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Synthesis of transition-metal complexes with heterodifunctional ligands derived of $NH(PPh_2)_2$. Crystal structure of $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}P,Se\text{-}Ph_2PNP(Se)Ph_2\}]\cdot CH_2Cl_2$

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Abstract

The uncoordinated P atom of the bis(diphenylphosphine)amine (dppa) ligand in complexes $[(ring)MCl_2(\eta^1\text{-}P\text{-}PPh_2NHPPh_2)]$ (M = Rh, Ir, Ru) reacts with sulphur or selenium to form $[(ring)MCl_2(\eta^1\text{-}P\text{-}PPh_2NHP(E)Ph_2)]$ (E = S (**1**–**3**), Se (**4**–**6**)) containing the P-coordinated monosulphide or monoselenide ligands. The selenium derivatives have also been directly prepared from the corresponding $[\{(ring)MCl_2\}_2]$ dimer and dppaSe. Chloride abstraction from rhodium and ruthenium complexes gives the neutral compounds $[(ring)MCl(\eta^2\text{-}P,E\text{-}PPh_2NP(E)Ph_2)]$ (**7**–**10**) whilst the iridium derivatives yield cationic complexes of the general formula $[\{\eta^5\text{-}C_5Me_5\}IrCl(\eta^2\text{-}P,E\text{-}PPh_2NHP(E)Ph_2)]^+$ (**11** and **12**). The crystal structure of complex $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}P,Se\text{-}PPh_2NP(Se)Ph_2\}]$ has been established by X-ray crystallography. The rhodium atom exhibits a distorted octahedral coordination with a $\eta^5\text{-}C_5Me_5$ group occupying the centre of three octahedral sites; a bidentate chelate P,Se-bonded ligand and a chloride atom complete the metal coordination sphere. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Iridium; Ruthenium; Bis(diphenylphosphine)amine complexes; Monochalcogenide complexes

1. Introduction

Transition-metal chemistry of bis(diphenylphosphine)amine, $NH(PPh_2)_2$, has attracted considerable interest in recent years [1], in part due to its chemical and structural proximity to the widely used diphosphine $CH_2(PPh_2)_2$ (dppm). This amine ligand is easily oxidised to form dichalcogenide derivatives $NH(EPPh_2)_2$ (E = O, S, Se) which, it turn, can be readily deprotonated with alkali metals or metal alcoxides (e.g. $KOBu^t$) to give the corresponding metal salts [2]. The anions formed, $[N(EPPh_2)_2]^-$, are versatile ligands able to form inorganic (carbon-free) chelate rings with a variety of transition metals [3].

In contrast, there are few examples of metal complexes containing monochalcogenide derivatives of the type $Ph_2PNHP(E)Ph_2$. These heterodifunctional ligands, containing two types of donor atoms, can show different coordination modes in their neutral or anionic form [3b]. Thus, they can act as unidentate P-bonded, P,E-chelating or bridging ligand with the formation, in the latter case, of bimetallic complexes [4].

Following our interest in the coordination behaviour of short-bite bidentate phosphine ligands [1b,3a,4e,5], we report in this paper the synthesis and characterisation of new mononuclear neutral complexes of general formula $[(ring)MCl_2(\eta^1\text{-}P\text{-}PPh_2NHP(E)Ph_2)]$ [(ring)-M = $(\eta^5\text{-}C_5Me_5)Rh$, $(\eta^5\text{-}C_5Me_5)Ir$, $(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)$-Ru; E = S, Se] and their reactions with chloride scavengers to form neutral or cationic derivatives of the types $[(ring)MCl(\eta^2\text{-}P,E\text{-}PPh_2NP(E)Ph_2)]$ (M = Rh, Ru) and $[(\eta^5\text{-}C_5Me_5)IrCl(\eta^2\text{-}P,E\text{-}PPh_2NHP(E)Ph_2)]$-

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BF_4. The crystal structure of [(η^5-C_5Me_5)RhCl{η^2-*P*,*Se*-$PPh_2NP(Se)Ph_2$}], determined by single-crystal X-ray diffraction, is also reported.

2. Experimental

2.1. General

All reactions were carried out under purified nitrogen by using Schlenk-tube techniques. Solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting complexes [{(η^5-C_5Me_5)MCl_2}$_2$] (M = Rh, Ir) [6], [{(η^6-*p*-$MeC_6H_4Pr^i$)$RuCl_2$}$_2$] [7], [(ring)MCl_2{η^1-*P*-$Ph_2PNHPPh_2$}] [(ring)M = (η^5-C_5Me_5)Rh, (η^5-C_5Me_5)Ir, (η^6-*p*-$MeC_6H_4Pr^i$)Ru] [8] and the ligands dppa [2c] and dppaE [$Ph_2PNHP(E)PPh_2$, E = S, Se] [4b], were prepared by published procedures. Elemental analyses (C, H, N, S) were made with a Fisons EA 1108 microanalyser. FTIR spectra were recorded in a Bruker Vector-22 spectrophotometer using KBr pellets. The NMR spectra were recorded in Bruker AC-200P or in Varian Unity 300 spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ (^{1}H) and 85% H_3PO_4 in D_2O (^{31}P, positive shifts downfield) as internal and external standards, respectively.

