ELSEVIER

Journal of Organometallic Chemistry 651 (2002) 90–97

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Chiral sulfur diphosphazanes derived from S-$(Ph_2P)_2N(CHMePh)$ and its rhodium(I), (III) and iridium(III) complexes. Crystal structures of $Ph_2P(S)N(CHMePh)PPh_2$, $\{Ph_2P(S)\}_2N(CHMePh)$ and $[(Cp^*)MCl\{\eta^2\text{-}P,S\text{-}Ph_2PNHP(S)Ph_2\}]BF_4$, $Cp^* = \eta^5\text{-}C_5Me_5$; M = Rh, Ir

Eugenio Simón-Manso [a,*], Mauricio Valderrama [a], Peter Gantzel [b], Clifford P. Kubiak [b]

[a] Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile
[b] Department of Chemistry and Biochemistry, 9500 Gilman Drive, University of California, San Diego, CA 92093-0358, USA

Received 18 July 2001; received in revised form 6 February 2002; accepted 7 February 2002

Abstract

The reaction of S-$(Ph_2P)_2N(CHMePh)$ with sulfur (1:1 molar ratio) in diethyl ether solution leads to S-$Ph_2P(S)N(CHMePh)PPh_2$ (**1**). The disulphide S-$\{Ph_2P(S)\}_2N(CHMePh)$ (**2**), was obtained when the reaction was carried out in tetrahydrofuran with an excess of sulfur (1:5 molar ratio). **1** reacts with the solvated rhodium (I) complex $[Rh(cod)S_x]BF_4$ to afford the cationic complex $[Rh(cod)\{\eta^2\text{-}S,P\text{-}Ph_2P(S)N(CHMePh)PPh_2\}]BF_4$ (**3**). However, when the above reaction was carried out with **2**, cleavage of the C–N bond of the ligand occurred, to yield the complex $[Rh(cod)(\eta^2\text{-}S,S\text{-}\{Ph_2P(S)\}_2NH)]BF_4$ (**4**). Reactions of **1** with the fragments of Rh (III) and Ir (III) $[Cp^*MCl_3]BF_4$ lead to cleavage of the C–N bond of the ligand yielding cationic complexes, $[(Cp^*)MCl\{\eta^2\text{-}P,S\text{-}Ph_2PNHP(S)Ph_2\}]BF_4$ (M = Rh, **5**; Ir, **6**]. Crystal structures of **1**, **2**, **5** and **6** have been determined by X-ray diffraction methods. Compounds **1** and **2** crystallize in the same space group $P2(1)2(1)2(1)$. The molecular structure of **1** shows a nearly trigonal planar nitrogen atom bound to two different phosphorus atoms and to the chiral carbon atom. Compound **2** acquires a twisted conformation with the two sulfur atoms adopting mutually trans positions with respect to the PNP backbone.

Keywords: Chiral diphosphazanes; Chalcogenide compounds; Rhodium and Iridium complexes; Synthesis; Crystal structures

1. Introduction

In the last decade, the coordination chemistry of the mono and dichalcogenides derived from bis(diphenylphosphino)amine, $Ph_2PNHP(E)Ph_2$ and $\{Ph_2P(E)\}_2NH$ (E = O, S, Se), has received considerable attention. These compounds are easily deprotonated, and in their anionic form are versatile ligands, able to form inorganic (carbon free) chelate rings [1–8].

In contrast, there are few examples of metal complexes containing these ligands as neutral derivatives [9,10]. Similarly, little attention has been paid to the transition metal coordination chemistry of neutral chalcogenides derived from substituted diphosphazanes $(Ph_2P)_2NR$ (R = Me, Ph) [11].

Recently, the synthesis and X-ray crystal structure of the chiral diphosphazane *N*,*N*-bis(diphenylphosphino)-*N*-{(S)-α-methylbenzyl}amine was described [12,13]. However, to the best of our knowledge, no chalcogenide derivatives of this chiral diphosphazane have been reported to date. Following our interest in the coordination properties of diphosphazanes and their chalcogenide derivatives [2,14–16], we report here the synthesis of the ligands S-$Ph_2P(S)N(CHMePh)PPh_2$ and S-$\{Ph_2P(S)\}_2N(CHMePh)$, and some of their complexes

* Corresponding author. Present address: Department of Chemistry and Biochemistry, University of California, San Diego (UCSD), 9500 Gilman Drive, Dept. 0358, La Jolla, CA 92093-0358, USA. Fax: +1-619-534-5383.
E-mail address: emismon@chem.ucsd.edu (E. Simón-Manso).

0022-328X/02/$ - see front matter
PII: S0022-328X(02)01317-7

with rhodium and iridium organometallic fragments. The molecular structures of S-$Ph_2P(S)N(CHMePh)$-PPh_2, S-$\{Ph_2P(S)\}_2N(CHMePh)$ and $[(Cp^*)MCl\{\eta^2$-P,S-$Ph_2PNHP(S)Ph_2\}]BF_4$ (M = Rh, Ir) were determined by single-crystal X-ray diffraction. A variable-temperature $^{31}P\{^1H\}$-NMR spectroscopy study of compounds S-$(Ph_2P)_2N(CHMePh)$ and S-$\{Ph_2P(S)\}_2$-N(CHMePh), is also reported.

2. Experimental

All reactions were carried out under purified nitrogen using Schlenk-tube techniques. Solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting materials, S-$(Ph_2P)_2N(CHMePh)$, $[\{Rh(\mu$-$Cl)(cod)\}_2]$ (cod = 1,5-cyclooctadiene) and $[\{(Cp^*)$-$MCl(\mu$-$Cl)Cl\}_2]$(M = Rh, Ir) were prepared according to published methods [2,17]. Elemental analyses (C, H, N and S) were conducted with a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. ^1H and $^{31}P\{^1H\}$-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. Optical rotations were measured with an Optical Activity LTD polarimeter equipped with a sodium lamp at 18 °C.

