

Synthesis and Spectroscopic Studies of Silver and Rhodium Mono- and Polynuclear Complexes with Multidentate Phosphines $(\text{Ph}_2\text{P})_2\text{CHR}$ ($\text{R} = \text{H}, \text{Me}, \text{PPh}_2$)

ANTHONIUS F. M. J. VAN DER PLOEG and GERARD VAN KOTEN*

Anorganisch Chemisch Laboratorium, J. H. van't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received February 12, 1981

Trinuclear $[\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CR}')_3]$, dinuclear $[\{(\text{Ph}_2\text{P})_2\text{CHR}\}\text{Ag}_2(\text{O}_2\text{CR}')_2]$, $[\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2\text{-Ag}_2](\text{BF}_4)_2$ and $[\text{Rh}_2(\text{Cl})(\text{CO})_2\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2][\text{RhCl}_2(\text{CO})_2]$, and mononuclear $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2](\text{BF}_4)$, $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2\text{HCl}](\text{BF}_4)$, $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$ and $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2\text{O}_2](\text{BF}_4)$ ($\text{R} = \text{H}, \text{Me}$) were synthesized from the phosphines tris(diphenylphosphino)methane $((\text{Ph}_2\text{P})_3\text{CH})$, bis(diphenylphosphino)methane $((\text{Ph}_2\text{P})_2\text{CH}_2)$ and 1,1-bis(diphenylphosphino)ethane $((\text{Ph}_2\text{P})_2\text{CHMe})$. The ^1H , ^{13}C and ^{31}P NMR spectra were investigated and for the mononuclear rhodium compounds compared with their 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane analogues. The ^{31}P NMR spectra of the silver complexes revealed besides normal values for $J(^{107}\text{Ag}-^{31}\text{P})$ (640 and 500 Hz for the AgP and AgP_2 systems, respectively) a small $^3J(^{107}\text{Ag}-^{31}\text{P})$ of about -4 Hz and an exceptionally large $^2J(^{31}\text{P}-^{31}\text{P})$ of 170 Hz. A large positive charge on the P-atoms in $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CR}')_2]$ and $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2](\text{BF}_4)_2$ was calculated from the chemical shifts of the methylene protons.

On the basis of ^{31}P NMR data methyl substitution in $(\text{Ph}_2\text{P})_2\text{CHR}$ resulted in formation of only one of the possible isomers for $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2](\text{BF}_4)_2$, $[\text{Rh}_2(\text{CO})_2(\text{Cl})\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2][\text{RhCl}_2(\text{CO})_2]$ and $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{O}_2](\text{BF}_4)$, but two isomers for $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2](\text{BF}_4)$ and $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{HCl}](\text{BF}_4)$. These results are interpreted in terms of metal–chelate ring puckering.

Introduction

Bis(diphenylphosphino)methane $((\text{Ph}_2\text{P})_2\text{CH}_2)$ has been extensively used as a ligand, its importance being related to its versatile coordination behaviour. On the one hand it can function as a bridging ligand and as such it can either stabilize unstable or

unfavourable metal–metal interactions such as the donative metal–metal bond in $[\text{Pt}_2\text{Me}_3\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2](\text{BF}_4)$ [1] or hold together two metal centers which can cooperate in reactions with small molecules as in $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-DMA})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2]$ (DMA = dimethylacetylenedicarboxylate) [2]. On the other hand it can function as a chelating ligand and as such it has a dramatic influence on the catalytic properties of its complexes, an effect which has been attributed to the resulting small chelate ring size [3].

In a previous paper we reported the effect of ligand geometry on the structure of silver complexes [4]. We found that tetranuclear silver complexes were obtained from reaction of 1,8-naphthalenedicarboxylatodisilver with PPh_3 , whereas dinuclear complexes were obtained from reactions of $\text{Ag}(\text{O}_2\text{-CMe})$ with the diphosphines $(\text{Ph}_2\text{P})_2\text{CH}_2$ and $\text{Ph}_2\text{-PCH}_2\text{CH}_2\text{PPh}_2$.

In order to study the effect of substituents at the methylene C-atom of $(\text{Ph}_2\text{P})_2\text{CH}_2$ on the molecular geometry and metal–metal interactions of the complexes formed, we carried out the reactions of silver and rhodium complexes with the phosphine ligands bis(diphenylphosphino)methane $(\text{Ph}_2\text{P})_2\text{CH}_2$, 1,1-bis(diphenylphosphino)ethane $(\text{Ph}_2\text{P})_2\text{CHMe}$, and tris(diphenylphosphino)methane $(\text{Ph}_2\text{P})_3\text{CH}$.

With rhodium as the centre metal atom bidentate phosphines can act as chelate or bridging ligands, thus the effect of substituents on the molecular geometry can be studied for both mononuclear and binuclear complexes.

In this paper we report i) the synthesis and characterization of di- and tri-nuclear silver carboxylates bridged by one, and dinuclear silver tetrafluoroborates bridged by two phosphines; ii) the synthesis and characterization of mono- and dinuclear rhodium complexes with two bridging or chelating phosphines $(\text{Ph}_2\text{P})_2\text{CHR}$; iii) detailed analyses of the ^1H , ^{13}C and ^{31}P NMR data in order to obtain more information about the effect of substituents at the methylene C-atom on the structure of the complexes as well as about the metal–phosphine interaction.

* Author to whom correspondence should be addressed.

Experimental

All reactions were carried out under a nitrogen atmosphere. Solvents were dried by standard techniques prior to use. ^1H NMR spectra were recorded on a Varian T-60, ^{13}C NMR spectra on a Bruker WP-80 and ^{31}P NMR spectra on a Varian XL-100 spectrometer. Spectral simulations and calculations were performed with the program ITRCAL, version 51200 [5]. Elemental analyses were carried out at the Institute for Organic Chemistry TNO, Utrecht. Analytical data for the silver complexes are given in Table II. The rhodium complexes did not give optimal analytical results, but were characterised with ^{31}P NMR data and IR spectra.

1,1-bis(diphenylphosphino)ethane $(\text{Ph}_2\text{P})_2\text{CHMe}$ was prepared from bis(diphenylphosphino)methane $(\text{Ph}_2\text{P})_2\text{CH}_2$ and methyl iodide in a procedure similar to that used for bis(diphenylphosphino)(trimethylsilyl)methane $(\text{Ph}_2\text{P})_2\text{CHSiMe}_3$ [6]. The synthetic procedures for the phosphines bis(diphenylphosphino)methane [7], tris(diphenylphosphino)methane $(\text{Ph}_2\text{P})_3\text{CH}$ [8] and bis(diphenylphosphino)(trimethylsilyl)methane [6] and the metal complexes $[\text{RhCl}(\text{CO})_2]_2$, $[\text{RhCl}(\text{CO})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2]$ [9] $[\text{RhCl}(\text{COT})_2]_2$ [10] (COT = cyclooctene), $[\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$ [11], $[\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{O}_2](\text{PF}_6)$, $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2]\text{Cl}$, $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2\text{O}_2]\text{Cl}$ and $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2\text{HCl}]\text{Cl}$ [12] are described in the literature.

Synthesis of the Silver Carboxylato Complexes
 $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{Ag}_2(\text{O}_2\text{CR})_2]$, $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2(\text{O}_2\text{CR})_2]$ and $[\{(\text{Ph}_2\text{P})_3\text{CH}\}_2\text{Ag}_3(\text{O}_2\text{CR})_3]$, $R = \text{Me}, \text{Et}, i\text{-Pr}, \text{C}_6\text{H}_5$

To a solution of the phosphine ligand $(\text{Ph}_2\text{P})_2\text{CH}_2$, $(\text{Ph}_2\text{P})_2\text{CHMe}$ and $(\text{Ph}_2\text{P})_3\text{CH}$ (0.5 mmol) in CH_2Cl_2 (10 ml) AgO_2CR (2, 2 and 3 equivalents, respectively) was added. The mixture was stirred for 4 h with exclusion of light. The reaction mixture was filtered and a layer of hexane was superposed on the filtrate. Slow diffusion of the solvents at -20°C resulted in the formation of a crystalline or microcrystalline precipitate. The white product was filtered off, washed with hexane and dried *in vacuo*. The yield ranged from 40 to 60%. A second fraction, although less pure, could be isolated from the filtrate. Purification by recrystallization was inadvisably owing to partial decomposition which occurred if a solution of the complexes was left standing for more than 24 h.

Synthesis of the Silvertetrafluoroborato Complexes
 $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{Ag}_2(\text{BF}_4)_2]$, $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2(\text{BF}_4)_2]$ and $[\{(\text{Ph}_2\text{P})_3\text{CH}\}_2\text{Ag}_3(\text{BF}_4)_3]$

AgBF_4 (1 equivalent for $(\text{Ph}_2\text{P})_2\text{CH}_2$ and $(\text{Ph}_2\text{P})_2\text{CHMe}$ and 1.5 equivalent for $(\text{Ph}_2\text{P})_3\text{CH}$) was added to a solution of the phosphine (0.5 mmol) in CH_2Cl_2

Cl_2 (10 ml). After stirring for 6 h with exclusion of light, a white suspension was obtained. Filtration gave a small yield of the complexes with $(\text{Ph}_2\text{P})_2\text{CH}_2$ and $(\text{Ph}_2\text{P})_2\text{CHMe}$. A second fraction could be obtained by addition of hexane to the filtrate.

