Pergamon

Polyhedron Vol. 14, No. 15–16, pp. 2239–2246, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 $9.50+0.00

0277–5387(94)00494–3

BIS(DIPHENYLPHOSPHINO)METHANE AND ITS SULPHIDE OR SELENIDE DERIVATIVES AS LIGANDS IN RUTHENIUM(II) AND RHODIUM(III) COMPLEXES: CRYSTAL STRUCTURE OF $[(\eta^6C_6Me_6)Ru\{\eta^3(SPPh_2)_2CH\}]ClO_4$

MAURICIO VALDERRAMA,* RAUL CONTRERAS, MANUEL BASCUÑAN and SERGIO ALEGRIA

Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago-22, Chile

and

DAPHNE BOYS

Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago, Chile

(*Received* 14 *October* 1994; *accepted* 21 *November* 1994)

Abstract—Reaction of complexes $[(\eta^6C_6Me_6)RuCl_2]_2$ and $[(\eta^5C_5Me_5)RhCl_2]_2$ with the ligands L = $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2PCH_2P(Se)Ph_2$ in benzene solutions led to neutral complexes with the general formula $[(ring)MCl_2(\eta^1L)]$. The reactivity of the uncoordinated P atom of dppm has been studied. When the reaction was carried out in methanol solutions, cationic complexes, with the ligands acting in their bidentate form, were obtained. Similar cationic perchlorate complexes were prepared using acetone as solvent in the presence of sodium perchlorate, yielding $[(ring)MCl(\eta^2L)]ClO_4$, where L = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2P(Se)Ph_2$ or $Ph_2P(S)CH_2P(S)Ph_2$. The complex $[(\eta^6C_6Me_6)RuCl\{\eta^2(SPPh)_2CH_2\text{-}S,S'\}]ClO_4$ reacted with sodium hydride in tetrahydrofuran or thallium pyrazolate in dichloromethane solution by deprotonation of the coordinated bidentate ligand giving the complex $[(\eta^6C_6Me_6)Ru\{\eta^3(SPPh_2)_2CH\text{-}C,S,S'\}]ClO_4$. The structure of this complex has been determined by single crystal X-ray diffraction methods. The complex contains a tridentate C,S,S′-bonded ligand occupying three coordination positions of a distorted octahedral ruthenium centre, with an $\eta^6C_6Me_6$ group completing the coordination sphere.

There is currently much interest in the synthesis and structure of transition metal complexes containing bidentate tertiary phosphine chalcogenides as ligands. Work has been mainly concentrated on reactions with derivatives of bis(diphenylphosphine)methane, and several complexes with the bidentate ligands $Ph_2PCH_2P(E)Ph_2$ and $Ph_2P(E)CH_2P(E)Ph_2$ (E = S,Se) have been described.[1–9] This type of ligand has been the subject of increasing interest because the methylene protons react with bases to yield an anionic derivative. When deprotonation was carried out on the coordinated ligand, the resulting complexes contain the anionic form acting as a *P,E*-[2–4,10], *E,E*-[9,11] or *C,E*-bonded chelate ligand[12] or as a *P,C,E*-bridging six-electron ligand.[3]

In this context we have recently reported the preparation of rhodium(III) and ruthenium(II) cationic complexes containing the ligand $Ph_2P(Se)CH_2P(Se)Ph_2$, of the type $[(ring)MCl\{\eta^2(SePPh_2)_2CH_2\text{-}Se,Se'\}]ClO_4$. Interestingly when deprotonation occurs on the coordinated ligand the methanide carbon formed displaces the chloride ligand and

---

*Author to whom correspondence should be addressed.

the anionic bis(diphenylphosphine)methanide diselenide group is bonded to the metal centre as a C,Se,Se′-tripod ligand.[13]

In this paper we describe the synthesis, characterization and reactivity of new ruthenium(II) and rhodium(III) complexes containing $Ph_2PCH_2PPh_2$ (dppm) or their sulphur or selenium derivatives, of different types: (a) neutral complexes with dppm or $Ph_2PCH_2P(Se)Ph_2$ acting as a unidentate P-donor ligand; (b) cationic complexes with dppm, $Ph_2PCH_2P(Se)Ph_2$ or $Ph_2P(S)CH_2P(S)Ph_2$ as bidentate ligands; and (c) cationic complex with deprotonated $Ph_2P(S)CH_2P(S)Ph_2$ as tridentate anionic ligand. The structure of the complex $[(\eta^6C_6Me_6)Ru\{\eta^3(SPPh_2)_2CH\text{-}C,S,S'\}]ClO_4$ has been established by X-ray diffraction studies.

EXPERIMENTAL

Elemental analyses were made with a Heraeus Mikro Standard and Perkin–Elmer 240B microanalysers. Infrared spectra were recorded on a Perkin–Elmer 567 spectrophotometer (over the range 4000–200 cm^{-1}) using KBr pellets. Conductivities were measured in *ca* 5×10^{-4} M acetone solutions using a WTW LF-521 conductimeter. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Brucker AC-200P spectrometer and chemical shifts are reported relative to $SiMe_4$ and 85% H_3PO_4 (positive shifts downfield), respectively.