2.1. S-$Ph_2P(S)N(CHMePh)PPh_2$ (1)

A solution of S-$(Ph_2P)_2N(CHMePh)$ (1.0 g; 2.05 mmol) and sulfur (66 mg; 2.05 mmol) in diethyl ether was heated under reflux for 45 min. During this time a white solid formed. The reaction mixture was evaporated to dryness and the residue was treated with diethyl ether (5 ml). The white solid was filtered, washed with diethyl ether (2 × 5 ml) and air-dried. Yield 718 mg (67%). M.p. 172–174 °C. Anal. Calc. for $C_{32}H_{29}NP_2S$: C, 73.70; H, 5.57; N, 2.69; S, 6.14. Found: 73.59; H, 5.59; N, 2.73; S, 6.00%. ^1H-NMR ($CDCl_3$, ppm): δ 1.84 (d, 3 H, $^3J(HH) = 6.96$ Hz, Me), 5.19 (m, 1 H, CH) and 7.50 (m, 25 H, Ph). $^{31}P\{^1H\}$ ($CDCl_3$, ppm): δ 51.4 [d, $^2J(PP) = 14.8$ Hz, P] and 71.1 (d, PS). FTIR (KBr, cm^{-1}): ν(PS), 673 (m). $[\alpha]_D = -68.75$ [c 2.4, $CHCl_3$]

2.2. S-$\{Ph_2P(S)\}_2N(CHMePh)$ (2)

A solution of S-$(Ph_2P)_2N(CHMePh)$ (1.0 g; 2.05 mmol) and sulfur (329 mg; 10.25 mmol) in tetrahydrofuran (40 ml) was heated under reflux for 2.5 h. The reaction mixture was cooled to −20 °C and the excess sulfur was filtered off. The solution was evaporated to dryness and the solid obtained was washed with methanol (15 ml). The compound was crystallized from chloroform-methanol. Yield 669 mg (59%). M.p. 115–117 °C. Anal. Calc. for $C_{32}H_{29}NP_2S_2$: C, 69,45; H, 5.24; N, 2.53; S, 11.57. Found: 69.67; H, 5.41; N, 2.59; S, 10.47%. ^1H-NMR ($CDCl_3$, ppm): δ 1.73 (d, 3 H, $^3J(HH) = 7.2$ Hz, Me), 5.34 (m, 1 H, CH) and 7.50 (m, 25 H, Ph). $^{31}P\{^1H\}$ ($CDCl_3$, ppm): δ 68.4 (s, br, PS). FTIR (KBr, cm^{-1}): ν(PS), 647 (s). $[\alpha]_D = 37.5$ [c 2.4, $CHCl_3$].

2.3. $[Rh(cod)\{\eta^2$-S,P-$Ph_2P(S)N(CHMePh)PPh_2\}]BF_4$ (3)

A mixture of the complex $[\{Rh(\mu$-Cl)(cod)$\}_2]$ (50 mg; 0.1 mmol), S-$Ph_2P(S)N(CHMePh)PPh_2$ (106 mg; 0.2 mmol) and $NaBF_4$ (22 mg; 0.2 mmol) in acetone (15 cm^3) was stirred for 1 h and solid NaCl was filtered off. This solution was concentrated to a small volume and the complex precipitated as a brown solid by addition of diethyl ether. Yield 90 mg (55%). Anal. Calc. for $C_{40}H_{41}BF_4NP_2RhS$: C, 58.63; H, 5.01; N, 1.71; S, 3.91. Found: C, 59.67; H, 5.15; N, 1.61; S, 4.32%. ^1H-NMR ($CDCl_3$, ppm): δ 1.10 (d, 3 H, $^3J(HH) = 7.22$ Hz, Me), 1.96–2.33 (m, 8 H, CH_2, cod), 2.92 (s, br, 1 H, =CH, cod), 3.34 (s, br, 1 H, =CH, cod), 5.0 (m, 1 H, CH), 5.72 (s, br, 2 H, =CH, cod) and 6.31 (d), 6.99 (t), 7.3–8.2 (m) assigned to aromatic H-rings. $^{31}P\{^1H\}$ ($CDCl_3$, ppm): δ 69.8 [d, $^2J(PP) = 66.1$ Hz, PS] and 103.0 [dd, $^1J(RhP) = 155.7$ Hz, P]. FTIR (KBr, cm^{-1}): ν(PS), 596(m), 588 (m).; $\nu(BF_4)$, ca. 1100(s), 520(m).

2.4. Reaction of $[\{Rh(\mu$-Cl)(cod)$\}_2]$ with S-$\{Ph_2P(S)\}_2N(C^*HMePh)$

A suspension of the dinuclear complex $[\{Rh(\mu$-Cl)(cod)$\}_2]$ (62 mg; 0.1 mmol) in acetone (10 ml) was treated with silver tetrafluoroborate (39 mg; 0.2 mmol). The mixture was stirred for 30 min in the absence of light and the AgCl formed was filtered off through Kieselguhr. A solution of S-$\{Ph_2P(S)\}_2N(CHMePh)$ (107 mg; 0.2 mmol) in acetone (10 ml) was added to the yellow filtrate, containing the solvated complex $[Rh(cod)(Me_2CO)_x]^+$. After stirring for 1 h at room temperature (r.t.), the mixture was evaporated to dryness and the residue was extracted with dichloromethane. Careful addition of diethyl ether induced precipitation of an orange solid. The solid obtained was characterized as. $[Rh(cod)(\eta^2$-S,S-$\{Ph_2P(S)\}_2$-NH)]BF_4 (**4**). Yield 65 mg (67%). Anal. Found: C, 51.42; H, 4.23; N, 1.81; S, 8.77. Calc. for $C_{32}H_{33}BF_4NP_2RhS_2$: C, 51.42; H, 4.45; N, 1.87; S, 8.58%. ^1H-NMR ($CDCl_3$, ppm): δ 1.9–2.4 (m, 8 H, CH_2, cod), 4.04 (s, br, 2 H, =CH, cod), 4.62 (s, br, 2 H, =CH, cod). $^{31}P\{^1H\}$ ($CDCl_3$, ppm): δ 35.9 (s). FTIR (KBr, cm^{-1}): ν(PS), 555 (s); $\nu(BF_4)$, ca. 1100(s), 510(m).

