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Group VIII transition metal complexes with the chiral diphosphazane ligand (S)-α-(Ph₂P)₂N(CHMePh): Synthesis and structural characterization

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Abstract

The chiral ligand S-(Ph₂P)₂N(CHMePh) reacts with Ni(CO)₄ in benzene solution to yield the mononuclear complex [Ni(CO)₂{κ²-(PPh₂)₂N(CHMePh)}] (**1**). The reactions of the chiral ligand with the solvated complexes [(η⁵-C₅Me₅)MCl(solvent)₂]BF₄ (M = Rh, Ir) or with the binuclear complex [{(η⁶-C₆Me₆)RuCl}₂(μ-Cl)] in the presence of a chloride scavenger, give cationic complexes of the type [(η^n-ring)MCl{κ²-(PPh₂)₂N(CHMePh)}]BF₄ [η^n-ring = η⁵-C₅Me₅; M = Rh (**2**), Ir (**3**). η⁶-C₆Me₆; M = Ru (**4**)]. The ³¹P NMR spectra of compounds **2**–**4** show two signals corresponding of two phosphorus nuclei with different chemical environments. The related complex [(η⁵-C₅H₅)Fe(CO){κ²-(PPh₂)₂N(CHMePh)}]BF₄ (**5**) was prepared by reaction of the ligand with the complex [(η⁵-C₅H₅)Fe(CO)₂I] in toluene following by a metathesis with AgBF₄. This compound exhibits only one signal in the ³¹P NMR spectra at room temperature, which splits into two signals at low temperature (213 K). The crystal structures of complexes **2**, **3** and **5** have been determined by X-ray diffraction studies. All complexes show the presence of an intramolecular π-stacking interaction. The separation between least-squares planes defined by the two intramolecularly stacked phenyl rings are in the range 3.318–3.649 Å.
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1. Introduction

The transition-metal chemistry of bis(diphenylphosphino)amine ligands NR(PPh₂)₂ (R = H, Me, Ph) has been developed rapidly in recent years due to its versatile coordination properties. In a similar form to the widely used bis(diphenylphosphino)methane (dppm, CH₂(PPh₂)₂) the phosphinoamine ligands can bind to metal atoms in different ways: monodentate, chelating or bridging [1–14].

Although Farrar et al. [9] suggest that the replacement of the methylene group in dppm with the smaller NH group may increase the ligand propensity to bridge two metal atoms, the formation of stable square-planar complexes of the type [M(dppa)₂]$^{n+}$ [M = Rh(I), Ir(I), Pt(II)] has been

described [15,16]. The influence of bulky substituents on the nitrogen atom which favour the chelation behaviour has been demonstrated in the case of alkyl substituted bisphosphinoamines NR(PPh₂)₂ (R = Me, ^{i}Pr) due to steric effects [7,10,17].

Recently, the synthesis and crystal structure of the chiral bisphosphinoamine (Ph₂P)₂N(CHMePh) has been described [18,19]. Moreover, the chelating behaviour of this ligand has been demonstrated in the formation of the square-planar compounds [Rh{(Ph₂P)₂N(CHMePh)}₂]BF₄ and [MCl₂{(Ph₂P)₂N(CHMePh)}] (Pt,Pd) [18,20]. Interestingly, selective cleavage of the P–N bond of the coordinated ligand is promoted by alcohols ROH (R = Me, Et) in platinum and palladium compounds [21].

Following our recent reports on the coordination chemistry of diphosphinoamines and their sulfur derivatives [2,22–25], in this paper we describe the behaviour as

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chelating ligand of the chiral diphosphine (S)-$(Ph_2P)_2N$-$(CHMePh)$ with the organometallic fragments $[Ni(CO)_2]$, $[(\eta^5$-$C_5Me_5)MCl]^+$ (M = Rh, Ir), $[(\eta^6$-$C_6Me_6)RuCl]^+$ and $[(\eta^5$-$C_5H_5)Fe(CO)]^+$.

The crystal structures of complexes $[(\eta^5$-$C_5Me_5)$-$MCl\{\kappa^2$-$(Ph_2P)_2N(C^*HMePh)\}]BF_4$ (M = Rh, Ir) and $[(\eta^5$-$C_5H_5)Fe(CO)\{\kappa^2$-$(Ph_2P)_2N(C^*HMePh)\}]BF_4$ are also reported. It is found that these compounds display an intramolecular π-stacking interaction between the phenyl groups of the bisphosphinoamine ligand.