The yield of the $(\text{Ph}_2\text{P})_3\text{CH}$ product was almost quantitative, but the isolated product did not give good elemental analysis. Purification by recrystallization was hampered by insolubility.

$[\text{Rh}_2\text{Cl}(\text{CO})_2\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2]/[\text{RhCl}_2(\text{CO})_2]$

$(\text{Ph}_2\text{P})_2\text{CHMe}$ (395 mg, 1.0 mmol) was added to a solution of $[\text{RhCl}(\text{CO})_2]_2$ (195 mg, 0.05 mmol) in acetone (5 ml). An orange precipitate was formed with gas evolution. The product was washed with hexane and dried *in vacuo*. Yield 530 mg, 90%.

Reactions of $(\text{Ph}_2\text{P})_3\text{CH}$ with Rhodium Complexes

Attempted reactions of $[\text{RhCl}(\text{COT})_2]_2$ and $[\text{RhCl}(\text{CO})_2]_2$ with $(\text{Ph}_2\text{P})_3\text{CH}$ did not lead to the isolation of well-defined products.

$[\text{RhL}_2](\text{BF}_4)$, $L = (\text{Ph}_2\text{P})_2\text{CH}_2$, $(\text{Ph}_2\text{P})_2\text{CHMe}$, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$

$[\text{RhCl}(\text{COT})_2]_2$ (90 mg, 0.25 mmol) was suspended in methanol (10 ml). The phosphine (1.0 mmol) and NaBF_4 (55 mg, 0.5 mmol) were added and the mixture stirred for 1 h. The orange suspension was filtered off and the solid $[\text{RhL}_2](\text{BF}_4)$ washed with hexane and dried *in vacuo*. Yield 90%.

Reaction of $[\text{RhCl}(\text{COT})_2]_2$ with $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$

$[\text{RhCl}(\text{COT})_2]_2$ (90 mg, 0.25 mmol) was suspended in methanol (10 ml). The phosphine (410 mg, 1.0 mmol) and NaBF_4 (55 mg, 0.5 mmol) were added and the mixture stirred for 1 h. The clear solution thus obtained was left standing overnight. Large red cubic crystals were formed, which were filtered off, washed with hexane and dried *in vacuo*. Yield 200 mg. *Anal. Calcd.* for $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}_2](\text{BF}_4) \cdot \frac{1}{2}\text{RhCl}(\text{COT})_2$: C, 62.38; H, 5.53; P, 10.36; Found: C, 62.6; H, 5.4; P, 10.2. The ^{31}P NMR spectrum evidenced the presence of only one phosphorus containing compound.

$[\text{RhL}_2\text{HCl}](\text{BF}_4)$, $L = (\text{Ph}_2\text{P})_2\text{CH}_2$, $(\text{Ph}_2\text{P})_2\text{CHMe}$, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$

A suspension of $[\text{RhL}_2](\text{BF}_4)$ (0.5 mmol) in methanol (10 ml) was freshly prepared by the above procedure. Gaseous HCl was bubbled through for 15 min. The suspension, which was cream coloured, was filtered off, washed with hexane and dried *in vacuo*, leading to the isolation of solid $[\text{RhL}_2\text{HCl}](\text{BF}_4)$. Yield 80%.

Reaction of $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{HCl}](\text{BF}_4)$ with Et_3N

$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{HCl}](\text{BF}_4)$ (50 mg, 0.05 mmol) was dissolved in CDCl_3 (0.5 ml). A small

TABLE I. ^1H , ^{31}P and ^{13}C NMR Data of the Phosphines $(\text{Ph}_2\text{P})_2\text{CHR}$ (R = H, Me, PPh₂, SiMe₃).^a

R	^1H NMR ^b			^{31}P NMR δ_{P}	^{13}C NMR					
	H_{aryl}	H_{CPX}	H_{Me}		Aryl group ^c			CHR ^d		R^{d}
					C(1)	C(2)	C(3)	C(4)	C(5)	
H	7.5	2.9(1.4)		-21.95	138.8(7.2)	132.7(21.6)	28.2(6.2)	128.5	27.9(32.2)	
Me	7.4	3.2	0.97(10.4)	-6.34	137.1(7.2)	134.3(22.0)	128.1 –	128.8	27.1(23.7)	13.6(8.5)
					136.2(9.8)	133.0(20.8)	127.9(7.4)	128.2		
PPh ₂	7.4	4.2		-9.49	136.4(12.0)	134.4(25.1)	127.6(7.6)	128.4	25.6(46.4)	
					(-11.0)	(-1.7)	(0)			
SiMe ₃	7.3	3.0	-0.17	-12.39	138.0(13.4)	134.1(22.0)	128.0(7.4)	128.5	18.1(45.8)	0.5(5.5)
					136.0(8.8)	133.9(23.2)	127.4(8.6)	128.1		

^aRecorded in CDCl₃; δ (in ppm) relative to TMS, H₃PO₄ and TMS, respectively. ^b $J(^{31}\text{P}-^1\text{H})$ between parentheses.

^cNumbers between parentheses indicate $|^xJ(^{31}\text{P}-^{31}\text{C}) + ^{2+x}J(^{31}\text{P}-^{13}\text{C})|$ for R = H, Me, SiMe₃; and $|^xJ(^{31}\text{P}-^{13}\text{C})|$ with $^{2+x}J(^{31}\text{P}-^{13}\text{C})$ for R = PPh₂. ^d $J(^{31}\text{P}-^{13}\text{C})$ between parentheses.

excess of Et₃N was added and the ^{31}P NMR spectrum was recorded. The product formed was identified as $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2]\text{BF}_4$ by comparison with the ^{31}P NMR data of the $(\text{Ph}_2\text{P})_2\text{CH}_2$ product obtained via the procedure starting from $[\text{RhCl}(\text{COT})_2]_2$.

$[\text{RhL}_2\text{O}_2](\text{BF}_4)$, $L = (\text{Ph}_2\text{P})_2\text{CH}_2$, $(\text{Ph}_2\text{P})_2\text{CHMe}$, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$

Oxygen gas was bubbled for 15 min through a freshly prepared suspension of $[\text{RhL}_2](\text{BF}_4)$ (0.5 mmol) in methanol (10 ml). The off-white precipitate formed was isolated by filtration, washed with hexane and dried *in vacuo*. Yield 80%.

$[\text{RhL}_2\text{Cl}(\text{HgCl})]\text{BF}_4$, $L = (\text{Ph}_2\text{P})_2\text{CH}_2$, $(\text{Ph}_2\text{P})_2\text{CHMe}$, $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 2, 3$)

HgCl₂ (130 mg, 0.5 mmol) was added to a freshly prepared suspension of $[\text{RhL}_2](\text{BF}_4)$ (0.5 mmol) in methanol (10 ml). The mixture was stirred for 1 h, and a yellow precipitate was formed. The product was filtered off, washed with hexane and recrystallized from CH₂Cl₂/hexane. Yield 60%.

For $L = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$, no colour change was observed and the ^{31}P NMR spectrum, recorded after work-up, did not show the presence of a Rh–Hg compound.

Analysis of the ^{31}P NMR Spectra of the Silver Complexes

The ^{31}P NMR spectra of the binuclear complexes $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{Ag}_2(\text{O}_2\text{CR})_2]$ and $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2(\text{O}_2\text{CR})_2]$ (R = Me, Et, i-Pr, C₆H₅) were interpreted as the sum of the A parts of different AA'XX' patterns resulting from each combination of the silver isotopes ^{107}Ag and ^{109}Ag , which have a natural abundance of 48 and 52%, respectively.

Calculation of the coupling constants was carried out with the following equations [13]:

$$\sqrt{(a-f)(c-d)} = |^1J(\text{Ag}-\text{P}) - ^3J(\text{Ag}-\text{P})| \quad (1)$$

$$|b-e| = |^1J(\text{Ag}-\text{P}) + ^3J(\text{Ag}-\text{P})| \quad (2)$$

and

$$|a-c| = |d-f| = |J(\text{P}-\text{P})| \quad (3)$$

The different symbols are indicated in Fig. 4a. A simulation of one of the spectra with the values thus calculated is shown in Fig. 4b. The results are summarized in Table IV.

The ^{31}P NMR spectra of the complexes $[\{(\text{Ph}_2\text{P})_3\text{CH}\}_2\text{Ag}_3(\text{O}_2\text{CR})_3]$ (R = Et, i-Pr) were considered to be the A part of the sum of various AA'A'XX'X' spin systems arising from the coupling of the phosphorus atoms to the silver atoms, which, as their isotopes, will be present in different combinations. With the assumption that $J(\text{Ag}-\text{Ag}) = 0$, the A part of each AA'A'XX'X' pattern in turn was considered to be a combination of a large number of a₂b sub patterns [14], where a and b stand for P atoms coordinated to silver atoms with spins in opposite direction. In Fig. 4c the spectrum of $[\{(\text{Ph}_2\text{P})_3\text{CH}\}_2\text{Ag}_3(\text{O}_2\text{C}-i\text{-Pr})_3]$ is shown. In view of the fact that $^1J(^{107}\text{Ag}-^{31}\text{P}) < ^1J(^{109}\text{Ag}-^{31}\text{P})$, the inner lines (b and c) originate from the P₃(^{107}Ag)₃ system, while the outer lines (a and d) came from the P₃(^{109}Ag)₃ system.