Table 1
Crystallographic data and structure refinement for compounds **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{32}H_{29}NP_2S$	$C_{32}H_{29}NP_2S_2$
Formula weight	521.56	553.62
Temperature (°C)	23	23
Wavelength (Å)	Mo–K_α (0.71073)	Mo–K_α (0.71073)
Crystal system	Orthorhombic	Orthorhombic
Space group	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
Unit cell dimensions		
a (Å)	10.969(5)	9.499(2)
b(Å)	15.131(7)	15.588(4)
c (Å)	16.964(9)	19.598(5)
V (Å^3)	2746(2)	2901.8(12)
Z	4	4
D_{calc} (Mg m^{-3})	1.262	1.267
Absorption coefficient (mm^{-1})	0.256	0.316
F(000)	1096	1160
Crystal size (mm)	0.80 × 0.50 × 0.30	0.60 × 0.50 × 0.50
θ Range for data collection (°)	1.80–22.50	1.67–22.50
Index ranges	$0 = h = 11$, $-1 = k = 16$, $1 = l = 18$	$-4 = h = 12$, $-1 = k = 20$, $0 = l = 25$
Reflections collected	2222	2413
Independent reflections	2211 ($R_{int} = 0.0352$)	2352 ($R_{int} = 0.0299$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2210/07266	2349/0/275
Goodness-of-fit on F^2	1.059	1.041
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0448$, $wR_2 = 0.0921$	$R_1 = 0.0468$, $wR_2 = 0.1089$
R indices (all data)	$R_1 = 0.0587$, $wR_2 = 0.1006$	$R_1 = 0.0534$, $wR_2 = 0.1140$
Absolute structure parameter	−0.02(18)	0.020(17)
Largest difference peak and hole (e Å^{-3})	0.204 and −0.195	0.256 and −0.276

2.5. *[(Cp*)MCl{η^2-P,S-Ph_2PNHP(S)Ph_2}]BF_4 (M = Rh **5**, Ir **6**)*

A solution of the binuclear complex [{(Cp*)MCl(μ-Cl)}$_2$] (0.16 mmol; Rh, 100 mg; Ir, 126 mg) and $AgBF_4$ (82 mg; 0.32 mmol) in a mixture chloroform-acetone (5:15 cm^3), was stirred for 2 h at r.t. in the absence of light. The precipitated silver chloride was removed by filtration. (S)-α-Ph_2PN(CHMePh)P(S)Ph_2 (167 mg; 0.32 mmol) dissolved in boiling diethyl ether (40 cm^3) 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 crystallized by diffusion of diethyl ether into a chloroform solution of compounds.

2.5.1. Complex **5**

Yield 180 mg, 72%. (Found: C, 52.4; H, 4.5; N, 1.9; S, 4.0. $C_{34}H_{36}BClF_4NP_2RhS$ requires C, 52.4; H, 4.7; N, 1.8; S, 4.1%). ν_{max} cm^{-1} (KBr): 588 (PS), 1100 and 520 (BF_4). δ_H ($CDCl_3$, 295 K) 1.5 [d, 15 H, ^4J(HP) = 3.68 Hz, C_5Me_5], 7.6 (m, 20 H, Ph). δ_P ($CDCl_3$, 295 K) 87.2 [dd, ^1J(RhP) = 139 Hz, ^2J(PP) = 39 Hz, PRh], 69.0 [d, PS].

2.5.2. Complex **6**

Yield 172 mg, 61%. (Found: C, 47.2; H, 4.2; N, 1.8; S, 3.5. $C_{34}H_{36}BClF_4NP_2IrS$ requires C, 47.1; H, 4.2; N, 1.6; S, 3.7%). ν_{max} cm^{-1} (KBr): 585 (PS), 1100 and 520 (BF_4). δ_H ($CDCl_3$, 295 K) 1. 57 [d, 15 H, ^4J(HP) = 2.48 Hz, C_5Me_5], 6.4–7.7 (m, 20 H, Ph). δ_P ($CDCl_3$, 295 K) 60.8 [d, ^2J(PP) = 32.5 Hz, PIr], 69.1 [d, PS].

2.6. *X-ray structure determination of compounds **1**, **2**, **5** and **6***

Suitable crystals for the X-ray diffraction studies were obtained by slow evaporation of a chloroform-methanol solution (**1** and **2**) and by vapor diffusion of ether into chloroform solution of **5** and **6**. Intensity crystal data were collected on a Siemens R3m/V diffractometer using graphite–monochromated Mo–K_α radiation in Wyckoff 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 [18]. Phenyl rings were treated as idealized D_{6h} symmetric rings with C–C = 1.395 Å and C–C–C = 120°. Crystal data and details of measurements and refinements are summarized in Tables 1 and 3.

