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Inorganica Chimica Acta 245 (1996) 243-249

Inorganica Chimica Acta

Synthesis and characterization of palladium(II) and rhodium(I) complexes coordinated with bis(diphenylphosphinomethyl) sulfide

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Received 15 May 1995, revised 11 September 1995

Abstract

Bis(chloromethyl) sulfide reacts with 2 moles of lithium diphenylphosphide in THF to give a white crystal, bis(diphenylphosphinomethyl) sulfide (dpms). This compound reacts with $Na_2[PdCl_4]$ in ethanol to afford a monomeric complex, $[PdCl_2(\text{dpms-}P,P')]$. The compound, dpms, reacts with a half mole of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to give a macrocyclic dinuclear complex, $[\{RhCl(CO)(\mu\text{-dpms})\}_2]$ (**3**). The dynamic property of **3** is investigated by means of temperature-dependent NMR spectroscopy. Treatment of **3** with a half mole of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ followed by the addition of $NaBPh_4$, gives a trinuclear complex, $[Rh_3(\mu\text{-}Cl)Cl(CO)_2(\mu\text{-dpms})_2](BPh_4)\cdot H_2O$. When **3** is treated with $AgClO_4$ and $[Cu(CH_3CN)_4]ClO_4$, hetero-trinuclear complexes, $M\{Rh_2Cl_2(CO)_2(\mu\text{-dpms})_2\}ClO_4\cdot(H_2O)n$ ($M = Ag$, $n = 0$; $M = Cu$, $n = 1$, respectively) are isolated as yellow powders.

Keywords: Phosphine-sulfide complexes, Tridentate ligand, Palladium complexes, Rhodium complexes, Metallamacrocycle, NMR spectroscopy

1. Introduction

Considerable interest has developed concerning metallamacrocyclic complexes owing to their unique coordination behaviors, or inclusion capability. Maverick and Klavetter [1] synthesized a macrocyclic dinuclear complex, bis[μ-2,6-bis(2,2-diacetylethyl)naphthalenato-$O,O':O'',O'''$]dicopper(II), which included chloroform or diamine. Balch and co-workers reported dinuclear metallamacrocyclic complexes containing bis(diphenylphosphinomethyl)phenylphosphine (dpmp) [2], bis(diphenylphosphinomethyl)phenylarsine (dpma) [3] or 2,6-bis(diphenylphosphino)pyridine (dppy) [4]. The diirida- and dirhodamacrocycles of dpma or dpmp incorporated the third metallic component to give unique trinuclear complexes [2–11].

One of the authors studied the preparation and coordination behavior of (benzylthiomethyl)diphenylphosphine (btmp). $Na_2[PdCl_4]$ and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ reacted with an excess amount of btmp to give mononuclear complexes, $[PdCl_2(\text{btmp-}P)_2]$ [12] and $[RhCl(CO)(\text{btmp-}P)_2]$ [13], respectively. The ligand btmp formed head-to-tail type binuclear complexes, $[\{PdCl(\mu\text{-btmp})\}_2]$ [12] and $[Rh_2(\mu\text{-}Cl)(\mu\text{-btmp})_2(CO)_2]X$ ($X = [RhCl_2(CO)_2]^-$ or BPh_4^-) [13], in which both phosphorus and sulfur in btmp served as coordinating atoms. We are interested in the fine difference of the coordinating abilities between the phosphorus and sulfur atoms. Bis(diphenylphosphinomethyl) sulfide (dpms) has one additional diphenylphosphinomethyl group in place of the benzyl group of the btmp ligand. Here, we report the coordinating behavior of the dpms ligand toward palladium(II) and rhodium(I) species and reactivity of a dirhodamacrocycle derived from the latter one.

2. Results and discussion

2.1. Preparation of bis(diphenylphosphinomethyl) sulfide and reaction with $Na_2[PdCl_4]$

Bis(diphenylphosphinomethyl) sulfide (dpms) was prepared as white crystals by reaction between bis(chloromethyl) sulfide and lithium diphenylphosphide in THF, and characterized fully by means of elemental analyses, IR and ^1H and $^{31}P\{^1H\}$ NMR data (Table 1), and mass spectrum. It is stable in a nitrogen atmosphere, but oxidized gradually in air yielding the corresponding phosphine oxides.