Examination of AB₂ patterns, reported in the literature [13, 15] concerning line positions and intensities, and comparison of these with the spectra of the silver phosphine compounds lead to the following equations:

$$|b-c| = 2(-3/4A + \sqrt{9/4A^2 - AB + B^2}) \quad (4)$$

and

$$|a-d| = 2(+3/4A + \sqrt{9/4A^2 + AC + C^2}) \quad (5)$$

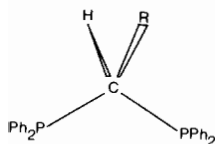


Fig. 1. Schematic view of the phosphine ligands $(\text{Ph}_2\text{P})_2\text{CHR}$ ($\text{R} = \text{H}, \text{Me}, \text{SiMe}_3, \text{PPh}_2$).

with $A = |J(^{31}\text{P}-^{31}\text{P})|$; $B = |J(^{107}\text{Ag}-^{31}\text{P})|$ and $C = |J(^{109}\text{Ag}-^{31}\text{P})|$. Bearing in mind that $J(^{109}\text{Ag}-^{31}\text{P}) = 1.149 J(^{107}\text{Ag}-^{31}\text{P})$ and calculating (a - d) and (b - c) from the spectra equations (4) and (5) are reduced to two equations with two unknowns: $J(^{31}\text{P}-^{31}\text{P})$ and $J(^{107}\text{Ag}-^{31}\text{P})$. The values thus calculated are indicated in Table V.

These values were used to simulate the spectra by adding together the different spin systems $\text{P}_3(^{107}\text{Ag})_3$, $\text{P}_3(^{107}\text{Ag})_2(^{109}\text{Ag})$, $\text{P}_3(^{107}\text{Ag})(^{109}\text{Ag})_2$ and $\text{P}_3(^{109}\text{Ag})_3$ with their statistical weight factor. The result for $\text{R} = i\text{-Pr}$ is shown in Fig. 4d. No attempt was made to optimize the simulation.

Results and Discussion

The Phosphine Ligands

The phosphine ligands $(\text{Ph}_2\text{P})_2\text{CHR}$ ($\text{R} = \text{H}, \text{PPh}_2, \text{Me}, \text{SiMe}_3$) used throughout this paper have in common two, and in one case three, Ph_2P units bonded to the same carbon atom (Fig. 1). Effects of substituents R at the central carbon atom on complex formation may be studied by several spectroscopic techniques. To help with spectral interpretation, we first studied in detail the ^1H , ^{13}C and ^{31}P NMR data of the non-coordinated ligands (Table I), some of which were reported previously [6-8].

The ^{13}C NMR data need special attention. The number of different phenyl groups observed for $(\text{Ph}_2\text{P})_2\text{CHR}$ is one when R is H or PPh_2 , and two when R is Me or SiMe_3 . This can be ascribed to the fact that in $(\text{Ph}_2\text{P})_2\text{CHR}$ ($\text{R} = \text{H}, \text{PPh}_2$) the phosphorus atoms are homotopic, while the phenyl groups are enantiotopic [16]. This results in isochronous chemical shifts and spin coupling equivalence for the ^{13}C nuclei in achiral solvents. However, in $(\text{Ph}_2\text{P})_2\text{CHR}$ ($\text{R} = \text{Me}, \text{SiMe}_3$) the phosphorus atoms are enantiotopic [16]. In this case the two aryl groups connected to each of these phosphorus atoms are diastereotopic because the third substituent to this phosphorus atom, *i.e.* the carbon centre $\text{CH}(\text{R})\text{-PPh}_2$, represents a centre of dissymmetry (see Fig. 2). This results in chemical shift and spin coupling non-equivalence for the ^{13}C nuclei of the two aryl groups. Appel, who synthesized $(\text{Ph}_2\text{P})_2\text{C}(\text{H})\text{SiMe}_3$ and studied its ^{13}C NMR spectrum, did not report this feature [6].

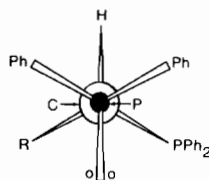


Fig. 2. Newman projection of $(\text{Ph}_2\text{P})_2\text{CHR}$ along one $\text{C}-\text{P}$ axis, showing the diastereotopic phenyl rings.

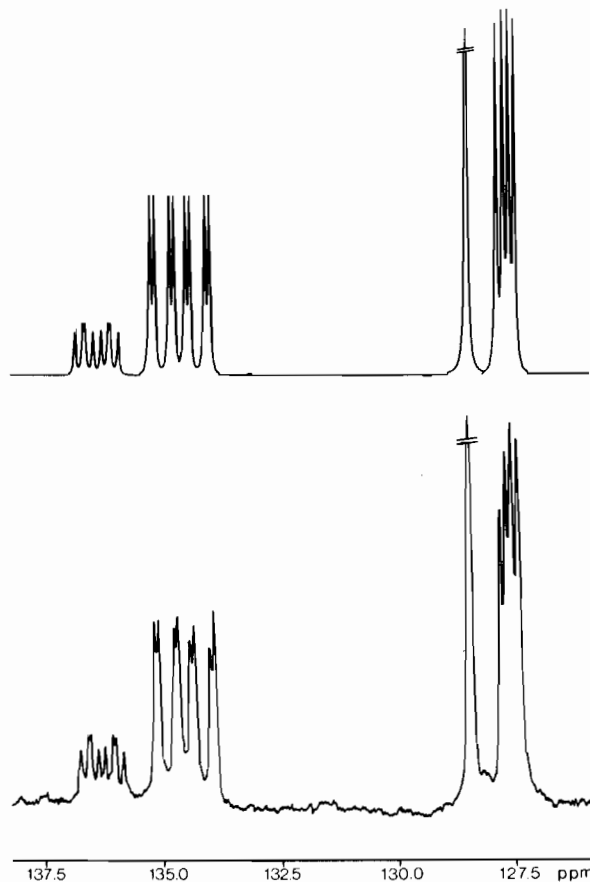


Fig. 3. The ^{13}C NMR spectrum of $(\text{PPh}_2)_3\text{CH}$ at ambient temperature (bottom) and computer simulation using calculated parameters (top).

As regards the $J(^{31}\text{P}-^{13}\text{C})$ coupling, observed for the different carbon atoms, only C_4 showed no such coupling. The resonance patterns observed for C_1 , C_2 and C_3 in $(\text{Ph}_2\text{P})_2\text{CHR}$ ($\text{R} = \text{H}, \text{Me}, \text{SiMe}_3$) were all quasi-triplets, due to virtual coupling between the phosphorus atoms in the $^{13}\text{CPP}'$ spin system. Simulation of the patterns gave the value of $|^xJ(^{31}\text{P}-^{13}\text{C}) + ^2+^xJ(^{31}\text{P}-^{13}\text{C})|$ [17].

The resonance patterns for C_1 , C_2 and C_3 in $(\text{Ph}_2\text{P})_3\text{CH}$ are more complicated, because we now deal with a $^{13}\text{CPP}'_2$ spin system. In this case, simulation of the observed resonance patterns yielded both

TABLE II. Analytical Data and Some Characteristic Infrared Absorptions for the Silver Phosphine Complexes.^a

Compound ^b	Found (calcd) %			IR absorptions (cm ⁻¹) ^c	
	C	H	P	$\nu(\text{CO}_2)_{\text{asymm.}}$	$\nu(\text{CO}_2)_{\text{symm.}}$
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CMe})_2$	46.54(48.60)	4.53(3.91)	8.44(8.38)	1550	1401
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CEt})_2$	49.48(49.90)	4.33(4.32)	8.55(8.30)	1560	1390
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$	51.03(51.18)	4.70(4.68)	8.25(8.00)	1560	1380
$\{[\text{Ph}_2\text{P})_2\text{CH}_2]\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$	49.59(49.37)	4.52(4.29)	7.43(7.60)		
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CC}_6\text{H}_5)_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$	53.16(53.60)	3.79(3.73)	7.43(7.00)	1555	1380
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CMe})_2 \cdot \text{CH}_2\text{Cl}_2$	45.02(45.75)	3.83(3.93)	7.51(7.63)	1560	1400
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CEt})_2 \cdot \text{CH}_2\text{Cl}_2$	48.44(48.61)	4.47(4.36)	7.80(7.72)	1565	1385
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$	50.17(49.86)	4.85(4.69)	7.81(7.47)	1560	1390
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CC}_6\text{H}_5)_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$	54.90(54.33)	3.97(3.91)	7.08(6.93)	1563	1385
$\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CMe})_3$	49.99(48.29)	4.14(3.74)	9.09(8.70)	1560	1410
$\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CEt})_3 \cdot \text{CH}_2\text{Cl}_2$	47.09(47.17)	4.15(4.01)	7.79(7.77)	1560	1385
$\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{C-i-Pr})_3 \cdot \text{CH}_2\text{Cl}_2$	48.83(48.48)	4.56(4.36)	7.99(7.50)	1555	1405
$\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CC}_6\text{H}_5)_3 \cdot \text{CH}_2\text{Cl}_2$	51.17(52.85)	3.52(3.58)	7.16(6.93)	1550	1385
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{BF}_4)_2$	51.19(51.84)	4.14(3.80)	9.82(10.70)		
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{BF}_4)_2$	51.89(52.64)	4.23(4.05)	9.46(10.45)		

^aAll compounds are white. ^bAmount of solvent molecule based on ¹H NMR spectra in CDCl₃. ^cIn KBr.