3. Results and discussion

3.1. Synthesis of sulfur diphosphazanes

The synthetic method of Krishnamurthy et al. [12] was used to synthesize the starting chiral diphosphazane S-$(PPh_2)_2N(CHMePh)$. The chiral diphosphazene S-$(Ph_2P)_2N(CHMePh)$ reacts with a stoichiometric amount of elemental sulfur in diethyl ether solution at reflux temperature, to give S-$Ph_2P(S)N(CHMePh)PPh_2$ (**1**) as an insoluble solid. The conversion is produced in moderate yield (67%) and minor amounts of disulphide $[Ph_2P(S)]_2N(CHMePh)$ and starting $(Ph_2P)_2N(CHMePh)$ compounds were detected in the diethyl ether solution. Compound **1** is soluble in toluene, chlorinated solvents, tetrahydrofuran and acetone. Its $^{31}P\{^1H\}$-NMR spectrum in $CDCl_3$ solution showed two sharp doublets at δ 51.4 and 71.1 ppm, assigned to phosphorus (III) and phosphorus (V) centers, respectively, with a $^2J(PP)$ coupling of 14.8 Hz. Evaporation of the solution gave the disulphide compound S-$[Ph_2P(S)]_2N(CHMePh)$ (**2**) in low yield (34%) when the reaction was carried out in a 1:2 molar ratio. At reflux temperature, a large amount (30%) of compound **1** was formed. Compound **2** was obtained in highest yield (59%) when the reaction was performed under refluxing tetrahydrofuran with an excess of sulfur (1:5 molar ratio). The $^{31}P\{^1H\}$-NMR spectrum of **2** in $CDCl_3$ solution showed a broad singlet at δ 68.4 ppm at room temperature.

Both compounds were isolated as stable white solids. The IR spectra showed the characteristic absorption band assigned to the ν(P=S) moiety (**1**, 674; **2**, 647 cm^{-1}).

3.2. Variable temperature NMR studies

The $^{31}P\{^1H\}$-NMR spectra of the starting ligand S-$(Ph_2P)_2N(CHMePh)$ and its sulfur derivative **2**, at room temperature, were broad singlet resonances at δ 52.5 and 68.4 ppm, respectively. Variable temperature experiment (Fig. 1) showed split of the signal into two sharp spin-coupled doublets (AB system) below 233 K for S-$(Ph_2P)_2N(CHMePh)$ and two uncouplet singlets below 213 K for **2**, respectively. This type of line-width/temperature behavior is characteristic of the exchange broadening by equilibrium involving minor component [23–25] (Scheme 1). Steric interactions prevent conformer of C2v′ from participating to any significant extend in conformational equilibrium [4].

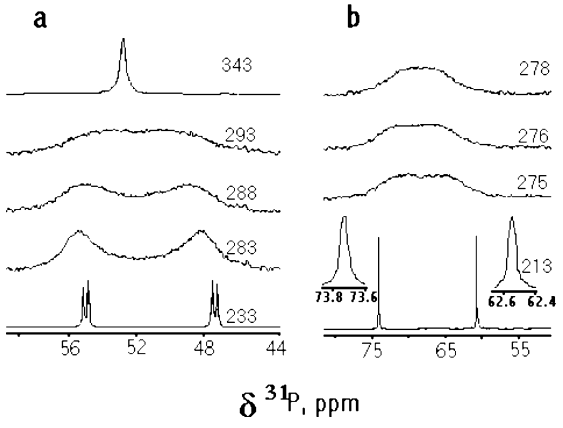
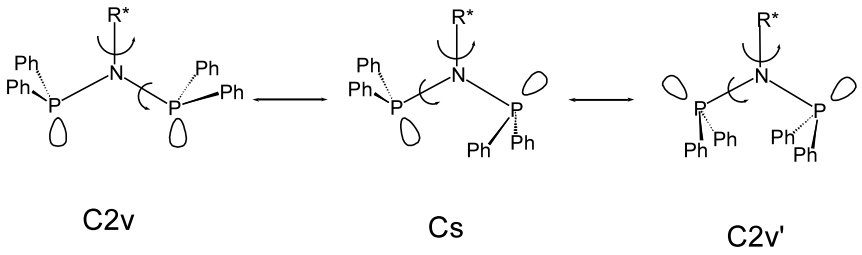


Fig. 1. Variable temperature $^{31}P\{^1H\}$-NMR. (a) S-$(Ph_2P)_2N(CHMePh)$; (b) S-$(Ph_2P(S))_2N(CHMePh)$, **2**.

Variable-temperature $^{31}P\{^1H\}$-NMR experiments of the chiral phosphazene and its sulfur derivative **2** show that, on cooling, the broad resonances (for starting compound and its sulfur derivative **2**) split into two broad signals. At 233 and 213 K, respectively, the exchange is sufficiently slow to separate two sharp doublet signals at δ 55.0 and 47.4 ppm [$^2J(PP) = 25.59$ Hz] for the starting compound and to uncoupled singlets at 73.7 and 62.5 ppm in case of **2**. Coalescence temperatures of these processes are 293 and 276 K, respectively. The free energy of activation $\Delta G^{\ddagger}_{Tc}$ for conformational changes between C_{2v} and C_s conformers were calculated using approximated rate constant at the coalescence point for the coalescence of singlets associated with uncoupled diasterotopic atoms or groups. a) $k_c = (\pi\sqrt{2^{-1}})\Delta\nu$ and for the coalescence of the coupled AB spin system to a singlet b) $k_c = (\pi\sqrt{2^{-1}})\sqrt{(\Delta\nu^2 + 6J^2)}$, $\Delta\nu$ is the difference of P signals (s^{-1}) and J is the coupling parameter [19]. $\Delta G^{\ddagger}_{Tc} = 12.92$ kcal mol^{-1} for the starting ligand and 11.93 kcal mol^{-1} for **2**. These quantities lie in the range for other P–N rotational barriers 9.4–12.7 kcal mol^{-1} in case of bulky alkyls and amides of main group elements [26].

The variable temperature ^{31}P-NMR spectra of S-$(Ph_2P)_2N(CHMePh)$ and **2** are very similar to those reported for of non chiral $Pr^iN(PPh_2)_2$ [25]. At low temperature, the presence of two different phosphorus resonances is ascribed to hindered P–N rotation and preference for C_s configuration. To support this, both of the ligands crystallize in the C_s conformation and low coupling parameter ($J_{PP} = 25.59$Hz) for the starting compound and the absence of coupling in **2** are indicative that at low temperature in solution the most stable conformer should be the C_s as have been shown by X-ray diffraction in other studies [4].