Treatment of dpms with $Na_2[PdCl_4]$ in ethanol at room temperature gave a yellow crystal, $[PdCl_2(\text{dpms-}P,P')]$ (**1**). The ^1H NMR spectrum of **1** showed a double doublet at δ 7.91, which was assigned to *o*-protons of the phosphine phenyl groups. This coupling pattern is characteristic of *cis*-

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SSDI 0020-1693(95)04819-8

Table 1
Selected NMR data of dpms and its complexes

Compound	^1H				$^{31}P\{^1H\}$	
	CH_2		o-CH(Ph)		δ[c]	J_{PRh} (Hz)
	δ[a]	^2J (Hz)	δ[a]	J (Hz)[b]		
dpms	3.22(d)	3	7.42(m)		−21.4(s)	
1	3.27(d)[d]	4.0	7.91(d d)[d]	12[e] 7[f]	8.2(s)[d]	
3	3.88(d)[d,g]	13.7	7.61(q)[d,g]	7	21.8(d)[d,g]	122.1
	5.18(d)[d,g]	13.7	8.01(q)[d,g]	7		
4	3.33(d)[g]	11	7.64(q)[g,h]	7	21.3(d)[g]	122.1
	4.45(d)[g]	11	7.70(q)[g,h]	7		
5	4.28(d)	11	7.79(br, q)	7	21.4(d)	122.0
	4.68(d)	11	7.90(br, q)	7		
6	4.03(br)[d]		7.61(q)[d]	7	24.7(d)[d]	122.1
	4.35(d)[d]	11	7.88(q)[d]	7		
7	3.89(d)	10.8	7.75(q)	6	19.7(d)	122.1
	4.70(d)	10.8	7.85(q)	6		

[a] δ value (400 MHz) in $CDCl_3$ at room temperature, unless noted elsewhere. Signal shape is given in parentheses.

[b] $^3J_{HH} = {}^3J_{HP} = {}^5J_{HP}$, except J values for **1**.

[c] δ value (161.9 MHz) from 85% H_3PO_4 in $CDCl_3$ at room temperature, unless noted elsewhere. Signal shape is given in parentheses.

[d] In CD_2Cl_2.

[e] $^3J_{HP}$.

[f] $^3J_{HH}$.

[g] At 0 °C.

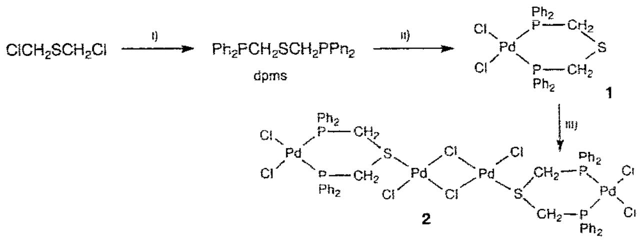
[h] The o-protons of the BPh_4 moiety resonate in the range of δ 7.42–7.53, overlapping with the p-protons of the PPh_2 moieties.

coordination of two equivalent diphenylphosphino moieties, lacking virtual coupling expected for two *trans*-coordinated diphenylphosphino moieties. Accordingly, **1** has a square planar structure in which the central palladium(II) atom is coordinated with the two *cis*-located phosphine moieties and two chloro ligands, and the sulfide moiety remains uncoordinated. The coordinating ability of the phosphine group is stronger than that of the sulfide one. The structure of **1** is very similar to that of $[PdCl_2(dpmp\text{-}P,P')]$ except for the sulfur atom in place of the phenylphosphine moiety in the latter complex [14].

Complex **1** reacted with $[PdCl_2(CH_3CN)_2]$ in dichloromethane to give a yellow powder, $[\{Pd_2Cl_4(dpms)\}_2]$ (**2**). Neither NMR data nor the molecular weight of **2** could be obtained owing to its poor solubility in organic solvents. In consideration of the uncoordinated sulfur atom in **1**, **2** was tentatively ascribed to a tetranuclear structure, in which the sulfur atom was coordinated to the other palladium atom, connecting the '$PdCl_2(dpms\text{-}P,P')$' moiety with the central Pd_2Cl_4 one (Scheme 1).

2.2. Preparation and dynamic property of a dirhodamacrocycle

Di-μ-chloro-tetracarbonyldirhodium(I) reacted with double molar amount of dpms in benzene at room temperature to give $[\{RhCl(CO)(\mu\text{-dpms})\}_2]$ (**3**). The IR spectrum of **3** showed strong bands at 1975, 1480 and 1435 cm^{-1}, attributable to $\nu(C{\equiv}O)$, C_6H_5 and $P\text{–}C_6H_5$, respectively. The band at 1975 cm^{-1} supports strongly the *trans*-coordination of the two phosphine groups rather than the *cis*-one in comparison with the $\nu(C{\equiv}O)$ bands of $[\{RhCl(CO)(\mu\text{-dpma})\}_2]$



Scheme 1. (i) $LiPPh_2$ in THF, (ii) $Na_2[PdCl_4]$, (iii) $[PdCl_2(CH_3CN)_2]$.

