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Diphosphinito-bridged ruthenium(II) and rhodium(III) complexes with stereogenic metal centers

Carmela G. Arena, Daniela Drago, Manuela Panzalorto, Giuseppe Bruno, Felice Faraone *

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica dell'Università, Salita Sperone 31, Villaggio S. Agata, I-98166 Messina, Italy

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Abstract

The bis-4-phosphinito ligands [(*p*-$Ph_2POC_6H_4)_2X$] (X = O, **1**; X = CMe_2, **2**; X = S, **3**) react with [Ru(η^6-*p*-cymene)$Cl_2]_2$ to form the binuclear complexes {[Ru(η^6-*p*-cymene)$Cl_2]_2$[μ-(*p*-$Ph_2POC_6H_4)_2X$]} (X = O, **4**; X = CMe_2, **5**; X = S, **6**) in good yields as red air stable solids. The crystal structures of **4**–**6** were determined by X-ray analysis. In acetonitrile and in the presence of $AgPF_6$ (1:1 equiv. with respect to Ru), complexes **4**–**6** undergo substitution to yield the cationic complexes {[Ru(η^6-*p*-cymene)Cl(CH_3CN)$]_2$[μ-(*p*-$Ph_2POC_6H_4)_2X$]}$[PF_6]_2$ (X = O, **7**; X = CMe_2, **8**; X = S, **9**), whose stability in solution is very limited. The acetonitrile ligand in complexes **7**–**9** can be easily replaced by carbon monoxide; the products {[Ru(η^6-*p*-cymene)Cl(CO)$]_2$[μ-(*p*-$Ph_2POC_6H_4)_2X$]}$[PF_6]_2$ (X = O, **10**; X = CMe_2, **11**; X = S, **12**) can only be detected in solution under a CO atmosphere and have limited stability. The reaction of [Rh(η^5-C_5Me_5)$Cl_2]_2$ with ligands **1**–**3** results in the formation of the complexes {[Rh(η^5-C_5Me_5)$Cl_2]_2$[μ-(*p*-$Ph_2POC_6H_4)_2X$]} (X = O, **13**; X = CMe_2, **14**; X = S, **15**), which have been isolated as red–orange air stable solids. The cationic complexes {[Rh(η^5-C_5Me_5)Cl(CH_3CN)$]_2$[μ-(*p*-$Ph_2POC_6H_4)_2X$]}$[PF_6]_2$ (X = O, **16**; X = CMe_2, **17**; X = S, **18**), in which the metal atoms are stereogenic centers, have been obtained from the corresponding complexes **13**–**15**, by treatment in CH_3CN with $AgPF_6$, and have been characterized only in solution by $^{31}P\{^1H\}$ NMR spectra and conductivity measurements. On reaction with ligands **1**–**3**, [Rh(η^5-C_5H_5)$(CO)_2$] was converted into the binuclear phosphinito-bridged complexes {[Rh(η^5-C_5H_5)(CO)$]_2$[μ-(*p*-$Ph_2POC_6H_4)_2X$]} (X = O, **19**; X = CMe_2, **20**; X = S, **21**). The reactions of the binuclear complex {[Rh(η^5-C_5H_5)(CO)$]_2$[μ-(*p*-$Ph_2POC_6H_4)_2S$]} (**21**) with CH_3I, *S*-(+)-1-bromo-2-methylbutane and racemic $PhCH(CH_3)Br$ were also studied. The products were the corresponding acyl derivatives. The reaction of **21** with neat CH_3I easily afforded the complex {[Rh(η^5-C_5H_5)($COCH_3$)I$]_2$[μ-(*p*-$Ph_2POC_6H_4)_2S$]} (**23**), whose structural determination by X-ray analysis is also reported.

Keywords: Crystal structures; Ruthenium complexes; Rhodium complexes; Diphosphinito-bridged complexes

1. Introduction

Three-legged piano stool complexes containing a stereogenic metal are very important species as they may undergo simple reactions, such as ligand substitution and migratory insertion, which could provide detailed information regarding the role that metal stereocenters play in the course of stereoselective transformations. The role of the stereogenic metal has been discussed previously, particularly in arene- and cyclopentadienyl-ruthenium(II) and pentamethylcyclopentadienyl-rhodium(III) complexes. In this context, of particular relevance are the stereochemical studies performed by Consiglio and Morandini [1] on η^5-cyclopentadienylruthenium(II) complexes containing the chiral ligand prophos (prophos = *R*-1,2-propanediylbis-(diphenylphosphine)). The chemistry of η^6-arene analogs has been less extensively studied, although Mashima et al. [2] reported several catalytic studies using η^6-areneruthenium(II) complexes containing the binap (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) ligand. Several detailed studies, particularly

* Corresponding author. Tel.: +39-090-676 5717; fax: +39-090-393 756.

E-mail address: faraone@chem.unime.it (F. Faraone)

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by Brunner et al. [3], consider the factors which confer an appreciable configurational stability on the metal atom.

A literature search reveals that the majority of the stereochemical investigations on chiral-at-metal half-sandwich species have concentrated on mononuclear complexes. Few examples of chiral-at-metal half-sandwich binuclear complexes of ruthenium(II) and rhodium(III) with one bridging diphosphine ligand have been reported [4].

This work deals with the synthesis of the bis-*p*-phosphinito ligands (p-$Ph_2POC_6H_4)_2X$ (X = O, **1**; X = CMe_2, **2**; X = S, **3**), designed to induce a bridging coordination in transition metal complexes, and their reactions with $[Ru(\eta^6$-*p*-cymene$)Cl_2]_2$, $[Rh(\eta^5$-$C_5Me_5)Cl_2]_2$, and $[Rh(\eta^5$-$C_5H_5)(CO)_2]$ to give binuclear complexes. The stereochemical course of some substitution and oxidative addition reactions is also reported. The molecular structures of the binuclear complexes $\{[Ru(\eta^6$-*p*-cymene$)Cl_2]_2[\mu$-(p-$Ph_2POC_6H_4)_2X]\}$ (X = O, CMe_2) and of the compound $\{[Rh_2(\eta^5$-$C_5H_5)_2$-$(COCH_3)_2I_2][\mu$-(p-$Ph_2POC_6H_4)_2S]\}$, obtained by oxidative addition of $\{[Rh_2(\eta^5$-$C_5H_5)_2(CO)_2][\mu$-(p-$Ph_2POC_6H_4)_2S]\}$ with CH_3I have been determined by X-ray diffractometry.

2. Experimental

An established method was used to prepare the compound $[Rh(\eta^5$-$C_5H_5)(CO)_2]$ [5]. All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. IR spectra were obtained as Nujol mulls on KBr plates using a Perkin–Elmer FT-IR 1720 spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX R300. ^1H NMR spectra were referenced to internal tetramethylsilane and $^{31}P\{^1H\}$ spectra to external 85% H_3PO_4; positive chemical shifts for all nuclei are to higher frequency. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milan.

2.1. Preparation of the ligands

2.1.1. (p-$Ph_2POC_6H_4)_2O$ (1)

A toluene solution of 4,4′-oxydiphenol (2.00 g, 9.89 mmol) and triethylamine (2.5 g, 24.7 mmol) was added at 0°C dropwise to a stirring solution (40 ml) of PPh_2Cl (4.37 g, 19.8 mmol) in the same solvent (50 ml). The mixture was allowed to stand at room temperature (r.t.) and was stirred for an additional 2 h; then was filtered and the solvent was removed at reduced pressure. The pure product was obtained as a colorless oil. Yield: 90%. ^1H NMR (C_6D_6): δ 6.8–7.85 (m, 28H, CH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 113.1(s).

2.1.2. (p-$Ph_2POC_6H_4)_2CMe_2$ (2)

This compound was obtained by an analogous procedure to **1**, as a white solid, starting from 4,4′-isopropylidendiphenol (2.5 g, 10.9 mmol). Yield: 95%. *Anal.* Calc. for $C_{39}H_{34}O_2P_2$: C, 78.51; H, 5.74. Found: C, 78.72; H, 5.44%. ^1H NMR (C_6D_6): δ 1.49 (s, 6H, CH_3,), 6.98–7.73 (m, 28H, CH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 111.3 (s).

2.1.3. (p-$Ph_2POC_6H_4)_2S$ (3)

This compound was obtained by an analogous procedure to **1**, as a colorless oil, starting from 4,4′-thiodiphenol (2.00 g, 9.16 mmol). Yield: 88%. ^1H NMR (C_6D_6): δ 6.9–7.95 (m, 28H, CH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 112.7 (s).