2. Experimental details

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 $[\{(\eta^5$-$C_5Me_5)MCl(\mu$-$Cl)\}_2]$ (M = Rh, Ir) [26], $[\{(\eta^6$-$C_6Me_6)RuCl(\mu$-$Cl)\}_2]$ [27], and the ligand (S)-$(Ph_2P)_2N(CHMePh)$ [18] were prepared by published procedures. Elemental analyses (C, H, N) were carried out by a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. The NMR spectra were recorded on a Bruker AC-200P spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4(^1H)$ and 85% $H_3PO_4(^{31}P$, positive shifts downfield) as internal and external standards, respectively.

2.2. Synthesis of complexes

2.2.1. $[Ni(CO)_2\{\kappa^2$-P,P-$(Ph_2P)_2N(CHMePh)\}]$ (1)

To a solution of $Ni(CO)_4$ (77 mg; 0.45 mmol) in benzene (10 mL) was added a solution of (S)-$(Ph_2P)_2N(CHMePh)$ (221 mg; 0.45 mmol) dissolved benzene (10 mL). The reaction mixture was heated under reflux for 15 min and then evaporated to a small volume. Yellow crystals were obtained by addition of *n*-pentane and cooling at −20 °C. Yield 213 mg, 78%. The complex was recrystallised as yellow thin plates from THF–diethyl ether at low temperature (−20 °C). (Found: C, 67.2; H, 5.0; N, 2.1. $C_{34}H_{29}NiNO_2P_2$ requires: C, 67.6; H, 4.8; N, 2.3%). FTIR (KBr, cm^{-1}): ν(CO), 1997 and 1936. ^1H NMR (C_6D_6, 295 K): δ0.93 [d, 3H, ^3J(HH) = 7.1 Hz, MeC], 4.5 (m, 1H, HC), 6.5–7.8 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, 295 K): δ 95.0 [s].

2.2.2. $[(\eta^5$-$C_5Me_5)MCl\{\kappa^2$-P,P-$(Ph_2P)_2N(CHMePh)\}]$-BF_4 (M = Rh 2, Ir 3)

A solution of the binuclear complex $[\{(\eta^5$-$C_5Me_5)$-$MCl(\mu$-$Cl)\}_2]$ (0.16 mmol; Rh, 100 mg; Ir, 126 mg) and $AgBF_4$ (82 mg; 0.32 mmol) in a chloroform-acetone mixture (5:15 mL), was stirred for 2 h at room temperature (r.t.) in the absence of light. The precipitated silver chloride was removed by filtration and (S)-$(Ph_2P)_2N(CHMePh)$ (157 mg; 0.32 mmol), dissolved in boiling diethyl ether (40 mL), was added to the resulting solution. After stirring

the reaction mixture for 30 min, the solution was filtered, evaporated to a small volume and the complex precipitated by adding diethyl ether. The complexes were recrystallized by diffusion of diethyl ether into a chloroform solution of the compounds. Complex 2: yield 214 mg, 78%. (Found: C, 59.3; H, 5.6; N, 1.6. $C_{42}H_{44}BClF_4NP_2Rh$ requires: C, 59.4; H, 5.2; N, 1.7%). FTIR (KBr, cm^{-1}): ν(BF_4) 1100 and 520. ^1H NMR (CDCl$_3$, 295 K): δ 1.42 [d, 3H, ^3J(HH) = 7.2 Hz, MeC], 1.6 [t, 15 H, ^4J(HP) = 4.10 Hz, C_5Me_5], 5.1 (m, 1H, HC), 6.9–7.4 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR (CDCl$_3$, 295 K): δ 72.8 [dd, ^1J(RhP) = 118 Hz, ^2J(PP) = 96 Hz], 65.6 [dd, ^1J(RhP) = 122 Hz]. Complex 3: yield 240 mg, 79%. (Found: C, 53.3; H, 4.9; N, 1.5. $C_{42}H_{44}BClF_4NP_2Ir$ requires: C, 53.7; H, 4.7; N, 1.5%). FTIR (KBr, cm^{-1}): ν(BF_4), 1100 and 520. ^1H NMR (CDCl$_3$, 295 K): δ 1. 45 [d, 3H, ^3J(HH) = 7.1 Hz, MeC], 1.63 [t, 15H, ^4J(HP) = 2.74 Hz, C_5Me_5], 5.1 (m, 1H, HC), 6.9–7.7 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR (CDCl$_3$, 295 K): δ 33.0 [d, ^2J(PP) = 57.5 Hz], 39.9 [d].