2.2. Preparation of [(ring)MCl_2{η^1-*P*-Ph_2PNH-*P*(S)Ph_2}] [(ring)M = (η^5-C_5Me_5)Rh (**1**), (η^5-C_5Me_5)Ir (**2**), (η^6-*p*-$MeC_6H_4Pr^i$)Ru (**3**)]

To a suspension of the corresponding [(ring)-MCl_2{η^1-*P*-($Ph_2PNHPPh_2$}] complex (0.14 mmol) in Et_2O (20 cm^3) was added sulphur (0.5 mg, 0.14 mmol). The suspension was stirred at 0 °C until complete reaction of the solid sulphur (ca. 3 h). The solution obtained was evaporated to dryness and the solid residue extracted with CH_2Cl_2. Addition of Et_2O caused the precipitation of the complexes.

1: Yield 76 mg (75%). Anal. Found: C, 55.9; H, 4.9; N, 2.0; S, 4.1. Calc. for $C_{34}H_{36}Cl_2NP_2RhS$: C, 56.2, H, 5.0; N, 1.9; S, 4.4%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.37 (15H, C_5Me_5, $^4J(P_AH) = 3.8$ Hz), 6.23 (s, br, NH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 51.3 (d, $^2J(P_AP_B) =$ 45.4 Hz, P_B), 65.4 (dd, $^1J(RhP_A) = 148$ Hz, P_A). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1101, 931, ν(PS) 623, 613.

2: Yield 75 mg (66%). Anal. Found: C, 50.3; H, 4.3; N, 1.6, S, 3.6. Calc. for $C_{34}H_{36}Cl_2NP_2IrS$: C, 50.1, H, 4.4; N, 1.7; S, 3.9%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.37 (d, 15H, C_5Me_5, $^4J(P_AH) = 2.4$ Hz), 6.54 (s, br, NH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 35.3 (d, $^2J(P_AP_B) =$ 41 Hz, P_A), 51.2 (d, P_B). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1103, 930, ν(PS) 624, 613.

3: Yield 84 mg (80%). Anal. Found: C, 56.2; H, 4.9; N, 1.9; S, 4.2. Calc. for $C_{34}H_{35}Cl_2NP_2RuS$: C, 56.4, H, 4.9; N, 1.9; S, 4.4%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 0.82 (6H, d, $^3J(HH) = 6.9$ Hz, 2 Me(Pr^i)), 1.88 (3H, s, Me), 2.49 (1H, sp, CH(Pr^i)), 5.07 (2H, d, AA′, $^3J(HH) = 6.0$ Hz), 5.33 (2H, dd, BB′, $^3J(HH) = 6.0$ Hz, $J(PH) = 1.5$ Hz), 5.88 (1H, dd, $^2J(PH) = 3.4$ Hz, $^2J(PH) = 3.0$ Hz, NH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 50.5 (d, $^2J(P_AP_B) = 44.7$ Hz, P_B), 61.6 (d, P_A). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1100, 848, ν(PS) 625, 613.

2.3. Preparation of [(ring)MCl_2{η^1-*P*-(Ph_2PNH-*P*(Se)Ph_2}] [(ring)M = (η^5-C_5Me_5)Rh (**4**), (η^5-C_5Me_5)Ir (**5**), (η^6-*p*-$MeC_6H_4Pr^i$)Ru (**6**)]

The complexes can be prepared by the following two methods:

(i) A solution of [{(η^5-C_5Me_5)MCl_2}$_2$] (0.14 mmol) in toluene (15 cm^3) was treated with the stoichiometric amount of dppaSe (130 mg, 0.28 mmol). The obtained solution was stirred at 0 °C for 1 h and then evaporated to dryness. The solid residue was dissolved in the minimal amount of $CHCl_3$ and the complexes were precipitated by adding *n*-hexane.

4: Yield 207 mg (85%). Anal. Found: C, 52.5; H, 4.7; N, 1.5. Calc. for $C_{34}H_{36}Cl_2NP_2RhSe$: C, 53.8, H, 4.8; N, 1.8%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.37 (d, 15H, C_5Me_5, $^4J(P_AH) = 3.8$ Hz), 6.29 (s, br, NH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 46.1 (d, $^2J(P_AP_B) = 46$ Hz, $^1J(PSe) = 776$ Hz, P_B), 67.2 (dd, $^1J(RhP_A) = 148.3$ Hz, P_A). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1099, 930, ν(PSe) 552.

5: Yield 163 mg (60%). Anal. Found: C, 47.3; H, 4.1; N, 1.4. Calc. for $C_{34}H_{36}Cl_2NP_2IrSe$: C, 47.3; H, 4.2; N, 1.6%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.37 (d, 15H, C_5Me_5, $^4J(P_AH) = 2.4$ Hz), 6.59 (s, br, NH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 36.6 (d, $^2J(P_AP_B) = 41.5$ Hz, P_A), 45.6 (d, $^1J(PSe) = 780$ Hz, P_B). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1102, 929, ν(PSe) 554.

