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Bis(diphenylphosphino)amine and their dichalcogenide derivatives as ligands in rhodium(III), iridium(III), and ruthenium(II) complexes. Crystal structures of [(η^5-C$_5$Me$_5$)MCl{η^2-(SePPh$_2$)$_2$N}] (M = Rh, Ir)

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This article is dedicated to Professor Martin A. Bennett, author of major advances on Organometallic Chemistry, on the occasion of his 65th birthday.

Abstract

Reaction of the dimers [{(η^5-C$_5$Me$_5$)MCl}$_2$(μ-Cl)$_2$] (M = Rh, Ir) or [{(η^6-arene)RuCl}$_2$(μ-Cl)$_2$] (arene = p-MeC$_6$H$_4^i$Pr, C$_6$Me$_6$) with NH(PPh$_2$)$_2$ in the presence of AgA (A = BF$_4$, PF$_6$) leads to the mononuclear cationic complexes [(η^5-C$_5$Me$_5$)MCl{η^2-(PPh$_2$)$_2$NH}]A (M = Rh (**1**), Ir (**2**)) or [(η^6-arene)RuCl{η^2-(PPh$_2$)$_2$NH}]A (arene = p-MeC$_6$H$_4^i$Pr (**3**), C$_6$Me$_6$ (**4**)). Similar reactions using the chalcogenide derivatives NH(EPPh$_2$)$_2$ (E = S, Se) yield the neutral complexes [(η^5-C$_5$Me$_5$)RhCl{η^2-(EPPh$_2$)$_2$N}] (E = S (**5**), Se (**6**)), [(η^5-C$_5$Me$_5$)IrCl{η^2-(EPPh$_2$)$_2$N}] (E = S (**7**), Se (**8**)), [(η^6-arene)RuCl{η^2-(SPPh$_2$)$_2$N}] (arene = C$_6$H$_6$ (**9**), p-MeC$_6$H$_4^i$Pr (**10**)) and [(η^6-arene)RuCl{η^2-(SePPh$_2$)$_2$N}] (arene = C$_6$Me$_6$ (**11**), p-MeC$_6$H$_4^i$Pr (**12**)). Chloride abstraction from complexes **5**–**8** with AgPF$_6$ in the presence of PPh$_3$ gives the cationic complexes [(η^5-C$_5$Me$_5$)Rh{η^2-(EPPh$_2$)$_2$N}(PPh$_3$)]PF$_6$ (E = S (**13**), Se (**14**)) and [(η^5-C$_5$Me$_5$)Ir{η^2-(EPPh$_2$)$_2$N}(PPh$_3$)]PF$_6$ (E = S (**15**), Se (**16**)). Complexes **13**–**16** can also be synthesised from the starting dinuclear complexes, AgPF$_6$, NH(EPPh$_2$)$_2$ and PPh$_3$. Using this alternative synthetic route the related ruthenium complexes [(η^6-C$_6$Me$_6$)Ru{η^2-(EPPh$_2$)$_2$N}(C$_5$H$_5$N)] BF$_4$ (E = S (**17**), Se (**18**)) can be prepared. All described compounds have been characterised by microanalysis and NMR (^{1}H, ^{31}P) and IR spectroscopy. The crystal structures of the neutral complexes [(η^5-C$_5$Me$_5$)MCl{η^2-(SePPh$_2$)$_2$N}] (M = Rh (**6**), Ir (**8**)) have been determined by X-ray diffraction methods. Both complexes exhibit analogous pseudo-octahedral molecular structures with a C$_5$Me$_5$ group occupying three coordination positions and a bidentate chelate Se,Se′-bonded ligand and a chloride atom completing the coordination sphere.

Keywords: Rhodium; Iridium; Ruthenium; Bis(diphenylphosphino)amine complexes; Dichalcogenide complexes; Crystal structures

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1. Introduction

The chemistry of the bis(diphenylphosphino)amine (NH(PPh$_2$)$_2$, dppa) and its chalcogenide derivatives (NH(EPPh$_2$)$_2$; E = O, S, Se) has been rapidly developed in recent years due to their versatile coordination properties. In a similar fashion to the widely employed bis(diphenylphosphino)methane, the dppa ligand can bind to metal atoms in different ways: monodentate [1], chelating [2], single bridging [3], double bridging [1,4] or tridentate bridging in its anionic form [5].

On the other hand, its chalcogenide derivatives can be regarded as non-carbon analogues of acetylacetones and their deprotonation reactions give the anions [(EPPh$_2$)$_2$N]$^-$ which undergo complexation with many

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metals to form inorganic (carbon-free) chelate rings [6]. A variety of transition metal compounds have been characterised crystallographically, showing that the ligands form non-planar metallacycles, in some cases with unusual coordination geometries at the metal centre [3]. The majority of the coordination studies have been developed with the sulphur derivative $[(SPR_2)_2N]^-$ due to the flexibility of the S–P–N–P–S backbone and its large S···S bite (3.7–4.0 Å). This bite is larger than that of 1,1-dithio ligands, $R_2PS_2^-$ (ca. 3.0 Å), which presents some uses in metal extractions, oil additives or biological activities [4]. However, only a few examples of transition metal dichalcogenoimidophosphinate complexes containing organometallic moieties have been described so far, $[AuR_2\{(SPPh_2)_2N\}]$ [5], $[Mn(CO)_4\{(SPPh_2)_2N\}]$ [4a] or $[Rh(cod)\{(SePPh_2)_2N\}]$ [4b] being some representative examples.

Here we describe the synthesis of cationic complexes of the type $[(\eta^n\text{-ring})MCl(\eta^2\text{-}P,P'\text{-dppa})]A$ $[(\eta^n\text{-ring})M = (\eta^5\text{-}C_5Me_5)Rh$, $(\eta^5\text{-}C_5Me_5)Ir$, $(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)Ru$, $(\eta^6\text{-}C_6Me_6)Ru$; $A = PF_6$, $BF_4]$, neutral complexes of the type $[(\eta^n\text{-ring})MCl\{\eta^2\text{-}(EPPh_2)_2N\}]$ $[(\eta^n\text{-ring})M = (\eta^5\text{-}C_5Me_5)Rh$, $(\eta^5\text{-}C_5Me_5)Ir$, $(\eta^6\text{-}C_6H_6)Ru$, $(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)Ru$, $(\eta^6\text{-}C_6Me_6)Ru$; E = S, Se] [7] and cationic complexes of general formula $[(\eta^5\text{-}C_5Me_5)M\{\eta^2\text{-}(EPPh_2)_2N\}(PPh_3)]PF_6$ (M = Rh, Ir; E = S, Se) and $[(\eta^6\text{-}C_6Me_6)Ru\{\eta^2\text{-}(EPPh_2)_2N\}(C_5H_5N)]BF_4$ (E = S, Se). The crystal structure of complexes $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}(SePPh_2)_2N\}]$ (M = Rh, Ir), determined by single-crystal X-ray diffraction, are also reported.

