (Å)	25.100(18)	14.9810(10)
c (Å)	14.043(4)	15.477(5)
β (°)	108.49(2)	95.39(3)
V (Å^3)	4073(3)	3098(1)
Z	4	4
D_{calc} (Mg m^{-3})	1.711	1.473
Absorption coefficient (mm^{-1})	1.251	0.825
$F(000)$	2036	1400
Crystal size (mm^3)	0.35 × 0.30 × 0.275	0.57 × 0.42 × 0.35
θ range for data collection (°)	1.53–24.98	1.32–24.96
Index ranges	$0 \le h \le 14$, $0 \le k \le 29$, $-16 \le l \le 15$	$0 \le h \le 15$, $0 \le k \le 17$, $-18 \le l \le 18$
Reflections collected	7592	5960
Independent reflections	7340 [$R_{int} = 0.0593$]	5656 [$R_{int} = 0.0261$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7337/1/991	5656/1/721
Goodness-of-fit on F^2	1.038	0.960
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0617$, $wR_2 = 0.1586$	$R_1 = 0.0509$, $wR_2 = 0.1363$
R indices (all data)	$R_1 = 0.0792$, $wR_2 = 0.1764$	$R_1 = 0.0668$, $wR_2 = 0.1570$
Absolute structure parameter	−0.02(8)	−0.02(8)
Largest difference peak and hole (e Å^{-3})	2.301 and −1.478	1.172 and −0.966

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

Compound **3**		Compound **5**	
Bond lengths			
Ru(11)–Ru(12)	2.815(2)	Rh(1)–C(1)	1.79(2)
Ru(11)–Ru(13)	2.733(2)	Rh(1)–P(12)	2.208(5)
Ru(11)–S(1)	2.366(5)	Rh(1)–S(1)	2.369(5)
Ru(11)–P(11)	2.357(5)	Rh(1)–Cl(1)	2.382(5)
Ru(11)–P(12)	2.344(4)	C(1)–O(1)	1.15(3)
Ru(11)–C(133)	1.82(2)	S(1)–P(11)	1.992(5)
Ru(11)–C(134)	1.94(2)	P(11)–N(1)	1.70(1)
Ru(12)–Ru(13)	2.711(2)	N(1)–P(12)	1.74(1)
Ru(12)–S(1)	2.341(5)		
Ru(12)–C(134)	2.47(2)		
Ru(12)–C(135)	1.90(2)		
Ru(12)–C(136)	1.87(3)		
Ru(12)–C(137)	1.94(2)		
Ru(13)–S(1)	2.344(5)		
Ru(13)–C(138)	1.84(2)		
Ru(13)–C(139)	1.93(3)		
Ru(13)–C(140)	1.94(2)		
P(11)–N(11)	1.71(1)		
Bond angles			
P(12)–N(11)–P(11)	101.7(7)	P(11)–N(1)–P(12)	110.1(8)
Ru(13)–Ru(11)–Ru(12)	58.5(1)	C(1)–Rh(1)–P(12)	92.8(7)
Ru(12)–Ru(13)–Ru(11)	62.3(1)	P(12)–Rh(1)–S(1)	89.2(2)
Ru(12)–S(1)–Ru(13)	70.7(1)	C(1)–Rh(1)–Cl(1)	87.5(7)
Ru(12)–S(1)–Ru(11)	73.5(1)	P(12)–Rh(1)–Cl(1)	172.9(2)
Ru(13)–S(1)–Ru(11)	71.0(1)	S(1)–Rh(1)–Cl(1)	90.0(2)
P(12)–Ru(11)–P(11)	68.1(2)	O(1)–C(1)–Rh(1)	169.5(2)