(ii) To a suspension of complex [(η^6-*p*-$MeC_6H_4Pr^i$)$RuCl_2${η^1-*P*-$Ph_2PNHPPh_2$}] (0.14 mmol) in Et_2O (20 cm^3) was added grey selenium (11 mg, 0.14 mmol). The mixture was worked up as described for complexes **1**–**3**.

6: Yield 91 mg (82%). Anal. Found: C, 53.4; H, 4.7; N, 1.8. Calc. for $C_{34}H_{35}Cl_2NP_2RuSe$: C, 53.0, H, 4.7; N, 1.8%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 0.84 (6H, d, $^3J(HH) = 6.9$ Hz, 2Me(Pr^i)), 1.87 (3H, s, Me), 2.49 (1H, sp, CH(Pr^i)), 5.07 (2H, d, AA′, $^3J(HH) = 6.2$ Hz), 5.70 (2H, dd, BB′, $^3J(HH) = 6.2$ Hz, $J(PH) = 1.5$ Hz), 5.95 (1H, dd, $^2J(PH) = 2.2$ Hz, $^2J(PH) = 2.2$ Hz, NH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 45.3 (d, $^2J(P_AP_B) =$ 45.7 Hz, $^1J(PSe) = 782$ Hz, P_B), 62.7 (d, P_A). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1100, 849, ν(PSe) 549.

2.4. Preparation of [(ring)MCl{η^2-*P*,*S*-Ph_2PN-*P*(S)Ph_2}] [(ring)M = (η^5-C_5Me_5)Rh (**7**), (η^6-*p*-$MeC_6H_4Pr^i$)Ru (**8**)]

To a solution of [{(ring)MCl_2}$_2$] (0.2 mmol) in a mixture of Me_2CO–CH_2Cl_2 (15 cm^3, 2:1 v/v) was added

dppaS (167 mg, 0.4 mmol) and $AgBF_4$ (79.4 mg, 0.4 mmol). The mixture was stirred for 1 h at room temperature (r.t.). The AgCl formed was filtered off through Kieselguhr and the solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2, chromatographed (Kieselgel) and eluted with CH_2Cl_2. The solution was concentrated to a small volume and the complexes were precipitated by adding Et_2O.

7: Yield 190 mg (69%). Anal. Found: C, 59.3; H, 5.2; N, 1.9; S, 4.4. Calc. for $C_{34}H_{35}ClNP_2RhS$: C, 59.2; H, 5.1; N, 2.0; S, 4.7%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.48 (d, 15H, C_5Me_5, $^4J(P_AH) = 3.0$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 61.9 (d, $^2J(P_AP_B) = 36$ Hz, P_B), 79.5 (dd, $^1J(RhP_A) = 127$ Hz, P_A). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1106, 931, ν(PS) 573.

8: Yield 133 mg (51%). Anal. Found: C, 59.1; H, 4.9; N, 2.0; S, 4.9. Calc. for $C_{34}H_{34}ClNP_2RuS$: C, 59.4; H, 5.0; N, 2.0; S, 4.7%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 0.80 (3H, d, $^3J(HH) = 6.9$ Hz, Me(Pr^i)), 1.13 (3H, d, $^3J(HH) = 6.9$ Hz, Me(Pr^i)), 2.10 (3H, s, Me), 2.53 (1H, sp, $J(HH) = 6.9$ Hz, CH(Pr^i)), 4.20 (1H, d, $^3J(HH) =$ 5.6 Hz), 5.14 (1H, d, $^3J(HH) = 6.2$ Hz), 5.47 (1H, d, $^3J(HH) = 5.6$ Hz), 5.78 (1H, d, $^3J(HH) = 6.2$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 71.1 (d, $J(P_AP_B) =$ 46.9 Hz, P_B), 85.4 (d, P_A). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1104, 839, ν(PS) 559.

Similar results were obtained reacting complexes **1** or **3** with $AgBF_4$ or $AgPF_6$ in Me_2CO solution and working up as described above.

*2.5. Preparation of [(ring)MCl{η²-P,Se-Ph₂PN-P(Se)Ph₂}] [(ring)M = (η⁵-(C₅Me₅)Rh (**9**), (η⁶-p-MeC₆H₄Pr^i)Ru (**10**)]*

To a solution of $[\{(ring)MCl_2\}_2]$ (0.2 mmol) in a mixture of CH_2Cl_2–Me_2CO (15 cm^3, 2/1 v/v) was added dppaSe (186 mg, 0.4 mmol) and $AgBF_4$ (79.4 mg, 0.4 mmol). The mixture was stirred for 1 h at r.t. The AgCl formed was filtered off through Kieselguhr and the solution was evaporated to dryness.