2. Experimental

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 materials $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ (M = Rh, Ir) [8], $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-}Cl)_2]$ (arene = C_6H_6 [9], $p\text{-}MeC_6H_4^iPr$ [10], C_6Me_6 [10]), and the ligands $NH(PPh_2)_2$ and $NH(EPPh_2)_2$ [4b,11] were prepared by published procedures. Elemental analyses (C, H, N, and S) were made with a Perkin–Elmer 240C microanalyser. IR spectra were recorded on a Perkin–Elmer 1330 spectrophotometer using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on Bruker AC-200P and Varian Unity 300 spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ (^1H) and 85% H_3PO_4 in D_2O (^{31}P, positive shifts downfield) as internal and external standards, respectively. Mass spectra were measured on a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode; ions were produced with the standard Cs^+ gun at ca. 30 kV and 3-nitrobenzylalcohol (NBA) was used as matrix.

2.1. Preparation of complexes

2.1.1. $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}(PPh_2)_2NH\}]PF_6$ (M = Rh (**1a**), Ir (**2a**))

To a solution of the dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ (0.162 mmol; Rh (100 mg), Ir (126 mg)) in CH_2Cl_2 (10 cm^3) was added a solution of $AgPF_6$ (82 mg; 0.324 mmol) in Me_2CO (10 cm^3). After stirring the mixture for 1 h at room temperature (r.t.), in the absence of light, the precipitated silver chloride was removed by filtration through Kieselghur. To the filtrate, $NH(PPh_2)_2$ (125 mg; 0.324 mmol) was added and the mixture stirred for 2 h. The resulting solution was evaporated to a small volume and the complex precipitated by adding *n*-hexane or pentane. The red solids were filtered off, washed with *n*-hexane and diethyl ether and dried under vacuum. Complex **1a**: yield, 208 mg, 84% (Found: C, 50.8; H, 5.1; N, 1.7. $C_{34}H_{36}ClF_6NP_3Rh$ requires C, 50.8; H, 4.5; N, 1.7%). ν_{max}/cm^{-1} (KBr) 3423 (NH), 838, 558 (PF_6^-). δ_H ($CDCl_3$) 1.49 [t, 30 H, C_5Me_5, $^4J(PH) = 4.1$ Hz], 7.24–7.59 (m, 20 H, Ph). δ_P ($CDCl_3$) 48.5 [d, $^1J(RhP) = 118.5$ Hz], −145.0 [sp, PF_6^-, $^1J(PF) = 714$ Hz]. Complex **2a**: yield, 176 mg, 61% (Found: C, 45.7; H, 4.1; N, 1.7. $C_{34}H_{36}ClF_6IrNP_3$ requires C, 45.7; H, 4.1; N, 1.6%). ν_{max}/cm^{-1} (KBr) 3443 (NH), 839, 560 (PF_6^-). δ_H ($CDCl_3$) 1.54 [t, 30 H, C_5Me_5, $^4J(PH) = 2.7$ Hz], 6.86–7.73 (m, 20 H, Ph), 8.8 (s, br, 1 H, NH). δ_P ($CDCl_3$) 16.8 (s), −145.0 [sp, PF_6^-, $^1J(PF) = 714$ Hz].

The related tetrafluoroborate complexes $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}(PPh_2)_2NH\}]BF_4$ (**1b**) and $[(\eta^5\text{-}C_5Me_5)IrCl\{\eta^2\text{-}(PPh_2)_2NH\}]BF_4$ (**2b**), were prepared using $AgBF_4$ (63 mg; 0.324 mmol) instead of $AgPF_6$, in $CHCl_3/Me_2CO$: 5/15 cm^3. The products were recrystallised from dichloromethane–diethyl ether. Complex **1b**: yield, 159 mg, 62% (Found: C, 52.6; H, 3.7; N, 2.0. $C_{34}H_{36}BClF_4NP_2Rh\cdot 0.5CH_2Cl_2$ requires C, 52.6; H, 4.0; N, 1.8%). ν_{max}/cm^{-1} (KBr) 3424 (NH), 1103 and 516 (BF_4^-). δ_H (CD_2Cl_2) 1.53 [t, 30 H, C_5Me_5, $^4J(PH) = 4.1$ Hz], 7.30–7.63 (m, 20 H, Ph). δ_P (CD_2Cl_2) 49.8 [d, $^1J(RhP) = 118.4$ Hz]. Complex **2b**: yield, 217 mg, 81% (Found: C, 48.2; H, 3.9; N, 1.7. $C_{34}H_{36}BClF_4IrNP_2$ requires C, 48.9; H, 4.4; N, 1.7%). ν_{max}/cm^{-1} (KBr) 3442 (NH), 1105 and 519 (BF_4^-). δ_H ($CDCl_3$) 1.54 [t, 30 H, C_5Me_5, $^4J(PH) = 2.7$ Hz], 6.86–7.73 (m, 20 H, Ph) and 8.7 (s, br, 1 H, NH). δ_P ($CDCl_3$) 16.7 (s).

2.1.2. $[(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)RuCl\{\eta^2\text{-}(PPh_2)_2NH\}]BF_4$ (**3**)

To a solution of the binuclear ruthenium complex $[\{(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)RuCl\}_2(\mu\text{-}Cl)_2]$ (100 mg; 0.163 mmol) in $CHCl_3$ (5 cm^3) was added a solution of $AgBF_4$ (64 mg; 0.326 mmol) in Me_2CO (15 cm^3). After stirring the mixture for 1 h at r.t., in the absence of light, the precipitated silver chloride was removed by filtration through Kieselghur. To the filtrate, $NH(PPh_2)_2$ (126 mg; 0.326 mmol) was added and the mixture stirred for 2 h. The resulting solution was evaporated to a small volume and the complex precipitated by adding *n*-hexane or pentane. The solid was filtered off, washed with *n*-hexane and diethyl ether and dried under vacuum. Yield: 220 mg, 86% (Found: C, 52.5; H, 4.6; N, 1.9. $C_{34}H_{35}BClF_4NP_2Ru\cdot 0.5CH_2Cl_2$ requires C, 52.7; H, 4.6; N, 1.8%). ν_{max}/cm^{-1} (KBr) 3442 (NH), 1102 and 519 (BF_4^-). δ_H ($CDCl_3$) 0.89 [d, 6 H, Me(^{i}Pr), ^3J(HH) = 6.5 Hz], 1.78 [s, 3 H, Me], 2.13 [sp, 1 H, CH(^{i}Pr)], 5.20 and 5.30 [4 H, AB system, J(HH) = 5.8 Hz], 5.41 [t, NH, ^2J(PH) = 4.65 Hz], 7.16–7.75 (m, 20 H, Ph). δ_P ($CDCl_3$) 60.7 (s).