2.2.3. $[(\eta^6$-$C_6Me_6)RuCl\{\kappa^2$-P,P-$(Ph_2P)_2N(CHMePh)\}]$-BF_4 (4)

A suspension of the binuclear complex $[\{(\eta^6$-p-MeC_6H_4-$Pr^i)RuCl(\mu$-$Cl)\}_2]$ (134 mg; 0.2 mmol), (S)-$(Ph_2P)_2N$-$(CHMePh)$ (196 mg; 0.4 mmol) and $NaBF_4$ (44 mg; 0.4 mmol) in methanol (15 mL) was stirred for 8 h at r.t. The solution obtained was evaporated to dryness and the solid residue extracted with the minimal amount of dichloromethane. The complex was precipitated as a yellow solid by addition of diethyl ether. Yield 172 mg, 49%. (Found: C, 56.0; H, 5.0; N, 1.6. $C_{44}H_{47}BClF_4NP_2Ru$ requires: C, 56.6; H, 5.1; N, 1.5%). FTIR (KBr, cm^{-1}): ν(BF_4), 1100 and 520. ^1H NMR (CDCl$_3$, 295 K): δ 1.38 [d, 3H, ^3J(HH) = 7.17 Hz, MeC], 1.93 [s, br, 18H, C_6Me_6], 5.05 [m, 1H, HC], 6.8–7.8 [m, 25H, Ph]. $^{31}P\{^1H\}$ NMR (CDCl$_3$, 295 K): δ 79.3 [d, ^2J(PP) = 87 Hz], 82.6 [d].

2.2.4. $[(\eta^5$-$C_6H_5)Fe(CO)\{\kappa^2$-P,P-$(Ph_2P)_2N(CHMePh)\}]BF_4$ (5)

Preparation of $[(\eta^5$-$C_6H_5)Fe(CO)\{\eta^2$-P,P-$(Ph_2P)_2N(CHMePh)\}]I$. A solution of $[(\eta^5$-$C_6H_5)Fe(CO)_2I]$ (304 mg: 1.0 mmol) and (S)-$(Ph_2P)_2N(CHMePh)$ (490 mg: 1.0 mmol) in toluene (50 mL) was heated under reflux for 2 h. The solid formed was filtered and washed with cold toluene. The yellow solid was dissolved in dichloromethane (10 mL) and the solution chromatographed on Silica gel 60. The complex was eluted with acetone and crystallized by addition of diethyl ether. Yield 700 mg, 91%. (Found: C, 59.5; H, 4.4; N, 1.8. $C_{37}H_{34}FeINOP_2$ requires: C, 59.6; H, 4.5; N, 1.8%).

Preparation of 5. To a solution of compound $[(\eta^5$-$C_6H_5)Fe(CO)\{\kappa^2$-P,P-$Ph_2P)_2N(CHMePh)\}]I$ (100 mg; 0.13 mmol) in acetone (20 mL) the stoichiometric amount of $AgBF_4$ (26 mg, 0.13 mmol) was added. After stirring the mixture for 1 h at r.t., the precipitated silver iodide was removed by filtration through Kieselguhr. The resulting solution was concentrated to a small volume and the complex crystallized by addition of diethyl ether. Orange

crystals were obtained from acetone–diethyl ether. Yield 62 mg, 65%. (Found: C, 62.5; H, 4.8; N, 1.8. $C_{38}H_{34}BF_4Fe$-NOP_2 requires: C, 62.7; H, 4.7; N, 1.9%). FTIR (KBr, cm^{-1}): v(CO), 1979. ^{1}H NMR (CDCl$_3$, 295 K): δ 1.1 [d, 3H, ^3J(HH) = 7.0 Hz, MeC], 4.3 [s, br, 5H, C$_5$H$_5$], 4.7 [s, br, 1H, CH], 6.6–7.8 [m, H, Ph]. ^{31}P{^{1}H} NMR (CDCl$_3$), 295 K: δ 08.9 (s); 213 K: δ 109.7 [d, ^2J(PP) = 112 Hz], 110.5 (d).

2.3. X-ray crystallography of complexes 2, 3 · CH₃CN and 5

Suitable crystals for the X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a chloroform solution of complex **2** and **5**, and from a mixture of acetonitrile–diethyl ether for complex **3**. Intensity crystal data were collected on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation in Wyck-off ω scan mode. The structures were solved by direct methods, and all of the non-hydrogen atoms refined with anisotropic displacement parameters. Refinement was by full-matrix least-squares methods on F^2. Calculations were performed using the program SHELXTL-PC [28]. Crystal data and refinement parameters are summarized in Table 1.