9: The residue was dissolved in the minimal amount of Me_2CO and the complex was precipitated by adding *n*-hexane. Yield 218 mg (74%). Anal. Found: C, 50.9; H, 4.4; N, 1.7. Calc. for $C_{34}H_{35}ClNP_2RhSe$: C, 51.7; H, 4.5; N, 1.7%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.49 (d, 15H, C_5Me_5, $^4J(P_AH) = 3.0$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 40.1 (d, $^2J(P_AP_B) = 41.2$, $^1J(PSe) = 458$ Hz, P_B), 79.7 (dd, $^1J(RhP_A) = 130$ Hz, P_A). IR (KBr, cm^{-1}):$\nu(P_2N)$ 1103, ν(PSe) 544.

10: The residue was dissolved in CH_2Cl_2, chromatographed (neutral aluminium oxide, Brockmann I) and eluted with CH_2Cl_2–Me_2CO (1:10). The solution obtained was evaporated to dryness, the residue dissolved in the minimal amount of CH_2Cl_2 and the complex was precipitated by adding Et_2O. Yield 147 mg (50%). Anal. Found: C, 56.1; H, 4.7; N, 1.9. Calc. for $C_{34}H_{34}ClNP_2RuSe$: C, 55.6; H, 4.7; N, 1.9%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 0.83 (3H, d, $^3J(HH) = 6.9$ Hz, Me(Pr^i)), 1.09 (3H, d, $^3J(HH) = 6.9$ Hz, Me(Pr^i)), 2.06 (3H, s, Me), 2.52 (1H, sp, CH(Pr^i)), 4.27 (1H, d, $^3J(HH) = 5.7$ Hz), 5.01 (1H, d, $^3J(HH) = 6.2$ Hz), 5.54 (1H, d, $^3J(HH) = 5.7$ Hz), 5.77 (1H, d, $^3J(HH) = 6.2$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 50.6 (d, $J(P_AP_B) = 52.4$ Hz, $^1J(PSe) = 468$ Hz, P_B), 86.3 (d, P_A). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1102, 839, ν(PSe) 546.

*2.6. Preparation of [(η⁵-C₅Me₅)IrCl(η²-P,E-Ph₂PNH-P(E)Ph₂)]BF₄. [E = S (**11**), Se (**12**)]*

The complexes can be prepared by the following two methods:

(i) To a solution of complex $[\{(\eta^5\text{-}C_5Me_5)IrCl_2\}_2]$ (100 mg, 0.13 mmol) in a 1:1 mixture of CH_2Cl_2–Me_2CO (20 cm^3) was added dppaE [0.25 mmol; E = S (105.2 mg), Se (113.5 mg)] and $AgBF_4$ (50 mg, 0.26 mmol). The mixture was stirred for 3 h at r.t. The AgCl formed was filtered off through Kieselguhr and the solution was concentrated to a small volume (ca. 2 cm^3) under reduced pressure. The complexes were precipitated by addition of Et_2O.

11: Yield 144 mg (66%). **12**. Yield 139 mg (61%).

(ii) To a solution of complex $[(\eta^5\text{-}C_5Me_5)IrCl_2(\eta^1\text{-}P\text{-}Ph_2PNHP(E)Ph_2)]$ (0.12 mmol) in a 2:1 mixture of CH_2Cl_2–Me_2CO (15 cm^3) was added $AgBF_4$ (25 mg 0.13 mmol). The mixture was stirred for 1 h at r.t. The AgCl formed was filtered off through Kieselguhr and the solution evaporated to dryness. The residue was dissolved in CH_2Cl_2, chromatographed (neutral aluminium oxide, Brockmann I) and eluted with CH_2Cl_2. The solution was concentrated to a small volume and the complexes were precipitated by the addition of Et_2O.

11: Yield 76 mg (63%). Anal. Found: C, 46.8; H, 4.2; N, 1.6; S, 3.6. Calc. for $C_{34}H_{36}ClNP_2BF_4IrS$: C, 47.1; H, 4.2; N, 1.6; S, 3.7%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.57 (d, 15H, C_5Me_5, $^4J(P_AH) = 2.4$ Hz), 8.68 (s, br, NH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 60.9 (d, $J(P_AP_B) = 32.0$ Hz, P_A), 69.0 (d, P_B). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1108, 941, ν(PS) 584.

12: Yield 79 mg (70%). Anal. Found: C, 45.0; H, 3.8; N, 1.3. Calc. for $C_{34}H_{36}ClNP_2BF_4IrSe$: C, 44.7; H, 4.0; N, 1.5%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.60 (d, 15H, C_5Me_5, $^4J(P_AH) = 2.5$ Hz), 8.72 (s, br, NH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 53.6 (d, $J(P_AP_B) = 34.0$ Hz, P_A), 63.8 (d, P_B). IR (KBr, cm^{-1}): $\nu(P_2N)$ 1104, 944, ν(PSe) 549.