displays a tetrahedral Ru_3S core in which an isosceles triangle of ruthenium atoms is almost symmetrically capped by a sulfur atom. The Ru11–Ru13 and Ru12–Ru13 bonds are of comparable length (2.733(2) and 2.711(2) Å) while Ru11–Ru12 bond is slightly longer (2.815(2) Å). The first two Ru–Ru distances are significantly shorter than those found in the selenium monocapped cluster $[Ru_3(\mu_3\text{-Se})(\mu_3\text{-CO})(CO)_7(PPh_3)_2]$ [20] and the unsubstituted sulfur monocapped cluster $[Ru_3(\mu_3\text{-S})(\mu_3\text{-CO})(CO)_9]$ [21]. The Ru–S bonds lie in the range 2.341–2.367 Å and are comparable to those found in other sulfur capped triruthenium clusters[15,21]. The Ru–P distances are unexceptional. The mean P–N bond distance (1.70(1) Å) is almost the same as that found in the free ligand $Ph_2PN(CHMePh)PPh_2$ (mean P–N distance 1.719(1) Å). However as a result of the chelate formation, the P–N–P angle is considerably narrowed to 101.7° as compared to that in the free ligand [22]. Of the seven terminal carbonyl lignads, the two ruthenium centers Ru12 and Ru13 each carry three terminal carbonyl ligands while one terminal carbonyl is attached to Ru11. There is one 'bent semi-bridging' carbonyl [23] between Ru11 and Ru12 which forms the largest side of the ruthenium triangle; the Ru12–C134 distance (2.47(2) Å) is longer than the Ru11–C134 distance (1.94(2) Å).

The crystal packing diagram shows an interesting helical arrangement of molecules in the crystal lattice (see Fig. B of Section 5). The helical array, formed by two independent molecules (molecules 1 and 2), consists of two strands which run parallel to each other. Each strand consists of molecules 1 and 2 packed one over the other. Both intra- and intermolecular hydrogen bonding provide the major source of stability. The helical arrays are connected by hydrogen-bonds; within each strand, molecules 1 and 2 are also connected by hydrogen bonds. The phenyl hydrogen atoms in the diphosphazane ligand act as hydrogen-bond donors and the oxygen atoms of the carbonyl ligands and sulfur atoms act as hydrogen-bond acceptors. The C–H···O distances and C–H···O angles lie in the range 3.19–3.85 Å and 124–167°, respectively. The C–H···S distances and C–H···S angles are in the range 3.46–3.74 Å and 145–156° (see Fig. C and Table C of Section 5).

3.5. Molecular structure of **5**

The structure of **5** has been confirmed by single crystal X-ray diffraction. The space group is identified as $P2_1$. The unit cell contains two crystallographically independent molecules. An ORTEP view of one of the molecule is shown in Fig. 2. Crystallographic information and the important bond lengths and bond angles are listed in Tables 2 and 3. Except the torsion angles around the chiral carbon atom, there are no significant differences in the bond lengths and bond angles of the two molecules.

The molecule has a square-planar geometry around rhodium, with the sulfur atom *trans* to carbon monoxide. The carbonyl ligand is slightly bent about the carbon atom with a Rh1–C1–O1 angle of 170(2)°. The Cl1–Rh1–P12 angle of 172.9(2)° shows that there is a slight shift from an idealised square planar geometry. The slightly large bond angle of 92.8(7)° for P12–Rh1–C1 is probably due to steric repulsion of the phenyl group of the diphosphazane with the carbonyl group. This results in a slight decrease of C1–Rh1–Cl1 angle of [87.5(7)°] from the ideal value of 90°. The angles S1–Rh1–Cl1 [90.0(2)°] and S1–Rh1–P12 [89.2(2)°] are close to 90°. The Rh–P and Rh–C1 distances in complex **5** are comparable to those observed for the bis(diphenylphosphino)methane monosulfide (dppmS) complex, *cis*-[Rh(CO)Cl{$Ph_2PCH_2P(S)Ph_2$-κ^2P,S}] [3]. However, the P–Rh–Cl and the Rh–C–O bond angles are more linear in the dppmS complex (177.7 and 179.4°, respectively) compared to the corresponding values in **5** (173 and 170°). The P–N bond distances [1.74(1) and 1.70(1) Å] do not vary significantly from those observed for the free ligand [1.749(4) and 1.695 (4) Å] [12] but the P–S bond distance [1.992(5) Å] increases by 0.04 Å [1.955(2) for free ligand]. Upon complexation the P–N–P bond angle [110.1(8)°] shows an appreciable decrease from that [124.3(2)°] for the free ligand; nevertheless, the geometry around the nitrogen atom is planar. An examination of the packing diagram and of intermolecular contacts of **5** shows that there are intermolecular hydrogen bonds between the hydrogen atoms of the phenyl groups and the chloride or the carbonyl oxygen of the neighboring molecule. The C–H···O distances and C–H···O angles are in the range 3.18–3.55 Å and 133–165°, respectively, the C–H···Cl distances and C–H···Cl angles are in the range 3.50–3.82 Å and 127–151° respectively (see Table E of the Section 5).