3. Results and discussion

We have recently reported that the reaction of the nickel tetracarbonyl complex Ni(CO)$_4$ with the ligand bis(diph-

enylphosphino)amine [dppa,(Ph$_2$P)$_2$NH] gives the binuclear complex [Ni$_2$(μ-CO)(CO)$_2$(μ-dppa)$_2$] [2]. When this reaction was carried out with the related diphosphazane ligand S-(Ph$_2$P)$_2$N(CHMePh) in refluxing benzene, the neutral mononuclear complex [Ni(CO)$_2${κ^2-(PPh$_2$)$_2$N-(CHMePh)}] was isolated as yellow solid. This compound was characterized by analytical and spectroscopic means. The molecular weight determined cryoscopically in benzene (M_{exp} = 585) coincides with that calculated for the mononuclear complex (M_{calc} = 605.7). In particular, its IR spectrum in solid state shows two strong bands at 1997 and 1936 cm^{-1}, and a doublet [δ_H 0.93, ^3J(HH) = 7.1 Hz, MeC], a multiplet (δ_H 4.5, HC) and one singlet (δ_P 95.0) as the most relevant data of the ^{1}H and ^{31}P NMR spectra, respectively. The formation of a mononuclear complex is probably due to the decrease of the P–N–P angle caused by the steric effect produced by the substituents of the N atom. In fact, we recently reported that the ^{31}P{^{1}H} NMR spectrum of the ligand S-(Ph$_2$P)$_2$N-(CHMePh) exhibits a broad resonance at δ 52.5 ppm, which splits into two sharp-spin-coupled peaks below 233 K. This behaviour is characteristic of the exchange broadening by equilibrium of the major configurations C$_s$ and C$_{2v}$ (Fig. 1) [25]. The X-ray diffraction [19] and the ^{31}P{^{1}H} NMR studies at low temperature demonstrate that the C$_s$ configuration is the most stable structure in solution. As in the coordination process the ligand changes this configuration from C$_s$ to C$_{2v}$ we modelled this

Table 1
Crystallographic data and structure refinement for compounds **2**, **3** and **5**

| Compound	**2**	**3**	**5**
Empirical formula	C$_{42}$H$_{44}$BClF$_4$NP$_2$Rh	C$_{44}$H$_{47}$BClF$_4$IrN$_2$P$_2$	C$_{38}$H$_{34}$BF$_4$FeNOP$_2$
Formula weight	849.89	980.24	725.29
Temperature (°C)	295(2)	295(2)	383(2)
Wavelength (Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P2(1)2(1)2(1)	P2(1)2(1)2(1)	P2(1)2(1)2(1)
Unit cell dimensions			
a (Å)	10.486(7)	10.565(18)	10.8988(15)
b (Å)	18.638(13)	18.650(12)	15.849(2)
c (Å)	20.547(12)	21.641(32)	19.466(3)
Volume (Å^3)	4016(5)	2901.8(12)	3362.4(8)
Z	4	4	4
Density (calc.) (Mg m^{-3})	1.406	1.319	1.441
Abs coeff (mm^{-1})	0.621	3.319	0.600
$F(000)$	1744	1960	1504
Crystal size (mm)	1.00 × 0.15 × 0.10	1.00 × 0.20 × 0.20	1.00 × 0.15 × 0.10
θ Range for data collection (°)	1.98–25.00	1.88–25.06	1.66–28.30
Index ranges	0 ⩽ h ⩽ 12,	0 ⩽ h ⩽ 12,	−14 ⩽ h ⩽ 14,
	−1 ⩽ k ⩽ 22,	−1 ⩽ k ⩽ 22,	−21 ⩽ k ⩽ 22,
	0 ⩽ l ⩽ 24	0 ⩽ l ⩽ 25	−25 ⩽ l ⩽ 21
Reflections collected	4208	4472	38 604
Independent reflections (R_{int})	4184 (0.0768)	4460 (0.0428)	8327 (0.0362
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4184/0/372	4459/0/278	8327/0/445
Goodness-of-fit on F^2	1.003	1.052	1.039
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0750, wR_2 = 0.1654	R_1 = 0.0658, wR_2 = 0.1375	R_1 = 0.0286, wR_2 = 0.675
R indices (all data)	R_1 = 0.1173, wR_2 = 0.1938	R_1 = 0.0996, wR_2 = 0.1632	R_1 = 0.0317, wR_2 = 0.0690
Absolute structure parameter	0.05(9)	−0.04(2)	0.000(3)
Largest difference in peak and hole (e Å^{-3})	0.760 and −0.492	2.760 and −1.057	0.408 and −2.207
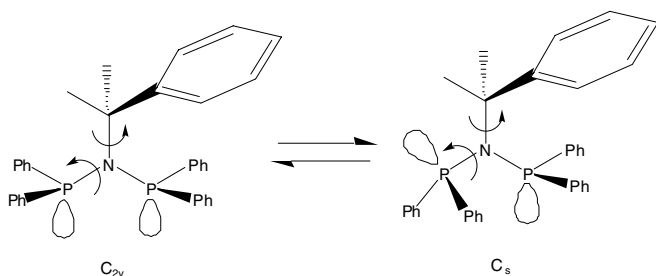
Fig. 1. $C_s \Longleftrightarrow C_{2v}$ inversion of the ligand (S)-(Ph₂P)₂N(CHMePh).