The room temperature spectra of S-$(Ph_2P)_2$-N(CHMePh) and **2** are, however, less really explained. The presence of chiral R*group on nitrogen makes the phosphorus atoms diastereotopic, yet only one resonance, albeit a broad one, is observed at room temperatures for both of the compounds. This may be due to accidental degeneracy of the resonances or to an inability to resolve the two peaks due to ^{14}N spin coupling witch is incompletely collapsed by ^{14}N quadrupolar relaxation and/or by the exchange broadening



Scheme 1.

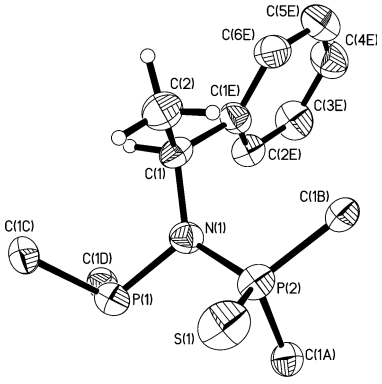


Fig. 2. ORTEP plot (50% probability ellipsoids) for compound $Ph_2P(S)N(CHMePh)PPh_2$.

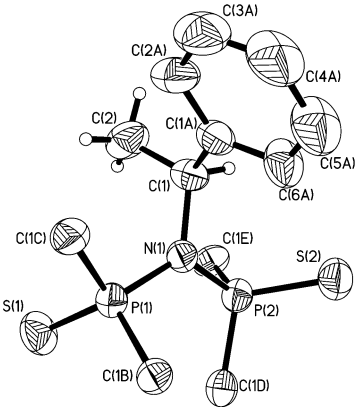


Fig. 3. ORTEP plot (50% probability ellipsoids) for compound $\{Ph_2P(S)_2N(CHMePh)\}$.

by equilibrium involving minor component of C_s conformer afford mentioned.

3.3. Molecular structures of *1* and *2*

Figs. 2 and 3 display the molecular structures of compounds **1** and **2**, respectively. Crystallographic Data and Structure Refinement for Compounds **1** and **2** and Selected bond lengths and bond angles for the structures are shown in Tables 1 and 2. From a crystallographic point of view, the crystal lattices and packing are identical in the space group $P2_12_12_1$.

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

1		**2**	
Bond distances (Å)			
P(1)–N(1)	1.749(4)	P(1)–N(1)	1.700(4)
P(2)–N(1)	1.695(4)	P(1)–S(1)	1.945(2)
N(1)–C(1)	1.499(6)	P(2)–N(1)	1.716(4)
P(2)–S(1)	1.955(2)	P(2)–S(2)	1.927(2)
		N(1)–C(1)	1.524(7)
Bond angles (°)			
P(1)–N(1)–P(2)	124.3(2)	P(2)–N(1)–P(1)	112.0(2)
P(1)–N(1)–C(1)	123.2(3)	N(1)–P(2)–S(1)	117.2(2)
P(2)–N(1)–C(1)	111.4(3)	P(1)–N(1)–C(1)	121.5(3)
N(1)–P(1)–S(1)	115.4(2)	P(2)–N(1)–C(1)	121.9(3)
N(1)–P(2)–S(2)	113.7(2)		

The molecular structure of **1** shows a nearly trigonal planar nitrogen atom bound to two different phosphorus atoms, $P^{III}(1)$ and $P^{V}(2)$, and to a chiral carbon atom. As expected, the P^{V}–N bond distance is shorter [P(2)–N, 1.695(4) Å] than the P^{III}–N bond [P(1)–N, 1.749(4) Å] and compares well with those found in the related compounds $[Ph_2P(S)]_2NH$ [P–N, average 1.676(7) Å] [20] and $(Ph_2P)_2N(CHMePh)$ [P–N, average 1.7192 Å] [13]. The P–S bond distance [1.955(2) Å] is indicative of the double bond character and is similar to those found in P_4S_{10} [P=S, 1.960 Å] [21] and $[Ph_2P(S)]_2NH$ [P–S, average 1.916(3) Å] [19]. The P–N–P bond angle [P–N–P, average 112.0°] is smaller than the P–N–P angle of the starting compound $(Ph_2P)_2N(CHMePh)$ [P–N–P, average 120.04°] [13].

Compound **2** acquires a twisted conformation with the two sulfur atoms adopting a mutually trans relationship with respect to the PNP skeleton. The P–S [1.945(2) and 1.927(2) Å] and P–N bond distances [1.700(4) and 1.716(4) Å], compare well with those showed in the similar compound $[Ph_2P(S)]_2NH$ [P–S, average 1.916(3) Å, P–N, average 1.676(7) Å] [20]. The P–N–P bond angle [124.3(2)°] is smaller than the P–N–P angle of the related compound $[Ph_2P(S)]_2NH$ [P–N–P, 131.7(5)°] [21]. However, it compares well with the value found in the starting compound $(Ph_2P)_2N(CHMePh)$ [P–N–P, average 120.04°] [13].

3.4. Synthesis of the metal complexes

Compound **1** reacts with the solvated complex $[Rh(cod)S_x]BF_4$ (prepared in situ from $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ and silver tetrafluoroborate in acetone or tetrahydrofuran) to give the cationic complex $[Rh(cod)\{\eta^2\text{-}S,P\text{-}Ph_2P(S)N(C^*HMePh)PPh_2\}]BF_4$ (**3**). As expected, in this compound, the mono sulphide (**1**) derivative behaves as heterobifunctional chelate ligand. Its $^{31}P\{^1H\}$-NMR spectrum shows a doublet resonance at δ 69.8 [$^2J(PP) = 66.1$ Hz] and a doublet of doublets at 103.0 ppm [$^1J(RhP) = 155.7$ Hz], assigned to $P^V(PS)$ and $P^{III}(P\text{–}Rh)$, respectively. The ^{1}H-NMR spectrum shows the expected resonances of the diolefin cod and the coordinated chiral ligand in the required proportions, supporting the proposed formulation.