2.2. Preparation of the complexes

2.2.1. {[Ru(η^6-*p*-cymene)$Cl_2]_2[\mu$-(p-$Ph_2POC_6H_4)_2O]$} (4)

A toluene solution of **1** (0.075 g, 0.131 mmol) was added to a suspension of $[Ru(\eta^6$-*p*-cymene$)Cl_2]_2$ (0.080 g, 0.131 mmol) in the same solvent. After 20 min the suspension disappeared and by stirring for an additional 15 min a red solid separated. This was isolated by filtration, washed with toluene (3 × 5 ml) and dried in vacuo. Yield: 80%. *Anal.* Calc. for $C_{56}H_{56}Cl_4O_3P_2Ru_2$: C, 56.86; H, 4.77; Cl, 11.99. Found: C, 56.59; H, 4.89; Cl, 11.73%. ^1H NMR ($CDCl_3$): δ 0.80 (d, 12H, J(HH) = 6.9 Hz, CH_3), 1.49 (s, CH_3, 6H), 2.48 (sept, 2H, J(HH) = 6.9 Hz, CH), 5.21 (m, 8H, CH), 6.9–7.28 (m, 20H, CH), 7.9–7.95 (m, 8H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 115.0 (s).

2.2.2. {[Ru(η^6-*p*-cymene)$Cl_2]_2[\mu$-(p-$Ph_2POC_6H_4)_2$-$CMe_2]$} (5)

This compound was obtained by an analogous procedure to **4**, as a red solid, starting from $[Ru(\eta^6$-*p*-cymene$)Cl_2]_2$ (0.100 g, 0.163 mmol) and **2** (0.097 g, 0.163 mmol). Yield: 85%. *Anal.* Calc. for $C_{59}H_{62}Cl_4O_2P_2Ru_2$: C, 58.61; H, 5.17; Cl, 11.73. Found: C, 58.35; H, 4.83; Cl, 11.40%. ^1H NMR ($CDCl_3$): δ 0.76 (d, 12H, J(HH) = 7.0 Hz, CH_3), 1.34 (s, 6H, CH_3) 1.47 (s, 6H, CH_3) 2.40 (sept, 2H, J(HH) = 7.0 Hz, CH), 5.20 (m, 8H, CH), 6.75–7.28 (m, 20H, CH), 7.89–7.93 (m, 8H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 113.5 (s).

2.2.3. {[Ru(η^6-*p*-cymene)$Cl_2]_2[\mu$-(p-$Ph_2POC_6H_4)_2S]$} (6)

This compound was obtained by an analogous procedure to **4**, as a red solid, starting from $[Ru(\eta^6$-*p*-cymene$)Cl_2]_2$ (0.090 g, 0.147 mmol) and **3** (0.086 g, 0.147 mmol). Yield: 82%. *Anal.* Calc. for $C_{56}H_{56}Cl_4O_2P_2SRu_2$: C, 56.10; H, 4.71; Cl, 11.83. Found: C, 56.35; H, 4.83; Cl, 11.50%. ^1H NMR ($CDCl_3$): δ 0.84 (d, 12H, J(HH) = 6.9 Hz, CH_3), 1.50 (s, 6H, CH_3) 2.52 (sept, 2H, J(HH) = 6.9 Hz, CH), 5.27

(m, 8H, CH), 6.79–7.36 (m, 20H, CH), 7.94–8.00 (m, 8H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 115.4 (s).

2.2.4. {[Ru(η^6-p-cymene)Cl(CH_3CN)]$_2$[μ-(p-Ph_2-POC_6H_4)$_2$O]}[PF_6]$_2$ (7)

To a stirring solution of **4** (0.080 g, 0.67 mmol) in acetonitrile (20 ml) was added solid $AgPF_6$ (0.034 g, 0.134 mmol). After 2 h, the reaction mixture was filtered and vacuum reduced to ca. 3 ml. A yellow solid was obtained by addition of diethyl ether (30 ml). This was separated by filtration, washed with diethyl ether and dried. Yield: 50%. Due to the instability of complex **7** reliable microanalysis could not be obtained. IR (KBr, Nujol) $\nu(PF_6^-)$ 840 cm^{-1}, ν(CN) 2278 cm^{-1}. ^1H NMR (CD_3CN): δ 0.9–1.4 (m, 12H, CH_3), 2.53 (m, 6H, CH_3CN), 2.14–2.24 (m, 6H, CH_3), 2.6–2.9 (m, 2H, CH), 5.41–5.95 (m, 8H, CH), 6.72–6.95 (m, 8H, C_6H_4), 7.38–8.92 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 125.3 (s), 125.5 (s) (1:1 ratio), -143.8 (sept, J(PF) = 716.8 Hz, PF_6^-). Λ (ohm^{-1} cm^2 mol^{-1}) (5×10^{-4}–10^{-3} M, CH_3CN) 242.

2.2.5. {[Ru(η^6-p-cymene)Cl(CH_3CN)]$_2$[μ-(p-Ph_2POC_6-H_4)$_2$$CMe_2$]}[$PF_6$]$_2$ (8)

This compound was obtained similarly to **7**, as a yellow solid, starting from **5** (0.070 g, 0.058 mmol) and $AgPF_6$ (0.029 g, 0.116 mmol). Yield: 48%. Due to the instability of complex **8** reliable microanalysis could not be obtained. IR (KBr, Nujol) $\nu(PF_6^-)$ 840 cm^{-1}, ν(CN) 2273 cm^{-1}. ^1H NMR (CD_3CN): δ 0.8–1.3 (m, 12H, CH_3), 1.6 (s, 6H, CH_3), 1.8–2 (m, 6H, CH_3CN) 2.5 (m, 6H, CH_3), 2.6–2.9 (m, 2H, CH), 5.41–5.95 (m, 8H, CH), 6.72–6.95 (m, 8H, C_6H_4), 7.38–8.92 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 122.8 (s), 123.5 (s) (1:1 ratio), -143.8 (sept, J(PF) = 716.8 Hz, PF_6^-. Λ (Ohm^{-1} cm^2 mol^{-1}) (5×10^{-4}–10^{-3} M, CH_3CN) 250.

2.2.6. {[Ru(η^6-p-cymene)Cl(CH_3CN)]$_2$[μ-(p-Ph_2POC_6-H_4)$_2$S]}[PF_6]$_2$ (9)

This compound was obtained similarly to **7**, as a yellow solid, starting from **6** (0.070 g, 0.05 mmol) and $AgPF_6$ (0.025 g, 0.100 mmol). Yield: 47%. Due to the instability of complex **9** reliable microanalysis could not be obtained. IR (KBr, Nujol) $\nu(PF_6^-)$ 840 cm^{-1}, ν(CN) 2275 cm^{-1}. ^1H NMR (CD_3CN): δ 0.9–1.3 (m, 12H, CH_3), 1.8–1.9 (m, 6H, CH_3CN), 2.45 (m, 6H, CH_3), 2.6–2.8 (m, 2H, CH), 5.5–6.15 (m, 8H, CH), 6.68–6.87 (m, 8H, C_6H_4); 7.40–8.90 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 124.4 (s), 125.8 (s) (1:1 ratio), -143.8 (sept, J(PF) = 716.8 Hz, PF_6^-). Λ (ohm^{-1} cm^2 mol^{-1}) (5×10^{-4}–10^{-3} M, CH_3CN) 245.

2.2.7. {[Rh(η^5-C_5Me_5)Cl_2]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$O]} (13)

A toluene solution (5 ml) of **1** (0.148 g, 0.259 mmol) was added to a suspension of [(η^5-C_5Me_5)$RhCl_2$]$_2$ (0.160 g, 0.259 mmol) in the same solvent (10 ml). The mixture was stirred for about 5 h at r.t. during which time a red solid was formed. The solid was isolated by filtration and washed with cold toluene (3 × 3 ml), hexane (2 × 5 ml) and dried. Yield: 80%. *Anal.* Calc. for $C_{56}H_{58}Cl_4O_3P_2Rh_2$: C, 56.59; H, 4.92; Cl, 11.93. Found: C, 56.71; H, 4.83; Cl, 11.65%. ^1H NMR ($CDCl_3$): δ 1.35 (d, 30H, ^3J(PH) = 3.9 Hz, CH_3), 6.8 (d, 4H, J(HH) = 8.8 Hz, C_6H_4), 7.2 (d, 4H, J(HH) = 8.8 Hz, C_6H_4), 7.28–7.4 (m, C_6H_5, 12H) 8.17–8.23 (m, C_6H_5, 8H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 114.1 (d, ^1J(RhP) = 169.6 Hz).

2.2.8. {[Rh(η^5-C_5Me_5)Cl_2]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$$CMe_2$]} (14)

This compound was obtained similarly to **13** as a red solid, by reaction of [η^5-C_5Me_5)$RhCl_2$]$_2$ (0.08 g, 0.129 mmol) with **2** (0.077 g, 0.129 mmol). Yield: 85%. *Anal.* Calc. for $C_{59}H_{64}Cl_4O_2P_2Rh_2$: C, 58.34; H, 5.31; Cl, 11.67. Found: C, 58.60; H, 5.60; Cl, 11.95%. ^1H NMR ($CDCl_3$): δ 1.31 (d, 30H, ^3J(PH) = 3.9 Hz, CH_3), 1.51 (s, 6H, CH_3), 6.5 (d, 4H, J(HH) = 8.7 Hz, C_6H_4), 6.9 (d, 4H, J(HH) = 8.7 Hz, C_6H_4), 7.13–7.28 (m, 12H, C_6H_5); 8.03–8.13 (m, 8H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 113.2 (d, ^1J(RhP) = 169.6 Hz).