TABLE III. ¹H NMR Data of the Silver Phosphine Complexes.^a

Compound	Phosphine ligand			Carboxylate		
	H _{aryl}	H _{CPx}	H _{Me}	H _α	H _β	¹ H _{ortho}
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CMe})_2$	7.3	3.1(10)t		1.91 s		
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CEt})_2$	7.3	3.3(10)t		2.2 q	1.0 t	
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2$	7.2	3.3(10)t		2.5 m	1.2 d	
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CC}_5\text{H}_6)_2$	7.2	2.8(10)t				8.1
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CMe})_2$	7.4	3.6 ^b	1.2(18) ^c	2.0 s		
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CEt})_2$	7.4	3.6 ^b	1.3(18) ^c	2.2 q	1.2 t	
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2$	7.2	3.7 ^b	1.2(18) ^c	2.5 m	1.2 d	
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CC}_5\text{H}_6)_2$	7.2	3.5 ^b	1.0(18) ^c			8.0
$\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CMe})_3$	7.0 and 7.6	4.4 ^b		2.16 s		
$\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CEt})_3$	7.0 and 7.6	4.6 ^b		2.4 q	1.2 t	
$\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{C-i-Pr})_3$	7.1 and 7.8	4.6 ^b		2.6 m	1.3 d	
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{Ag}_2(\text{BF}_4)_2$	7.3	3.4 ^b				
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2(\text{BF}_4)_2$	7.2	3.5 ^b	1.0 ^b			

^aRecorded in CDCl₃; δ (in ppm) relative to TMS; J(³¹P-¹H) between parentheses. ^bBroad. ^cDoublet of triplets; J(¹H-¹H)_{vicinal} = 7 Hz.

^xJ(³¹P-¹³C) and ^{2+x}J(³¹P'-¹³C) together with their relative signs (See Fig. 3).

Inspection of the obtained values reveals no correlation between the coupling constants and the number of bonds separating the two coupled nuclei. Nevertheless, it is clear that $|\text{}^x\text{J}(\text{}^{31}\text{P}-\text{}^{13}\text{C})|$ drops drastically when $x \geq 4$.

Furthermore, the sum of $|\text{}^x\text{J}(\text{}^{31}\text{P}-\text{}^{13}\text{C}) + \text{}^{x+2}\text{J}(\text{}^{31}\text{P}'-\text{}^{13}\text{C})|$ calculated for C₂ and C₃ in (Ph₃P)₃CH corresponds well with those observed for the ligands (Ph₂P)₂CHR (R = H, Me, SiMe₃). For C₁ this correlation is less good; clearly $|\text{}^x\text{J}(\text{}^{31}\text{P}-\text{}^{13}\text{C})|$ is most sensitive to substitution at the central bridging carbon atom (C₅).

TABLE IV. ^{13}C NMR Data of Carboxylatosilver Phosphine Complexes.^a

Compound	Aryl group ^b			CHR ^c (C(5))	R ^c (C(6))	Carboxylate		
	C(2)	C(3)	C(4)			C _{CO₂}	C _{CH}	C _{CH₃}
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2$	133.0(17.2)	128.7(9.8)	130.5	28.4(11.9)		183.9	36.6	20.5
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2$	134.2(16.9)	129.0(12.2)	131.2	29.0(13.5)	14.5(5.5)	184.3	36.7	20.5
	134.1(17.1)	128.5(12.2)	130.8					
$\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{C-i-Pr})_3$	135.0(19.5)	128.5(11.1)	130.9	29.7(br)		183.8	36.6	20.6

^aRecorded in CDCl_3 : δC (in ppm) relative to TMS. ^b $|^x\text{J}(^{31}\text{P}-^{13}\text{C}) + ^{2+x}\text{J}(^{31}\text{P}-^{13}\text{C})|$ between parentheses. ^c $|^1\text{J}(^{31}\text{P}-^{13}\text{C})|$ between parentheses.

The Silver Carboxylato Complexes

Reaction of the different phosphines with silver carboxylates gave compounds of formulae $\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CR})_2$, $\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CR})_2$ and $\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CR})_3$ (R = Me, Et, i-Pr, C_6H_5), as evidenced by elemental analytical and spectroscopic data (Tables II and III). They crystallized with solvent molecules in the lattice and this was confirmed by the ^1H NMR spectra. The compound $\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CMe})_2$ was reported by ourselves in a previous paper [4]. Reactions of $(\text{Ph}_2\text{P})_2\text{CH}_2$ with halogeno silver compounds AgX (X = Cl, Br, I) are reported to give both 1:1 and 1:2 complexes [18].

The present complexes have a rather good solubility in most common polar solvents, which increases from R = Me to R = i-Pr, and as a result the ^1H NMR spectra could be recorded which establish the phosphine-carboxylato ratio. The chemical shifts for the R groups of the carboxylato ligands are almost insensitive to the phosphine ligand used (Table III), which points to similar structural features in these complexes. Also from the similarity of the $\nu(\text{CO}_2)$ frequencies in the IR spectra (Table II) one can deduce that the carboxylato groups in these complexes are bonded in the same way.

For the most soluble derivatives, *i.e.* $\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2$, $\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2$ and $\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{C-i-Pr})_3$, the ^{13}C NMR spectra were recorded and these results are in Table IV. The spectra reveal the presence of both carboxylato groups and phosphine ligands. The chemical shifts of the carboxylato groups are very similar for the three compounds, indicating that their coordination modes may be related.

As in the free ligands, one set of phenyl groups is again observed for the $(\text{Ph}_2\text{P})_2\text{CH}_3$ and $(\text{Ph}_3\text{P})_3\text{CH}$ complexes. This indicates that the metal atoms must possess a symmetrical arrangement with respect to the ligand on the NMR time scale otherwise the phenyl groups would have become diastereotopic. The observation of diastereotopic phenyl groups for

$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{C-i-Pr})_2$, as in the free ligand, can be explained by the dissymmetry of the central carbon atom.

The $\text{J}(^{31}\text{P}-^{13}\text{C})$ coupling constants within the ligands have changed upon coordination to the silver carboxylates, namely a decrease for C_2 , C_5 and C_6 and an increase for C_3 . These features are generally observed for phenylphosphino ligands coordinated to transition metals [19].

The ^{31}P NMR spectra of all compounds showed a temperature dependence which is normally observed for silver phosphino complexes [4, 20]. At ambient temperature one broadened line was observed. On lowering the temperature this broad line split into two broad bands and finally sharpened into a doublet of multiplets at about -50°C . It was possible to simulate these multiplets using the A part of the sum of AA'XX' spin systems for the compounds $\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CR})_2$ and $\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CR})_2$, and AA'A''XX'X'' spin systems for the compounds $\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CR})_3$, with all combinations of silver isotopes ^{107}Ag and ^{109}Ag . The procedure used is outlined in the Experimental Section and the results are summarized in Table V. Examples for both systems are shown in Fig. 4.

From these calculations there is a large $\text{J}(^{107}\text{Ag}-^{31}\text{P})$ coupling constant of about 650 Hz, which is comparable with the $^1\text{J}(^{107}\text{Ag}-^{31}\text{P})$ coupling constants observed for other complexes with one phosphorus atom coordinated to each silver atom [4]. For the compounds $\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CR})_2$ and $\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CR})_2$ $^1\text{J}(^{107}\text{Ag}-^{31}\text{P})$ and $^1\text{J}(^{109}\text{Ag}-^{31}\text{P})$ could be calculated independently and their ratio (1.153) is fairly close to the gyromagnetic ratio of 1.149 of the two silver isotopes.