In contrast, when the above reaction was carried out with the disulphide ligand $S\text{-}\{Ph_2P(S)\}_2N(CHMePh)$, the coordination of the phosphine-sulphide groups to the metal center occurs simultaneously with the cleavage of the carbon–nitrogen bond of the ligand, affording the cationic complex $[Rh(cod)(\eta^2\text{-}S,S\text{-}\{Ph_2P(S)\}_2NH)]BF_4$ (**4**). This complex was fully characterized by elemental analysis, IR and NMR spectroscopies. Same complex was obtained by reaction of disulphide ligand $HN\{P(S)Ph_2\}_2$ [22] with the solvated complex $[Rh(cod)S_x]BF_4$.

On the other hand, the reaction of compound **1** with solvated complex $[Cp^*MClS_x]BF_4$, M = Rh, Ir (prepared in situ from binuclear complexes $[\{Cp^*MCl(\mu\text{-}Cl)\}_2]$ and silver tetrafluoroborate in acetone or tetrahydrofuran) give the cationic complexes $[Cp^*MCl\{\eta^2\text{-}S,P\text{-}Ph_2P(S)NHPPh_2\}]BF_4$, M = Rh (**5**), Ir (**6**) with the consequent loss of the chiral R* group, shown by ^{1}H-NMR and X diffraction studies.

The ^{31}P-NMR spectra of the crude product for both complexes **5** and **6** (Fig. 4) show a duplicated pattern (relative intensity ~60:40), having the same coupling parameters with the less intense signals, appearing at

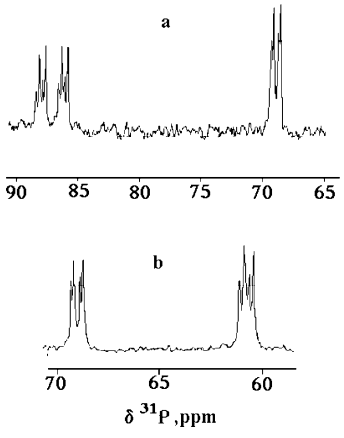


Fig. 4. ^{31}P-MR spectra of the crude product (a) rhodium and (b) irridium complexes. Notice the duplicated pattern of the spectra.

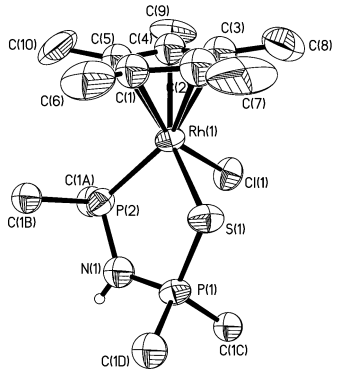


Fig. 5. ORTEP plot (50% probability ellpsoids) for $[(Cp^*)RhCl\{\kappa^2\text{-}P,S\text{-}Ph_2PNHP(S)Ph_2\}]BF_4$, **5**.

lower fields. The ^{31}P-NMR spectrum on a well shaped crystals, obtained by diffusion of ether into chloroform solution of the complex doesn't show the afford mentioned duplicated pattern. This could be explained by the existence in solution of structural conformer at a five membered chelate ring and its interconversion during the crystallization process.

Addition of a base (NEt_3) leads to loss of the acidic imine proton in both complexes to give neutral species, as shown by comparison of the ^{31}P-NMR chemical shift with the one of iridium neutral complex $[Cp^*IrCl\{\eta^2\text{-}P,S\text{-}Ph_2PNP(S)Ph_2\}]$ [31]. When both forms (neutral and cationic) are present in solution a fast proton exchange occurs at NMR time scale to give broad ^{31}P signal at room temperature. Lowering the temperature to −50 °C make the proton exchange process, at nitrogen atom, slow enough to resolve the spectra in to sharp signals corresponding to cationic and neutral species, respectively.

3.5. Molecular structures of 5 and 6

Figs. 5 and 6 display the molecular structures of compounds **5** and **6**, respectively. Crystallographic information and relevant bond lengths and bond angles are given in Tables 3 and 4, respectively. In both

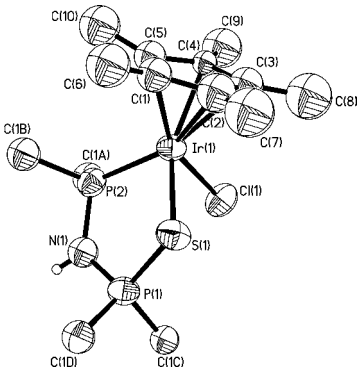


Fig. 6. ORTEP plot (50% probability ellpsoids) for $[(Cp^*)IrCl\{\kappa^2\text{-}P,S\text{-}Ph_2PNHP(S)Ph_2\}]BF_4$, **6**.