4. Conclusions

The present study demonstrates that the oxidative chalcogen transfer reactions of diphosphazane monochalcogenides with $[Ru_3(CO)_{12}]$ may proceed by a different pathway from that observed for the analogous

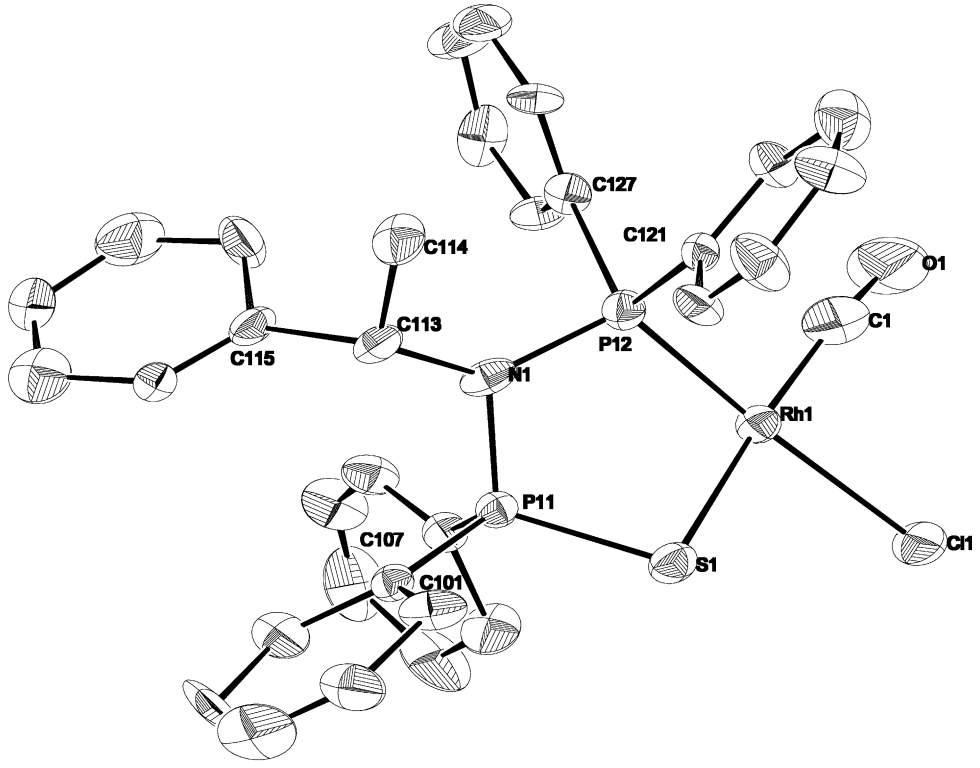


Fig. 2. A view of the molecular structure of [RhCl(CO){Ph_2PN{((*S*)-*CHMePh) $P(S)Ph_2$-κ^2P,S}] (**5**) (molecule 1 only shown) with the atomic labeling scheme.

reactions of diphosphazane dichalcogenides although the available information on these systems is admittedly limited. The synthetic methodology reported in this paper can be extended to other chiral diphosphazane monosulfides and monoselenides to prepare chalcogen monocapped ruthenium carbonyl clusters, especially those containing a streogenic centre at the phosphorus or the substituent(s) attached to phosphorus. These ruthenium clusters as well as the rhodium, palladium and platinum complexes, (which are readily formed by the intact monosulfides), in particular the chiral complexes, may find applications in enantioselective catalysis [2,24].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 133688 and 189175 for compounds **3** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

6. Note added in proof

The synthesis of the chiral ligand **1** and its Pd and Pt chloride complexes have been reported recently by Faller et al. [J.W. Faller, J. Lloret-Fillol, J. Parr, New J. Chem. 29 (2002) 883].

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