All reactions were carried out by Schlenk techniques under purified nitrogen. Reagent grade solvents were dried, distilled and stored under a nitrogen atmosphere. The ligands $Ph_2PCH_2P(Se)Ph_2$, $Ph_2P(S)CH_2P(S)Ph_2$, and the starting binuclear complexes $[(\eta^6C_6Me_6)RuCl_2]_2$ and $[(\eta^5C_5Me_5)RhCl_2]_2$ were prepared by published procedures.[14–16]

Carbon and hydrogen analyses, colours, yields and conductivities are listed in Table 1. ^1H NMR and $^{31}P\{^1H\}$ NMR data are listed in Table 2.

Preparation of $[(ring)MCl_2(\eta^1dppm\text{-}P)]$ $[(ring)M = (\eta^6C_6Me_6)Ru$ (I), $(\eta^5C_5Me_5)Rh$ (II)]

To a suspension of the binuclear complex $[(ring)MCl_2]_2$ (0.150 mmol) in benzene (20 cm^3) was added a slight excess of the ligand dppm (0.303 mmol). After stirring for 7 h, the mixture was filtered through cellulose and concentrated to a small volume (5 cm^3). The addition of diethylether gave orange solids, which were filtered off, washed with diethylether and dried *in vacuo*. The complexes were recrystallized in benzene–diethylether forming red needles.

Preparation of $[(\eta^6C_6Me_6)RuCl_2(\eta^1Ph_2PCH_2P(Se)Ph_2\text{-}P)]$ (**III**)

A mixture of $[(\eta^6C_6Me_6)RuCl_2]_2$ (100 mg, 0.15 mmol) and $Ph_2PCH_2P(Se)Ph_2$ (140 mg, 0.303 mmol) in benzene (30 cm^3) was stirred for 4 h. The solution obtained was evaporated to dryness and the solid residue extracted with dichloromethane (5 cm^3). The solution was filtered through cellulose and the complex precipitated by addition of n-hexane. Recrystallization in dichloromethane gave red–brown crystals.

Preparation of $[(\eta^5C_5Me_5)RhCl_2(\eta^1Ph_2PCH_2P(Se)Ph_2\text{-}P)]$ (**IV**)

A suspension of the binuclear complex $[(\eta^5C_5Me_5)RhCl_2]_2$ (100 mg, 0.162 mmol) in benzene (20 cm^3) was treated with the ligand $Ph_2PCH_2P(Se)Ph_2$ (150 mg, 0.324 mmol) and the mixture stirred for 5 h. The orange solid formed was filtered off and washed with diethylether. The mother liquor obtained was evaporated to a small volume (5 cm^3), and the careful addition of diethylether gave a second crop of solid. The complex was recrystallized from benzene–diethylether.

Preparation of $[(ring)MCl_2(\eta^1Ph_2PCH_2P(S)Ph_2\text{-}P)]$ $[(ring)M = (C_6Me_6)Ru$ (**V**), $(C_5Me_5)Rh$ (**VI**)]

A mixture of complex **I** or **II** (0.209 mmol) with an excess of sulphur (7.0 mg, 0.219 mmol) was boiled under reflux in benzene (20 cm^3), with stirring, for 4 h. The resulting solution was evaporated to a small volume (5 cm^3) and the complexes precipitated by addition of n-hexane. The solids were filtered off, washed with carbon disulfide (2×5 cm^3) and diethylether, and dried *in vacuo*. Red crystals were obtained from dichloromethane–n-hexane.

Preparation of $[(\eta^6C_6Me_6)RuCl(\eta^2L)]Cl$ [L = dppm-P,P (**VII**), $Ph_2PCH_2P(Se)Ph_2$-P,Se (**VIII**)]

A solution of $[(\eta^6C_6Me_6)RuCl_2]_2$ (100 mg, 0.15 mmol) and the corresponding ligand L (0.324 mmol) in methanol (30 cm^3) was boiled under reflux for 2 h. The resulting solution was evaporated to a small volume and the complexes were precipitated by addition of diethylether. The solids were washed with diethylether (3×10 cm^3) and dried *in vacuo*. The complexes were recrystallized from dichloromethane–n-hexane (**VII**) or dichloromethane–diethylether (**VIII**).

Table 1. Analytical results, colours, yields and molar conductivities of the isolated ruthenium(II) and rhodium(III) complexes