2.2.9. {[Rh(η^5-C_5Me_5)Cl_2]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$S]} (15)

This compound was obtained similarly to **13**, as a red solid, by reaction between [η^5-C_5Me_5)$RhCl_2$]$_2$ (0.100 g, 0.162 mmol) and **3** (0.095 g, 0.162 mmol). Yield: 78%. *Anal.* Calc. for $C_{56}H_{58}Cl_4O_2P_2SRh_2$: C, 55.83; H, 4.85; Cl, 11.77. Found: C, 55.70; H, 4.91; Cl, 11.65%. ^1H NMR ($CDCl_3$): 1.33 (d, 30H, ^3J(PH) = 3.9 Hz, CH_3), 6.5 (d, 4H, J(HH) = 8.7 Hz, C_6H_4), 7.0 (d, 4H, J(HH) = 8.7 Hz, C_6H_4), 7.25–7.36 (m, 12H, C_6H_5); 8.18–8.24 (m, 8H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 114.3 (d, ^1J(RhP) = 169.6 Hz).

2.2.10. {[Rh(η^5-C_5Me_5)Cl(CH_3CN)]$_2$[μ-(p-Ph_2POC_6-H_4)$_2$O]}[PF_6]$_2$ (16)

To a stirring solution of **13** (0.050 g, 0.050 mmol) in acetonitrile (10 ml) was added solid $AgPF_6$ (0.025 g, 0.10 mmol). After 16 h, the reaction mixture was filtered and vacuum reduced to ca. 3 ml. A yellow–orange solid was obtained by addition of diethyl ether (30 ml). This was separated by filtration, washed with diethyl ether and dried. Yield: 45%. The stability of this compound is very low in the solid state so it was characterized only by NMR spectroscopy. ^1H NMR (CD_3CN): δ 1.4 (d, 30H, ^3J(PH) = 3.9 Hz, CH_3), 2.4 (s, 6H, CH_3CN), 6.3–7.0 (m, 8H, CH), 7.25–7.36 (m, 12H, CH); 8.18–8.24 (m, 8H, CH). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 121.5 (d, ^1J(RhP) = 169.6 Hz), -143.8 (sept, J(PF) = 716.8 Hz, PF_6^-). Λ (ohm^{-1} cm^2 mol^{-1}) (5×10^{-4}–10^{-3} M, CH_3CN) 275.

*2.2.11. {[Rh(η⁵-C_5Me_5)Cl(CH_3CN)]$_2$[μ-(p-$Ph_2POC_6H_4)_2CMe_2$]}[PF_6]$_2$ (**17**)*

This compound was obtained similarly to **16** starting from **14** (0.060 g, 0.058 mmol) and $AgPF_6$ (0.029 g, 0.116 mmol).Yield: 47%. ^{1}H NMR (CD_3CN): δ 1.5 (d, 30 H, ^3J(PH) = 3.9 Hz, CH_3), 1.61 (s, 6H, CH_3), 2.51 (s, 6H, CH_3CN), 6.3–7.1 (m, 8H, CH), 7.26–7.36 (m, 12H, CH); 8.18–8.24 (m, 8H, CH). ^{31}P{^{1}H} NMR (CD_3CN): δ 120.5 (d, ^1J(RhP) = 169.6 Hz), −143.8 (sept, J(PF) = 716.8 Hz, PF_6^-). Λ (ohm^{-1} cm^2 mol^{-1}) (5×10^{-4}–10^{-3} M, CH_3CN) 270.

*2.2.12. {[Rh(η⁵-C_5Me_5)Cl(CH_3CN)]$_2$[μ-(p-$Ph_2POC_6H_4)_2S$]}[PF_6]$_2$ (**18**)*

This compound was obtained similarly to **16** starting from **15** (0.070 g, 0.068 mmol) and $AgPF_6$ (0.035 g, 0.137 mmol). Yield: 43%. ^{1}H NMR (CD_3CN): δ 1.5 (d, 30 H, ^3J(PH) = 3.9 Hz, CH_3), 2.49 (s, 6H, CH_3CN), 6.4–7.1 (m, 8H, CH), 7.36–7.46 (m, 12H, CH); 8.18–8.24 (m, 8H, CH). ^{31}P{^{1}H} NMR (CD_3CN): δ 121.0 (d, ^1J(RhP) = 169.5 Hz), −143.8 (sept, J(PF) = 716.8 Hz, PF_6^-). Λ (ohm^{-1} cm^2 mol^{-1}) (5×10^{-4}–10^{-3} M, CH_3CN) 278.

*2.2.13. {[Rh(η⁵-C_5H_5)CO]$_2$[μ-(p-$Ph_2POC_6H_4)_2O$]} (**19**) and {Rh(η⁵-C_5H_5)[μ-(p-$Ph_2POC_6H_4)_2O$]}$_n$ (**22**)*

[Rh(η⁵-C_5H_5)(CO)$_2$] (obtained in heptane from [Rh(CO)$_2$Cl]$_2$ (0.250 g, 0.643 mmol) and an excess of Tl(C_5H_5)) and a slight excess of **1** were refluxed in toluene (150 ml) for about 5 h. During this time a color change from yellow to orange occurred. The completion of the reaction was checked by the disappearance of ν(CO) absorptions for [Rh(η⁵-C_5H_5)(CO)$_2$]. The solution was then concentrated to ca. 30 ml and chromatographed on a neutral alumina column (2 × 20 cm) saturated with a mixture of dichloromethane/diethyl ether 1:1. Elution with the same solvent mixture and collection of the first orange band, followed by slow evaporation of the solvent, gave the product **19** as an orange powder in a 60% yield. *Anal.* Calc. for $C_{48}H_{38}O_5P_2Rh_2$: C, 59.89; H, 3.98. Found: C, 60.15; H, 4.08%. IR (KBr, Nujol) ν(CO) 1953 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.02 (s, 10H, C_5H_5), 6.89–7 (m, 8H, C_6H_4), 7.3–7.42 (m, 12H, C_6H_5), 7.7–7.9 (m, 8H C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 150.7 (d, ^1J(RhP) = 223.7 Hz).

Elution with dichloromethane/diethyl ether 10:1 gave the product **22** as an orange powder. Yield: 20%. *Anal.* Calc. for $C_{41}H_{33}O_3P_2Rh$: C, 66.68; H, 4.5. Found: C, 66.59; H, 4.31%. ^{1}H NMR ($CDCl_3$): δ 5.01 (s, 10H, C_5H_5), 6.85–6.93 (m, 8H, C_6H_4), 7.3–7.45 (m, 12H, C_6H_5), 7.7–7.8 (m, 8H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 151.0 (d, ^1J(RhP) = 198.8 Hz).

*2.2.14. {[Rh(η⁵-C_5H_5)CO]$_2$[μ-(p-$Ph_2POC_6H_4)_2CMe_2$]} (**20**)*

In a similar manner to the preparation of **19**, the compound **20** was synthesized by the reaction of [Rh(η⁵-C_5H_5)(CO)$_2$] and **2**. Yield: 58%. *Anal.* Calc. for $C_{51}H_{44}O_4P_2Rh_2$: C, 61.96; H, 4.49. Found: C, 62.05; H, 4.52%. IR (KBr, Nujol) ν(CO) 1950 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.42 (s, CH_3, 6H), 5.0 (s, C_5H_5, 10H), 6.87–6.92 (m, 8H, C_6H_4), 7.28–7.42 (m, C_6H_5, 12H), 7.7–7.9 (m, 8H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 149.9 (d, ^1J(RhP) = 223.9 Hz). By elution with dichloromethane/diethyl ether 10:1 no further product, similar to **22**, has been obtained.

*2.2.15. {[Rh(η⁵-C_5H_5)CO]$_2$[μ-(p-$Ph_2POC_6H_4)_2S$]} (**21**)*

In a similar manner to the preparation of **19**, compound **21** was synthesized by the reaction of [Rh(η⁵-C_5H_5)(CO)$_2$] with **3**. Yield: 70%. *Anal.* Calc. for $C_{48}H_{38}O_4SP_2Rh_2$: C, 58.91; H, 3.91. Found: C, 58.71; H, 3.68%. IR (KBr, Nujol) ν(CO) 1950 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.05 (s, C_5H_5, 10H), 6.85–6.92 (m, C_6H_4, 8H), 7.25–7.40 (m, C_6H_5, 12H), 7.7–7.9 (m, C_6H_5, 8H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 151.1 (d, ^1J(RhP) = 224.5 Hz). By elution with dichloromethane/diethyl ether 10:1 no further product, similar to **22**, has been obtained.