*2.7. Crystal structure of complex [(η⁵-C₅Me₅)RhCl{η²-P,Se-Ph₂PNP(Se)Ph₂}]·CH₂Cl₂ (**9**)*

A summary of crystal data, and refinement parameters for the structural analysis is reported in Table 1. Suitable crystals were obtained from a slow diffusion of

Et_2O into CH_2Cl_2 solution of complex **9**; a yellow irregular block ($0.25 \times 0.18 \times 0.15$ mm) was mounted on a four-circle diffractometer (Siemens P4) working with graphite-monochromated Mo–K_α radiation ($\lambda =$ 0.71073 Å) and operating at 200 K. Precise lattice parameters were determined by least-squares fit from 94 centred reflections in the region $25 \leq 2\theta \leq 38°$. Three standard reflections were monitored every 97 measured reflections to check crystal and instrument stability throughout data collection; a 2.46% decay of the intensities was observed. All data were corrected for Lorentz and polarisation effects, and a semiempirical (ψ-scan method) absorption correction was also applied [9a]. The structure was solved by Patterson and conventional Fourier techniques, and refined by full-matrix least-squares methods on F^2 (SHELXL-97) [9b] with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms for methyl groups were included in calculated positions (C–H = 0.98 Å), and the remaining hydrogens were located in difference Fourier maps; all were included in the refinement riding on their respective carbon atom with two different common isotropical thermal parameters.

Table 1
Crystallographic data and structure refinement parameters for complex **9**

Empirical formula	$C_{34}H_{35}ClNP_2RhSe{\cdot}CH_2Cl_2$
Formula weight	821.82
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.6592(6)
b (Å)	11.1095(8)
c (Å)	19.0300(14)
α (°)	86.928(5)
β (°)	82.696(5)
γ (°)	70.593(5)
V (Å^3)	1712.5(3)
Z	2
D_{calc} (Mg m^{-3})	1.594
μ (mm^{-1})	1.915
θ Range for data collection (°)	2.16–27.50
Index ranges	$-1 \leq h \leq 11$, $-13 \leq k \leq 14$, $-24 \leq l \leq 24$
Reflections collected	9713
Independent reflections	7823 ($R_{int} = 0.0352$)
Data/restraints/parameters	7823/0/395
Goodness-of-fit on F^2	1.000
R_1 [a] $[I > 2\sigma(I)]$	0.0455
wR_2 [b] (all data)	0.0828
Largest difference peak and hole (e Å^{-3})	0.579 and −0.527

[a] $R_1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$ for 5155 reflections.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0275P)^2 + 0.4909P]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$.

3. Results and discussion

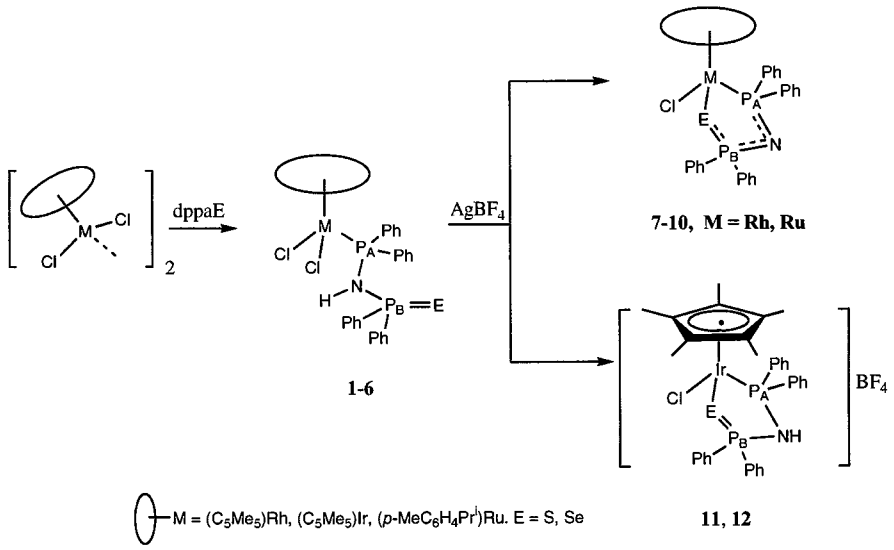
The dinuclear complexes $[\{(ring)MCl_2\}_2]$ ((ring)M = (η^5-C_5Me_5)Rh, (η^5-C_5Me_5)Ir and (η^6-*p*-$MeC_6H_4Pr^i$)-Ru) reacted with bis(diphenylphosphino)-amine [NH-(PPh_2)$_2$, dppa] in toluene by cleavage of the chlorine bridges to yield neutral complexes with the dppa acting as a monodentate P-donor ligand [8].

$$1/2[\{(ring)\})MCl_2\}_2] + NH(PPh_2)_2 \rightarrow [(ring)MCl_2(\eta^1\text{-}P\text{-}Ph_2PNHPPh_2)] \quad (1)$$