Complex	Colour	Yield (%)	Analysis [found (calc.) (%)]		Λ_M ($cm^2\ ohm^{-1}\ mol^{-1}$)
			C	H	
$[(\eta^6C_6Me_6)RuCl_2(\eta^1dppm\text{-}P)]$ **(I)**	Red	75	61.5 (61.8)	5.9 (5.6)	—
$[(\eta^5C_5Me_5)RhCl_2(\eta^1dppm\text{-}P)]$ **(II)**	Red–purple	81	59.4 (60.5)	5.3 (5.4)	—
$[(\eta^6C_6Me_6)RuCl_2\{\eta^1Ph_2PCH_2P(Se)Ph_2\text{-}P\}]$ **(III)**	Red brownish	66	55.5 (55.7)	5.1 (5.1)	—
$[(\eta^5C_5Me_5)RhCl_2\{\eta^1Ph_2PCH_2P(Se)Ph_2\text{-}P\}]$ **(IV)**	Red	93	54.6 (54.4)	4.7 (4.8)	—
$[(\eta^6C_6Me_6)RuCl_2\{\eta^1Ph_2PCH_2P(S)Ph_2\text{-}P\}]$ **(V)**	Red	50	59.6 (59.2)	5.5 (5.4)	—
$[(\eta^5C_5Me_5)RhCl_2\{\eta^1Ph_2PCH_2P(S)Ph_2\text{-}P\}]$ **(VI)**	Red	81	57.0 (57.9)	5.3 (5.1)	—
$[(\eta^6C_6Me_6)RuCl(\eta^2\text{-}dppm\text{-}P,P)]Cl$ **(VII)**	Yellow	94	61.1 (61.8)	5.5 (5.6)	126
$[(\eta^6C_6Me_6)RuCl\{\eta^2Ph_2PCH_2P(Se)Ph_2\text{-}P,Se\}]Cl$ **(VIII)**	Yellow	89	60.3 (60.6)	5.5 (5.4)	118
$[(\eta^5C_5Me_5)RhCl(\eta^2dppm\text{-}P,P)]Cl$ **(IX)**	Red	87	55.2 (55.7)	5.5 (5.1)	127
$[(\eta^5C_5Me_5RhCl\{\eta^2Ph_2PCH_2P(S)Ph_2\text{-}P,Se\}]Cl$ **(X)**	Red	77	54.6 (54.4)	4.9 (4.8)	117
$[(\eta^6C_6Me_6)RuCl(\eta^2dppm\text{-}P,P)]ClO_4$ **(XI)**	Yellow	88	56.7 (56.8)	5.0 (5.1)	137
$[(\eta^6C_6Me_6)RuCl\{\eta^2(SePPh_2)_2CH_2\text{-}Se,Se'\}]ClO_4$ **(XII)**	Red	94	51.9 (51.6)	4.8 (4.7)	143
$[(\eta^6C_6Me_6)RuCl\{\eta^2(SPPh_2)_2CH_2\text{-}S,S'\}]ClO_4$ **(XIII)**	Yellow orange	79	52.4 (52.5)	4.8 (4.8)	136
$[(\eta^5C_5Me_5)RhCl(\eta^2dppm\text{-}P,P)]ClO_4$ **(XIV)**	Yellow	87	55.3 (55.5)	5.1 (4.9)	138
$[(\eta^5C_5Me_5)RhCl\{\eta^2Ph_2PCH_2P(Se)Ph_2\text{-}P,Se\}]ClO_4$ **(XV)**	Red orange	94	50.3 (50.3)	4.4 (4.5)	137
$[(\eta^5C_5Me_5)RhCl(\eta^2(SPPh_2)_2CH_2\text{-}S,S'\}]ClO_4$ **(XVI)**	Red	87	50.9 (51.2)	4.9 (4.5)	137
$[(\eta^6C_6Me_6)Ru\{\eta^3CH(Ph_2PS)_2\}\text{-}C,S,S'\}]ClO_4$ **(XVII)**	Red orange	79	54.5 (54.8)	4.9 (4.8)	120

Preparation of $[(\eta^5C_5Me_5)RhCl(\eta^2L)]Cl$ [L = dppm-P,P **(IX)**, $Ph_2PCH_2P(Se)Ph_2$-P,Se **(X)**]

A suspension of $[(\eta^5C_5Me_5)RhCl_2]_2$ (100 mg, 0.163 mmol) and the corresponding ligand L (0.324 mmol) in methanol (30 cm^3) was boiled under reflux for 2 h. The solution obtained was evaporated to a small volume ($\sim$5 cm^3) and the complexes were precipitated by addition of diethylether. The solids were washed with diethylether (3 × 10 cm^3) and dried *in vacuo*. The complexes were recrystallized from dichloromethane–diethylether **(IX)** or dichloromethane–n-hexane **(X)**.

Preparation of $[(\eta^6C_6Me_6)RuCl(\eta^2L)]ClO_4$ [L = dppm-P,P **(XI)**, $Ph_2PCH_2P(Se)Ph_2$-P,Se **(XII)**, $Ph_2P(S)CH_2P(S)Ph_2$-S,S′ **(XIII)**]

The complexes were prepared by the following two routes:

(i) A slurry of complex **VII** or **VIII** (0.16 mmol) and a slight excess of $NaClO_4$ (0.17 mmol) in acetone (30 cm^3) was boiled under reflux for 5 h. The obtained mixture was evaporated to dryness, extracted with dichloromethane (15 cm^3) and filtered through cellulose to eliminate the NaCl formed and the excess of $NaClO_4$.