(1978 cm^{-1}) [3], [{RhCl(CO)(μ-dppp)}$_2$] (dppp = 1,3-bis-(diphenylphosphino)propane, 1958 cm^{-1}) and *cis*-[RhCl(CO)(dppe)] (dppe = 1,2-bis(diphenylphosphino)-ethane, 2010 cm^{-1}) [15]

The ^{1}H NMR spectrum of **3** at 0 °C showed two broad doublets at δ 3 88 and 5.18 ($^2J_{HH}$ = 13 7 Hz) due to unequivalent methylene protons The doublet at δ 5 18 changed to a broad singlet at −20 °C, which diminished in the temperature range −40 to −60 °C At −90 °C, two broad signals appeared at δ 4 38 and 6 17 The doublet at δ 3 88 broadened near −40 °C and split into two broad signals at δ 3 44 and 4.17 at −90 °C Thus, the ^{1}H NMR spectra exhibited remarkable temperature dependency At 0 °C, the spectrum showed two quartets ($^3J_{HH}$ = $^3J_{HP}$ = $^5J_{HP}$ = 7 Hz) at δ 7 61 and 8 01, which were assigned to the *o*-protons of the phosphine phenyl groups. This indicates that the *o*-protons couple not only with the neighboring *m*-proton, but also with two phosphorus atoms by virtual coupling This virtual coupling implies that the two phosphine groups are coordinated *trans* to each other, but not *cis* (vide infra) Accordingly, the two dpms ligands in **3** act as bridges, combining two rhodium atoms and forming a twelve-membered macrocycle, so called dirhodamacrocycle (Scheme 2) In the macrocycle, the four phosphine groups act as ligands, whereas the two dialkyl sulfide ones remain uncoordinated These facts imply unambiguously that the phosphine group acts as a stronger ligand also to the Rh(I) center than the dialkyl sulfide one. Our ligand, dpms, is very similar to dpma, dpmp and dppy, since these four ligands have a common structure of Ph$_2$P–C–E–C–PPh$_2$ (E = hetero atom with coordinating ability) Thus, the twelve-membered dirhodamacrocycle of **3** is similar to that of [{RhCl(CO)(μ-dpma)}$_2$], which was confirmed by X-ray structure analysis [3] Furthermore, dppy and dppp formed analogous twelve-membered dirhodamacrocycles, [{RhCl(CO)(μ-dppy)}$_2$] [4] and [{RhCl(CO)(μ-dppp)}$_2$] [15], respectively.

The ^{31}P{^{1}H} NMR spectra of **3** were also dependent on temperature (Fig 1) The spectrum at −90 °C showed four doublets ($^1J_{PRh}$ = 122 Hz) at δ 16 9, 19 1, 24 0 and 26 2 with intensity ratio of about 0 8:1 6 1.7 1 0, respectively, indicating clearly that all the phosphine groups are ligated to the rhodium atom and there is actually no free phosphine in the solution. The four doublets diminished actually to noise level near −60 °C, and a broad doublet ($^1J_{PRh}$ = 122 Hz) appeared at δ 21 8 at −20 °C Only one fairly sharp doublet was observed near δ 21.8 at room temperature. The ^{1}H and ^{31}P{^{1}H} NMR data are explained as follows, corresponding to the stereochemical non-rigidity of **3** as pictured in Fig. 2 At −90 °C, bond rotation at the sulfur atoms is quenched actually, and **3** consists of two symmetric isomers **3a** and **3b** and one asymmetric one **3c** Thus, these three conformational isomers **3a–c** show four kinds of phosphorus resonances at δ 16 9, 19 1, 24 0 and 26 2 (vide ante) The two resonances at δ 19 1 and 24 0 correspond to two kinds of phosphorus atoms

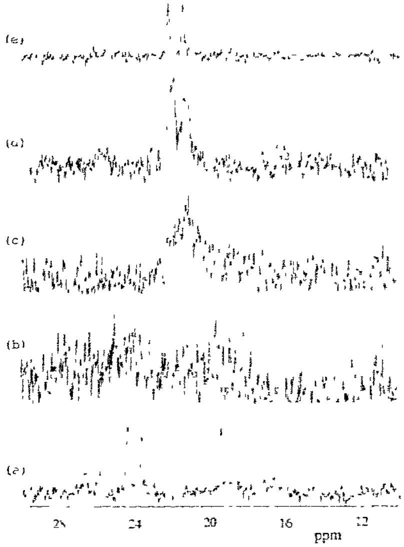
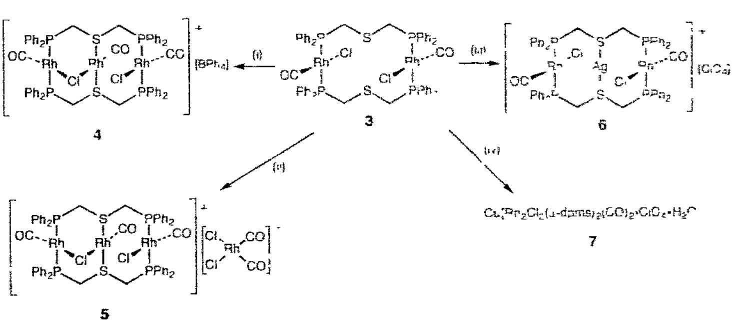


Fig 1 ^{31}P{^{1}H} NMR spectra of 3 in CD$_2$Cl$_2$ (161 9 MHz) at (a) −90, (b) −60, (c) −40, (d) −20, (e) 30 °C