*2.2.16. {[Rh(η⁵-C_5H_5)($COCH_3$)I]$_2$[μ-(p-$Ph_2POC_6H_4)_2S$]} (**23**)*

CH_3I (2 ml) was added to compound **21** (0.090 g, 0.092 mmol). The resulting mixture was stirred for 1 h at r.t. On monitoring the reaction by IR spectroscopy, the disappearance of ν(CO) bands of the starting material and the appearance of new ν(CO) bands were observed. The volume of the reaction mixture was then reduced to ca. 3 ml and hexane (20 ml) was added. The dark red solid obtained was isolated by filtration and dried. Yield: 82%. *Anal.* Calc. for $C_{50}H_{44}I_2O_4SP_2Rh_2$: C, 47.57; H, 3.51. Found: C, 47.69; H, 3.67%. IR (KBr, Nujol) ν(CO) 1790 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.64 (s, CH_3, 6H), 5.11 (s, C_5H_5, 10H), 6.99 (d, C_6H_4, J(HH) = 8.7 Hz, 4H), 7.17 (d, C_6H_4, J(HH) = 8.7 Hz, 4H), 7.25–7.40 (m, C_6H_5, 12H), 7.9–8.1 (m, C_6H_5, 8H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 143.8 (d, ^1J(RhP) = 189.7 Hz).

2.3. Crystal data and data collection

Suitable crystals of compounds **4**, **5** and **23** were obtained, respectively, by slow evaporation of diethyl ether/acetone, diethyl ether/$CHCl_3$ and CH_2Cl_2/hexane solutions. Diffraction data were collected at r.t. with a Siemens R3μV automated four-circle single-crystal diffractometer. Crystals of compounds **5** and **23** were enveloped by a glue surface to avoid solvent loss during data collection.

A summary of the crystallographic data and structure determination is given in Table 1. Reflection intensities were evaluated by profile fitting of a 96-step peak scan [6] and then corrected for Lorentz and

Table 1
Crystal data and structure determination summary for **4**, **5** and **23** [a]

	4	**5**	**23**
Formula	$C_{56}H_{56}Cl_4O_3P_2Ru_2$	$C_{59}H_{62}Cl_4O_2P_2Ru_2 \cdot 1/3[(CH_3CO)+2(C_2H_5)_2O]$	$C_{50}H_{60}Cl_2I_2O_4P_2SRh_2 \cdot 2/3CH_2Cl_2$
M_r	1182.89	1268.5	1399.9
Temperature (K)	293	293	293
Crystal system	monoclinic	triclinic	monoclinic
Space group	$C2$	$P\bar{1}$	$C2/c$
a (Å)	14.446(4)	14.106(5)	35.184(7)
b (Å)	13.464(2)	14.235(3)	9.541(2)
c (Å)	26.730(6)	18.173(5)	18.967(4)
α (°)		92.58(2) (**2**)	
β (°)	91.16(2)	94.48(2)	116.52(3)
γ (°)		107.84(2)	
V (Å^3)	5198(2)	3453.9(2)	5697(2)
Z	4	2	4
$F(000)$	2408	1200	2640
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
D_{calc} (g cm^{-3})	1.512	1.221	1.634
μ (mm^{-1})	0.892	0.67	1.886
θ Range (°)	2.19–28.56	2.59–25.05	2.23–25.05
Reflections collected	6799	12209	5233
Unique reflections	6425	11410	5025
Reflection ($I>4\sigma(I)$)	4658	5222	2592
No. refined parameters	594	678	329
GOF on F^2	0.885	0.943	0.725
R_1 (on F, $I>4\sigma(I)$)	0.0340	0.0590	0.0516
wR_2 (on F^2, all data)	0.055	0.1311	0.0997

[a] $R_1 = [\Sigma||F_o|-|F_c||]/\Sigma|F_o|$. $wR_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = n/(\sigma^2(F_o)$; GOF $= [\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

polarization effects. An absorption correction was applied for **4** by an empirical method [7] using azimuthal scan data. No absorption corrections were applied for **5** or **23** because of the rapid decay (24% for **5** and 31% for **23**) of the crystal under X-ray exposure; and this reduced the accuracy of the data as can be seen from crystal data and details of measurement for **5**.

The structure of complex **4** was first solved in the monoclinic space group $C2/c$, but many systematic absence violations, related to a glide plane, revealed the space group $C2$. Statistical considerations suggested the acentric packing with two half molecules in special positions, as confirmed by the successful refinement.

The structures were solved by standard Patterson methods, subsequently completed by a combination of least-squares technique and Fourier syntheses [8] and refined by the full-matrix least-squares on F^2 [9]. Anisotropic displacement factors were used for all non-hydrogen atoms except those that were disordered.

For complex **5**, the difference Fourier map of the crystallographic asymmetric unit revealed significant electron density residuals isolated from the molecule that were interpreted as three co-crystallized solvent molecules, one of acetone and two of diethyl ether. Site occupation factors of the solvent groups were fixed at 0.3 value into the following usual refinement.

For complex **23**, during the refinement, it became apparent that some residual peaks in the difference Fourier map located next to positions of the acetyl moiety and of the iodine atom indicated co-crystallization of both diastereomers (*RR*, *SS* and *RS*). A correction for these residuals was introduced by splitting atoms in two staggered positions having different site occupancy factors (0.8 and 0.2) and refining acetyl groups with restrained geometry. In addition, there is co-crystallized dichloromethane. This CH_2Cl_2 appeared disordered over two positions. They were refined with site occupation factors of 0.3 and with restrained distances.

Hydrogens were placed at their geometrically calculated positions and refined 'riding' on the corresponding carbon atoms, with fixed isotropic displacement parameters ($U_{iso} = 0.08$ Å^2). Data reduction, structure solution and drawings were performed with the SHELXTL-PLUS [8,9] package and geometrical calculations with the PARST [10] program. All calculations were performed on either a μ-VAX 3400 or a AXP DecStation 3000/400.

2.3.1. Computational details

All calculations were accomplished with the AMPAC (MOPAC) program [11]. Full geometry optimizations of the ligands were carried out by using the PM3 Hamiltonian parameters.

Table 2
Structural parameters by semi-empirical geometry optimization for **1**, **2** and **3**

	P···P (Å)	P–O (Å)	POC (°)	Valence angle (°)	CCXC (°) X = [O, $C(CH_3)_2$, S]
1	11.506	1.614	122.6	115.9	125.5–140.6
2	9.848	1.613	122.8	106.9	49.2–51.7
3	11.04	1.613	123.0	100.3	119.5–109.3

3. Results and discussion

3.1. Synthesis of ligands

The bis-4-phosphinito ligands **1**–**3** (Fig. 1) were synthesized in a satisfactory yield by reaction of the corresponding 4,4′-bisphenol with Ph_2PCl, in toluene, in the presence of triethylamine as an acid acceptor. Compounds **1**–**3** were obtained as colorless oils, except **2**, which is a white solid that is moderately stable in air. In solution their stability is diminished because formation of the corresponding oxides occurs easily. In the $^{31}P\{^1H\}$ NMR spectra of **1**–**3** a singlet was observed in the range δ 111–113 ppm, consistent with the proposed structures. These resonances are in the region expected for phosphinito derivatives. The ^1H NMR spectra of **1** and **3**, in C_6D_6, exhibit resonances for the phenyl groups together with those for *p*-substituted aromatic rings. In the spectrum of compound **2** a singlet at δ 1.49 ppm due to the methyl groups is also present.

The geometries of ligands **1**–**3** were predicted by semi-empirical calculation [11] (Table 2). All molecular modeling calculations show that the P–O bond distances are nearly the same for all the ligands indicating that the X-group has only a minor influence on the electronic properties of the phosphorus donor. Interestingly the P···P separation ranges from 9.848 Å for **2** to 11.506 Å for **1**, indicating that *cis* or *trans* chelation to one metal atom is hindered for these ligands. The C–X–C angles range from 100.3° for X = S to 115.9° for X = O and their values are not directly related to the P···P separation.