Table 2. NMR chemical shifts (δ, ppm) and coupling constants (Hz) of isolated complexes[a]

Complex	^{1}H NMR		$^{31}P\{^1H\}$ NMR
	Ring	$CH_2(L)$	
I	1.7 (d) $^4J(P_AH) = 0.6$	3.5 (dd) $^2J(P_AH) = 8.4$; $^2J(P_BH) = 2.2$	$-27.4(d,P_B)$, $26.9(d,P_ARu)$ $^2J(P_AP_B) = 25.6$
II	1.4 (d) $^4J(P_AH) = 3.5$	3.7 (dd) $^2J(P_AH) = 9.0$; $^2J(P_BH) = 1.6$	$-26.8(d,P_B)$, $30.1(dd,P_ARh)$ $^2J(P_AP_B) = 28.1$; $^1J(P_ARh) = 140.9$
III	1.7 (d) $^4J(P_AH) = 0.6$	4.4 (dd) $^2J(P_AH) = 9.4$; $^2J(P_BH) = 11.1$	$23.5(d,P_BSe)$, $25.5(d,P_ARu)$ $^2J(P_AP_B) = 38.5$; $^1J(P_BSe) = 741.7$
IV	1.3 (d) $^4J(P_AH) = 3.6$	4.7 (at) $^2J(PH) = 11.0$	$23.5(dd,P_BSe)$, $26.9(dd,P_ARh)$ $^2J(P_AP_B) = 38.6$; $^1J(P_ARh) = 140.3$ $^3J(P_BRh) = 5.2$
V	1.7 (d) $^4J(P_AH) = 0.4$	4.2 (at) $^2J(PH) = 10.1$	$24.7(d,P_ARu)$,$34.4(d,P_BS)$ $^2J(P_AP_B) = 38.8$
VI	1.3 (d) $^4J(P_AH) = 3.5$	4.5 (at) $^2J(PH) = 10.3$	$26.2(dd,P_ARh)$, $34.2(dd,P_BS)$ $^2J(P_AP_B) = 37.7$; $^1J(P_ARh) = 144.9$ $^3J(P_BRh) = 3.6$
XI	2.0 (t) $^4J(PH) = 0.9$	4.4 (m,H_a) 4.9 (m,H_b)	1.6 (s)
XII	1.9 (d) $^4J(PH) = 0.7$	3.9 (m,H_a) 4.4 (m,H_b)	$32.4(d,P_BSe)$, $50.4(d,P_ARu)$ $^2J(P_AP_B) = 35.5$; $^1J(P_BSe) = 561.0$
XIII[b]	2.1 (s)	4.9 (m,H_a) 5.2 (m,H_b)	38.1 (s)
XIV	1.8 (t) $^4J(PH) = 4.1$	4.5 (m,H_a) 4.8 (m,H_b)	-5.9 (d) $^1J(P_ARh) = 114.3$
XV	1.6 (d) $^4J(PH) = 3.8$	4.4 (m,H_a) 4.7 (m,H_b)	$32.9(d,P_BSe)$, $44.1(dd,P_ARh)$ $^2J(P_AP_B) = 38.5$; $^1J(P_ARh) = 138.6$ $^1J(P_BSe) = 566.9$
XVI	1.8 (s)	4.7 (m,H_a) 5.3 (m,H_b)	37.1 (s)

[a] Measured in $CDCl_3$ at room temperature. Chemical shifts relative to Me_4Si and H_3PO_4 (85%) as external. s, singlet; d, doublet; dd, doublet of doublets; t, triplet; at, apparent triplet; m, multiplet. All complexes show multiplets in the region 6.8–8.6 ppm corresponding to phenyl groups of the ligands.

[b] $^{13}C\{^1H\}$ NMR: δ 93.9 (s,C_6Me_6), 15.4(s,C_6Me_6) and 25.8$(t,CH_2,{}^1J_{PC} = 45.1$ Hz) ppm.

The solution obtained was concentrated to a small volume and the complexes **XI** or **XII** were precipitated by addition of diethylether. The solids were washed with diethylether (3×10 cm^3), dried under vacuum and recrystallized from dichloromethane–n-hexane.

(ii) A slurry of $[(\eta^6C_6Me_6)RuCl_2]_2$ (200 mg, 0.298 mmol), the ligand $Ph_2P(S)CH_2P(S)Ph_2$ (0.598 mmol) and $NaClO_4$ (73 mg, 0.598 mmol) in acetone (35 cm^3) was boiled under reflux for 17 h. The solution was filtered through Kieselguhr, concentrated to a small volume and the complex (**XIII**) was precipitated by addition of diethylether. The complex was recrystallized from ethanol.

Preparation of $[(\eta^5C_5Me_5)RhCl(\eta^2L)]ClO_4$ [L = dppm-P,P (**XIV**), $Ph_2PCH_2P(Se)Ph_2$-P,Se (**XV**), $Ph_2P(S)CH_2P(S)Ph_2$-S,S′ (**XVI**)]

To a suspension of $[(\eta^5C_5Me_5)RhCl_2]_2$ (100 mg, 0.162 mmol) in acetone (25 cm^3) was added the ligand L (0.324 mmol) and $NaClO_4$ (40 mg, 0.324 mmol). After the mixture was boiled under reflux for several hours (**XIV** 2 h, **XV** 2 h, **XVI** 15 h) the solution was filtered through Kieselgel (HF_{254}, type 60) and concentrated to a small volume. The slow addition of diethylether caused the precipitation of the corresponding complexes which were washed with diethylether and dried *in vacuo*. The complexes were recrystallized from dichloromethane–diethylether.