*2.1.3. [(η^6-C_6Me_6)RuCl{η^2-$(PPh_2)_2NH$}]PF_6 (**4**)*

To a solution of complex [{(η^6-C_6Me_6)RuCl}$_2$(μ-Cl)$_2$] (100 mg; 0.15 mmol) in CH_2Cl_2 (10 cm^3) was added a solution of $AgPF_6$ (76 mg; 0.30 mmol) in Me_2CO (10 cm^3). The mixture was worked up as described for complex **3**, using 116 mg (0.30 mmol) of the ligand $NH(PPh_2)_2$. Yield: 191 mg, 77% (Found: C, 51.9; H, 4.8; N, 1.7. $C_{36}H_{39}ClF_6NP_3Ru$ requires C, 52.2; H, 4.8; N, 1.7%). ν_{max}/cm^{-1} (KBr) 3443 (NH), 837 and 557 (PF_6^-). δ_H [$(CD_3)_2CO$] 2.07 (s, 18 H, C_6Me_6), 7.52–7.87 (m, 20 H, Ph). δ_P [$(CD_3)_2CO$] 58.4 (s), -145.0 [sp, PF_6^-, ^1J(PF) = 714 Hz].

*2.1.4. [(η^5-C_5Me_5)MCl{η^2-$(EPPh_2)_2N$}] (M = Rh; E = S (**5**), Se (**6**). M = Ir; E = S (**7**), Se (**8**))*

To a solution of the binuclear complex [{(η^5-C_5Me_5)MCl}$_2$(μ-Cl)$_2$] (0.1 mmol; Rh (62 mg), Ir (80 mg)) in CH_2Cl_2 (10 cm^3) a solution of $AgBF_4$ (41 mg; 0.21 mmol) in Me_2CO (10 cm^3) was added. After stirring the mixture for 1 h, the AgCl formed was filtered off through Kieselguhr. The filtrate was treated with the ligand $NH(EPPh_2)_2$ (0.2 mmol; E = S (90 mg), Se (108 mg)) and the resulting solution stirred for 2 h. The mixture was evaporated to dryness and the residue extracted with the minimal amount of CH_2Cl_2. The solution was chromatographed on neutral Al_2O_3 (90% activity) using CH_2Cl_2 as eluent. The red solution obtained was concentrated to a small volume and the complexes crystallised by careful addition of diethyl ether. Complex **5**: yield, 176 mg, 75% (Found: C, 56.3; H, 4.8; N, 2.0; S, 8.9. $C_{34}H_{35}ClNP_2RhS_2$ requires C, 56.6; H, 4.9; N, 1.9; S, 8.9%). ν_{max}/cm^{-1} (Nujol) 570 (PS), 1145 and 805 (P_2N). δ_H ($CDCl_3$) 1.38 (s, 30 H, C_5Me_5), 6.90–8.20 (m, 20 H, Ph). δ_P ($CDCl_3$) 36.45 (s). Complex **6**: yield, 165 mg, 78% (Found: C, 49.9; H, 4.4; N, 1.8. $C_{34}H_{35}ClNP_2RhSe_2$ requires C, 50.1; H, 4.3; N, 1.7%). ν_{max}/cm^{-1} (Nujol) 535 (PSe), 1165 and 785 (P_2N). δ_H ($CDCl_3$) 1.39 (s, 30 H, C_5Me_5), 7.20–7.95 (m, 20 H, Ph). δ_P ($CDCl_3$) 24.9 (s, ^1J(PSe) = 570 Hz). Complex **7**: yield, 145 mg, 67% (Found: C, 50.1; H, 4.5; N, 1.7; S, 7.4. $C_{34}H_{35}ClIrNP_2S_2$ requires C, 50.3; H, 4.4; N, 1.7; S, 7.9%). ν_{max}/cm^{-1} (Nujol) 560 (PS), 1165 and 800 (P_2N). δ_H ($CDCl_3$) 1.36 (s, 30 H, C_5Me_5), 7.04–8.20 (m, 20 H, Ph). δ_P ($CDCl_3$) 31.6 (s). Complex **8**: yield, 124 mg, 65% (Found: C, 45.3; H, 4.0; N, 1.5. $C_{34}H_{35}ClIrNP_2Se_2$ requires C, 45.1; H, 3.9; N, 1.6%). ν_{max}/cm^{-1} (Nujol) 530 (PSe), 1170 and 780 (P_2N). δ_H (CD_2Cl_2) 1.37 (s, 30 H, C_5Me_5), 7.05–8.20 (m, 20 H, Ph). δ_P (CD_2Cl_2) 18.4 (s, ^1J(PSe) = 578 Hz).

*2.1.5. [(η^6-arene)RuCl{η^2-$(EPPh_2)_2N$}] (E = S; arene = C_6H_6 (**9**), p-Me$C_6H_4^i$Pr (**10**). E = Se; arene = C_6Me_6 (**11**), p-Me$C_6H_4^i$Pr (**12**))*