Furthermore, for these compounds further $\text{J}(^{107,109}\text{Ag}-^{31}\text{P})$ couplings were obtained with much smaller absolute value and of opposite sign to the former one. The latter is likely to be the three bond coupling occurring via the phosphine skeleton: $\text{Ag}-\text{P}-\text{C}-\text{P}'$. $^3\text{J}(\text{M}-\text{P}-\text{C}-\text{P}')$ couplings can be expected to be present in several other $(\text{Ph}_2\text{P})_2\text{CH}_2$

TABLE V. ^{31}P NMR Data for Silver Phosphine Complexes.^a

	δ	$2J(^{31}\text{P}-^{31}\text{P})$	$1J(^{107}\text{Ag}-^{31}\text{P})$	$1J(^{109}\text{Ag}-^{31}\text{P})$	$3J(^{107}\text{Ag}-^{31}\text{P})^c$	$3J(^{109}\text{Ag}-^{31}\text{P})^c$
A Dinuclear silver carboxylato complexes^b						
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CMe})_2]$	6.5	175	634	732	-5.9	-7.2
$\{[\text{Ph}(\text{C}_2\text{P})_2\text{CH}_2]\text{Ag}_2(\text{O}_2\text{CET})_2]$	5.7	177	629	725	-6.2	-7.8
$\{[\text{Ph}(\text{C}_2\text{P})_2\text{CH}_2]\text{Ag}_2(\text{O}_2\text{C}-i\text{-Pr})_2]$	6.5	157	543	743	-3.8	-4.6
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CC}_5\text{H}_6)_2]$	5.0	165	659	755	-12.3	-14.0
$\{[\text{Ph}(\text{C}_2\text{P})_2\text{CHMe}]\text{Ag}_2(\text{O}_2\text{CMe})_2]$	25.2	170	636	735	-4.5	-5.2
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CET})_2]$	24.5	168	636	735	-3.7	-5.1
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{C}-i\text{-Pr})_2]$	23.9	167	635	733	-3.2	-5.2
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CC}_5\text{H}_6)_2]$	24.8	175	649	750	-4.9	-6.0
B Trinuclear silver carboxylato complexes^d						
$\{[\text{Ph}_2\text{P}_3\text{CH}]\text{Ag}_3(\text{O}_2\text{CMe})_3]^e$	18.6		633			
$\{[\text{Ph}_2\text{P}_3\text{CH}]\text{Ag}_3(\text{O}_2\text{CET})_3]$	20.8	121	625	718		
$\{[\text{Ph}_2\text{P}_3\text{CH}]\text{Ag}_3(\text{O}_2\text{C}-i\text{-Pr})_3]$	20.1	112	630	724		
C Dinuclear silver tetrafluoroborate complexes^d						
$\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{Ag}_2(\text{BF}_4)_2$	11.5	129	505	583	-0.6	-1.5
$\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2(\text{BF}_4)_2$	25.2	146	493	572	-3.4	-3.8

^a δ (in ppm) relative to H_3PO_4 ; coupling constants calculated by the procedure given in the experimental section. ^bRecorded in CDCl_3 . ^cAccuracy in coupling constants not better than ± 0.5 Hz. ^dRecorded in CD_2Cl_2 . ^eSpectrum incompletely resolved.

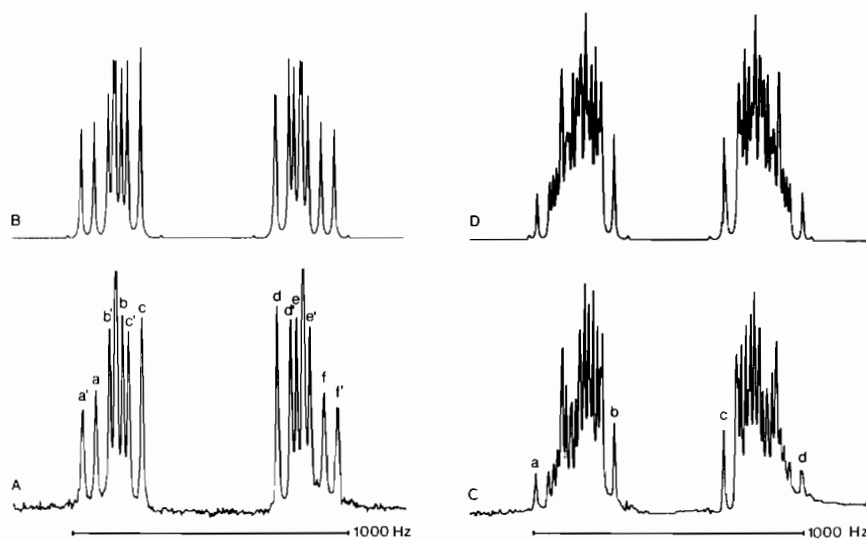


Fig. 4. The ^{31}P NMR spectra of $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{C-}i\text{-Pr})_2]$ in CDCl_3 at -60°C (a) and of $[\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{C-}i\text{-Pr})_3]$ in CD_2Cl_2 at -80°C (c) and the computer simulations (b and d, respectively) using calculated parameters. The indicated symbols are used in the calculation (see Experimental Section).

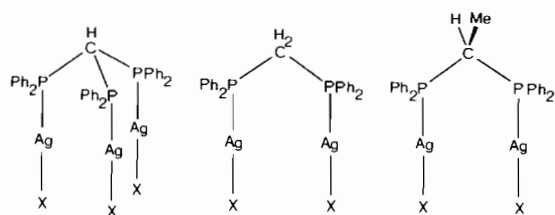


Fig. 5. Schematic representation of the structure of the phosphine silver carboxylates. X denotes the carboxylate groups (see text).

complexes, but in most cases it cannot be separated from other contributory coupling mechanisms [9, 39]. Although the values now obtained for these couplings are not particularly accurate, the average $J(^{109}\text{Ag}-^{31}\text{P})/J(^{107}\text{Ag}-^{31}\text{P})$ ratio is close to the theoretical gyromagnetic ratio for $^{109}\text{Ag}/^{107}\text{Ag}$ and thus gives confidence to our assignment.

In addition to these silver–phosphorus couplings, a $^2J(^{31}\text{P}-^{31}\text{P})$ coupling constant is obtained of about 170 Hz for $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CR})_2]$ and $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CR})_2]$ and of 120 Hz for $[\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CR})_3]$.

The above data indicate that the coupling constants are rather insensitive to the substituent at the carboxylate group. Substitution at C_5 resulted in a noticeable change of $^2J(^{31}\text{P}-^{31}\text{P})$ only when $\text{R} = \text{PPh}_2$.

Structural implications

From the present results it is concluded that in the phosphino silver carboxylates each silver atom is coordinated to one phosphorus atom. Thus, dinuclear

and trinuclear silver phosphine units are formed (Fig. 5).

Similar dinuclear phosphine structures have been reported for $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Au}_2\text{Cl}_2]$ [21] and $[\text{MeN}(\text{PPh}_2)_2\text{Ag}_2\text{Br}_2]_2$ [18a]. The coordination around the silver atoms will be completed by coordination of the carboxylate groups either as chelating ligands or as bridging ligands within one phosphine silver unit or between two different units.

This requires for the $\{(\text{Ph}_2\text{P})_3\text{CH}\}$ complexes that the silver atoms must lie at the same side of the ligand, which is supported by the ^{13}C NMR data (*vide supra*). Structural models indicate not only that this is possible but that, furthermore, adjacent phenyl rings on neighbouring phosphorus atoms are likely to be co-parallel. Such graphite-like interactions are observed in many complexes with $(\text{Ph}_2\text{P})_2\text{CH}_2$ as a bridging ligand [17, 22, 23]. This feature is found with concomitant puckering of the metal–ligand ring $\text{MPCP}'\text{M}'$. Graphite-like interactions are also observed in compounds containing three PPh_2 units such as in $[(\text{triphos})\text{Co}(\eta^8\text{-C}_7\text{H}_8)](\text{ClO}_4)$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) [24]. It is of interest that the latter complex and $[\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ag}_3(\text{O}_2\text{CR})_3]$ have as a common structural feature that the three PPh_2 units are connected to the same atom, *i.e.* the Co-atom and the C-atom, respectively. Recently, the carbonyl complexes $[\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Rh}_4(\text{CO})_9]$ [25a] and $[\{(\text{Ph}_2\text{P})_3\text{CH}\}\text{Ni}_3(\text{CO})_6]$ [25b] have been reported to contain $(\text{Ph}_2\text{P})_3\text{CH}$ as a tri-metal bridging ligand while the compound $[\{\text{MeSi}(\text{PBu}_2)_3\}\text{Ru}_3(\text{CO})_9]$ also contains a triangle of metal atoms captured by a ligand containing a P_3X unit [25c].

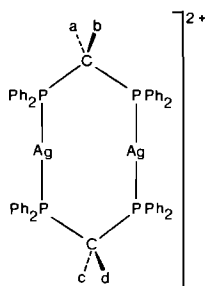


Fig. 6. Schematic structure of the dimeric dication $[\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2\text{Ag}_2]^{2+}$, R = H: one isomeric form with a, b, c, d = H. R = Me: two isomeric forms: a, c = H, b, d = Me, and a, d = H, b, c = Me.

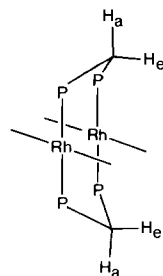


Fig. 7. Illustration of the puckering of the M-P-C-P'-M' units in double bridged dinuclear $(\text{Ph}_2\text{P})_2\text{CH}_2$ compounds.