Table 3
Crystallographic data and structure refinement for compounds **5** and **6**

Compound	**5**	**6**
Empirical formula	$C_{34}H_{36}BClF_4NP_2RhS$	$C_{34}H_{36}BClF_4IrNP_2S$
Formula weight	777.81	867.10
Temperature (°C)	23	22
Wavelength (Å)	Mo–K_α (0.71073)	Mo–K_α (0.71073)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pca*2(1)	*Pca*2(1)
Unit cell dimensions		
a (Å)	16.791(5)	16.752(4)
b(Å)	10.966(3)	10.957(2)
c (Å)	19.010(6)	18.959(4)
V (Å^3)	3500.4(19)	3480.0(12)
Z	4	4
D_{calc} (Mg m^{-3})	1.476	1.655
Absorption coefficient (mm^{-1})	0.762	4.112
F(000)	1584	1712
Crystal size (mm)	0.35 × 0.35 × 0.20	0.80 × 0.30 × 0.10
θ Range for data collection (°)	1.86–27.50	1.86–27.53
Index ranges	$-1 < h < 21,\ 0 < k < 14,\ -24 < l < 0$	$-1 \le h \le 21,\ -4 \le k \le 14,\ -24 \le l \le 0$
Reflections collected	4411	4416
Independent reflections	4138 ($R_{int} = 0.0318$)	4416 ($R_{int} = 0.0376$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4137/1/277	4118/1/152
Goodness-of-fit on F^2	1.028	1.022
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0661,\ wR_2 = 0.1316$	$R_1 = 0.0641,\ wR_2 = 0.1405$
R indices (all data)	$R_1 = 0.1215,\ wR_2 = 0.1626$	$R_1 = 0.1215,\ wR_2 = 0.1744$
Absolute structure parameter	0.08(9)	0.03(2)
Largest difference peak and hole (e Å^{-3})	0.637 and −0.512	2.729 and −0.761

structures Rh and Ir atoms have distorted coordination spheres. The centroid of the pentamethylcyclopentadienyl ligand occupies the center of three octahedral sites. The heterobifunctional chelate ring bonded to the metal center through a phosphorus and sulfur atoms and a chlorinate atom complete the coordination sphere. Complexes **5** and **6** crystallize as a racemic mixture S and R [50:50%] imposed by space group *Pca*2(1) requirement [27].

The distances Rh–P and Rh–Cl [Rh–P, 2.293(4); Rh–Cl, 2.389(3)Å] are slightly shorter than in the neutral complex [Cp*RhCl{η^2-P,Se-($Ph_2PNP(Se)Ph_2$}] [Rh–P, 2.3295(11); Rh–Cl, 2.3992(15) Å] [31] and in the [Cp*RhCl{prophos}] [Rh–P, 2.325(1); Rh–Cl, 2.393(1) Å] [28]. The Rh–S and P–S [Rh–S, 2.404(3); P–S, 1.997(4) Å] distances are very close to those in the Rh(I) complex [(COD)Rh{$Ph_2P(S)\}_2CH_2$]ClO_4, [Rh–S, 2.403(5); P–S, 2.001(6) Å] [29]. For the iridium complex **6** the Ir–P and Ir–Cl distances [Ir–P, 2.263(6); Ir–Cl, 2.398(5) Å] are in range of the cationic complex [Cp*IrCl{η^2-P,S-$Ph_2PCH_2P(S)Ph_2$}]$BF_4 \cdot Me_2CO$ [Ir–P, 2.303(3); Ir–Cl, 2.381(2) Å] [30]. The Ir–C and Ir–S distances [Ir–C(C_5Me_5)$_{av.}$, 2.201; Ir–S, 2.407(5)Å] are very close to the one for the mentioned before complex [Ir–C(C_5Me_5)$_{av.}$, 2.161/2.238; Ir–S, 2.402(3) Å].

Finally, the coordination reaction of the disulphide ligand **2** with the solvated compound [Cp*MClS_x]BF_4 was carried out with a simultaneously cleavage of the C–N bond to afford the recently described neutral complexes [Cp*MCl($(SPPh_2)_2N$)] [2]. In this case the ligand is co-ordinated in its very stable bidentate anionic

Table 4
Selected bond distances (Å) and angles (°) for complexes [Cp*RhCl{κ^2-P,S(Ph_2P NHP(S)Ph_2)}]BF_4, **5**; [Cp*IrCl{κ^2-P,S(Ph_2PNHP-(S)Ph_2)}]BF_4, **6**

5		**6**	
Bond distances (Å)			
Rh(1)–S(1)	2.404(3)	Ir(1)–S(1)	2.407(5)
Rh(1)–P(2)	2.293(4)	Ir(1)–P(2)	2.263(6)
P(1)–N(1)	1.650(11)	P(1)–N(1)	1.64(2)
P(2)–N(1)	1.698(10)	P(2)–N(1)	1.69(2)
P(1)–S(1)	1.997(4)	P(1)–S(1)	2.000(8)
P(1)–C(1C)	1.790(7)	P(1)–C(1C)	1.781(12)
P(1)–C(1D)	1.777(8)	P(1)–C(1D)	1.764(12)
Rh(1)–Cl(1)	2.389(3)	Ir(1)–Cl(1)	2.398(5)
Rh(1)–$C_{(1-5)av}$	2.197	Ir(1)–$C_{(1-5)av}$	2.201
Bond angles (°)			
P(1)–N(1)–P(2)	121.1(6)	P(1)–N(1)–P(2)	122.5(11)
S(1)–Rh(1)–P(2)	88.32(12)	S(1)–Ir(1)–P(2)	88.6(2)
P(2)–Rh(1)–Cl(1)	87.63(12)	P(2)–Ir(1)–Cl(1)	87.7(2)
S(1)–Rh(1)–Cl(1)	91.59(12)	S(1)–Ir(1)–Cl(1)	89.2(2)

form, which is considered as non-carbon analogues of acetylacetonate.

4. Conclusions

Sulfur chalcogenide derivatives of diphosphazanes S-$Ph_2P(S)N(CHMePh)PPh_2$ and S-$\{Ph_2P(S)\}_2N$-(CHMePh) have been synthesized and fully characterized using spectroscopic techniques and by elemental analysis. Their structures have been determined by X-ray diffraction method. Variable temperature experiments with the starting ligand and its sulfur derivative S-$\{Ph_2P(S)\}_2N(CHMePh)$ show exchange broadening by equilibrium involving two conformers. Calculated barriers from NMR data are $\Delta G^{\ddagger}_{Tc} \sim 12.92$ and 11.93 kcal mol^{-1}, respectively.