To a solution of the binuclear complex [{(η^6-arene)RuCl}$_2$(μ-Cl)$_2$] (0.1 mmol; C_6H_6 (49 mg), *p*-Me$C_6H_4^i$ Pr (61 mg), C_6Me_6 (67 mg)) in CH_2Cl_2 (10 cm^3) a solution of $AgBF_4$ (41 mg; 0.21 mmol) in Me_2CO (10 cm^3) was added. After stirring the mixture for 1 h, the AgCl formed was filtered off through Kieselguhr. The filtrate was treated with the ligand $NH(EPPh_2)_2$ (0.2 mmol; E = S (90 mg), Se (108 mg)) and the resulting solution stirred for 2 h. During this time the solution changed from red to a sort of green colour. The solution was evaporated to dryness, the residue extracted with the minimal amount of CH_2Cl_2 and the solution chromatographed on neutral Al_2O_3 (90% activity) using CH_2Cl_2 as eluent. The red solution obtained was concentrated to a small volume and the complexes crystallised by careful addition of diethyl ether. Complex **9**: yield, 87 mg, 63% (Found: C, 53.4; H, 5.2; N, 2.0; S, 9.2. $C_{30}H_{36}ClNP_2RuS_2$ requires C, 53.5; H, 5.4; N, 2.1; S, 9.5%). ν_{max}/cm^{-1} (Nujol) 550 (PS), 1170 and 795 (P_2N). δ_H ($CDCl_3$) 5.17 (s, 6 H, C_6H_6), 7.10–8.30 (m, 20 H, Ph). δ_P ($CDCl_3$) 38.2 (s). Complex **10**: yield, 76 mg, 75% (Found: C, 56.9; H, 4.4; N 1.9; S, 8.4. $C_{34}H_{34}ClNP_2RuS_2$ requires C, 56.8; H, 4.8; N, 2.0; S, 8.9%). ν_{max}/cm^{-1} (Nujol) 555 (PS), 1180 and 800 (P_2N). δ_H ($CDCl_3$) 1.19 [d, 6 H, Me(^{i}Pr), ^3J(HH) = 6.9 Hz], 2.06 (s, 3 H, Me), 2.78 [m, 1 H, CH(^{i}Pr)], 4.82 and 5.00 [4 H, AB system, J(HH) = 5.9 Hz], 7.30–7.88 (m, 20 H, Ph). δ_P ($CDCl_3$) 36.2 (s). Complex **11**: yield, 78 mg, 62% (Found: C, 51.8; H, 4.7; N, 1.6. $C_{36}H_{38}ClNP_2RuSe_2$ requires C, 51.4; H, 4.6; N, 1.7%). ν_{max}/cm^{-1} (Nujol) 535 (PSe), 1150 and 780 (P_2N). δ_H ($CDCl_3$) 1.80 (s, 18 H, C_6Me_6), 6.94–8.10 (m, 20 H, Ph). δ_P ($CDCl_3$) 24.8 [s, ^1J(PSe) = 587 Hz]. Complex **12**: yield, 212 mg, 80% (Found: C, 50.2; H, 3.9; N, 2.2. $C_{34}H_{34}ClNP_2RuSe_2$ requires C, 50.2; H, 4.2; N, 1.7%). ν_{max}/cm^{-1} (Nujol) 530 (PSe), 1170 and 780 (P_2N). δ_H ($CDCl_3$) 1.07 [d, 6 H, Me(^{i}Pr), ^3J(HH) = 5.8 Hz], 1.88 (s, 3 H, Me), 2.73 [m, 1 H, CH(^{i}Pr)], 4.75 and 4.90 [4 H, AB system, J(HH) = 4.6 Hz], 6.96–8.24 (m, 20 H, Ph). δ_P ($CDCl_3$) 29.4 [s, ^1J(PSe) = 563 Hz].

*2.1.6. [(η^5-C_5Me_5)M{η^2-$(EPPh_2)_2N$}(PPh_3)]PF_6 (M = Rh; E = S (**13**), Se (**14**). M = Ir; E = S (**15**), Se (**16**))*

The complexes can be alternatively prepared by the two methods described below.

(i) To a solution of complexes **5**–**8** (0.1 mmol) in CH_2Cl_2 (20 cm^3) the stoichiometric amount of $AgPF_6$ (25.8 mg; 0.1 mmol) in Me_2CO (10 cm^3) was added. The mixture was boiled under reflux for 4 h. The AgCl formed was filtered off through Kieselguhr and PPh_3 (26.3 mg; 0.1 mmol) was added to the obtained solution. The resulting solution was stirred for 1 h, concentrated to a small volume and the addition of diethyl ether caused the precipitation of the compounds. Recrystallisation from acetone–diethyl ether led to orange crystals.

(ii) To a solution of the dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ (0.1 mmol; Rh (62 mg), Ir (80 mg)) in CH_2Cl_2 (20 cm^3) was added $AgPF_6$ (103.2 mg; 0.4 mmol) in Me_2CO (10 cm^3). The mixture was boiled under reflux for 2 h. The AgCl formed was filtered off through Kieselguhr and to the obtained solution $NH(EPPh_2)_2$ (0.2 mmol; E = S (90 mg), Se (108 mg)) and PPh_3 (52.6 mg; 0.2 mmol) were added. After stirring for 1 h, the solution was evaporated to dryness, the residue extracted with the minimal amount of CH_2Cl_2 and the solution chromatographed on neutral Al_2O_3 (90% activity) using CH_2Cl_2 as eluent. The obtained solution was concentrated under reduced pressure to a small volume and the complexes crystallised by addition of diethyl ether.

Method (i). Complex **13**: yield, 59 mg, 54% (Found: C, 56.6; H, 4.5; N, 1.2; S, 5.6. $C_{52}H_{50}F_6NP_4RhS_2$ requires C, 57.1; H, 4.6; N, 1.3; S, 5.9%). ν_{max}/cm^{-1} (KBr) 525 (PS), 1177 and 798 (P_2N), 840 and 565 (PF_6^-). δ_H ($CDCl_3$) 1.18 [d, 30 H, C_5Me_5, $^4J(P_AH) = 3.5$ Hz)], 6.83–8.16 (m, 20 H, Ph). δ_P ($CDCl_3$) 30.3 [dt, $^1J(RhP_A) = 134$ Hz, $^3J(P_BP_A) = 17$ Hz], 31.5 [d, P_B] − 145.0 [sp, PF_6^-, $^1J(PF) = 714$ Hz]. Complex **14**: yield, 60 mg, 51% (Found: C, 53.4; H, 4.1; N, 1.1. $C_{52}H_{50}F_6NP_4RhSe_2$ requires C, 52.8; H, 4.3; N, 1.2%). ν_{max}/cm^{-1} (KBr) 509 (PSe), 1196 and 789 (P_2N), 839 and 558 (PF_6^-). δ_H ($CDCl_3$) 1.30 [d, 30 H, C_5Me_5, $^4J(P_AH) = 3.6$ Hz)], 6.80–8.10 (m, 20 H, Ph). δ_P ($CDCl_3$) 32.1 [dt, $^1J(RhP_A) = 140$ Hz, $^3J(P_BP_A) = 17$ Hz], 20.1 [d, P_B, $^1J(P_BSe) = 566$ Hz], − 145.0 [sp, PF_6^-, $^1J(PF) = 714$ Hz]. Complex **15**: yield, 67 mg, 56% (Found: C, 52.2; H, 4.3; N, 1.2; S, 5.2. $C_{52}H_{50}F_6IrNP_4S_2$ requires C, 52.6; H, 4.2; N, 1.2; S, 5.4%). ν_{max}/cm^{-1} (KBr) 530 (PS), 1175 and 805 (P_2N), 840 and 564 (PF_6^-). δ_H ($CDCl_3$) 1.20 [d, 30 H, C_5Me_5, $^4J(P_AH) = 2.5$ Hz], 6.83–8.14 (m, 20 H, Ph). δ_P ($CDCl_3$) − 2.95 [t, $^3J(P_BP_A) = 19$ Hz], 25.6 [d, P_B], − 145.0 [sp, PF_6^-, $^1J(PF) = 714$ Hz]. Complex **16**: yield, 63 mg, 49% (Found: C, 48.9; H, 3.9; N, 1.1. $C_{52}H_{50}F_6IrNP_4Se_2$ requires C, 48.9; H, 4.0; N, 1.1%). ν_{max}/cm^{-1} (KBr). δ_H ($CDCl_3$) 1.31 [d, 30 H, C_5Me_5, $^4J(P_AH) = 2.2$ Hz], 6.83–8.03 (m, 20 H, Ph). δ_P ($CDCl_3$) − 2.3 [t, $^3J(P_BP_A) = 19$ Hz], 25.6 [d, P_B, $^1J(P_BSe) = 558$ Hz], − 145.0 [sp, PF_6^-, $^1J(PF) = 714$ Hz].