Scheme 2 (i) [Rh$_2$(μ-Cl)$_2$(CO)$_4$] and NaBPh$_4$; (ii) [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (iii) AgClO$_4$, (iv) [Cu(CH$_3$CN)$_4$]ClO$_4$

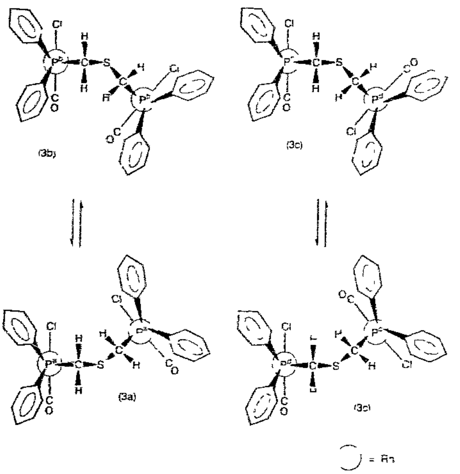


Fig. 2. Intramolecular motion of 3. The molecules are drawn in the top view from the P–Rh–P line.

(P^c and P^d) of the asymmetric isomer since P^c and P^d exist in leveled circumstances, whereas the two remaining resonances correspond to phosphorus atoms (P^a and P^b) of the two symmetric isomers. It is noted that the symmetric isomers **3a** and **3b** and the asymmetric one **3c** exist in a population ratio of about 1:0.8:3.3 or 0.8:1:3.3 on the basis of the intensity ratio mentioned above. The three isomers exhibit four kinds of methylene protons at δ 3.44, 4.17, 4.38 and 6.17 in approximately equal intensities, although eight kinds of methylene protons are expected for the three isomers, strictly speaking. Chemical shifts of four kinds of methylene protons in **3c** coincide actually with those of protons in analogous chemical circumstances in **3a** and **3b**.

Upon increasing temperature, bond rotation at the sulfur atom begins to take place. Thus, isomers **3a** and **3b** interchange with each other, whereas isomer **3c** moves intramolecularly. Above −20 °C, bond rotation is rapid enough to unite the four signals corresponding to P^a, P^b, P^c and P^d, leaving only one doublet in the $^{31}P\{^1H\}$ NMR spectra. At the limit of the rapid rotation, all the phosphorus atoms are virtually equivalent. Thus, the two phosphine groups are coordinated *trans* to the rhodium atom but not *cis*, because *cis*-coordination of the two phosphine groups to the 'RhCl(CO)' moiety would give rise to two double doublets in the $^{31}P\{^1H\}$ NMR spectrum at room temperature [15]. The ^1H NMR spectra change corresponding to the $^{31}P\{^1H\}$ NMR ones, and show two doublets at δ 3.88 and 5.18 near 20 °C (vide ante). This indicates that the methylene protons neighboring on the chloro and the carbonyl ligands do not interchange with each other. Accordingly, the RhCl(CO) moiety does not rotate actually around the P–Rh–P axis at room temperature. Sanger [15] reported that $[\{RhCl(CO)(\mu\text{-dppp})\}_2]$ existed as two conformational isomers, a major asymmetric one and a minor symmetric one at −50 °C, but detailed analysis was not done. As for $[\{RhCl(CO)(\mu\text{-dpma})\}_2]$, the dirhodamacrocyclic skeleton was flexible, but plural conformational isomers were not detected [3].

2.3. Cationic trirhodium complexes

As discussed above, **3** holds the twelve-membered macrocycle, which forms a similar cavity to the case of $[\{RhCl(CO)(\mu\text{-dpma})\}_2]$ [3] or $[\{RhCl(CO)(\mu\text{-dppy})\}_2]$ [4]. Furthermore, **3** possesses the two uncoordinated sulfide groups, which are able to ligate a third metallic component. Accordingly, **3** is expected to incorporate the third metallic component into the cavity to form a homo- or hetero-trinuclear complex.

The dirhodamacrocycle **3** reacted with a half molar amount of $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ in the presence of $NaBPh_4$ at room temperature to give a cationic trirhodium complex, $[Rh_3Cl_2(CO)_3(\mu\text{-dpms})_2]BPh_4 \cdot H_2O$ (**4**). The IR spectrum of **4** exhibited a strong band at 1980 cm^{-1} and a shoulder at 1990 cm^{-1}, assigned to $\nu(C{\equiv}O)$, but there was no band near 1800 cm^{-1} ascribable to the bridging carbonyl. Similar chloro derivatives $[Rh_3(\mu\text{-Cl})Cl(CO)_3(\mu\text{-dpmp})_2]^+$ and $[Rh_3(\mu\text{-Cl})Cl(CO)_3(\mu\text{-dpma})_2]^+$ contained also no bridging carbonyl ligand. However, the iodo derivatives $[Rh_3(\mu\text{-I})_2(\mu\text{-CO})(CO)_2(\mu\text{-dpmp})_2]^+$ and $[Rh_3(\mu\text{-I})_2(\mu\text{-CO})(CO)_2)(\mu\text{-dpma})_2]^+$ involved one bridging carbonyl, whereas the bromo derivative $[Rh_3(\mu\text{-Br})Br(CO)_3(\mu\text{-dpmp})_2]^+$ yielded two forms: a tan form had one bridging carbonyl and the other violet one lacked it [5].