transition by computer methods [29], varying the dihedral angle C–P–N–C of the C_s structure and optimizing all the values to obtain an energy pattern. In the structure of the ligand there are four crystallographically independent structures with more or less different geometries that imply the presence of several minima of potential energy. The structures with C–P–N–C angles between 100° and 150° are consistent with the geometry in which the electron pairs of the phosphorus atoms are in a *cis* disposition (C_{2v}). This structure is less stable, ~8 kcal/mol, than that of the C_s conformer. On the other hand, the calculated barrier rotation through the P–N bond, even if is not in agreement with the calculated value by NMR (~5 kcal/mol), is sufficiently small to be overcome by with the energy of the thermal vibrations. These results prove that the presence of a bulky group bonded to the N atom implies a steric repulsion to hinder the free rotation of the PPh₂ group through P–N bond, producing a large distortion of the P–N–P angle from 120° to 100°. This value is smaller than those shown by the dppa ligand in the binuclear complex [Ni₂(μ-CO)-(CO)₂(μ-dppa)₂], P–N–P = 118.1(1) [2], and explains the unsuccessful formation of a similar binuclear compound in the reaction with Ni(CO)₄.

In order to study the coordination behaviour of the chiral ligand in the formation of pseudo-octahedral complexes, we carried out the reaction of binuclear complexes [{(η⁵-C₅Me₅)MCl}₂(μ-Cl)] (M = Rh, Ir) with silver tetrafluoroborate in 1:2 molar ratio in acetone–chloroform solution to form silver chloride and, most probably, the solvated complex [(η⁵-C₅Me₅)MCl(solvent)₂]⁺. This further reacted with S-(Ph₂P)₂N(CHMePh) to give cationic complexes of the type [(η⁵-C₅Me₅)MCl{κ²-(PPh₂)₂N-(CHMePh)}]BF₄ (M = Rh **2**, Ir **3**). On the other hand, the complex [{(η⁶-C₆Me₆)RuCl}₂(μ-Cl)] reacted with the chiral ligand in methanol solution in the presence of sodium tetrafluoroborate to give the complex [(η⁵-C₅Me₅)-RuCl{κ²-(PPh₂)₂N(CHMePh)}]BF₄ (**4**). All compounds were isolated as stable microcrystalline solids and characterized by elemental analyses, IR and NMR spectroscopy. The IR spectra showed the presence of the uncoordinated anion (BF₄⁻, ca. 1100 and 520 cm⁻¹). The ¹H NMR spectra of these complexes are in agreement with the proposed formulation showing the expected resonances of the C₅Me₅ or C₆Me₆ coordinated ring and the CHMePh group in the required proportions (see Section 2). The ³¹P{¹H} NMR at

room temperature showed two doublet of doublets for complex **2** [δ 72.8 and 65.7 ppm, ^2J(PP) = 96 Hz, ^1J(RhP) = 122 Hz] and two doublets for complexes **3** [δ 33.0 and 39.2 ppm, ^2J(PP) = 57.5 Hz] and **4** [δ 79.3 and 82.6 ppm, ^2J(PP) = 8 Hz]. These results indicate the existence of two phosphorus nuclei with different chemical environments, probably due to the existence of a high rotation barrier of the chiral group R* = CHMePh through the C–N bond. This behaviour, observed even at high temperature (80 °C) in deuterated acetonitrile, shows that the ligand caused an asymmetric induction on the metal centre.

3.1. X-ray crystal structures of [(η⁵-C₅Me₅)MCl{κ²-P,P-(Ph₂P)₂N(CHMePh)}]BF₄

To obtain a complete characterisation of complexes **2** and **3**, and to explain the formation of the different environments of P atoms, two analyses by X-ray diffraction methods were carried to establish the molecular structures and to obtain information on bonding parameters. Figs. 2 and 3 display the molecular representation of the cations of complexes **2** and **3**, 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 with comparable cell parameters. Both metal centres exhibit distorted pseudo-octahedral environments with the pentamethylcyclopentadienyl group occupying three formal coordinate sites, with the chelating N,N-bis(diphenylphosphino)-N-{(S)-α-methylbenzylamine}amine ligand bonded to the metal through two phosphorus atoms, and with a chloride atom completing the coordination sphere.