3.2. Reactions of ligands *1*–*3* with *[Ru(η⁶-p-cymene)Cl₂]₂*

The reaction of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ with ligands **1**–**3** in the molar ratio 1:1, in toluene, results in the formation of the binuclear complexes $\{[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2X]\}$ (X = O, **4**; X = CMe_2, **5**; X = S, **6**), which have been isolated in good yields as red air stable solids. No other species were detected even when the reactions were carried out using a different molar ratio. All the complexes **4**–**6** are soluble in chlorinated solvents, benzene, and acetone and are nonconducting in acetone solution. They have been characterized by microanalysis, IR, NMR spectroscopy and X-ray diffraction studies[1] (details are given in Section 2). The $^{31}P\{^1H\}$ NMR spectra of complexes **4**–**6**, in $CDCl_3$ solution, show a single resonance in the range δ 113–115 ppm indicating chemical equivalence of the phosphorus atoms in the coordinated ligands. The ^1H NMR spectra are very similar and show resonances for aromatic, isopropyl, and methyl protons in the correct integration ratio, in accordance with the proposed structure. The *cis* or *trans* disposition of the η^6-*p*-cymene and η^5-cyclopentadienyl ligands with respect to the metal–metal axis in complexes **4**–**6**, in the solid state, is due to packing effects and is not a consequence of the requirement of the bridging ligands. In fact molecular models indicate that *cis*–*trans* interconversion between the isomers should occur by rotation of 180° around the P–O bond of a ruthenium atom. The energy required for such a rotation in free ligands was calculated [11] to be about 6.0 kcal mol^{-1}; on this basis, a low rotational barrier value can also be expected for complexes **4**–**6**.

The full structural characterization in the solid state of complexes **4**–**6** has been undertaken by X-ray diffraction.

In acetonitrile and in the presence of $AgPF_6$ (1:1 equiv. with respect to Ru), complexes **4**–**6** undergo a substitution reaction with CH_3CN to produce the cationic complexes $\{[Ru(\eta^6\text{-}p\text{-cymene})Cl(CH_3CN)]_2[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2X]\}[PF_6]_2$ (X = O, **7**; X = CMe_2, **8**; X = S, **9**). It was also shown that the presence of Ag(I)

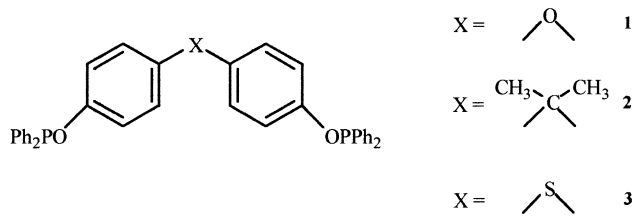

Fig. 1. Ligands **1**–**3**.

[1] The crystal structure of **6** was not fully determined owing to extensive crystal decay. However, the data permit assignment of a structure with *trans* disposition of the *p*-cymene groups with respect to Ru–Ru axis. Some geometric parameters of **6** will be considered in the discussion of the structure of **23**. Crystal data for **6**: $C_{56}H_{56}Cl_4O_2P_2SRu_2$, triclinic, space group $P\bar{1}$, $a = 13.919(5)$, $b = 14.311(3)$, $c = 17.881(6)$ Å, $\alpha = 85.98(2)$, $\beta = 89.25(3)$, $\gamma = 72.86(2)°$.

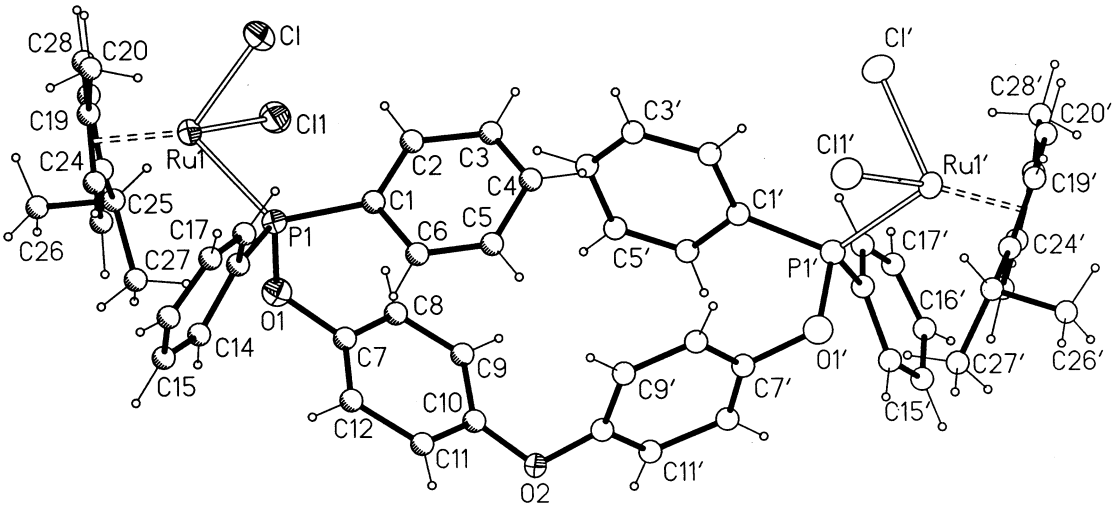

Fig. 2. View of the structure of complex **4** with the atom numbering scheme.

does not promote redox reactions. Compounds **7**–**9** are yellow solids, soluble in methanol and their stability in solution is limited very likely owing to CH_3CN dissociation. The lability of the acetonitrile ligands in the mononuclear cationic complexes $[(\eta^6\text{-}C_6H_6)RuCl(CH_3CN)_2]^+$ and $[(\eta^6\text{-}C_6H_6)Ru(PPh_3)(CH_3CN)Cl]^+$ has been clearly demonstrated [12]. In CH_3CN solution, compounds **7**–**9** are 1:2 electrolytes. In complexes **7**–**9** both ruthenium atoms become stereogenic centers. In principle these compounds can give rise to a pair of enantiomers ($R_{Ru}R_{Ru}$ and $S_{Ru}S_{Ru}$) and the *meso* form ($R_{Ru}S_{Ru}$, $S_{Ru}R_{Ru}$) In some cases $^{31}P\{^1H\}$ NMR spectroscopy allows diastereomers to be distinguished [13]. The $^{31}P\{^1H\}$ NMR spectra of **7**–**9**, in $CDCl_3$ solution, show two resonances of comparable intensity in the range δ 122.8–125.5 ppm, indicating the presence in solution of a pair of enantiomers and the *meso* form in equal amounts.

Compounds **7**–**9** can be very useful starting materials for the synthesis of complexes in which two [Ru(η^6-*p*-cymene)] moieties, containing stereogenic ruthenium atoms, are held together by the bridging phosphinito ligands **1**–**3**. The acetonitrile ligands in complexes **7**–**9** can be easily replaced by carbon monoxide. When CO was bubbled into an acetonitrile solution containing complexes **7**–**9** a fast reaction occurs. The progress of the CH_3CN substitution reaction was monitored by IR spectroscopy. The reaction is complete in about 1 h for all the substrates.

The compounds $\{[Ru(\eta^6\text{-}p\text{-cymene})Cl(CO)]_2[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2X]\}[PF_6]_2$ (X = O, **10**; X = CMe_2, **11**; X = S, **12**) show one ν(CO) band, in CH_3CN, in the range 2033–2020 cm^{-1}. Complexes **10**–**12** can be detected only in solution, under a CO atmosphere, and have limited stability. Starting from **7**–**9** or **10**–**12**, all attempts to obtain complexes in which the ruthenium centers are bridged by two binucleating **1**–**3** ligands to give bi- or tetra-nuclear species failed. Very likely, the presence of two bridging ligands induces strong repulsive interactions between the phenyl groups of the phosphinito ligands and the isopropyl moiety of the *p*-cymene groups and prevents the formation of these species. Using dppe (dppe = 1,2-bis(diphenylphosphino)ethane) as a bidentate ligand the complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl(dppe)]PF_6$ [14] was obtained, with the phosphinito ligands being displaced by the more basic dppe.

*3.3. Description of the crystal structure of {[Ru(η^6-p-cymene)Cl_2]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$O]} (**4**)*

A view of the molecular structure of $\{[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2O]\}$ with the atom-labeling scheme is shown in Fig. 2. Selected bond distances and angles are given in Table 3.

The geometry around the ruthenium atom is that of a 'three legged piano stool' in which the η^6-coordinated arene ligand occupies the 'stool' position, while the Cl atoms and the P atom occupy the three 'leg' positions.

In the binuclear complex the η^6-*p*-cymene planes are arranged in the *cis* position with respect to the Ru–Ru axis, with an angle of 23° to each other. The angle between the weighted least-squares planes through the two phenolic rings of the ligand is 77.9°.

The molecule possesses *C*2 symmetry, and in the asymmetric unit there are two half molecules with oxygen atoms in special positions. Both chlorine atoms are oriented towards the Ru–Ru axis, to minimize the interaction with the phenyl rings of the ligand. Since the two half molecules show very similar geometric parameters, in the following discussion we report only both values if necessary.