The ^1H NMR spectrum of **4** at 0 °C showed two doublets at δ 3.33 and 4.45 ($^2J_{HH} = 11$ Hz), assignable to two unequivalent methylene protons. The *o*-protons of the phosphine phenyl groups resonated as two slightly broad quartets (each, $^3J_{HH} = {^3J_{HP}} = {^5J_{HP}} = 7$ Hz) at δ 7.64 and 7.70, implying that **4** held both the *trans* P–Rh–P structures and the dirhodamacrocycle. The $^{31}P\{^1H\}$ NMR spectrum exhibited one doublet ($^1J_{PRh} = 122.1$ Hz) at δ 21.3, indicating that the four phosphorus atoms were actually equivalent in accord with the ^1H NMR data. The ^1H and $^{31}P\{^1H\}$ NMR spectra did not change actually in the temperature range of 30 to −90 °C. In the $^{13}C\{^1H\}$ NMR spectrum of **4**, a doublet ($^1J_{CRh} = 78.3$ Hz) at δ 182 is assigned to the carbonyl carbon coordinated to the sulfur-bonded rhodium atom, whereas a triplet of doublet ($^2J_{CP} = 14$ Hz, $^1J_{CRh} = 78.3$ Hz) at δ 187.5 is due to those coordinated to the phosphine-bonded rhodium atoms. The coupling constant of 14 Hz indicates *cis*-coordination of the carbonyl ligand to the two phosphine ones, which were situated *trans* to each other. Complex **4** showed a conductivity of 7.0×10^{-3} Sm^2 mol^{-1} in 1.0×10^{-3} mol dm^{-3} acetone, comparable to about 10 Sm^2 mol^{-1} for a typical 1:1 electrolyte, confirming its ionic structure.

On the basis of the data mentioned above, we propose that **4** is a cationic trirhodium complex, as illustrated in

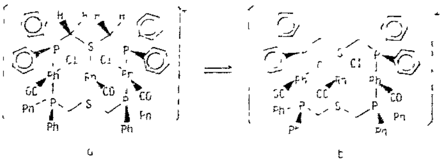


Fig 3 Bridge/terminal interchange of the chloro ligands in the trirhodium cation

Scheme 2 However, the structure of **4** shown in Scheme 2 seems to be asymmetric, having two kinds of [RhCl(CO)(PPh_2CH_2)$_2$] moieties in different chemical circumstances This contradiction is explained by rapid interchange between bridging and terminal chloro ligands, as shown in Fig 3. It looks as though the energy barrier between the two structures **a** and **b** is comparatively low, since the distance between the central rhodium atom and the bridging chloro ligand is not greatly different from that between the central rhodium atom and the terminal chloro ligand. A similar bridge/terminal interchange of chloro ligands was reported for cationic trirhodium complexes, [Rh_3(μ-Cl)Cl(CO)$_3$(μ-dpmp)$_2$]BPh_4 and [Rh_3(μ-Cl)Cl(CO)$_3$(μ-dpma)$_2$]BPh_4 [5]

The dirhodamacrocycle **3** reacted with an equal molar amount of [Rh_2(μ-Cl)$_2$(CO)$_4$] in benzene at room temperature to give a violet precipitate, [Rh_3Cl_2(μ-dpms)$_2$(CO)$_3$][$RhCl_2(CO)_2$] (**5**). Complex **5** also precipitated directly when dpms was added to the solution involving an equal molar amount of [Rh_2(μ-Cl)$_2$(CO)$_4$] to dpms. The IR spectrum of **5** showed a sharp and strong band at 2060 cm^{-1} and a slightly broad and very strong one at 1980 cm^{-1} The former band was ascribed to symmetric $\nu(C\equiv O)$ absorption of the anionic [$RhCl_2(CO)_2$]$^-$ moiety, whereas the latter one was due to overlap of the $\nu(C\equiv O)$ absorptions of the cationic trirhodium moiety and the asymmetric $\nu(C\equiv O)$ of the [$RhCl_2(CO)_2$]$^-$ moiety [16] The spectrum exhibited no band near 1800 cm^{-1}, assignable to the bridged carbonyl. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **5** indicate that the four methylene groups are actually equivalent and the four phosphorus atoms are also so Rapid bridge/terminal interchange of the chloro ligands takes place in the dichlorotrirhodium moiety similarly to the case of **4**