The Silver Tetrafluoroborato Complexes

In addition to the silver carboxylates the complex formation of AgBF_4 with the $(\text{Ph}_2\text{P})_2\text{CHR}$ ligands was also investigated, in order to study the possible formation of salt-like structures containing, for example, $\text{Ag}_2\text{L}_2^{2+}$ cations. Such cations would have structural features quite similar to those of $[(\text{Ph}_2\text{P})_2\text{CH}_2]$ bridged dinuclear compounds of Pt [26] and Rh [22, 23] (*vide infra*).

Reaction of AgBF_4 with the various phosphines gave compounds of the formulae $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_n\text{Ag}_n](\text{BF}_4)_n$, $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_n\text{Ag}_n](\text{BF}_4)_n$ and $[\{(\text{Ph}_2\text{P})_3\text{CH}\}_2\text{Ag}_3](\text{BF}_4)_3$. Evidence for these formulations came from elemental analytical data (Table II), IR and in some instances NMR spectroscopy. The IR absorption pattern for the BF_4 ion was similar to that reported for KBF_4 [27] and this indicates that in the solid no abnormal distortions are present *i.e.* coordination of BF_4 to silver is absent or only very weak [28].

Detailed analysis of the structure of the compound $[\{(\text{Ph}_2\text{P})_3\text{CH}\}_2\text{Ag}_3](\text{BF}_4)_3$ in solution by NMR spectroscopy was hampered by its insolubility. For the other two compounds the ^{31}P NMR spectra could be recorded and showed to consist of the A parts of different AA'XZ''A''X' patterns as the result of different combinations of silver isotopes. The observation of such patterns can be interpreted by a structure for these complexes consisting of two silver atoms bridged by two phosphine ligands, which would result in a linear coordination around each silver atom by two phosphorus atoms (Fig. 6). Unraveling the spectra in a fashion similar to that described above for the dinuclear carboxylato complexes yielded $J(^{107,109}\text{Ag}-^{31}\text{P})$ and $J(^{31}\text{P}-^{31}\text{P})$ coupling constants as summarised in Table V. The observed reduction of $^1J(^{107,109}\text{Ag}-^{31}\text{P})$ compared with the carboxylato compounds having only one P-atom coordinated to each Ag atom is in agreement with the proposed structure. Recently, $[\text{Ag}\{\text{P}(\text{mesityl})_3\}_2]\text{X}$ has been reported, for which a linear P-Ag-P coordination geometry about Ag was adopt-

ed, and this has a $^1J(^{107}\text{Ag}-^{31}\text{P})$ value of 425 Hz [29].

On the basis of the above deduced dimeric structure the dication $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2]^{2+}$ can exist in two distinct stereoisomeric forms; one isomer has the methyl groups at the same side of the molecular plane, while the second isomer has the methyl groups at opposite sides of this plane (Fig. 6). In principle these stereoisomers have different NMR spectra. However, only one ^{31}P pattern was observed for $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2](\text{BF}_4)_2$, which suggests either that only one isomer is present in solution, or that the chemical shift difference between the two stereoisomers is too small to be observed.

An indication for the first possibility might be obtained from the following considerations, concerning puckering of the M-P-C-P'-M' fragments. Several crystal structures of double bridged dinuclear $\text{M}_2\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2$ compounds, including many Pt and Rh complexes, show puckering in such a way that the two CH_2 units bend out of the molecular plane in the same direction (see Fig. 7). Meanwhile the phenyl groups on the other side of the molecular plane are bent towards each other resulting in a graphite like interaction [2, 11, 23]. This puckering results in inequivalent CH_2 H atoms, because two H atoms (H_a) have an axial while the others (H_e) have an equatorial orientation (Fig. 7). With regard to this, substitution of either H_a or H_e by a methyl group might result in an energy difference for the possible stereoisomers. If the energy difference is large enough, substitution will be regioselective. In that case only one isomer, *i.e.* either the $\text{H}_a\text{H}_e'$ or $\text{H}_a\text{H}_a'$ substituted compound might be formed for $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{Ag}_2](\text{BF}_4)_2$. Evidence in favour of the second possibility is that the methyl groups are a long way from the stereochemical determining site *i.e.* Ag.

Unfortunately, the ^1H NMR spectrum did only show a very broad unresolved methyl resonance, while the low solubility of the compound hampered the study of the ^{13}C NMR spectra, which might have

TABLE VI. Characteristic Infrared Absorptions for the Rhodium Phosphine Complexes (cm^{-1}).^a

Complex	Frequency (cm^{-1})	Mode	Reference
$[\text{Rh}_2\text{Cl}(\text{CO})_2\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2][\text{RhCl}_2(\text{CO})_2]$	2059, 1998, 1980 312, 284	$\nu(\text{CO})$ $\nu(\text{H}-\text{Cl})$	
$[\text{RhCl}(\text{CO})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2]$	1970	$\nu(\text{CO})$	
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{HCl}](\text{BF}_4)$	2105, 2099	$\nu(\text{M}-\text{H})$	
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{HCl}](\text{BF}_4)$	2078	$\nu(\text{M}-\text{H})$	
$[\text{Rh}\{(\text{Ph}_2\text{P})(\text{CH}_2)_2\text{PPh}_2\}_2\text{HCl}](\text{BF}_4)$	2078	$\nu(\text{M}-\text{H})$	
$[\text{Rh}\{(\text{Ph}_2\text{P})(\text{CH}_2)_3\text{PPh}_2\}_2\text{HCl}](\text{BF}_4)$	2110	$\nu(\text{M}-\text{H})$	
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{O}_2](\text{BF}_4)$	870	$\nu(\text{O}_2)$	
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{O}_2](\text{BF}_4)$	875, 869	$\nu(\text{O}_2)$	
$[\text{Rh}\{(\text{Ph}_2\text{P})(\text{CH}_2)_2\text{PPh}_2\}_2\text{O}_2](\text{BF}_4)$	880	$\nu(\text{O}_2)$	
$[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2\text{O}_2](\text{BF}_4)$	885	$\nu(\text{O}_2)$	
$[\text{RhCl}_2(\text{CO})_2]^-$	2060, 1975 318, 291	$\nu(\text{CO})$ $\nu(\text{M}-\text{Cl})$	22
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{HCl}]\{\text{BPh}_4\}$	2080	$\nu(\text{M}-\text{H})$	33
$[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2\text{HCl}]\text{Cl}$	2090	$\nu(\text{M}-\text{H})$	36
$[\text{Rh}(\text{CO})_2(\mu\text{-Cl})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}](\text{BF}_4)$	1995, 1978	$\nu(\text{C}-\text{C})$	22

^aRecorded in KBr disk.

shown the number of different phenyl groups and thus the number of isomers.

Bonding Properties of the Silver-Phosphine Complexes

In order to study the silver-phosphorus interaction for the Ag-P system in $[\{(\text{Ph}_2\text{P})_2\text{CHR}\}\text{Ag}_2(\text{O}_2\text{CR})_2]$ and the P-Ag-P system in $[\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2\text{Ag}_2](\text{BF}_4)$, we compared these complexes with some P-X systems described in the literature.

Grim and Walton stated that the chemical shifts of the bridging methylene protons in $[\text{H}_2\text{C}(\text{PPh}_2\text{X})(\text{PPh}_2\text{Y})]$ (X, Y = O, S, Se, Me or electron lone pair) can be used to infer bonding properties of the adjacent X-P and Y-P bonds [30]. They derived the equation

$$\delta_{\text{CH}_2}(\text{ppm}) = 1.57 \sum q_i + 2.65$$

where q_i is the charge generated on each phosphorus atom. When the above silver complexes obey this equation, the following charges can be deduced from the observed chemical shifts for the C(5) hydrogen atoms: +0.20 charge for $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CR})_2]$ and +0.24 charge for $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{Ag}_2](\text{BF}_4)_2$. Since the downfield shift of 0.55 ppm in $[\{(\text{Ph}_2\text{P})_2\text{CHMe}\}\text{Ag}_2(\text{O}_2\text{CR})_2]$ is comparable with that of 0.59 ppm in $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CR})_2]$, the generated charge will be of the same order of magnitude. The values of q_i , which provide an indica-

tion of the charge delocalisation in the P-Ag bonds, therefore seem to be reasonable.

For the binuclear unit $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{Ag}_2]^{2+}$, in which each silver cation is coordinated by two phosphorus atoms, we can deduce that almost 50% of the positive charge of each silver cation is delocalised over those two phosphorus atoms. The fact that in neutral $[\{(\text{Ph}_2\text{P})_2\text{CH}_2\}\text{Ag}_2(\text{O}_2\text{CR})_2]$ a +0.20 charge is still generated at each phosphorus atom might be an indication of a high covalent character for the Ag-P bond in that compound, which is in line with the observation of a large $J(^{107,109}\text{Ag}-^{31}\text{P})$ coupling constant (*vide supra*).

The ^{13}C NMR data of the isobutyrate complexes support these conclusions (Table IV) with the carbon atoms of the phenyl groups being shifted downfield as compared with the free ligand systems. This deshielding, which is most pronounced for C₄, is in line with the following canonical forms:



These canonical forms will have a high contribution to the overall electron distribution in the silver complexes *i.e.* when a positive charge is generated on the phosphorus atom by coordination.