Preparation of $[(\eta^6C_6Me_6)Ru\{\eta^3(SPPh_2)_2CH\text{-}C,S,S'\}]ClO_4$ (**XVII**)

The complex was prepared by the following two methods:

(i) To a solution of complex $[(\eta^6C_6Me_6)RuCl(\eta^2(SPPh_2)_2CH_2\text{-}S,S')]ClO_4$ (**XIII**) (150 mg, 0.177 mmol) in tetrahydrofuran (20 cm^3) was added an excess of sodium hydride (4.7 mg of 80% dispersion in mineral oil). After the mixture was stirred for 3 h at 0°C, the solution was evaporated to dryness. The solid residue was extracted with dichloromethane (15 cm^3), filtered through cellulose and concentrated to a small volume. The addition of n-hexane caused the precipitation of the complex, which was washed with diethylether (3 × 10 cm^3) and dried *in vacuo*. The complex was recrystallized from dichloromethane–n-hexane.

(ii) To a solution of complex $[(\eta^6C_6Me_6)RuCl(\eta^2(SPPh_2)_2CH_2\text{-}S,S')]ClO_4$ (**XIII**) (150 mg, 0.177 mmol) in dichloromethane was added the stoichiometric amount of thallium pyrazolate[17] (32 mg, 0.177 mmol). The mixture was stirred for 6 h. During this time solid thallium chloride is formed and the solution gradually changed from red to orange. The thallium chloride was filtered off, the solution was concentrated to a small volume and the addition of n-hexane caused the precipitation of the complex. Yield 61%.

Crystal structure determination of XVII

A deep-orange, prismatic-shaped crystal of average dimension $0.18 \times 0.20 \times 0.26$ mm^3, obtained from a slow diffusion of n-hexane into a dichloromethane solution of complex **XVII**, was selected for structure determination by X-ray diffraction. Intensity data were collected on a Siemens R3m/V four-circle diffractometer, using a θ–2θ scan technique and graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Two standard reflections, monitored every 48 reflections, showed no significant intensity variation during data collection. A total of 6032 reflections were collected with $3.0 \leqslant 2\theta \leqslant 60.0°$ ($0 \leqslant h \leqslant 14$, $-6 \leqslant k \leqslant 21$, $-16 \leqslant l \leqslant 16$) and merged to give 5524 independent reflections of which 3681, with $I > 2\sigma(I)$, were considered observed. Corrections were applied for Lorentz and polarization effects. Semi-empirical correction for absorption was applied with maximum and minimum transmission factors of 0.9606 and 0.7273, respectively.

A summary of crystal data is given in Table 3. The structure was solved using direct methods and refined on F. All non-H atoms were refined anisotropically by full-matrix least-squares methods. H atoms were placed in idealized positions with C—H = 0.96 Å, riding on their parent C atoms, with their equivalent isotropic U, except for the methanide hydrogen which was determined from a Different synthesis. A comment should be made regarding the space group assigned to the complex. The structure was initially refined in the acentric space group $P2_1$ but, at an early stage, a symmetry plane in the cation became evident. While the chlorine atom (located in the mirror plane of the cation) and all other atoms in the cation refined well in the centric space group $P2_1/m$, oxygen atoms of the anion proved difficult to refine, in either space group, due to the high positional disorder commonly exhibited by perchlorates. None of the possible models tested for the disorder of the oxygens proved successful, so the structure was finally refined in centric space group $P2_1/m$. The disordered anion was constrained to be a regular tetrahedron, with equal refinable Cl—O distances, satisfying the symmetry conditions imposed by the crystallographic mirror plane of the centric space group. Refinement converged to final R and R_w values of 0.043 and 0.045, respectively (weighting scheme $w^{-1} = \sigma^2(F) + 0.0014F^2$). The total number of parameters refined was 221. All calculations were performed with the Siemens SHELXLT Plus system (PC version).[18] Lists of bond lengths and angles, anisotropic thermal parameters, H-atom coordinates, least-squares planes and dihedral angles, and observed and calculated structure factors have been deposited with the Editor as supplementary material.

Table 3. Crystal data for $[(\eta^6C_6Me_6)Ru\{\eta^3(SPPh_2)_2CH\}]ClO_4$

Empirical formula	$C_{37}H_{39}ClO_4P_2RuS_2$
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	
a (Å)	10.192(1)
b (Å)	15.131(2)
c (Å)	11.850(1)
β (°)	90.75(1)
Volume (Å^3)	1827.1(3)
Z	2
Formula weight (g mol^{-1})	810.3
Density (calc.)(Mg m^{-3})	1.473
Absorption coefficient (mm^{-1})	0.742
$F(000)$	832