The phosphinito ligand **1** possesses a large valence angle; in **4** the valence angle C(10)–O(2)–C(10) for

Table 3
Selected bond lengths (Å) and angles (°) for **4** [a]

Bond lengths (Å)			
Ru(1)–P(1)	2.303(3)	P(1)–C(13)	1.794(11)
Ru(1)–C*	1.714	P(1)–C(1)	1.815(9)
Ru(1)–Cl(1)	2.415(4)	O(1)–C(7)	1.461(12)
Ru(1)–Cl	2.416(4)	O(2)–C(10)	1.344(13)
P(1)–O(1)	1.644(9)	Ru(1′)–P(1′)	2.287(3)
Ru(1′)–C*′	1.716	P(1′)–C(1′)	1.806(11)
Ru(1′)–Cl(1′)	2.389(4)	O(1′)–C(7′)	1.337(13)
Ru(1′)–Cl(′)	2.400(3)	O(2′)–C(10′)	1.445(11)
P(1′)–O(1′)	1.627(8)	P(1′)–C(13′)	1.841(13)
Bond angles (°)			
C*–Ru(1)–Cl	124.1	P(1)–Ru(1)–Cl	89.1(1)
C*–Ru(1)–Cl(1)	127.2	C*–Ru(1)–P(1)	127.8
C(13)–P(1)–C(1)	104.5(5)	P(1)–Ru(1)–Cl(1)	86.1(1)
C(7)–O(1)–P(1)	121.9(6)	Cl(1)–Ru(1)–Cl	90.0(1)
C*′–Ru(1′)–Cl′	123.8	C*′–Ru(1′)–Cl(1′)	128.2
C*′–Ru(1′)–P(1′)	127.0	C(13′)–P(1′)–C(1′)	112.5(4)
P(1′)–Ru(1′)–Cl(′)	89.3(1)	P(1′)–Ru(1′)–Cl(1′)	86.8(1)
Cl(1′)–Ru(1)–Cl(′)	89.4(1)	C(7′)–O(1′)–P(1′)	124.2(6)

[a] C*, centroid of the six-membered ring of the η^6-*p*-cymene.

both independent molecules is 116.0(12) and 118.4(13)°. The nonbonded Ru(1)···Ru(1A) separation is 13.09 Å, while P(1)···P(1A) is 10.259 Å, this last value being shorter than that calculated for the ligand (11.51 Å) by semi-empirical calculations [11].

The ruthenium atom is in a pseudo-octahedral environment. Considering the η^6-*p*-cymene ring to occupy three coordination centers, represented by its centroid (C^*_{Ar}), the angles formed by it and the other ruthenium ligands are, respectively: C^*_{Ar}–Ru(1)–Cl(1) = 127.2°, C^*_{Ar}–Ru(1)–Cl = 124.1°, C^*_{Ar}–Ru(1)–P(1) = 127.8°. The values of the angles P(1)–Ru(1)–Cl and P(1)–Ru(1)–Cl(1) are 89.1(1) and 86.1(1)°. The deviations from the regular arrangement are in the range normally found for areneruthenium(II) complexes. Other significant geometric parameters concerning the ruthenium atom and its coordination sphere include the following: Ru(1)–C^*_{Ar} = 1.714 Å, Ru(1)–P(1) = 2.303(3) Å, Ru(1)–Cl(1) = 2.415(4) Å, Ru(1)–Cl = 2.416(4) Å which are comparable to those observed for similar compounds [15].

Also the bond lengths related to the phosphinito ligand are in good agreement with literature values [16].

3.4. Description of the crystal structure of {[Ru(η^6-*p*-cymene)Cl_2]$_2$[μ-(*p*-$Ph_2POC_6H_4$)$_2$$CMe_2$]} (**5**)

A view of the molecular structure of {[Ru(η^6-*p*-cymene)Cl_2]$_2$[μ-(*p*-$Ph_2POC_6H_4$)$_2$$CMe_2$]} with the atom-labeling scheme is shown in Fig. 3. Selected bond distances and angles are given in Table 4.

{[Ru(η^6-*p*-cymene)Cl_2]$_2$[μ-(*p*-$Ph_2POC_6H_4$)$_2$$CMe_2$]} is homologous with complex **4**, except for the presence of one methylenic group between the phenolic rings in the ligand instead of the oxygen atom. In contrast to **4**, in **5** the η^6-*p*-cymene groups are in a *trans* position with respect to the Ru–Ru axis and lie in two planes nearly perpendicular with each other; the angle between these planes is 101.5°. The angle between the weighted least-squares planes through two phenolic rings is 89.6°.

The nonbonded Ru(1)···Ru(1A) separation is 12.807 Å, while the distance P(1)···P(1A) is 11.714 Å, longer than the corresponding value in the free ligand (9.848 Å) as found from the geometry optimization [11]. The P(1)–O(1)–C(1) angle is 128.5(5)°, and the P(1)–O(1)–C(1)–C(6) dihedral angle is −170.5(2)°. The valence angle C(4)–C(1′)–C(4A) is 109.8(7)°, and the dihedral angle around the methylenic carbon atom C(4)–C(1′)–C(4A)–C(5A) is 117.8(10)°.

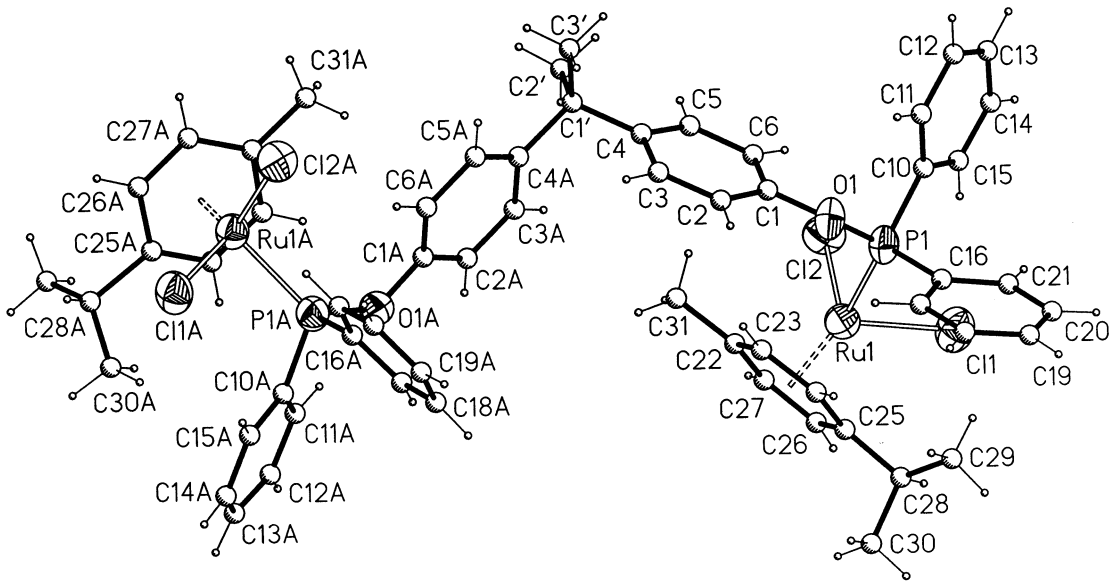

Fig. 3. View of the structure of complex **5** with the atom numbering scheme.

Table 4
Selected bond lengths (Å) and angles (°) for **5** [a]

Bond lengths (Å)			
Ru(1)–P(1)	2.314(2)	Ru(1A)–P(1A)	2.313(2)
Ru(1)–Cl(1)	2.400(2)	Ru(1A)–Cl(1A)	2.417(2)
Ru(1)–Cl(2)	2.400(2)	Ru(1A)–Cl(2A)	2.418(2)
Ru(1)–C*	1.709	Ru(1A)–C*	1.719
P(1)–O(1)	1.618(5)	P(1A)–O(1A)	1.626(5)
P(1)–C(16)	1.796(7)	P(1A)–C(16A)	1.822(8)
P(1)–C(10)	1.817(8)	P(1A)–C(10A)	1.815(8)
C(4)–C(1′)	1.532(11)	C(4A)–C(1′)	1.555(11)
Bond angles (°)			
C*–Ru(1)–P(1)	128.5	CA*–Ru(1A)–P(1A)	127.8
C*–Ru(1)–Cl(2)	125.8	CA*–Ru(1A)–Cl(2A)	121.9
C*–Ru(1)–Cl(1)	125.1	CA*–Ru(1A)–Cl(1A)	127.8
P(1)–Ru(1)–Cl(2)	90.7(1)	P(1A)–Ru(1A)–Cl(2A)	94.47(8)
P(1)–Ru(1)–Cl(1)	86.0(1)	P(1A)–Ru(1A)–Cl(1A)	84.11(7)
Cl(1)–Ru(1)–Cl(2)	88.2(1)	Cl(1A)–Ru(1A)–Cl(2A)	87.25(8)
O(1)–P(1)–C(1)	128.5(5)	C(1A)–O(1A)–P(1A)	127.5(5)
O(1)–P(1)–Ru(1)	114.5(2)	O(1A)–P(1A)–Ru(1A)	115.6(2)
C(4)–C(1′)–C(2′)	110.7(8)	C(4A)–C(1′)–C(2′)	109.9(9)
C(3′)–C(1′)–C(2′)	107.4(9)	C(4)–C(1′)–C(4A)	109.8(7)

[a] C*, centroid of the six-membered ring of the η^6-*p*-cymene.