Binuclear Rhodium Complexes

Reactions of $(\text{Ph}_2\text{P})_2\text{CH}_2$ and related ligands, such as $(\text{Ph}_2\text{As})_2\text{CH}_2$, with $[\text{RhCl}(\text{CO})_2]_2$ are reported

TABLE VII. ^{31}P NMR Data of the Rhodium Phosphine Complexes.^a

A Dinuclear Rhodium Complexes				
$[\text{RhCl}(\text{CO})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}]_2$				16.0(114)
$[\text{Rh}_2\text{Cl}(\text{CO})_2\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2][\text{RhCl}_2(\text{CO})_2]$				34.1(111)
$[\text{Rh}_2\text{Cl}(\text{CO})_2\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2](\text{BPh}_4)$				16.1(113) ^b
B Mononuclear Rhodium Complexes				
Compound: Phosphine (L)	$[\text{RhL}_2](\text{BF}_4)$	$[\text{RhL}_2\text{HCl}](\text{BF}_4)$	$[\text{RhL}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$	$[\text{RhL}_2\text{O}_2](\text{BF}_4)$
$(\text{Ph}_2\text{P})_2\text{CHMe}$	-6.52(116) ^k -2.92(118) ^k	-4.28(85) ^k +2.57(81) ^k		-1.14(112) -17.43(83) (31) ^c
$(\text{Ph}_2\text{P})_2\text{CH}_2$	-23.61(115)	-16.38(83) ^d	-25.14(77) (390) ^e	-13.40(109) -30.49(80) (35) ^{c,f}
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	57.89(133) ^g	+52.36(94)	42.62(87.5) (387) ^e	51.3 (126) 44.3 (92) (7.7) ^{c,g}
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$	8.08(131) ^h	2.96(91) ⁱ		15.52(123) -12.40(85) (30) ^{c,j}

^aRecorded in CDCl_3 ; δ (in ppm) relative to H_3PO_4 ; $J(^{103}\text{Rh}-^{31}\text{P})$ between parentheses. ^bRef. 32. ^c $J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{B})$. ^d-16 δ (83 Hz) ref. 33. ^e $J(^{199}\text{Hg}-^{31}\text{P})$. ^f $\text{A}_2\text{B}_2\text{X}$ pattern of decomposition product: -25.8 δ (95 Hz); -43.3 δ (75 Hz); $J(^{31}\text{P}-^{31}\text{P})$ 31 Hz. ^gValues from ref. 37. ^h $X = \text{Cl}$ 6.4 δ (132 Hz), ref. 38. ⁱ $X = \text{Cl}$, 1.9 δ (90 Hz), ref. 38. ^j $X = \text{Cl}$, -15.0 δ (122 Hz), -13.8 δ (85 Hz) $J(^{31}\text{P}-^{31}\text{P})$ 30 Hz, ref. 38. ^kTwo isomers.

TABLE VIII. ^{13}C NMR Data of Rhodium Phosphine Complexes.^a

Compound	Aryl group ^b			CHR (C(5))	R (C(6))
	C(2)	C(3)	C(4)		
$[\text{RhCl}(\text{CO})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}]_2$	134.1	129.4	132.0	-	
$[\text{Rh}(\text{CO})_2\text{Cl}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2][\text{RhCl}_2(\text{CO})_2]$	135.8	129.5	132.5	25.9	12.1
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{HCl}](\text{BF}_4)$	131.6	128.7	131.0	-	
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{HCl}](\text{BF}_4)$	132.9	129.1	131.8	-	
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{HCl}](\text{BF}_4)$	132.8	128.5	131.3	-	
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{HCl}](\text{BF}_4)$	135.8 ^c	128.7	128.3	132.1 ^c	-
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{HCl}](\text{BF}_4)$	131.6 ^c	128.4	128.1	-	-
$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$	133.6	130.2	132.4	-	
	131.3	128.7	131.8	-	

^aRecorded in CDCl_3 ; δ C (in ppm) relative to TMS. ^bSecond order patterns due to virtual coupling between the various phosphorus atoms. ^cBroad, due to overlap of the resonances of different phenyl C atoms.

to give binuclear complexes with two bridging ligands [9, 31]. Therefore, complex formation of $(\text{Ph}_2\text{P})_2\text{-CHR}$ ligands was investigated with rhodium compounds in addition to the silver complexes, in order to study the influence of R on the conformations of the dimers.

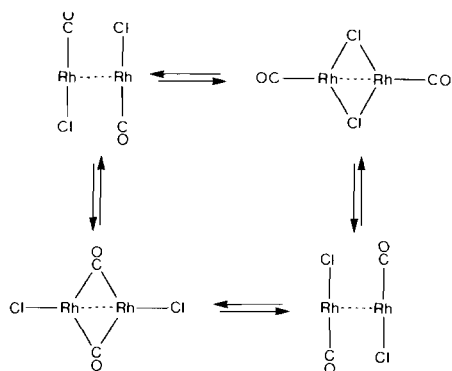
Reaction of $[\text{RhCl}(\text{CO})_2]_2$ with two equivalents of diphosphine, $(\text{Ph}_2\text{P})_2\text{CH}_2$ or $(\text{Ph}_2\text{P})_2\text{CHMe}$, resulted in formation of compounds with the for-

mulae $[\text{RhCl}(\text{CO})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}]_2$ and $[\text{Rh}_2\text{Cl}(\text{CO})_2\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2][\text{RhCl}_2(\text{CO})_2]$, respectively, based on elemental analytical data and IR data (Table VI). $[\text{RhCl}(\text{CO})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}]_2$ is reported to have a binuclear structure with two bridging phosphine ligands [9]. Ionic $[\text{Rh}_2\text{Cl}(\text{CO})_2\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2](\text{BF}_4)$ has also a binuclear structure but in addition to two bridging $(\text{Ph}_2\text{P})_2\text{CH}_2$ ligands the two rhodium atoms are bridged by one chlorine atom [22]. In the case

of $(\text{Ph}_2\text{P})_2\text{CHMe}$, instead of $(\text{Ph}_2\text{P})_2\text{CH}_2$, a similar arrangement could theoretically result in the formation of three isomeric forms, two having the methyl groups at the same side of the molecular plane, but with the bridging chlorine atom either at the same or opposite side, and a third having the methyl groups at opposite sides of that plane.

The ^{31}P NMR spectra of $[\text{RhCl}(\text{CO})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}]_2$ and $[\text{Rh}_2\text{Cl}(\text{CO})_2\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2][\text{RhCl}_2(\text{CO})_2]$ appeared to be very similar. Both consisted of the A part of one AA'XA''A'''X' pattern with $J(^{103}\text{Rh}-^{31}\text{P})$ coupling constants of comparable magnitude (Table VII), suggesting the presence of only one of the three possible isomers for the $(\text{Ph}_2\text{P})_2\text{CHMe}$ compound. This prompted us to investigate the ^{13}C NMR spectra of the two Rh compounds, the data of which are reported in Table VIII.

For the $(\text{Ph}_2\text{P})_2\text{CH}_2$ complex one set of phenyl groups was observed, which is remarkable in view of the close proximity of these groups to coordinated CO and Cl. This might be explained by either i) a too small difference generated by CO and Cl or ii) a fast exchange between CO and Cl. Since the generation of chemical shift differences between geminal adjacent phenyl groups has been observed for other substituents at rhodium (*i.e.* H, Cl and Hg, Cl, *vide infra*) explanation i) seems less likely. An exchange between CO and Cl, which might involve either bridging carbonyls or bridging halogens, as depicted in Scheme I, seems more likely, because related dinuclear compounds with either a bridging halogen



Scheme I. Exchange mechanism for CO and Cl in $[\text{RhCl}(\text{CO})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}]_2$.

or carbonyl have been reported [22, 31]. Furthermore, an exchange process between bridging and terminal carbonyl groups was proposed for the reversible coordination reaction of CO to the chlorine bridged compound $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2](\text{PF}_6)$ [32].

For the $(\text{Ph}_2\text{P})_2\text{CHMe}$ complex two sets of phenyl groups were observed in the ^{13}C NMR spectrum

(Table VIII). This result is in agreement with the existence of only one isomeric form, in which two sets of phenyl groups are innerrelated by a twofold axis or a molecular mirror plane. Formation of only one isomer might be the result of puckering effects, as discussed for the silver tetrafluoroborate complexes (*vide supra*). Moreover, in $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2](\text{BF}_4)$ the methylene groups are bent towards the bridging chlorine atom [22] and thus may cause an even larger energy difference for substitution of either H_a or H_e .

Conversely, methyl substitution might have strengthened the puckering effect, thus expelling one chlorine atom from the starting compound, resulting in the chlorine bridged complex as the only product.