When the ligand dppa acts as a unidentate P-donor ligand, the second uncoordinate P atom has proved to remain reactive. Thus, the mononuclear complexes reacted with elemental sulphur or selenium in diethyl ether creating the P-coordinate monosulphide or monoselenide ligands and leading to complexes of the type $[(ring)MCl_2\{\eta^1\text{-}P\text{-}Ph_2PNHP(S)Ph_2\}]$ ((ring)M = (η^5-C_5Me_5)Rh (**1**), (η^5-C_5Me_5)Ir (**2**), (η^6-*p*-$MeC_6H_4Pr^i$)Ru (**3**)) and $[(ring)MCl_2\{\eta^1\text{-}P\text{-}Ph_2PNHP(Se)Ph_2\}]$ ((ring)M = (η^5-C_5Me_5)Rh (**4**), (η^5-C_5Me_5)Ir (**5**), (η^6-*p*-$MeC_6H_4Pr^i$)Ru (**6**)). Alternatively, complexes **1**–**6** can be prepared by reaction of the dimeric complexes $[\{(ring)MCl_2\}_2]$ with the stoichiometric amounts of the ligands $Ph_2PNHP(S)Ph_2$ and $PPh_2NHP(Se)Ph_2$, previously synthesised.

Interestingly, treatment of these complexes with $AgBF_4$ or $AgPF_6$ in a 1:1 molar ratio affords two different types of complexes. When the reaction was carried out starting from Rh(**1**, **4**) or Ru (**3**, **6**) derivatives, neutral complexes of general formula $[(ring)MCl\{\eta^2\text{-}P,E\text{-}Ph_2PNP(E)Ph_2\}]$ (E = S; (ring)M = (η^5-C_5Me_5)Rh (**7**), (η^6-*p*-$MeC_6H_4Pr^i$)Ru (**8**); E = Se; (ring)M = (η^5-C_5Me_5)Rh (**9**), (η^6-*p*-$MeC_6H_4Pr^i$)Ru (**10**)) were obtained. In these reactions, the easy loss of the amine proton is caused by the increase of its acidity produced by the coordination of the free PE group to the metal centre. Similar results were obtained treating the starting dimeric complexes $[\{(ring)MCl_2\}_2]$ with the monochalcogenide ligands $Ph_2PNHP(S)Ph_2$ (dppaS) and $Ph_2PNHP(Se)Ph_2$ (dppaSe) in the presence of silver salts. However, reactions performed with the iridium complexes (**2**, **5**) yield the cationic compounds $[(\eta^5\text{-}C_5Me_5)IrCl(\eta^2\text{-}P,E\text{-}Ph_2PNHP(E)Ph_2)]BF_4$ [E = S (**11**), Se (**12**)]. These results confirm that the iridium centre is softer than the corresponding Rh or Ru centres and, in this case, the acidity of the amine proton is not en-hanced enough by the η^2-coordination of the ligand. All these reactions are summarised in Scheme 1.

All complexes were isolated as stable microcrystalline solids. Their solid-state IR spectra in KBr pellets showed the characteristic absorptions of the P_2N moiety, together with the absorption of the uncoordinated or coordinated P=E groups. The P_2N fragment



Scheme 1.

Table 2
$^{31}P\{^{1}H\}$-NMR chemical shifts (δ ppm) and coupling constants (Hz) of the isolated complexes [a]

Complex [b]	P_A	P_B	$^{2}J(P_AP_B)$
(1) $[(\eta^5\text{-}C_5Me_5)RhCl_2\{\eta^1\text{-}P\text{-}Ph_2PNHP(S)Ph_2\}]$ [c]	65.4 (dd)	51.3 (d)	45.4
(2) $[(\eta^5\text{-}C_5Me_5)IrCl_2\{\eta^1\text{-}P\text{-}Ph_2PNHP(S)Ph_2\}]$	35.3 (d)	51.2 (d)	41.0
(3) $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)RuCl_2\{\eta^1\text{-}P\text{-}Ph_2PNHP(S)Ph_2\}]$	61.6 (d)	50.5 (d)	44.7
(4) $[(\eta^5\text{-}C_5Me_5)RhCl_2\{\eta^1\text{-}P\text{-}Ph_2PNHP(Se)Ph_2\}]$ [d]	67.2 (dd)	46.1 (d)	46.0
(5) $[(\eta^5\text{-}C_5Me_5)IrCl_2\{\eta^1\text{-}P\text{-}Ph_2PNHP(Se)Ph_2\}]$ [e]	36.6 (d)	45.6 (d)	41.5
(6) $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)RuCl_2\{\eta^1\text{-}P\text{-}Ph_2PNHP(Se)Ph_2\}]$ [f]	62.7 (d)	45.3 (d)	45.7
(7) $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}P,S\text{-}Ph_2PNP(S)Ph_2\}]$ [g]	79.5 (dd)	61.9 (d)	36.0
(8) $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)RuCl\{\eta^2\text{-}P,S\text{-}Ph_2PNP(S)Ph_2\}]$	85.4 (d)	71.1 (d)	46.9
(9) $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}P,Se\text{-}Ph_2PNP(Se)Ph_2\}]$ [h]	79.7 (dd)	40.1 (d)	41.2
(10) $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)RuCl\{\eta^2\text{-}P,Se\text{-}Ph_2PNP(Se)Ph_2\}]$ [i]	86.3 (d)	50.6 (d)	52.4
(11) $[(\eta^5\text{-}C_5Me_5)IrCl\{\eta^2\text{-}P,S\text{-}Ph_2PNHP(S)Ph_2\}]BF_4$	60.9 (d)	69.0 (d)	32.0
(12) $[(\eta^5\text{-}C_5Me_5)IrCl\{\eta^2\text{-}P,Se\text{-}Ph_2PNHP(Se)Ph_2\}]BF_4$	53.6 (d)	63.8 (d)	34.0