2.1.7. *$[(\eta^6\text{-}C_6Me_6)Ru\{\eta^2\text{-}(EPPh_2)_2N\}(C_5H_5N)]BF_4$ (E = S (**17**), Se (**18**))*

To a solution of the dinuclear complex $[\{(\eta^6\text{-}C_6Me_6)RuCl\}_2(\mu\text{-}Cl)_2]$ (66.9 mg; 0.1 mmol) in CH_2Cl_2 (20 cm^3) was added $AgBF_4$ (79.4 mg; 0.4 mmol) in Me_2CO (10 cm^3). The mixture was boiled under reflux for 2 h. The AgCl formed was filtered off through Kieselguhr and to the obtained solution $NH(EPPh_2)_2$ (0.2 mmol; E = S (90 mg), Se (108 mg)) and C_5H_5N (16 μl, 0.2 mmol) were added. After stirring for 1 h, the solution was concentrated under reduced pressure to a small volume and the complexes crystallised by addition of diethyl ether. Orange–red crystals were obtained from acetone–diethyl ether. Complex **17**: yield, 81 mg, 46% (Found: C, 55.7; H, 5.0; N, 3.1; S, 6.9. $C_{41}H_{43}BF_4N_2P_2RuS_2$ requires C, 56.1; H, 4.9; N, 3.2; S, 6.6%). ν_{max}/cm^{-1} (KBr) 568 (PS), 1176 and 798 (P_2N), 1100 and 514 (BF_4^-). δ_H ($CDCl_3$) 1.81 (s, 18 H, C_6Me_6), 7.20–7.80 (m, 20 H, Ph), 6.81 (t, C_5H_5N), 8.38 (d, C_5H_5N). δ_P ($CDCl_3$) 24.1 (s). Complex **18**: yield, 93 mg, 48% (Found: C, 49.9; H, 4.4; N, 2.8. $C_{41}H_{43}BF_4N_2P_2RuSe_2$ requires C, 50.8; H, 4.5; N, 2.9%). ν_{max}/cm^{-1} (KBr) 505 (PSe), 1178 and 786 (P_2N), 1100 and 539 (BF_4^-). δ_H ($CDCl_3$) 1.83 (s, 18 H, C_6Me_6), 7.21–7.90 (m, 20 H, Ph), 6.77 (t, C_5H_5N), 8.40 (d, C_5H_5N). δ_P ($CDCl_3$) 20.9 [s, $^1J(PSe) = 576$ Hz].

2.2. *Crystal structure determination of $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}(SePPh_2)_2N\}]$ (**6**) and $[(\eta^5\text{-}C_5Me_5)IrCl\{\eta^2\text{-}(SePPh_2)_2N\}]$ (**8**)*

Suitable crystals for the X-ray analyses were obtained by slow diffusion of diethyl ether into acetone solutions of complexes **6** and **8**. Crystal data and refinement parameters are summarised in Table 1. Data were collected on a Siemens–Stoe AED-2 (**6**) or on a Siemens P4 (**8**) diffractometer with graphite-monochromated Mo–K_α radiation, using the ω–2θ scan method. Three standard reflections were monitored every 55 min (**6**) or every 97 measured reflections (**8**) throughout data collection; no significant variations were observed. All data were corrected for Lorentz and polarisation effects, and for absorption using a semiempirical method (ψ scan) [12]; minimum and maximum transmission factors are listed in Table 1. All structures were solved by Patterson method and Fourier techniques, and refined by full-matrix least squares on F^2 (SHELXL-97) [13]. Absolute structure was checked in both cases using the Flack parameter ($x = -0.013(10)$ **6** and $-0.018(12)$ **8**) [14]. The function minimised was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program [13].

2.2.1. Complex *6*

Anisotropic displacement parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms of the pentamethylcyclopentadienyl methyl groups were included in calculated positions; all the remaining ones were obtained from difference Fourier maps. All the hydrogens were refined riding on carbon atoms with two common displacement parameters (phenyl and methyl groups). The refinement converged to $R(F)=0.0464$ $[F^2>2\sigma(F^2)]$ and $wR(F^2)=0.1010$ (all data), with weight parameters $x=0.0427$ and $y=1.8372$. Residual peaks in the final difference map were in the range 0.662 and −0.637 e Å^{-3}.

2.2.2. Complex *8*

After refinement of all non-hydrogen atoms with anisotropic displacement parameters, the hydrogen atoms of the pentamethylcyclopentadienyl ligand and some of the phenyl groups were included in calculated positions; the remaining ones were obtained from difference Fourier maps. All the hydrogens were refined riding on carbon atoms with two common thermal parameters, one for phenyl groups and another for methyl groups. The refinement converged to $R(F)=0.0411$ $[F^2>2\sigma(F^2)]$ and $wR(F^2)=0.0993$ (all data), with weight parameters $x=0.0391$ and $y=6.6804$. The highest residual peaks in the final difference map, lower than 1.136 e Å^{-3}, were situated close to the metal centre.

Table 1
Crystallographic data and refinement details for $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}(SePPh_2)_2N\}]$ (M = Rh (**6**), Ir (**8**))

	6	**8**
Crystal colour, habit	Dark red, prismatic block	Red, block
Crystal size (mm)	0.40 × 0.34 × 0.23	0.33 × 0.24 × 0.18
Formula	$C_{34}H_{35}ClNP_2RhSe_2$	$C_{34}H_{35}ClIrNP_2Se_2$
M	815.85	905.14
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
T (K)	293(2)	293(2)
a (Å)	8.9245(7)	8.931(2)
b (Å)	17.7607(13)	17.740(4)
c (Å)	20.575(3)	20.627(4)
V/ (Å^3)	3261.2(6)	3268.1(12)
Z	4	4
μ(mm^{-1})	2.961	6.518
θ Range (°)	1.51–27.53	1.51–25.02
No. collected reflections	9425	8194
No. unique reflections	7518 ($R_{int}=0.0275$)	5740 ($R_{int}=0.0479$)
Min., max. transmission factors	0.384, 0.549	0.222, 0.387
Data/restraints/parameters	7518/0/377	5740/0/377
$R(F)$ $[F^2>2\sigma(F^2)]$ [a]	0.0464	0.0411
$wR(F^2)$ (all data) [b]	0.1010	0.0993

[a] $R(F)=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$ for 6116 and 4913 observed reflections, respectively.