The mono-sulfur chalcogenide behaves as a neutral ligand with fragment $[Rh(cod)S_x]BF_4$ to afford the cationic complex $[Rh(cod)\{\eta^2$-S,P-$Ph_2P(S)N$-$(CHMePh)PPh_2\}]BF_4$ (**3**). However, cleavage of the C–N bond of the ligand occurred to yield the complex $[Rh(cod)(\eta^2$-S,S-$\{Ph_2P(S)\}_2NH)]BF_4$ (**4**) when the above reaction was carried out with S-$\{Ph_2P(S)\}_2$-N(CHMePh).

Reactions of S-$Ph_2P(S)N(CHMePh)PPh_2$ with the fragments of Rh (III) and Ir (III) $[Cp^*MClS_x]BF_4$ lead to cleavage of the C–N bond of the ligand affording cationic complexes, $[(Cp^*)MCl\{\eta^2$-P,S-$Ph_2PNHP(S)Ph_2\}]BF_4$ (M = Rh, **5**; Ir, **6**].

4.1. Supporting information available

X-ray crystallographic files, in CIF format for the structure determination at the Cambridge Crystallographic Data Centre and allocated the deposition numbers **1**, 165206; **2**, 165207; **5**, 165473; **6**, 165474.

Acknowledgements

We are grateful for the financial support provided by 'Fondo de Desarrollo Científico y Tecnológico (FONDECYT)', Chile (Projectos No. 2980031, 4000002 and 8980007). E.S.-M. thanks Professor Joanne Stewart for useful discussions.

References

[1] J. Parr, M.B. Smith, A.M.Z. Slawin, J. Organomet. Chem. 588 (1999) 99.
[2] M. Valderrama, R. Contreras, M.P. Lamata, F. Viguri, D. Carmona, F.J. Lahoz, S. Elipe, L.A. Oro, J. Organomet. Chem. 607 (2000) 3.
[3] J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996) 2893, and references therein.
[4] P. Bhattacharyya, J.D. Woollins, Polyhedron 14 (1996) 3367 (and references therein).
[5] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, J. Chem. Soc. Dalton Trans. (1998) 2467.
[6] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, J.D. Woollins, Inorg. Chem. 35 (1996) 3675.
[7] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996) 1283.
[8] R. Rösler, J.E. Drake, C. Silvestru, J. Yang, I. Haiduc, J. Chem. Soc. Dalton Trans. (1996) 391.
[9] J. Cuadrado, M. Morán, Trans. Met. Chem. 9 (1984) 96.
[10] R.O. Day, R.R. Holmes, A. Schmidtpeter, K. Stoll, L. Howe, Chem. Ber. 124 (1991) 2443.
[11] M.S. Balakrishna, R. Klein, S. Uhlenbrock, A.A. Pinkerton, R.G. Cavell, Inorg. Chem. 32 (1993) 5676.
[12] R.P.K. Babu, S.S. Krishnamurthy, M. Nethaji, Tetrahedron: Asymmetry 6 (1995) 427.
[13] F. Robert, Y. Gimbert, M.T. Averbuch-Pouchot, A.E. Greene, New Cryst. Struct. 215 (2000) 233.
[14] E. Simón-Manso, M. Valderrama, V. Arancibia, Y. Simón-Manso, D. Boys, Inorg. Chem. 39 (2000) 1659.
[15] M. Valderrama, R. Contreras, A. Arancibia, P. Muñóz, Bol. Soc. Chil. Quím. 45 (2000) 227.
[16] M. Valderrama, V. Arancibia, R. Contreras, C. Soto, J. Coord. Chem. 54 (2001) 389.
[17] (a) J. Chatt, M.L. Venanzi, J. Chem. Soc. (1957) 4735.;
(b) P.M. Maitlis, Acc. Chem. Res. 11 (1978) 301.
[18] G.M. Sheldrick, SHELXTL-PC, Siemens Analytical X-Ray Instruments Inc., Madison, WI, USA, 1990.
[19] D. Kost, E.H. Carlson, M. Raban, Chem. Commun. (1971) 656.
[20] P.B. Hitchcock, J.F. Nixon, I. Silaghi-Dumitrescu, I. Haiduc, Inorg. Chim. Acta 96 (1985) 77.
[21] A. Vasand, E.M. Wiebenga, Acta Crystallogr. 8 (1955) 217.
[22] F.T. Wand, J. Najdzionek, K.L. Leneker, H. Wasserman, D.M. Braitsch, Synth. React. Inorg. Met. Org. Chem. 8 (1978) 119.
[23] F.A.L. Anet, V.J. Basus, J. Magn. Res. 32 (1978) 339.
[24] N. Okazawa, T.S. Sorenson, Can. J. Chem. 56 (1978) 2737.
[25] R. Keat, L. Manojlovic-Muir, K.W. Muir, D.S. Rycroft, J. Chem. Soc. Dalton Trans. (1981) 2192.
[26] H. Goldwhite, P.P. Power, Org. Mag. Res. 11 (1978) 499.
[27] W. Massa, Crystal Structure Determination, Springer-Verlag, Berlin, Heidelberg, Germany, 2000.
[28] M.T. Pinillos, M.T. Jarauta, D. Carmona, L.A. Oro, C. Apreda, C. Foses-Foses and, F.H. Cano, J. Organomet. Chem. 345 (1998) C13.
[29] M.S. Abbasioun, P.A. Chaloner, C. Claver, P.B. Hitchcock, A.M. Masdeu, A. Ruiz, T. Saballs, J. Organomet. Chem. 403 (1991) 229.
[30] M. Valderrama, R. Contreras, D. Boys, Polyhedron (1997) 16, 11, 1811.
[31] M. Valderrama, R. Contreras, M. Muñoz, M.P. Lamata, D. Carmona, F.J. Lahoz, S. Elipe, L.A. Oro, J. Organomet. Chem. 633 (2001) 182.