The most salient feature of these molecular structures is the existence of an intramolecular π-stacking interaction
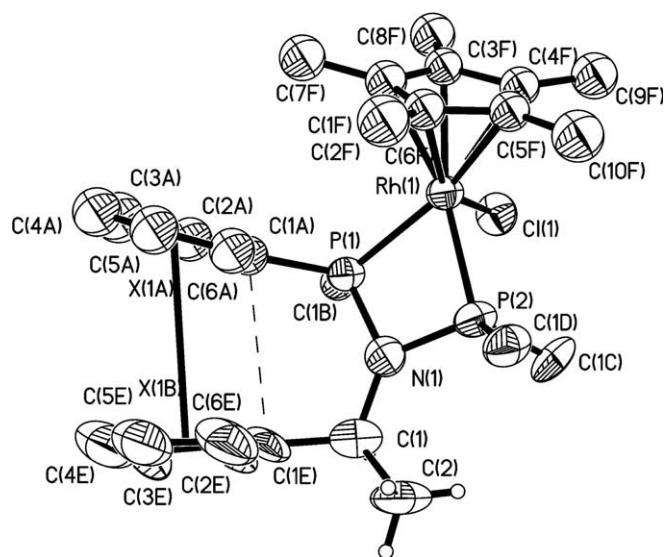

Fig. 2. Ortep plot of the cation of complex **2**, with the labelling scheme used. The phenyl groups of P(2) and one of P(1) are omitted for clarity. D(X1A–X1B) = 3.618 Å, d[C(1A)–C(1E)] = 3.263 Å.
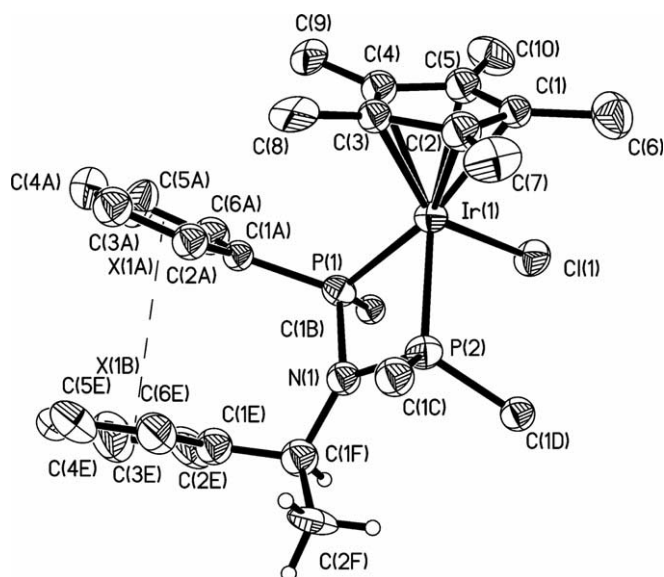
Fig. 3. Ortep plot of the cation of complex **3**, with the labelling scheme used. The phenyl groups of P(2) and one of P(1) are omitted for clarity. D(X1A–X1B) = 3.649 Å, d[C(1A)–C(1E)] = 3.273 Å.

Table 2
Selected bond lengths (Å) and bond angles (°) of complexes **2** and **3**

2		**3**	
Bond distances (Å)			
Rh–P(1)	2.290(4)	Ir–P(1)	2.296(6)
Rh–P(2)	2.279(4)	Ir–P(2)	2.291(5)
Rh–Cl(1)	2.382(4)	Ir–Cl(1)	2.395(6)
Rh–C(1–5)av	2.229(13)	Ir–C(1–5)av	2.242(13)
P(1)–N(1)	1.713(12)	P(1)–N(1)	1.750(2)
P(2)–N(1)	1.712(12)	P(2)–N(1)	1.690(2)
P(1)–C(1A)	1.817(14)	P(1)–C(1A)	1.814(10)
P(1)–C(1B)	1.805(14)	P(1)–C(1B)	1.823(10)
P(1)–C(1C)	1.848(16)	P(1)–C(1C)	1.819(11)
P(1)–C(1D)	1.818(16)	P(1)–C(1D)	1.829(12)
N(1)–C(1F)	1.502(18)	N(1)–C(1F)	1.530(2)
Bond angles (°)			
P(1)–Rh–Cl(1)	90.63(14)	P(1)–Ir–Cl(1)	90.2(2)
P(1)–Rh–P(2)	67.07(14)	P(1)–Ir–P(2)	69.4(2)
P(2)–Rh–Cl(1)	90.63(14)	P(2)–Ir–Cl(1)	89.8(2)
P(1)–N(1)–P(2)	98.30(6)	P(1)–N(1)–P(2)	98.9(8)

between the phenyl groups of the CHMePh and the Ph_2P moieties. The distances between the centres of the planes of the phenyl groups are 3.318 and 3.649 Å for complexes **2** and **3**, respectively. These distances are similar to the distances found between aromatic rings in Pt(II) complexes [range 3.30–3.48 Å] [30].