RESULTS AND DISCUSSION

The binuclear complexes $[(\eta^6C_6Me_6)RuCl_2]_2$ and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ react with the ligands L = 1,2-bis(diphenylphosphino)methane (dppm) or (diphenylphosphinomethyl)diphenylphosphino selenide ($Ph_2PCH_2P(Se)Ph_2P$) in benzene solution, by cleavage of the chlorine bridges to yield neutral complexes with L acting as unidentate P-donor ligand, in accord with the general equation:

$$1/2[(\text{ring})MCl_2]_2 + L \rightarrow [(\text{ring})MCl_2(\eta^1L)] \quad (1)$$

When the ligand dppm acts as a unidentate ligand is may be possible react the uncoordinated P atom. Thus, these complexes reacted with elemental selenium or sulphur in refluxing toluene, thereby creating the P-coordinated monoselenide or monosulphide ligands and led to the complexes **III**, **IV**, $[(\eta^6C_6Me_6)RuCl_2(\eta^1Ph_2PCH_2P(S)Ph_2\text{—}P)]$ (**V**) and $[(\eta^5C_5Me_5)RhCl_2(\eta^1Ph_2PCH_2P(S)Ph_2\text{—}P)]$ (**VI**).

The complexes were isolated as stable microcrystalline solids. The solid-state IR spectra of complexes **III**, **IV**, **V** and **VI** in KBr pellets, showed the characteristic absorptions of the non-coordinated P=Se or P=S groups at 530, 540 and 600 cm^{-1}, respectively. The ^1H NMR spectra of the mononuclear complexes exhibited the expected doublet signal for the permethylated rings and a doublet of doublets for the methylene protons or an apparent triplet in the case of the complexes **IV**–**VI**. The $^{31}P\{^1H\}$ NMR spectra showed two doublet resonances corresponding to the different phosphorus atoms, where the P bonded to the metal resonated at lower field than the non-coordinated P or P=E groups.

When the reaction in eq. (1) was carried out in methanol solutions at reflux temperature, cationic complexes with the ligand L acting in their bidentate form were obtained:

$$1/2[(\text{ring})MCl_2]_2 + L \xrightarrow{\text{MeOH}} [(\text{ring})MCl(\eta^2L)]Cl \quad (2)$$

(VII–X)

Similar perchlorate salts were obtained by reactions of the binuclear starting complexes with the ligands L = dppm, $Ph_2PCH_2P(Se)Ph_2$ or $Ph_2P(S)CH_2P(S)Ph_2$ in acetone solution at reflux temperature in the presence of $NaClO_4$:

$$1/2[(\text{ring})MCl_2]_2 + L + NaClO_4 \rightarrow [(\text{ring}MCl(\eta^2L)]ClO_4 + NaCl \quad (3)$$

(XI–XVI)

All cationic complexes were isolated as stable microcrystalline solids and behave as 1 : 1 electrolytes in acetone solutions. In all cases, the solid-state IR spectra showed the presence of the uncoordinated anion (ClO_4^- *ca* 1100 and 620 cm^{-1}) together with the absorption bands corresponding to the P=S or P=Se bonds. As expected, the ν(P=S) stretching vibrations are shifted to lower frequency (575–580 cm^{-1}) relative to free ligand (620 cm^{-1}), however the ν(P=Se) absorption showed no important variations of the frequency with respect to the free ligand (*ca* 530 cm^{-1}). Their ^1H NMR spectra in deuterated chloroform exhibited the expected resonances corresponding to the phenyl groups and permethylated rings, together with two different multiplet resonances in the range δ 3.93–5.40 ppm which indicated non-equivalent methylene protons, H_a and H_b. The proton *endo* to the chlorine atom is labelled H_a and is tentatively assigned to the highest field resonance, on the basis of results obtained for the similar iridium(III) complexes[19] and those reported for methylene protons of the bis(diphenylphosphine)methane ligand in the platinum(II) complex $[Pt_2X_2(\mu\text{-}S)(\mu\text{-dppm})_2]$(X = Cl, Br, I).[20] The proton decoupled ^{31}P NMR spectra showed only one signal for the complexes with the symmetrical bidentate ligands L = dppm and $Ph_2P(S)CH_2P(S)Ph_2$ corresponding to equivalent phosphorus atoms. The complexes containing the unsymmetrical $Ph_2PCH_2P(Se)Ph_2$ ligand exhibited the expected two different resonances. The phosphorus atom (P_B) bonded to the selenium resonates as a doublet at higher field than the phosphorus bonded to the metal (P_A), which showed a doublet for the ruthenium complex (**XII**) with $^2J(P_AP_B)$ = 35.5 Hz or a doublet of doublets for the rhodium complex (**XV**) with $^2J(P_AP_B)$ = 38.5 Hz and $^1J(P_ARh)$ = 138.62 Hz.