2.4. *Dirhodamacrocycles involving d^{10} metal ion*

The dirhodamacrocycle **3** reacted with silver(I) perchlorate in a dichloromethane–ethanol mixed solvent to afford a yellow complex, [Ag{$Rh_2Cl_2(CO)_2$(μ-dpms)$_2$}]ClO_4 (**6**) The IR spectrum of **6** was actually similar to that of **3** except for a strong band at 1095 cm^{-1}, assignable to ν(ClO). Furthermore, the spectrum lacked a band near 870–990 cm^{-1}, assignable to the ν_2-type Cl–O stretching vibration of a unidentate or bidentate perchlorate group [17]. This implies that the perchlorate group exists in a free state, but is not coordinated to the silver atom in a unidentate or bidentate fashion The ^1H NMR spectrum exhibited also two quartets at δ 7.61 and 7.88 (J = ~7 Hz) and two signals at δ 4.03 (broad) and 4.35 (d, $^2J_{HH}$ = 11 Hz) The $^{31}P\{^1H\}$ NMR spectrum showed only one doublet at δ 24.7 with a coupling constant J_{PRh} = 122.1 Hz, implying that the phosphine groups were coordinated with the rhodium atom, but not with the silver one These data indicate that **6** is a cationic hetero-trinuclear complex which holds the dirhodamacrocycle structure, and the silver(I) ion is trapped by the two sulfur atoms forming linear S–Ag–S coordination. Examples of linear L–Ag(I)–L coordination are bis(tertiary phosphine)silver(I) ions such as [Ag{P(C_6H_4-Me-p)$_3$}$_2$]$^+$ [18], [Ag(PBu^t_3)$_2$]$^+$ [19] and [Ag{P(mes)$_3$}$_2$]$^+$ (mes = mesityl) [20]. Balch et al [6] reported that [{RhClCO)(μ-dpma)}$_2$] reacted with AgCl in dichloromethane to yield [AgCl{$Rh_2Cl_2(CO)_2$(μ-dpma)$_2$}], which contained a three-sites-ligating silver(I) ion, As–Ag(Cl)–As unit

The dirhodamacrocycle **3** reacted with [Cu(CH_3CN)$_4$]ClO_4 in dichloromethane to give Cu{Rh_2Cl_2(CO)$_2$(μ-dpms)$_2$}$ClO_4 \cdot H_2O$ (**7**) The IR spectrum of **7** was fairly similar to that of **6** except for broad bands near 1620 and 3500 cm^{-1} due to water, and the lack of a band near 870–990 cm^{-1}, assignable to the unidentate or bidentate perchlorate group [17] Acetonitrile was not involved as a ligand to the copper atom. Since the ^1H and $^{31}P\{^1H\}$ NMR spectra of **7** were also analogous to the corresponding ones of **6** it is certain that **7** holds the dirhodamacrocycle structure and the copper(I) ion is trapped by the two sulfide groups, forming S–Cu–S coordination However, it is not certain whether water is coordinated to the copper ion or not, although the perchlorate ion appears to exist in a free state

3. Experimental

The starting complexes [Rh_2(μ-Cl)$_2$(CO)$_4$] [21], [$PdCl_2(CH_3CN)_2$] [22] and [Cu(CH_3CN)$_4$]ClO_4 [23] were prepared according to literature methods Solvents were purified by the usual methods and stored under dry nitrogen The other reagents were commercially available and used without further purification General procedures were described in the previous paper [24].

3.1 *Preparation of dpms*

Lithium (1.10 g) was formed into a ribbon shape and set in deaerated THF (150 cm^3) in a three-necked flask, filled with dry nitrogen A THF solution (30 cm^3) of chlorodiphenylphosphine (12.5 g) was added gradually to the flask with vigorous stirring. The reaction mixture was maintained under reflux for 5 h, then cooled to room temperature, and filtered through absorbent cotton to eliminate lithium chloride and unreacted lithium. A THF solution (40 cm^3) of bis(chloromethyl) sulfide (3.0 g) was added gradually to the blood-red filtrate The reaction mixture changed to a pale yellow suspension containing white precipitates, and was stirred for 5 h and filtered again through absorbent cotton. One cm^3 of methanol was added to the filtrate, and the solvent was evaporated. 20 cm^3 of benzene were added to the concentrated solution. The benzene solution was filtered, diluted with hexane, and set in a refrigerator to give 6.8 g of white crystals, $(Ph_2PCH_2)_2S$ (dpms). Yield 58%. M.p. 64–66 °C. IR (KBr, cm^{-1}): 3050 (m, aromatic C–H), 2890 (w, CH_2), 1950 (w, C_6H_5), 1880 (w, C_6H_5), 1810 (w, C_6H_5), 1755 (w, C_6H_5), 1480 (vs, C_6H_5), 1430 (vs, P-C_6H_5), 745 (vs, C_6H_5), 695 (vs, C_6H_5). $^{13}C\{^1H\}$ NMR (δC, 100.6 MHz, $CDCl_3$): 31.5 (2C, dd, $^1J_{CP}=22.5$ Hz, $^3J_{CP}=8.8$ Hz, PCH_2), 128.5 (8C, d, $^3J_{PC}=7.9$ Hz, *m*-C), 128.9 (4C, s, *p*-C), 132.9 (8C, d, $^2J_{CP}=19.5$ Hz, *o*-C), 137.6 (4C, d, $^1J_{CP}=15.6$ Hz, *ipso*-C). *Anal.* Found: C, 72.50; H, 5.67%; M^+, 430. Calc. for $C_{26}H_{24}P_2S$: C, 72.54; H, 5.62%; *M*, 430.48.