[a] Measured in $CDCl_3$ at room temperature. Chemical shifts relative to H_3PO_4 (85%) in D_2O as external standard.
[b] ^{31}P-NMR of free ligands $\{(CD_3)_2SO\}$: dppaS, δ 27.6 (d, $^{2}J(PP) = 86$ Hz, P) and 60.9 (d, PS); dppaSe, δ 29.3 (d, $^{2}J(PP) = 93$ Hz, P) and 58.2 (d, $^{1}J(PSe) = 757$ Hz, PSe) [4b].
[c] $^{1}J(RhP) = 148$ Hz.
[d] $^{1}J(RhP) = 148.3$ Hz, $^{1}J(PSe) = 776$ Hz.
[e] $^{1}J(PSe) = 780$ Hz.
[f] $^{1}J(PSe) = 782$ Hz.
[g] $^{1}J(RhP) = 127$ Hz.
[h] $^{1}J(RhP) = 130$ Hz, $^{1}J(PSe) = 458$ Hz.
[i] $^{1}J(PSe) = 468$ Hz.

shows two bands in the ranges 1099–1108 and 839–940 cm^{-1}, reflecting the increase of the P–N bond order compared with the free ligands [dppaS, $\nu_{asym}(P_2N) = 791$ and $\nu_{sym}(P_2N) = 696$ cm^{-1}; dppaSe, $\nu_{asym}(P_2N) = 790$ and $\nu_{sym}(P_2N) = 686$ cm^{-1}] [4b]. As expected, the ν(PS) stretching in complexes **7**, **8**, and **11** [$\nu(PS) = 584–559$ cm^{-1}] were shifted to lower frequencies relative to those observed in complexes **1**–**3** [$\nu(PS) = 613–625$ cm^{-1}] and in the free ligands [$\nu(PS) = 634$ cm^{-1}] [4b], most likely as a consequence of the decrease of the bond order upon coordination. However, the ν(PSe) absorption in complexes **9**, **10**, and **12** [$\nu(PSe) = 546–549$ cm^{-1}], showed no significant variations with respect to complexes **4**–**6** [$\nu(PSe) = 552–554$ cm^{-1}] or to the free ligand [$\nu(PSe) = 551$ cm^{-1}] [4b].

The $^{31}P\{^{1}H\}$-NMR data for the complexes **1**–**12** are given in Table 2. Couplings with the ^{77}Se and ^{103}Rh nuclei help us in the spectral assignments. As a consequence of the coordination, a large deshielding was observed for the P_A phosphorus nucleus with respect to the free ligand. The smaller shifts for the iridium com-

plexes **2** and **5** are consistent with the usual for ligands attached to heavier transition metals [10]. The P_B atom of complexes **7** and **8** shows a large deshielding upon coordination of the sulphur atom to the metal centre. This shift is probably due to the chelate ring stabilising effect [11]. Interestingly, the ^1J(PSe) coupling decreases ca. 300 Hz when the selenium coordinates to the metal. This reduction could be related to a decreasing of the P=Se double bond character upon coordination [4d].

The ^{1}H-NMR spectra of complexes **1**–**12** exhibited the expected resonances corresponding to the coordinated C_5Me_5 and *p*-$MeC_6H_4Pr^i$ groups. Moreover, complexes **11** and **12** show a broad singlet at δ 8.68 and 8.72 ppm, respectively, assigned to the amine proton.

3.1. Molecular structure of [(η^5-C_5Me_5)-RhCl{η^2-*P*,*Se*-$Ph_2PNP(Se)Ph_2$}]·CH_2Cl_2 (9)

A view of the neutral complex **9**, including the atom numbering scheme, is shown in Fig. 1. The most relevant bond distances and angles are collected in Table 3. In these complexes, the rhodium atom exhibits a distorted octahedral coordination sphere with the pentamethylcyclopentadienyl ligand formally occupying three octahedral sites; a heterodifunctional chelate ligand bonded to the metal centre through a phosphorus and a selenium atom, and a chloride atom complete the coordination sphere. This particular coordination makes each rhodium centre chiral, although, obviously, both enantiomers are present in the crystal structure.