The coordinated symmetric $Ph_2P(S)CH_2P(S)Ph_2$ ligand in complex **XIII** reacted with sodium hydride in tetrahydrofuran or with thallium pyrazolate in dichloromethane solutions by deprotonation of the methylene group giving a new cationic complex, according to eq. (4):

$$[(\eta^6C_6Me_6)RuCl\{\eta^2(SPPh_2)_2CH_2\text{—}S,S']ClO_4 \xrightarrow[\text{THF}]{\text{NaH}} [(\eta^6C_6Me_6)Ru\{\eta^3(SPPh_2)_2CH\text{—}C,S,S'\}]ClO_4 \quad (4)$$

This result is similar to those obtained by deprotonation reactions of the related complexes $[(\eta^6C_6Me_6)\ RuCl\ \{\eta^2(SePPh_2)_2CH_2\text{—}Se,Se'\}]\ ClO_4$ and $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2(SePPh_2)_2CH_2\text{—}Se,Se'\}]$ ClO_4. In both cases the new cationic complexes obtained contain the anionic ligand acting as a tripod ligand with an C,Se,Se′-donor set.[13] The formation of these compounds occurs *via* an intramolecular process, where the methanide carbon of the deprotonated phosphine chalcogenides displaces the chlorine ligand with formation of a methanide carbon—metal bond.

The complex **XVII** was isolated as a stable microcrystalline solid and behaved as a 1 : 1 electrolyte in acetone solutions. IR spectra showed the absorption of the coordinated P═S group and the uncoordinated ClO_4^- anion. The ^1H NMR spectrum showed a multiplet resonance at δ 2.83 ppm, corresponding to the methanide system, confirming that the methylene group in the starting complex undergoes deprotonation in the reaction with sodium hydride and the $^{31}P\{^1H\}$ NMR spectrum showed a single resonance at δ 55.97 ppm. Recently, Browning *et al.*[11] reported the $^{13}C\{^1H\}$ NMR spectrum of the anionic ligand in the lithium salt, $(SPPh_2)_2CHLi$, and in the neutral complex $[Rh(cod)\{\eta^2(SPPh_2)_2CH—S,S\}]$, indicating that the methanide carbon shifts occur at δ 19.9(t) and 14.4(t) ppm, respectively. In our case, the $^{13}C\{^1H\}$ NMR spectrum showed that the formation of the metal—carbon bond produced a large increase in shielding of the methanide carbon, which appeared as a triplet at δ -33.2 ppm ($^1J_{PC} = 51$ Hz), together with the resonances of the phenyl groups in the δ 130 ppm region and two singlets at δ 94.3 and 15.7 ppm corresponding to the η^6-coordinate hexamethylbenzene ring.

As expected, the methanide moiety of complex **XVII** reacted with aqueous HCl in acetone solution (5 h, room temperature), regenerating the starting complex **XVI**.

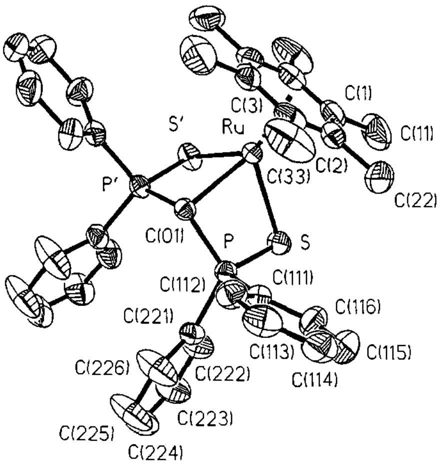

Fig. 1. ORTEP view of the structure of the cationic complex $[(\eta^6C_6Me_6)Ru\{\eta^3(SPPh_2)_2CH\}]^+$ (**XVII**), showing the atom numbering. Hydrogen atoms have been omitted for clarity.

In order to obtain an unambiguous characterization of the complex **XVII**, an X-ray diffraction study was undertaken. Table 4 lists the relevant bond distances and angles. Figure 1 shows a perspective ORTEP view of the cation, showing the metal centre with a pseudo-octahedral geometry, commonly referred as 'three-legged piano stool' configuration, with a centroid of the hexamethylbenzene ligand occupying the centre of three octahedral sites and the bis(diphenylphosphine) methanide disulphide ligand bonded to the ruthenium atom through to the two sulphur atoms and the methanide carbon atom.

The methyl subtituents of the benzene ring are bent away from the ruthenium atom and the Ru—C(ring) distances, ranging from 2.208(4) to 2.220(4) Å, compare well with those found in other hexamethylbenzene–ruthenium(II) complexes.[17,21] The Ru—S distances [2.443(1) Å] are slightly larger than those found in the thiolate complex $[Ru\{(SC_6H_4NHCH)_2\}_2(PPh_3)]$ [Ru—S : 2.371(3) and 2.375(2) Å][22] and the Ru—C(01) distance [2.238(4) Å] is similar to the Ru—C bond distance present in

Table 4. Selected bond distances (Å) and bond angles (°)

Ru—S	2.443(1)	S—P	2.003(1)
Ru—C(01)	2.238(4)	P—C(01)	1.775(2)
Ru—C(1)	2.220(4)	P—C(111)	1.805(4)
Ru—C(2)	2.208(4)	P—C(221)	1.809(4)
Ru—C(3)	2.208(4)		
S—Ru—S′	84.8(1)	S—P—C(01)	102.6(1)
S—Ru—C(01)	78.1(1)	S—P—C(111)	111.7(1)
S′—Ru—C(01)	78.1(1)	S—P—C(221)	111.0(1)
Ru—S—P	81.4(1)	C(01)—P—C(111)	108.5(2)
Ru—C(01)—P	92.5(1)	C(01)—P—C(221)	117.9(2)
P—C(01)—P′	120.1(2)	C(111)—P—C(221)	105.3(2)

Prime stands for symmetrically related atom.

the complex $[(C_5Me_5)Ru(CH_2C_5Me_4)]BPh_4 \cdot CH_2Cl_2$ [Ru—C: 2.270(3) Å].[23]

The bond angles Ru—C(01)—P [92.5(1)°] and P—C(01)—P′ [120.0(2)°] reveal the highly distorted tetrahedral environment of the methanide carbon.