As shown in Fig. 2, the usual 'three-legged piano stool' coordination is also observed for **5**. The coordination geometry and the metal–ligand distances are almost the same as for **4**. The values of the angles formed by the centroid (C^*_{Ar}) of the *p*-cymene phenyl ring and the other ruthenium ligands are: C^*_{Ar}–Ru(1)–Cl(1) = 125.1°, C^*_{Ar}–Ru(1)–Cl(2) = 125.8°, and CC^*_{Ar}–Ru(1)–P(1) = 128.5°.

3.5. Reaction of ligands *1*–*3* with $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ and $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$

We studied the reaction of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ with ligands **1**–**3** as pentamethylcyclopentadienylrhodium(III) complexes are isoelectronic with areneruthenium(II) complexes. The reaction of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ with ligands **1**–**3** in toluene results in the formation, in a good yield, of the complexes $\{[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2X]\}$ (X = O, **13**; X = CMe_2, **14**; X = S, **15**) which have been isolated as red–orange, air-stable solids, soluble in chlorinated solvents, benzene, and acetone. They have been characterized by microanalysis, IR and NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra of **13**–**15**, in $CDCl_3$ solution, show a doublet centered in the range δ 113–114 ppm ($^1J(RhP) = 169.6$ Hz). The ^1H NMR spectra of **13**–**15**, in $CDCl_3$, show resonances of the protons of the coordinated phosphinito ligand together with those of C_5Me_5 protons in the correct integration ratio. The latter appear as a doublet with $^3J(PH) = 3.9$ Hz.

The cationic complexes $\{[Rh(\eta^5\text{-}C_5Me_5)Cl(CH_3CN)]_2[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2X]\}[PF_6]_2$ (X = O, **16**; X = CMe_2, **17**; X = S, **18**), in which the metal atoms are stereogenic centers, have been obtained from the corresponding complexes **13**–**15** by treatment in CH_3CN with $AgPF_6$, and have been characterized only in solution by $^{31}P\{^1H\}$ NMR spectra and conductivity measurements. The compounds are stable only in CH_3CN solution very likely owing to CH_3CN dissociation. The mechanism of solvent exchange on the half-sandwich solvento species $\{[Rh(\eta^5\text{-}C_5H_5)Cl(CH_3CN)_3]^{2+}$ provide a model for the reactivity of half-sandwich compounds [17]. The $^{31}P\{^1H\}$ NMR spectra of **16**–**18**, in CH_3CN solution, show a doublet centered at about δ 121 ppm ($^1J(RhP) = 169.5$). It is not known whether only one of the two possible diastereomers ($R_{Rh}R_{Rh}$, $S_{Rh}S_{Rh}$) and ($R_{Rh}S_{Rh}$, $S_{Rh}R_{Rh}$) is present or whether the ^{31}P chemical shifts of the two species are experimentally indistinguishable. This would seem to be supported by the line width value of the $^{31}P\{^1H\}$ NMR peaks of 34 Hz (9 Hz for **7**–**9**). In the analogous *p*-cymeneruthenium(II) complexes **7**–**9** the $^{31}P\{^1H\}$ chemical shifts of the diastereomeric pairs differ only by 0.2 ppm.

We carried out the reactions of $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ with the ligands **1**–**3** with the aim of obtaining binuclear rhodium(I) complexes able to give, by oxidative addition of alkyl halides, the corresponding rhodium(III) species containing stereogenic metal centers. The $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ was converted into the binuclear phosphinito-bridged complexes by reaction with ligands **1**–**3**, in toluene, at about 80°C. The reaction was followed by IR and NMR spectroscopy and it appears that $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ is initially transformed into a carbonyl derivative, although a further compound was obtained by loss of CO. The reaction was stopped when the ν(CO) bands of the starting material disappeared. Spectroscopic IR and NMR data indicated that the crude product, obtained by evaporation of the solvents, contains a mixture of two compounds. For X = O, they have been separated by column chromatography on neutral alumina saturated with dichloromethane–diethyl ether. On the basis of analytical and spectroscopic data, they have been formulated as $\{[Rh(\eta^5\text{-}C_5H_5)(CO)]_2[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2X]\}$ (X = O, **19**; X = CMe_2, **20**; X = S, **21**) and $\{Rh(\eta^5\text{-}C_5H_5)[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2X]\}_n$, (X = O, **22**). In accordance with their formulation complexes **19**–**21** show, in the IR spectrum (Nujol mull), a ν(CO) band in the range of 1953–1960 cm^{-1} and in the $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$ solution, a doublet in the range δ 150–151 ppm ($^1J(RhP) = 223$–228 Hz). In the ^1H NMR spectrum, in $CDCl_3$ solution, the cyclopentadienyl protons resonance appears at δ about 5.0 ppm (singlet) to-

gether with the resonances for the protons of the coordinated ligands in the correct integration ratio. Spectroscopic data for **22** are very similar to those for the corresponding compound **19**, except for the lack of the ν(CO) band in the IR spectrum. The very similar values of the $^{31}P\{^1H\}$ chemical shifts indicate the same character of the Rh–P bond in both types of compounds. For compound **22** we suggest a structure in which the Rh(η^5-C_5H_5) moieties are held together by bridged diphosphinito ligands.

The reaction of [Rh(η^5-C_5H_5)(CO)L] (L = tertiary phosphine, phosphite) with alkyl halides RX have been extensively studied [18], and shown to proceed by formation of the ionic intermediate [Rh(η^5-C_5H_5)(CO)RL]X which affords the neutral final product [Rh(η^5-C_5H_5)(COR)LX]. Both the ionic intermediate and the acyl derivative possess a stereogenic rhodium(III) atom.

We studied the reactions of the binuclear complex {[Rh(η^5-C_5H_5)(CO)]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$S]} (**21**), with CH_3I, *S*-(+)-1-bromo-2-methylbutane and racemic PhCH(CH_3)Br. The reaction with CH_3I appears to be irreversible, while those with the other alkyl halides reach equilibrium conditions. The products were the acyl derivatives although following the reaction course by IR and NMR spectroscopy the ionic intermediates {[Rh(η^5-C_5H_5)(CO)R]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$S]}[X]$_2$ (X = Br, I) were detected. The reaction of **21** with neat CH_3I easily affords the complex {[Rh(η^5-C_5H_5)(COCH$_3$)I]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$S]} (**23**), as a red–brown solid, soluble in chlorinated solvents, benzene, and acetone. Its acetone solutions are not conducting. In accordance with its formulation the IR spectrum shows a broad ν(CO) band at 1690 cm^{-1} and in the ^1H NMR spectrum, in $CDCl_3$ solution, a singlet at δ 5.11 ppm due to cyclopentadienyl protons and a singlet at δ 2.64 ppm, due to the acyl protons, have been evidenced. In the $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$ solution, the compound exhibits only a doublet centered at δ 143.8 ppm (^1J(RhP) = 189.7 Hz) indicating the presence either of the *meso* form ($R_{Rh}S_{Rh}$, $S_{Rh}R_{Rh}$) or of the pair of enantiomers $R_{Rh}R_{Rh}$ and $S_{Rh}S_{Rh}$. The structural determination by X-ray analysis allowed the assignment of compound **23** as a mixture of both stereoisomeric ($S_{Rh}S_{Rh}$, $R_{Rh}R_{Rh}$) and *meso* forms. We unsuccessfully checked the mother liquor and the crystallization solution for the presence of the $R_{Rh}S_{Rh}$ (*meso*) form. However, it could be that the $^{31}P\{^1H\}$ chemical shifts of the *meso* form and of the enantiomeric pair differ very little; in this case, the *meso* form would not be detectable.

The reaction of **21** with neat *S*-(+)-1-bromo-2-methylbutane at r.t. is very slow. Raising the temperature the starting material was still not completely converted to the acyl derivative. However, after about 12 h, the IR and NMR spectra indicated the presence in the reaction mixture of only the starting material and the acyl derivative. Interestingly, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, in $CDCl_3$ solution, exhibits together with the resonances due to the presence of **21**, two doublets centered at δ 150.9 ppm (^1J(RhP) = 225.8 Hz) and δ 150.1 ppm (^1J(RhP) = 225.4 Hz). The complex {[Rh(η^5-C_5H_5)(COCH$_2$-CH(CH_3)C_2H_5)Br]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$S]} (**24**), can give rise to a pair of diastereoisomers ($R_{Rh}S_CS_CR_{Rh}$ and $S_{Rh}S_CS_CS_{Rh}$) and to the diastereoisomer $R_{Rh}S_CS_CS_{Rh}$. The existence of two doublets in the $^{31}P\{^1H\}$ NMR spectrum supports [12] either the presence of a pair of diastereoisomers or of the diastereoisomer $R_{Rh}S_CS_CS_{Rh}$ in which the phosphorus atoms are diastereotopic.