[b] $R_w(F^2)=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

3. Results and discussion

The dinuclear complexes $[\{(\eta^n\text{-ring})MCl\}_2(\mu\text{-}Cl)_2]$ reacted in dichloromethane–acetone with silver salts AgA of non-coordinating anions ($A=PF_6^-$, BF_4^-) in a 1:2 molar ratio, to form silver chloride and, most probably, the solvate complex $[(\eta^n\text{-ring})MCl(solvent)_2]^+$, which further reacted with $NH(PPh_2)_2$ to give cationic compounds of the type $[(\eta^n\text{-ring})MCl\{\eta^2\text{-}(PPh_2)_2NH\}]A$ $[(\eta^n\text{-ring})M=(\eta^5\text{-}C_5Me_5)Rh$; $A=PF_6^-$ (**1a**), BF_4^- (**1b**). $(\eta^n\text{-ring})M=(\eta^5\text{-}C_5Me_5)Ir$; $A=PF_6^-$ (**2a**), BF_4^- (**2b**). $(\eta^n\text{-ring})M=(\eta^6\text{-}p\text{-}MeC_6H^i_4Pr)Ru$; $A=BF_4^-$ (**3**). $(\eta^n\text{-ring})M=(\eta^6\text{-}C_6Me_6)Ru$; $A=PF_6^-$ (**4**)]. Complexes **1–4** were isolated as stable microcrystalline solids and characterised by elemental analyses, IR and NMR spectroscopy. The IR spectra showed the presence of the uncoordinated anion (PF_6^-: ca. 840, 560 cm^{-1}; BF_4^-: ca. 1050, 510 cm^{-1}) together with a broad absorption band, in the 3423–3443 cm^{-1} region, corresponding to the N–H bond. The ^{1}H-NMR spectra of complexes **1a** and **2a**, in deuterated chloroform, exhibited a singlet resonance at δ 1.49 (**1a**) or 1.53 ppm (**2a**) attributed to the C_5Me_5 group and two multiplets in the 7.24–7.59 ppm region corresponding to the phenyl protons of the phosphine ligand. For complex **2a**, the NH amine proton was observed as a broad singlet centred at δ 8.8 ppm. The ^{31}P-NMR spectra of complexes **1a** and **2a** showed a doublet resonance at δ 48.5 ppm with a ^1J(RhP) coupling of 118.5 Hz and a singlet at δ 16.8 ppm, respectively.

Analogously, the ^{1}H-NMR spectra of compounds **3** and **4** showed the presence of the arene and $NH(PPh_2)_2$ resonances in the required proportions. In particular, a triplet centred at δ 5.41 ppm with a ^2J(PH) coupling constant of 4.65 Hz denoted the presence of the NH functionality in the (p-$MeC_6H^i_4Pr$)Ru compound **3**. The ^{31}P-NMR spectra of the cations consisted of a singlet at 60.7 or 58.4 ppm for **3** and **4**, respectively.

On the other hand, the reactions of the starting dinuclear complexes $[\{(\eta^n\text{-ring})MCl\}_2(\mu\text{-}Cl)_2]$ with the chalcogenide ligands $NH(EPPh_2)_2$ (E = S, Se) in dichloromethane–acetone, in the presence of silver hexafluorophosphate or tetrafluoroborate, yielded neutral complexes of the general formula $[(\eta^n\text{-ring})MCl\{\eta^2\text{-}(EPPh_2)_2N\}]$ $[(\eta^n\text{-ring})M=(\eta^5\text{-}C_5Me_5)Rh$; E = S (**5**), Se (**6**). $(\eta^n\text{-ring})M=(\eta^5\text{-}C_5Me_5)Ir$; E = S (**7**), Se (**8**). $(\eta^n\text{-ring})M=(\eta^6\text{-}C_6H_6)Ru$, E = S (**9**). $(\eta^n\text{-ring})M=(\eta^6\text{-}p\text{-}MeC_6H^i_4Pr)Ru$, E = S (**10**). $(\eta^n\text{-ring})M=(\eta^6\text{-}C_6Me_6)Ru$, E = Se (**11**). $(\eta^n\text{-ring})M=(\eta^6\text{-}p\text{-}MeC_6H^i_4Pr)Ru$, E = Se (**12**)]. The spontaneous loss of hydrogen hexafluorophosphate or tetrafluoroborate confirmed that the acidity of the amine proton of the chalcogenide ligands was enhanced by coordination and, as expected, is higher than that of the amine proton in the dppa ligand. The neutral complexes were isolated as microcrystalline solids. In all cases their IR spectra in Nujol mulls showed the absorption bands corresponding to P_2N and P=E groups. The ν(PS) and ν(PSe) stretching bands were shifted to lower frequencies ($\nu(PS) = 550$–570 cm^{-1} and $\nu(PSe) = 530$–535 cm^{-1}) relative to that of the free neutral ligand ($\nu(PS) = 625$ cm^{-1} and $\nu(PSe) = 546$ cm^{-1}) [4b,15], as a consequence of the decrease in the bond order. The $\nu_{asym}(P_2N)$ bands of the dithioimidophosphinate complexes **5**, **7**, **9**, and **10** are in the ranges 1145–1180 and 795–805 cm^{-1} (935 and 932 cm^{-1} in the free ligand) and those of the diselenoimidophosphinates **6**, **8**, **11**, and **12** in the ranges 1150–1180 and 780–785 cm^{-1} (1114 and 781 cm^{-1} in the free ligand) [16], reflecting the increase in the P–N bond order. The mass spectrum of complex **8** (FAB$^+$ mode) showed a peak at *m*/*z* 905, with an isotopic distribution that matched the calculated for the proposed neutral formulation.

The ^{1}H-NMR spectra of complexes **5**–**12** were in good agreement with the proposed formulations showing the expected resonances of the C_5Me_5 or arene coordinated rings and the phenyl groups of the chalcogenide ligands in the required proportions (see Section 2). Their ^{31}P-NMR spectra exhibited a single resonance in the range δ 18.4–32.6 ppm, with the expected phosphorus–selenium coupling for the diselenoimidophosphinate complexes ranging between 563 and 578 Hz.

Complexes **5**–**8** reacted with silver hexafluorophosphate in refluxing dichloromethane–acetone leading to the cationic solvate intermediate $[(\eta^5\text{-}C_5Me_5)M\{\eta^2\text{-}(EPPh_2)_2N\}(solvent)]^+$, which in turn reacted with triphenylphosphine to yield the cationic complexes $[(\eta^5\text{-}C_5Me_5)M\{\eta^2\text{-}(EPPh_2)_2N\}(PPh_3)]PF_6$ (M = Rh; E = S (**13**), Se (**14**). M = Ir; E = S (**15**), Se (**16**)). Similar results were obtained by treatment of the intermediate solvate complex $[(\eta^5\text{-}C_5Me_5)M(solvent)_3]^{2+}$, prepared from $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ and $AgPF_6$, with equimolar amounts of $NH(EPPh_2)_2$ and PPh_3.