3.2. $^{31}P\{^1H\}$ NMR data of oxidized products of dpms

The diphosphine dpms was gradually oxidized in air. The $^{31}P\{^1H\}$ NMR data of the oxidized products are as follows. $Ph_2PCH_2SCH_2P(=O)Ph_2$: δ (161.9 MHz, $CDCl_3$) −21.3 (1P, s, PPh_2), 28.3 (1P, s, $P(=O)Ph_2$). $[Ph_2(O=)PCH_2]_2S$: δ 28.9 (2P, s, $P(=O)Ph_2$).

3.3. Preparation of $[PdCl_2(dpms)]$ (1)

A 90% aqueous ethanol solution (120 cm^3) of $Na_2[PdCl_4]$ (2.2 mmol) and an ethanol solution (110 cm^3) of dpms (1.02 g) were added together gradually to 110 cm^3 of ethanol stirred rigorously in a three-necked 500 cm^3 flask. The resulting yellow precipitates were washed with ethanol and diethyl ether to give a yellow solid, $[PdCl_2(dpms)]$ (**1**). Yield 76%. M.p. 260–270 °C (decomp.). IR (KBr, cm^{-1}): 1480 (C_6H_5), 1435 (P–C_6H_5), 1380 (P–CH_2). *Anal.* Found: C, 50.80; H, 3.98. Calc. for $C_{26}H_{24}Cl_2P_2PdS$: C, 51.38; H, 3.78%.

3.4. Preparation of $[\{Pd_2Cl_4(dpms)\}_2]$ (2)

A dichloromethane solution (50 cm^3) of $[PdCl_2(CH_3CN)_2]$ (64 mg, 0.25 mmol) was added to a dichloromethane solution (100 cm^3) of **1** (300 mg, 0.49 mmol). The reaction mixture was stirred at room temperature for 20 h. The resulting yellowish orange suspension was filtered with a glass filter. The yellow precipitates were washed with dichloromethane to give 295 mg of $[\{Pd_2Cl_4(dpms)\}_2]$ (**2**). Yield 100%. M.p. 270–280 °C (decomp.). IR (KBr, cm^{-1}): 1480 (C_6H_5), 1430 (P–C_6H_5), 1380 (P–CH_2). *Anal.* Found: C, 39.48; H, 3.34. Calc. for $C_{52}H_{48}Cl_8P_4Pd_4S_2$: C, 39.77; H, 3.08%.

3.5. Preparation of $[Rh_2Cl_2(\mu\text{-dpms})_2(CO)_2]$ (3)

A benzene solution (10 cm^3) of $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (109 mg, 0.28 mmol) was added to dpms (242 mg, 0.56 mmol) in a flask in a nitrogen atmosphere. The yellow solution changed gradually to a yellow suspension. After stirring at room temperature for 4 h, the reaction mixture was filtered to give a pale yellow solid, $[Rh_2Cl_2(CO)_2(\mu\text{-dpms})_2]$ (**3**). Yield 320 mg (95%). M.p. 250 °C. IR (KBr, cm^{-1}): 1975 (C≡O), 1480 (C_6H_5), 1435 (P–C_6H_5). *Anal.* Found: C, 54.31; H, 4.15. Calc. for $C_{54}H_{48}Cl_2O_2P_4Rh_2S_2$: C, 54.33; H, 4.05%.