On reaction of **21** with racemic PhCH(CH_3)Br, in $CHCl_3$ solution, the product {[Rh(η^5-C_5H_5)-(COCH(CH_3)Ph)Br]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$S]} (**25**), was obtained together with the starting material. In the $^{31}P\{^1H\}$ NMR spectrum four doublets of different intensity (0.3:0.8:1:1) and with the same ^1J(RhP) were observed instead of those expected for the formation of all possible diastereoisomers; we were not able to separate and fully characterize the diastereoisomers formed in the reaction and to assign their configurations.

Consiglio and Morandini [19] studied the reactions of η^5-cyclopentadienyl and η^5-indenyl rhodium(I) complexes of the type [(η^5-C_5H_5)Rh(P–P*)] and [(indenyl)Rh(P–P*)], in which P–P* are chiral C_1 and C_2 chelating diphosphines, with methyl iodide. The reaction products are the cationic [(η^5-C_5H_5)Rh(P–P*)-(CH_3)]I and [(indenyl)Rh(P–P*)(CH_3)]I, in which the metal is a stereogenic center. The extent of diastereoselectivity is complete only with the C_1 chiral ligands prophos and cycphos (prophos = 1,2-bis-(diphenylphosphino)propane; cycphos = 1,2-bis(diphenylphosphino)-1-cyclohexylethane) and seems to be mostly dependent on steric factors due to the diphosphine ligand. The stereochemical course of the reactions reported here is more complicated than those reported by Consiglio et al. [19], because the formation of the ionic product is followed by the nucleophilic attack of the iodide on the rhodium(III) center affording the neutral acyl-derivative; the last step of the reaction also follows a stereochemical course. The stereochemical configurations of **23**–**25** are the result of two processes, each of which has a stereochemical course.

*3.6. Description of the crystal structure of {[Rh(η^5-C_5H_5)(COMe)I]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$S]} (**23**)*

A view of the molecular structure of {[(Rh(η^5-C_5H_5)(COMe)I]$_2$[μ-(p-$Ph_2POC_6H_4$)$_2$S]} with the atom-labeling scheme is shown in Fig. 4. Selected bond distances and angles are given in Table 5.

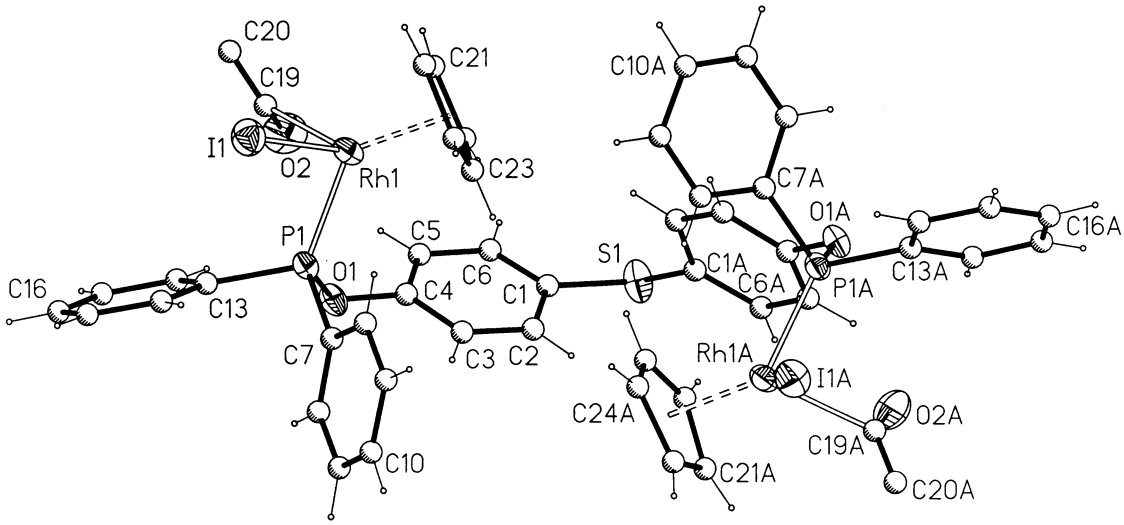

Fig. 4. View of the structure of complex **23** with the atom numbering scheme.

Table 5
Selected bond lengths (Å) and angles (°) for **23** [a,b]

Bond lengths (Å)			
Rh(1)–I(1)	2.655(1)	Rh(1)–C*	1.955
Rh(1)–P(1)	2.246(2)	O(1)–C(4)	1.394(8)
S(1)–C(1)	1.774(7)	P(1)–O(1)	1.643(5)
P(1)–C(7)	1.821(7)	P(1)–C(13)	1.813(7)
Bond angles (°)			
C*–Rh(1)–P(1)	125.5	C(13)–P(1)–Rh(1)	120.7(2)
C*–Rh(1)–I(1)	120.2	C(7)–P(1)–Rh(1)	116.1(2)
C*–Rh(1)–C(19)	129.8	C(1)–S(1)–C(1)*	101.9(5)
P(1)–Rh(1)–I(1)	91.30(6)	C(6)–C(1)–S(1)	119.6(6)
P(1)–Rh(1)–C(19)	90.3(5)	C(2)–C(1)–S(1)	121.7(6)
I(1)–Rh(1)–C(19)	90.1(2)	C(4)–O(1)–P(1)	123.2(4)
O(1)–P(1)–C(13)	96.8(3)	O(1)–P(1)–C(7)	102.0(3)
O(1)–P(1)–Rh(1)	115.8(2)		

[a] C*, centroid of the η^5-cyclopentadienyl ring.
[b] C(1)*, symmetric atom.

The crystals of {[(Rh(η^5-C_5H_5)(COMe)I]$_2$[μ-(*p*-$Ph_2POC_6H_4)_2$S]} build up by co-crystallization of the complex and CH_2Cl_2 of solvation. Solvent is omitted in the figure for clarity.

The X-ray analysis shows the existence of **23** in the solid state as a mixture of ($S_{Rh}S_{Rh}$, $R_{Rh}R_{Rh}$) and ($R_{Rh}S_{Rh}$, $S_{Rh}R_{Rh}$) diastereomers.

The asymmetric unit of the cell is represented by a half discrete molecule of the complex which is constituted by one Rh(III) atom coordinated to I(1), [μ-(*p*-$Ph_2POC_6H_4)_2$S] (via the P atom), and a η^5-cyclopentadienyl ring. Considering the C_5H_5-ring to occupy three coordination sites, the rhodium coordination geometry might be described as distorted octahedral; the angles formed by the carbocyclic ring centroid (Cp*) and the other rhodium ligands are Cp*–Rh(1)–I(1) = 120.2°, Cp*–Rh(1)–C(19) = 129.8°, Cp*–Rh(1)–P(1) = 125.5°. The distances between the rhodium and the cyclopentadienyl carbons are in a range from 2.241(6) to 2.34(5) Å with a mean value of 2.293(6) Å and a Rh-centroid separation of 1.955 Å. The Rh(1)–I(1) distance of 2.655(1) Å, and Rh(1)–C(acyl) distance of 2.293(6) Å are comparable with the values reported for {(η^5-C_5H_5)Rh[C(O)Me][(*S*)-(PPh$_2$-NHCH–(Me)Ph]}I [20], the slight differences being due to positional disorder. The Rh(1)–I(1) bond distance is shorter than the value reported for the complex {Rh[$Ph_2P(CH_2)_3PPh_2$][C(O)Me]I_2} [21]. The Rh(1)–P(1) bond distance (2.246(2) Å) is significantly shorter than that reported for [(η^5-C_5H_5)Rh(PPh_3)Cl_2] [22] (2.3089(9)) Å.

In the complex the η^5-cyclopentadienyl rings are in the *trans* position with respect to the metal–metal axis and lie in two planes which form an angle of 146° with each other, while the angle between the weighted least-squares planes through two phenolic rings is 65.72°.

The Rh(1)···Rh(1A) separation of 8.879 Å and the P(1)···P(1A) separation of 9.577 Å are shorter than the metal–metal (12.55 Å) and P···P (11.61 Å) separations found in **6**. The P(1)···P(1A) separation is shorter than that calculated for the free ligand [11] (11.04 Å). The P(1)–O(1)–C(4) angle is 123.4(4)°, and the dihedral angle C(1A)–S(1)–C(1)–C(6) is 139.3(7)°. The valence angle C(1)–S(1)–C(1A) of 101.9(5)° is larger than that in **6** (101.3)°. This value, as well as the S(1)–C(1) distance of 1.774(7) Å, compare well with those respectively of 103.2° and 1.769 Å reported [23] for [2,18-diphenyl-1,3,17,19-tetraoxa-10,26-dithia-2,18-diphospha (3.1.3.1)paracyclophane].

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