The ^{1}H-NMR spectra of complexes **13**–**16** showed the expected doublet for the C_5Me_5 groups due to P_A–H coupling (P_APh_3) and the ^{31}P-NMR spectra of the rhodium complexes **13** and **14** exhibited a doublet of triplets (P_A) and a doublet (P_B), due to Rh–P_A and P_A–P_B couplings $[N(EP_BPh_2)_2]$ centred at δ 30.3 and 31.5 ppm and at δ 32.05 and 20.1 ppm, respectively. The spectrum of complex **14** presents, moreover, the corresponding P–Se coupling. The ^{31}P-NMR spectra of the iridium complexes **15** and **16** consisted of a triplet and a doublet assigned to P_A and P_B nuclei, centred at δ -2.95 and 25.6 ppm and at -2.3 and 25.6 ppm, respectively, with a P_A–P_B coupling of 19 Hz. The difference in the chemical shift for the phosphorus nucleus of the PPh_3 ligand between the rhodium and the iridium compounds (about 34 ppm) reflects the softer character of the iridium atom.

Attempts to obtain similar cationic arene–ruthenium complexes, through the abstraction of the chloride ligand on complexes **9**–**12** with silver salts and subsequent reaction with triphenylphophine, were unsuccessful. In all cases, the reaction gave rise to a mixture of uncharacterised solids. However, the reactions of the solvate intermediate complex $[(\eta^6\text{-}C_6Me_6)Ru(solvent)_3]^{2+}$ with the appropriate chalcogenide ligands and a stronger σ-donor ligand such as pyridine, yielded the corresponding cationic derivatives $[(\eta^6\text{-}C_6Me_6)Ru\{\eta^2\text{-}(EPPh_2)_2N\}(NC_5H_5)]^+$ which were isolated as tetrafluoroborate salts (E = S (**17**), Se (**18**)). The ^{1}H-NMR spectra showed a singlet for the C_6Me_6 protons together with a triplet and a doublet corresponding to the pyridine ligand. The expected additional triplet for the pyridine protons is masked by two broad multiplets attributable to the phenyl groups of the chalcogenide ligands. Their ^{31}P-NMR spectra consisted of one singlet with the expected P–Se coupling (576 Hz) for complex **18**.

All cationic compounds **13**–**18** were isolated as stable microcrystalline solids. Their IR spectra showed the characteristic bands of the PE and P_2N bonds, the coordinated ligands PPh_3 and C_5H_5N, together with the bands corresponding to the uncoordinated anion.

*3.1. X-ray crystal structures of $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}(SePPh_2)_2N\}]$ (**6**) and $[(\eta^5\text{-}C_5Me_5)IrCl\{\eta^2\text{-}(SePPh_2)_2N\}]$ (**8**)*

Although the spectroscopic data in the solid state and in solution suggest the loss of the aminic proton of the chalcogenide ligands upon coordination, two analyses by X-ray diffraction methods were carried out to establish the molecular structures and to obtain additional information on bonding parameters. Figs. 1 and 2 display the molecular representation of complexes **6** and **8**, respectively. Table 2 collects selected bond distances and angles for both structures.

From a crystallographic point of view, both crystal structures are isostructural, packed in the same space group and with comparable cell parameters. At a molecular level, both metal complexes are also rather similar; although some of the molecular parameters (bond lengths and angles) are statistically different, none of them evince a significant diversity that could be potentially associated with chemical distinctions. Both metal centres exhibit highly distorted pseudo-octahedral environments with the pentamethylcyclopentadienyl group occupying three formal coordination sites, with the chelating tetraphenyldiselenoimidodiphosphinate ligand bonded to the metal through two selenium

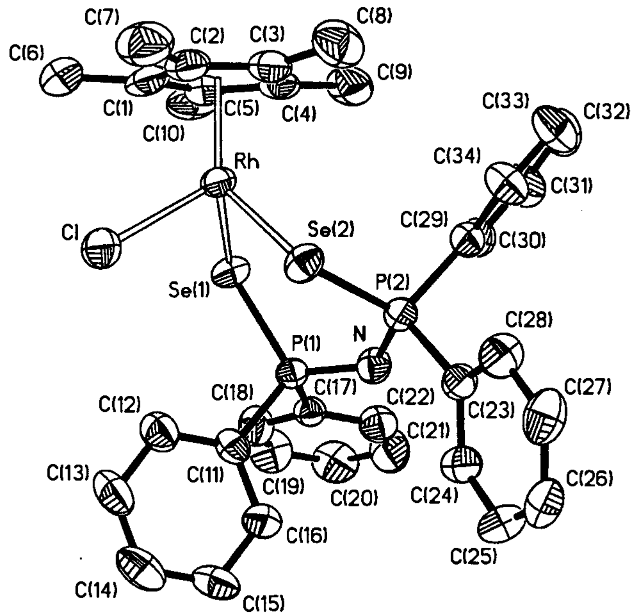

Fig. 1. Molecular diagram of the complex [(η^5-C_5Me_5)RhCl{η^2-($SePPh_2)_2N$}] (**6**), together with the numbering scheme used.

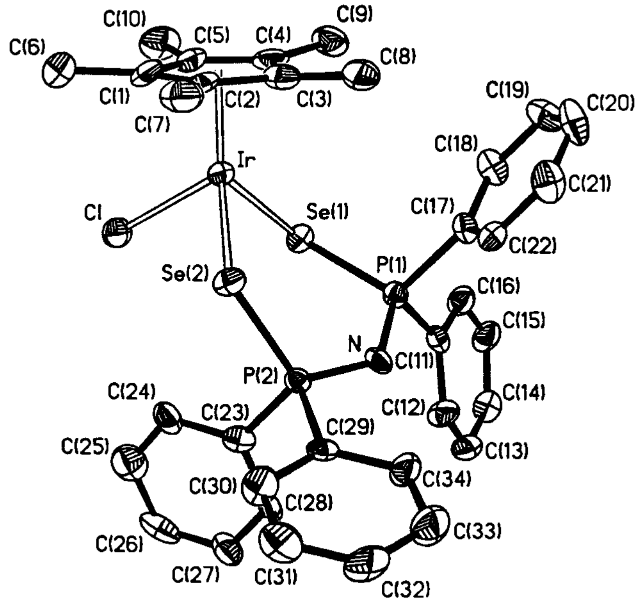

Fig. 2. Molecular representation of the neutral complex [(η^5-C_5Me_5)IrCl{η^2-($SePPh_2)_2N$}] (**8**), with the labelling scheme used.

atoms, and with a chloride atom completing the coordination sphere.