The methyl substituents are bent away from the rhodium atom and the Rh–G (C_5Me_5 centroid) distance is 1.839(5) Å [individual Rh–C bond distances range from 2.171(5) to 2.231(4) Å] and compares well with the values reported for related pentamethylcyclopentadienyl rhodium(III) compounds [(η^5-C_5Me_5)Rh{η^3-*Se*,*Se*′,*C*-$(SePPh_2)_2CH$}]ClO_4 [1.807(10) Å] [12] and [(η^5-C_5Me_5)Rh(η^2-S_2PPh_2)(η^1-$SPPh_2$)] [1.852(3) Å] [13]. The Rh–Cl [2.3991(12) Å] and Rh–Se [2.5067(6) Å] distances are slightly shorter than those reported for the

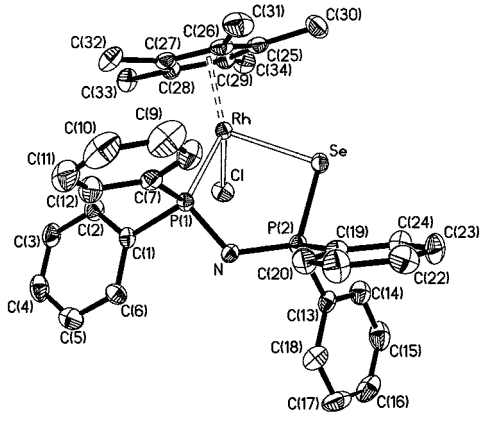


Fig. 1. Molecular representation of the neutral complex **9** with the labelling scheme used (H atoms omitted for clarity).

Table 3
Selected bond lengths (Å) and bond angles (°) for complex **9**

Bond lengths			
Rh–Cl	2.3991(12)	Se–P(2)	2.1940(12)
Rh–Se	2.5067(6)	P(1)–N	1.642(3)
Rh–P(1)	2.3195(11)	P(1)–C(1)	1.826(4)
Rh–C(25)	2.224(4)	P(1)–C(7)	1.838(4)
Rh–C(26)	2.171(4)	P(2)–N	1.582(3)
Rh–C(27)	2.206(4)	P(2)–C(13)	1.809(4)
Rh–C(28)	2.195(4)	P(2)–C(19)	1.820(4)
Rh–C(29)	2.230(4)		
Bond angles			
Cl–Rh–Se	91.09(3)	Rh–P(1)–C(7)	114.58(14)
Cl–Rh–P(1)	87.23(4)	N–P(1)–C(1)	104.33(12)
Cl–Rh–G*	122.98(16)	N–P(1)–C(7)	102.92(19)
Se–Rh–P(1)	88.18(3)	C(1)–P(1)–C(7)	102.21(19)
Se–Rh–G*	121.36(14)	Se–P(2)–N	113.46(13)
P(1)–Rh–G*	133.80(14)	Se–P(2)–C(13)	112.52(15)
Rh–Se–P(2)	98.86(3)	Se–P(2)–C(19)	107.02(14)
P(1)–N–P(2)	121.0(2)	N–P(2)–C(13)	109.8(2)
Rh–P(1)–N	115.89(13)	N–P(2)–C(19)	110.85(19)
Rh–P(1)–C(1)	115.15(14)	C(13)–P(2)–C(19)	102.67(19)

*G represents the centroid of the η^5-C_5Me_5 ligand.

symmetrical complex [(η^5-C_5Me_5)RhCl{η^2-*Se*,*Se*′-$(SePPh_2)_2N$}] [Rh–Cl: 2.4365(18), Rh–Se: average 2.563(1)Å] [3a]. The Rh–Cl and Rh–P(1) [2.3195(11) Å] distances agree well with the values found in the related complex [(η^5-C_5Me_5)RhCl{prophos}]BF_4 [Rh–Cl: 2.393(1)Å, Rh–P: 2.325(1) Å] [14].

The bidentate chelate ligand forms an approximately planar pentaatomic metallacycle. The bonding parameters within the RhP_2NSe ring [P(2)–Se: 2.1940(12) Å, P(2)–N: 1.582(3)Å, P(1)–N: 1.642(3) Å and P(1)–N–P(2): 121.0(2)°] indicate some grade of π-delocalisation over the fragment Se–P–N–P (P–Se in neutral ligand $NH(SePPh_2)_2$: 2.100(3) Å [15]; single covalent bond P–N: 1.78 Å [16]). Similar P–N–P bond sequences, with comparable bond lengths are commonly found in tri- or tetracyclophosphacenes [17]. These bonding parameters are similar to those in *cis*-[Pt{η^2-*P*,*Se*-$Ph_2P(Se)NPPh_2$}$_2$] [P–Se: 2.200(2) Å, P(2)–N: 1.584(7)Å, P(1)–N: 1.635(6) Å and P(1)–N–P(2): 123.3(4)°] [2b] and *trans*-[ReO(OEt){$Ph_2P(Se)NPPh_2$}$_2$] [P–Se: 2.208(3) Å, P(2)–N: 1.579(8)Å, P(1)–N: 1.639(8) Å and P(1)–N–P(2): 122.0(5)°] [18].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 154780 for compound **9**. Copies of the 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://ccdc.ca.ac.uk).

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