The Rh–C(ring) and Ir–C(ring) distances span the ranges 2.216(13)–2,258(13) and 2.233(13)–2.253(13) Å, respectively, and compare well with the those found in other pentamethylcyclopentadienylrhodium or iridium (III) complexes [25,31–33]. The Rh–P [2.290(4) and 2.279(4) Å] and Rh–Cl [2.382(4) Å] distances are similar to those found in related rhodium (III) complexes, such as $[(\eta^5$-$C_5Me_5)RhCl(\kappa^2$-prophos)]BF_4 [Rh–P = 2.314(1) and 2.335(1), Rh–Cl = 2.393(1) Å] [31] and $[(\eta^5$-$C_5Me_5)RhCl\{\kappa^2$-$(PPh_2)_2NMe\}]$-BF_4 [Rh–P = 2.297(2) and 2.303(2), Rh–Cl = 2.376(2) Å]

[32]. Similarly, the Ir–P [2.296(6) and 2.291(5) Å] and Ir–Cl [2.395(6) Å] distances are comparable to the corresponding values observed for similar Ir(III) complexes, $[(\eta^5$-$C_5Me_5)$-IrCl$(\kappa^2$-$Ph_2PCH_2SPh)]BF_4$ [Ir–P = 2.303(3) and Ir–Cl = 2.381(2) Å] [33] and $[(\eta^5$-$C_5Me_5)IrCl\{\kappa^2$-$Ph_2PNHP(S)Ph_2\}]$-BF_4 [Ir–P = 2.263(6) and Ir–Cl = 2.398(5) Å] [25].

In the coordinated chelate ligand the mean P–N bond lengths [**2**: av 1.7125(12); **3**: av 1.720(2) Å] are comparable with those found in the chelated diphosphazane [PdCl$_2\{\kappa^2$-$(PPh_2)_2N(CHMePh)\}$] [P–N = av 1.709(7) Å] [18] and in the free ligand [P–N = av 1.718(2) Å] [32]. In the coordinated ligand, the P(1)–N–P(2) angles [**2**: 98.30(6); **3**: 98.90(8)°] are smaller than the P–N–P angle of the free ligand [119.97(9)°] and similar to those found in the above mentioned palladium complex [P–N–P = 98.2(4)°].

On the other hand, with the aim of studying the properties of the ligand in coordination to a first row transition metal, we carried out the reaction of complex $[(\eta^5$-$C_5H_5)Fe(CO)_2I]$ with the chiral ligand S-$(Ph_2P)_2N(CHMePh)$. These compounds react in refluxing toluene to yield the complex $[(\eta^5$-$C_5H_5)Fe(CO)\{\kappa^2$-$(PPh_2)_2N(CHMePh)]I$, which in turn reacts with the stoichiometric amount of silver tetrafluoroborate in acetone solution, to give the complex $[(\eta^5$-$C_5H_5)$-Fe(CO)$\{\kappa^2$-$(PPh_2)_2N(CHMePh)]BF_4$ (**5**). Its IR spectrum in KBr shows the carbonyl band ν(CO) at 1979 cm^{-1}. The ^1H NMR spectrum shows a broad singlet centred at δ 4.3 ppm assigned to the C_5H_5 group together with the characteristic protons signals of the coordinated diphosphazane ligand. The ^{31}P NMR spectrum exhibits at room temperature (295 K) a singlet signal at δ 108.9 ppm, indicating equivalent P atoms, possibly due to a low energy value of the N–C rotation barrier. The ^{31}P NMR spectrum at low temperature (213 K) shows the splitting of the signal into two doublets at δ 109.7 and 110.5 ppm [^2J(PP) = 112 Hz], indicating that at low temperature the rotation barrier through the N–C bond is not overcome and two different environments on the phosphorus atoms are observed.

3.2. X-ray crystal structure of $[(\eta^5$-$C_5H_5)Fe(CO)$-$\{\kappa^2$-$(PPh_2)_2N(CHMePh)\}]BF_4$ (**5**)

A perspective view of the structure of the cation of complex **5** with the labelling of the atoms is shown in Fig. 4. Table 3 lists relevant bond distances and angles. The iron atom has a distorted octahedral co-ordination sphere, commonly referred as a "three legged piano stool" configuration, with the centred of the cyclopentadienyl ligand occupying the centre of three octahedral sites, with the chelating N,N-bis(diphenylphosphino)-N-{(S)-α-methylbenzylamine} amine ligand bonded to the metal through two phosphorus atoms, and with a carbon atom of the carbon monoxide completing the coordination sphere.