The two M–G (C_5Me_5 centroid) distances, 1.804(7) Å in **6** (Rh–C range 2.158(6)–2.195(7) Å) and 1.811(11) Å for complex **8** (Ir–C range 2.175(11)–2.202(11) Å), are identical within the experimental error and compare well with the values found in related pentamethylcyclopentadienyl rhodium(III) [17] and iridium(III) [18] complexes. The Rh–Cl (2.4366(17) Å) and Ir–Cl (2.447(3) Å) bond lengths are also very similar, but are slightly longer than the distances observed in analogous cationic complexes containing the '(η^5-C_5Me_5)M' moiety, such as in [(η^5-C_5Me_5)RhCl(prophos)]BF_4 (2.393(1)Å) [19], [(η^5-C_5Me_5)RhCl(phen)]ClO_4 (2.386(1) Å) [20] or in [(η^5-C_5Me_5)IrCl{η^2-Ph_2PCH_2SPh}]BF_4 (2.381(2) Å) [18a] and [(η^5-C_5Me_5)IrCl{L-histidine] (2.402(5) Å) [21].

In both structures, the MSe_2P_2N six-membered rings adopt analogous puckered conformations. This puckering twists the metallacycles towards a slightly distorted boat conformation, with a selenium and a phosphorus atom at the stern and bow of the boat ($Q = 0.909(2)$ Å, $\theta = 82.8(2)$ and $\phi = 69.2(2)°$ **6**; $Q = 0.927(3)$ Å, $\theta = 81.5(3)$ and $\phi = 67.6(4)°$ **8**) [22]. Within both metallacycles, none of the bond distances or angles reflect any structural or chemical difference. The Rh–Se bond distances (2.5317 and 2.5266(8) Å) are slightly shorter than those found in the closely related cationic complex

Table 2
Selected bond distances (Å) and angles (°) for complexes [(η^5-C_5Me_5)MCl{η^2-($SePPh_2)_2N$}] (M = Rh (**6**), Ir (**8**))

	6 (M = Rh)	**8** (M = Ir)
M–Cl	2.4366(17)	2.447(3)
M–Se(1)	2.5317(8)	2.5361(11)
M–Se(2)	2.5266(8)	2.5396(11)
M–G [a]	1.804(7)	1.811(11)
M–C(1)	2.175(6)	2.190(10)
M–C(2)	2.158(6)	2.188(11)
M–C(3)	2.177(6)	2.175(11)
M–C(4)	2.170(6)	2.202(11)
M–C(5)	2.195(7)	2.176(10)
Se(1)–P(1)	2.1693(16)	2.199(3)
Se(2)–P(2)	2.1771(16)	2.184(3)
P(1)–N	1.594(5)	1.601(7)
P(2)–N	1.597(5)	1.596(8)
Cl–M–Se(1)	95.93(5)	85.43(8)
Cl–M–Se(2)	86.26(5)	93.70(7)
Cl–M–G [a]	120.2(2)	120.7(4)
Se(1)–M–Se(2)	96.65(3)	96.46(4)
Se(1)–M–G [a]	120.5(2)	128.7(3)
Se(2)–M–G [a]	128.5(2)	121.8(3)
M–Se(1)–P(1)	111.43(5)	108.57(8)
M–Se(2)–P(2)	109.17(5)	111.77(8)
P(1)–N–P(2)	127.7(3)	128.1(5)
Se(1)–P(1)–N	118.08(19)	117.1(3)
Se(1)–P(1)–C(11)	111.2(2)	104.7(3)
Se(1)–P(1)–C(17)	105.86(19)	112.4(3)
N–P(1)–C(11)	111.9(3)	106.1(4)
N–P(1)–C(17)	104.8(3)	107.5(5)
C(11)–P(1)–C(17)	103.5(3)	108.6(4)
Se(2)–P(2)–N	117.43(19)	117.9(3)
Se(2)–P(2)–C(23)	105.2(2)	111.4(4)
Se(2)–P(2)–C(29)	112.4(2)	106.6(3)
N–P(2)–C(23)	106.0(3)	111.7(5)
N–P(2)–C(29)	107.4(3)	104.6(4)
C(23)–P(2)–C(29)	107.8(3)	103.1(5)

[a] G represents the centroid of the pentamethylcyclopentadienyl ring.

$[(\eta^5\text{-}C_5Me_5)Rh\{\eta^3\text{-}(SePPh_2)_2CH\}]ClO_4$ (mean 2.563(1) Å) [18b] but longer than those found in selenolato or selenido complexes such as $[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}C,Se\text{-}CH_3CH_2Se)(P^iPr_3)]$ (average 2.461(1) Å) [23], or $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu_3\text{-}Se)\}_4]$ (mean 2.459(1) Å) [24]. In the case of complex **8**, the Ir–Se bond lengths (2.5361 and 2.5396(11) Å) compare well with the distances observed in the Ir(III) diselenium complex $[Ir(Se_2)(dppe)_2]Cl$ (2.534(2) Å) [25], but are also longer than those found in the tetraselenido derivative $[(\eta^5\text{-}C_5Me_5)Ir(\eta^2\text{-}Se_4)(PMe_3)]$ (mean 2.469(1) Å) [26].

Interestingly, the P–Se bond distances (2.1771 and 2.1693(16) Å, **6**, and 2.199(3) and 2.184(3) Å, **8**) show a significant lengthening if compared with the values found in the neutral free ligand (average 2.093(1) Å). Additionally, the P–N bond lengths (1.597(5) and 1.594(5) Å in **6**; 1.601(7) and 1.596(8) Å in **8**) are markedly shorter than in free ligand (average 1.682(3) Å) [27]. This structural behaviour has also been reported for this bidentate anionic ligand in the related bis-homoleptic compounds $[Sn\{(SePPh_2)_2N\}_2]$ (P–Se average 2.175(6)Å) [28] and $[Pd\{(SePPh_2)_2N\}_2]$ (means: P–Se 2.184(3) Å; P–N 1.591(11) Å) [27], or in the related Pd(II) complex $[Pd(C_9H_{12}N)\{(SePPh_2)_2N\}_2]$ (2.184(2) and 1.598(5) Å) [27], and evidences some degree of π-delocalisation over the six-membered ring MSe_2P_2N. In fact the P–N bond distances observed in **6** and **8** are markedly longer than the mean length reported for P=N double bonds (1.540(22) Å) [29] in coordinated iminophosphines and are similar to those showed in tetrameric cyclophosphazene $[(Ph_2PN)_4]$ (average 1.590(3) Å) [30]. The values of the P–N–P bond angles in **6** (127.7(3)°) and **8** (128.1(5)°) are reduced respect to the neutral ligand (132.3(2)°) [27] and are slightly larger than those found in the square-planar platinum and palladium complexes $[M\{(SePPh_2)_2N\}_2]$ (Pt, 123.3(5)°; Pd, 122.9.(5)°) [27]. The bond angles at selenium and phosphorus atoms are similar to those reported for the coordinated ligand in the above mentioned homoleptic complexes [27,28].

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 137547 and 137548 for compounds **6** and **8**, respectively. See http://www.rsc.org/suppdata/dt/for crystallographic files in .cif format.

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