3.6. Preparation of $[Rh_3Cl_2(\mu\text{-dpms})_2(CO)_3]BPh_4\cdot H_2O$ (4)

40 mg (0.10 mmol) of $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ were added to a dichloromethane solution (20 cm^3) containing 230 mg (0.19 mmol) of **3** in a nitrogen atmosphere. The yellow solution of **3** changed immediately to reddish violet. After 1 h, a methanol solution (15 cm^3) of $NaBPh_4$ (132 mg, 0.39 mmol) was added to the reddish violet solution. After the solution had been stirred at room temperature for 23 h, diethyl ether was added to the solution to give a reddish violet solid, $[Rh_3Cl_2(CO)_3(\mu\text{-dpms})_2]BPh_4\cdot H_2O$. Yield 192 mg (51%). M.p. 145–150 °C. IR (KBr, cm^{-1}): 1990 (sh, C≡O), 1980 (vs, C≡O), 1482 (C_6H_5), 1435 (P–Ph). $^{13}C\{^1H\}$ NMR (δC, 100.6 MHz, $CDCl_3$): 35.5 (4C, s, PCH_2), 121.9 (4C, s, *p*-C), 126.0 (8C, s, *m*-C), 128.7 (8C, s, *m*-C), 129.1 (8C, s, *m*-C), 129.8 (4C, t, $^1J_{CP}={}^3J_{CP}=25$ Hz, *ipso*-C(PPh)), 131.4 (4C, s, *p*-C), 131.7 (4C, s, *p*-C), 131.8 (4C, t, $^1J_{CP}={}^3J_{CP}=25$ Hz, *ipso*-C(PPh)), 132.4 (8C, br-s, *o*-C(PPh)), 134.0 (8C, br-s, *o*-C(PPh)), 136.0 (8C, s, *o*-C(BPh_4)), 164.3 (4C, four signals, $^1J(C^{11}B)=50$ Hz, *ipso*-C(BPh_4)), 182.0 (1C, d, $^1J_{CRh}=78.3$ Hz, S–Rh–CO), 187.5 (2C, dt, $^1J_{CRh}=78.3$ Hz, $^2J_{CP}=14$ Hz, P–Rh–CO). Conductivity ($C=1.0\times10^{-3}$ mol dm^{-3}, acetone): 7.0×10^{-3} S m^2 mol^{-1}. *Anal.* Found: C, 57.59; H, 4.22. Calc. for $C_{79}H_{70}BCl_2O_4P_4Rh_3S_2$: C, 57.13; H, 4.25%.

3.7. Preparation of $[Rh_3Cl_2(\mu\text{-dpms})_2(CO)_3][RhCl_2(CO)_2]$ (5)

A benzene solution (10 cm^3) of $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (50 mg, 0.13 mmol) was added to 44 mg (0.13 mmol) of dpms and stirred. Violet precipitates were formed during the first 15 min of the reaction. After stirring for 3 h, the precipitates were collected and washed with hexane to give $[Rh_3Cl_2(\mu\text{-dpms})_2(CO)_3][RhCl_2(CO)_2]$ (**5**). Yield 65 mg (54%). M.p. 245–255 °C (decomp.). IR (KBr, cm^{-1}): 2060 (C≡O), 1980 (C≡O), 1480 (C_6H_5), 1430 (P–C_6H_5). *Anal.* Found: C, 43.15; H, 3.13. Calc. for $C_{57}H_{48}Cl_4O_5P_4Rh_4S_2$: C, 44.04; H, 3.11%.

3.8. Preparation of $[Ag\{Rh_2Cl_2(CO)_2(\mu\text{-dpms})_2\}]ClO_4$ (6)

An ethanol solution (10 cm^3) of $AgClO_4$ (100 mg, 0.48 mmol) was added to a dichloromethane solution (25 cm^3) of **3** (250 mg, 6.21 mmol). The reaction mixture was stirred at room temperature for 20 h, and diluted with ethanol to give yellow precipitates. The precipitates were recrystallized from dichloromethane and diethyl ether to afford a yellow solid,

$[Ag\{Rh_2Cl_2(CO)_2(\mu\text{-dpms})_2\}]ClO_4$ (**6**) Yield 58% M p 210–220 °C (decomp) IR (KBr, cm^{-1}) 1990 (CO), 1440 ($P–C_6H_5$), 1095 (ClO) *Anal* Found C, 46 62, H, 3 62 Calc for $C_{54}H_{48}AgCl_3O_6P_4Rh_2S_2$, C, 46 29, H, 3 45% Conductivity ($C = 1\ 0 \times 10^{-3}$ mol dm^{-3}, acetone) $12\ 0 \times 10^{-3}$ Sm^2 mol^{-1}

3 9 Preparation of $Cu\{Rh_2Cl_2(CO)_2(\mu\text{-dpms})_2\}ClO_4\ H_2O$ (7)

A dichloromethane solution (5 cm^3) of $[Cu(CH_3CN)_4]ClO_4$ (28 mg, 0 084 mmol) was added to a dichloromethane solution (10 cm^3) of **3** (100 mg, 0 084 mmol) After the reaction mixture had been stirred for 24 h at room temperature it was concentrated under reduced pressure and diluted with diethyl ether to give a yellow precipitate, $Cu\{Rh_2Cl_2(CO)_2(\mu\text{-dpms})_2\}ClO_4\ H_2O$ (**7**) Yield 68 mg (60%) M p 245–250 °C (in vacuum, decomp) IR (KBr, cm^{-1}) 1990 (CO), 1430 ($P–C_6H_5$) 1380 ($P–CH_2$), 1100 (Cl–O) *Anal* Found C, 46 99, H, 3 58 Calc. for $C_{54}H_{50}Cl_3CuO_7P_4Rh_2S_2$ C, 47 18 H, 3 67% Conductivity ($C = 1\ 0 \times 10^{-3}$ mol dm^{-3}, acetone) $5\ 0 \times 10^{-3}$ Sm^2 mol^{-1}

Acknowledgements

The authors thank Shoei Chemical Industry Inc for its financial support of the present work

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