The P—S [2.003(1) Å] and P—C(01) [1.775(2) Å] distances of the coordinated anionic ligand are similar to those found in the related complexes [Rh(η^4cod){η^2($(SPPh_2)_2CH$}—S,S′] [P—S: average 2.036(4) and P—C: 1.705(11) Å] and [Ir(η^4cod){η^2($(SPPh_2)_2CH$}—S,S′] [P—S: average 2.039(3) and P—C: 1.711(6) Å].[11] Angles involving the P atoms reflect a tetrahedral geometry, and it is noteworthy that the S—P—C(01) is smaller than the S—P—C(111) and S—P—C(221) angles.

Acknowledgement—The authors thank the Fondo Nacional de Ciencia y Tecnología (FONDECYT-Chile, Grant No. 798/91 and No. 460/93) and the Fundación Andes for financial support.

REFERENCES

1. T. S. Lobana, M. K. Sandhu, M. J. Lidell and E. R. T. Tiekink, *J. Chem. Soc. Dalton Trans.* 1990, 691.
2. D. E. Berry, J. Browning, K. R. Dixon and R. W. Hilts, *Can. J. Chem.* 1988, **66**, 1272.
3. R. Uson, A. Laguna, M. Laguna, M. N. Fraile, P. G. Jones and C. Freire. *J. Chem. Soc. Dalton Trans.* 1989, 73.
4. J. Browning, G. W. Bushnell, K. R. Dixon and R. W. Hilts, *J. Organometal. Chem.* 1993, **452**, 205.
5. E. W. Ainscough, A. M. Brodie and E. Mentzer, *J. Chem. Soc. Dalton Trans.* 1973, 2167.
6. E. W. Ainscough, H. A. Bergen, A. M. Brodie and K. A. Brown, *J. Chem. Soc. Dalton Trans.* 1976, 1649.
7. A. Laguna, M. Laguna, A. Rojo and M. N. Fraile, *J. Organometal. Chem.* 1988, **315**, 269.
8. M. S. Abassioun, P. A. Chaloner, C. Claver, P. B. Hitchcock, A. M. Masdeu, A. Ruiz and T. Saballs, *J. Organometal. Chem.* 1991, **403**, 229.
9. R. Contreras, M. Valderrama and S. Yañez, *Trans. Met. Chem.* 1993, **18**, 73.
10. M. Lusser and P. Peringer, *Inorg. Chim. Acta* 1987, **127**, 151.
11. J. Browning, G. W. Bushnell, K. R. Dixon and R. W. Hilts, *J. Organometal. Chem.* 1992, **434**, 241.
12. J. Browning, G. W. Bushnell, K. R. Dixon and A. Pidcock, *Inorg. Chem.* 1983, **22**, 2226.
13. M. Valderrama, R. Contreras, M. Bascuñan and D. Boys, *Polyhedron* 1994, **13**, 1101.
14. S. O. Grim and E. D. Walton, *Inorg. Chem.* 1980, **19**, 1982.
15. M. A. Bennett, T. N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.* 1982, **21**, 74.
16. P. M. Maitlis, *Acc. Chem. Res.* 1978, **11**, 301.
17. M. Scotti, M. Valderrama, R. Moreno, R. López and D. Boys, *Inorg. Chim. Acta* 1994, **216**, 67.
18. G. M. Sheldrick, SHELXTL Plus, release 4.2 for Siemens Crystallographic Research System. Siemens Analytical X-Ray Instruments, Inc., Madison, WI (1990).
19. M. Valderrama and R. Contreras, *Bol. Soc. Chil. Quim.* 1995, **40**, 111.
20. (a) M. P. Brown, J. R. Fisher, R. Puddephat and K. R. Seddon, *Inorg. Chem.* 1979, **18**, 2808; (b) S. Muralidharan, J. H. Espenson and S. A. Ross, *Inorg. Chem.* 1986, **25**, 2557.
21. G. A. Van Albada, R. A. G. De Graaf, R. Hage, J. Reedijk, E. Buchholtz and W. Kläui. *Polyhedron* 1991, **10**, 1091.
22. D. Sellmann, U. Reineke, G. Huttner and L. Zsolnai, *J. Organometal. Chem.* 1986, **310**, 83.
23. A. I. Yanowsky, Yu. T. Struchkow, A. Z. Kreindlin and M. I. Rybinskaya, *J. Organometal. Chem.* 1989, **369**, 125.