This molecular structure, similarly for complexes **2** and **3**, shows the existence of the intramolecular π-stacking interaction. The separation between least-squares planes defined by the two intramolecularly stacked phenyl rings is 3.62 Å.
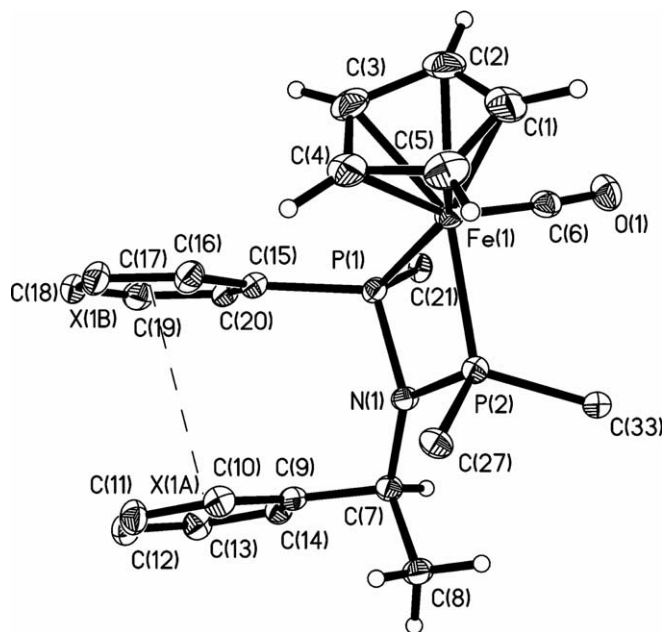
Fig. 4. Ortep plot of the cation of complex **5**, together with the numbering scheme used. The phenyl groups of P(2) and one of P(1) are omitted for clarity. D(X1A–X1B) = 3.62 Å, d[C(9)-C(15)] = 3.257 Å.

Table 3
Selected bond lengths (Å) and bond angles (°) of complex **5**

Bond distances (Å)	
Fe(1)–P(1)	2.2002(5)
Fe(1)–C(6)	1.7556(17)
P(2)–N(1)	1.6977(13)
C(6)–O(1)	1.1390(2)
Fe(1)–P(2)	2.1838(5)
P(1)–N(1)	1.7155(13)
N(1)–C(7)	1.5067(19)
Fe(1)–C(1–5)av	2.0969(17)
Bond angles (°)	
P(1)–Fe(1)–P(2)	71.906(17)
P(2)–Fe(1)–C(6)	92.200(5)
P(1)–Fe(1)–C(6)	90.940(5)
P(1)–N(1)–P(2)	97.900(7)

The distances Fe–C(Cp) [av 2.0969(17) Å], Fe–P [av 2.1922(5) Å], Fe-C(6) [1.7556(17) Å], N–P [av 1.7066(13) Å] and the angles P–N–P [97.900(7)°] and P–Fe–P [71.906(17)°] compare quite well with analogous distances in complex $[(\eta^5-C_5H_5)Fe(CO)\{\kappa^2-(PPh_2)_2NH\}]I$ [Fe–C(Cp) = av 2.098 Å, Fe-P = av 2.197(5) Å, Fe–C = 1.74(2) Å, N–P = av 1.7125 Å, P–N–P = 97.3(7)° and P–Fe–P = 71.7(2)°] [34].

4. Conclusions

Complexes containing the diphosphazane ligand, S-$(Ph_2P)_2N(CHMePh)$, and the organometallic fragments $Ni(CO)_2$ (**1**), Cp*M [Rh (**2**), Ir (**3**)], $(C_6Me_6)Ru$ (**4**) and CpFeCO (**5**) have been synthesized and fully characterized by analytical and spectroscopic means. The molecular structures of complexes **2**, **3** and **5** have been determined by X-ray diffraction methods.

The presence of the chiral CHMePh group on nitrogen causes a decrease of the P–N–P angle, leading to only a mononuclear square-planar complex with the fragment $Ni(CO)_2$, instead of the formation of a dinuclear complex with diphosphazane acting as a bridged ligand, as occurs with $(Ph_2P)_2NH$.

For the pseudo-octahedral complexes **2**–**5**, the presence of the chiral group makes two different chemical environments for the phosphorus atoms, generating an asymmetric induction on the metal centre. All the crystal structures show the existence of an intramolecular π-stacking interaction between the phenyls of the CHMePh group and the Ph₂P moiety.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 281828, 281829 and 281830 for complexes **2**, **3** and **5**, respectively. Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccd.cam.ac.uk).

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