Mononuclear Rhodium Complexes

Thus far we have concentrated on complexes in which the phosphine ligands act as bridges between two or three metal centres, resulting in di- or trinuclear metal complexes. With rhodium as the central atom, bidentate phosphines can also act as chelating ligands, resulting in mononuclear compounds. We investigated the formation of such mononuclear compounds with $(\text{Ph}_2\text{P})_2\text{CH}_2$ and $(\text{Ph}_2\text{P})_2\text{CHMe}$ in order to obtain more information about i) the influence of methylene substituents on formation of different structural isomers and ii) the influence of substituents at rhodium on phenyl carbon chemical shifts. Furthermore, it seemed to be of interest to compare the results of this study with those for similar compounds, in which $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (1,2-bis(diphenylphosphino)ethane) and $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (1,3-bis(diphenylphosphino)propane) acted as ligands (for references see Table VII). Because of the expected difference in geometry the following mononuclear rhodium complexes have been studied: $[\text{RhL}_2](\text{BF}_4)$ (square planar), $[\text{RhL}_2\text{HCl}](\text{BF}_4)$ (octahedral, *cis* or *trans* H and Cl), $[\text{RhL}_2\text{O}_2](\text{BF}_4)$ (trigonal bipyramidal) and $[\text{RhL}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$ (octahedral, *trans* Cl and HgCl) in which $\text{L} = (\text{Ph}_2\text{P})_2\text{CHMe}$, $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 1, 2, 3$).

$[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{HCl}]\text{X}$ was the first Rh compound reported in the literature to have chelating $(\text{Ph}_2\text{P})_2\text{CH}_2$ ligands [33]. It was then isolated with a BPh_4 counterion as a by product in the reaction of $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})\{(\text{Ph}_2\text{P})_2\text{CH}_2\}](\text{BPh}_4)$ with SO_2 . However, it can also be prepared directly from $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2](\text{BF}_4)$ and gaseous HCl, as done in this study. $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2](\text{BF}_4)$, in turn, can be liberated from $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{HCl}](\text{BF}_4)$ by reaction with triethylamine in chloroform. It was also prepared from $[\text{RhCl}(\text{COT})_2]_2$, $(\text{Ph}_2\text{P})_2\text{CH}_2$ and NaBF_4 in methanol, a procedure which is very similar to that recently reported by Pignolet *et al.* [3].

The O_2 and HgCl_2 products were synthesized via direct reactions of these reagents with $[\text{Rh}\{(\text{Ph}_2\text{P})_2-$

$\text{CH}_2\}_2\text{BF}_4$. The $(\text{Ph}_2\text{P})_2\text{CHMe}$ analogues and $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$ were prepared via similar procedures. To date we have not been able to synthesize the compound $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$.

All the compounds were characterized by ^{31}P NMR (Table VII) and IR spectra (Table VI) and for known compounds the results were compared with those reported in the literature. The formation of the HCl oxidative addition products $[\text{RhL}_2\text{HCl}](\text{BF}_4)$ was inferred from the $\nu(\text{M}-\text{H})$ frequencies in the IR spectra; $\nu(\text{O}-\text{O})$ absorptions near 880 cm^{-1} were observed for the O_2 adducts $[\text{RhL}_2\text{O}_2](\text{BF}_4)$. The presence of a Rh-Hg bond in $[\text{RhL}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$, by analogy with the Rh-Hg compounds reported by Vrieze *et al.* [34] was inferred from the ^{31}P NMR spectra which showed both $J(^{103}\text{Rh}-^{31}\text{P})$ and $J(^{199}\text{Hg}-^{31}\text{P})$ for the four equivalent phosphorus atoms (see Table VII).

^{31}P NMR spectra of the mononuclear Rhodium compounds

The ^{31}P NMR spectral data (summarised in Table VII b) need some general comment. For all the compounds a wide spread is observed for the ^{31}P chemical shifts of the various coordinated phosphines. Such a feature is generally accepted to be principally due to ring contributions, which are dependent on the size of the chelate-ligand-metal ring [35]. Within each series of compounds $[\text{RhL}_2\text{Y}](\text{BF}_4)$ the $J(^{103}\text{Rh}-^{31}\text{P})$ coupling constants are always smaller for the $(\text{Ph}_2\text{P})_2\text{CH}_2$ and $(\text{Ph}_2\text{P})_2\text{CHMe}$ than $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ and $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ ligands. The difference, which ranges from 5 to 20 Hz, may be caused by a ring effect on $^1J(^{103}\text{Rh}-^{31}\text{P})$ and by a very likely contribution of $^3J(^{103}\text{Rh}-^{31}\text{P})$ via the phosphine skeleton, which will have an opposite sign to that of $^1J(^{103}\text{Rh}-^{31}\text{P})$.

$[\text{RhL}_2](\text{BF}_4)$. For the compounds $[\text{RhL}_2](\text{BF}_4)$ one ^{31}P doublet was observed for $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$, $x = 1, 2, 3$, and two doublets for $\text{L} = (\text{Ph}_2\text{P})_2\text{CHMe}$. These doublets indicate that the four phosphorus atoms of the two diphosphine ligands are in equivalent environments, which is in accord with a square planar coordination around rhodium. In this context it is obvious that each of the two isomeric structures for $\text{L} = (\text{Ph}_2\text{P})_2\text{CHMe}$, which have the two methyl groups either at the same side or on opposite sides of the molecular plane, respectively (Fig. 8), will give rise to a different doublet resonance.

The observed intensity difference for the two doublets may be an indication of a difference in stability of the two isomers.

The values observed for $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2](\text{BF}_4)$ ($8.08\ \delta$, $J = 131\text{ Hz}$) are close to those reported for $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2\text{Cl}](\text{BF}_4)$ ($6.4\ \delta$, $J = 132\text{ Hz}$) at ambient temperature [36]. This supports the

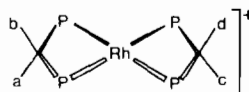
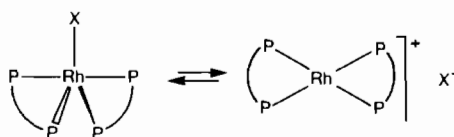


Fig. 8. Schematic representation of $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2](\text{BF}_4)$. For $\text{R} = \text{Me}$ two isomeric forms are possible: $a, c = \text{H}$, $b, d = \text{Me}$; and $a, d = \text{H}$, $b, c = \text{Me}$.

proposal by Baird [36] that an equilibrium between a trigonal bipyramidal and a square planar structure, involving rupture of the $\text{M}-\text{X}$ bond (Scheme II), will lie far towards the latter structure at ambient temperature.



Scheme II. Equilibrium between trigonal bipyramidal and square planar geometry for $[\text{Rh}(\text{PP})_2]\text{X}$.

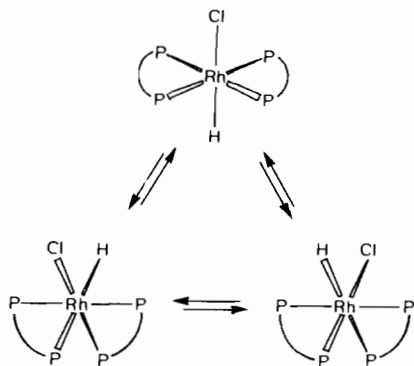
$[\text{RhL}_2\text{HCl}](\text{BF}_4)$. A single doublet is observed for the compound $[\text{RhL}_2\text{HCl}](\text{BF}_4)$ $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$, $x = 1, 2, 3$, and two doublets for $\text{L} = (\text{Ph}_2\text{P})_2\text{CHMe}$, pointing to an octahedral structure with H and Cl in *trans* positions. Such a structure was indeed observed for $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{HCl}](\text{BPh}_4)$ in the solid state [33].

That this structure is static on the NMR timescale for $\text{L} = (\text{Ph}_2\text{P})_2\text{CH}_2$ was indicated by the ^{13}C NMR spectrum, which showed the presence of two inequivalent sets of phenyl groups (Table VIII).

A similar rigid structure can also explain the observation of two doublets in the ^{31}P NMR spectrum, several phenyl groups in the ^{13}C NMR spectrum and two IR $\nu(\text{M}-\text{H})$ absorptions for $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{HCl}](\text{BF}_4)$: different isomers, with the methyl groups at the same side of the P_4Rh plane as either H or Cl, or at different sides, will be present.

By contrast, Baird showed that $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2\text{HCl}]\text{Cl}$ was dynamic at ambient temperature, and that the rigid structure at low temperature had H and Cl in *cis* positions [36]. The above results suggest that the energy difference of this *cis* and *trans* isomers and, as a result, the equilibrium between these isomers (Scheme III), will be delicately influenced by the ring size and ring substituents of the chelate.

$[\text{RhL}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$. $[\text{RhL}_2\text{Cl}(\text{HgCl})](\text{BF}_4)$ are the first Rh-Hg compounds with chelating phosphine ligands. They may be formed by oxidative addition of a Hg-Cl bond and, similar to the compounds with monodentate phosphines reported by



Scheme III. Equilibrium between *cis* and *trans* isomers for $[\text{Rh}(\text{PP})_2\text{HCl}]\text{X}$.

Vrieze *et al.* [34] have Cl and Hg in *trans* positions as evidenced by the ^{31}P NMR and ^{13}C NMR spectra. The ^{31}P NMR spectra for the compounds with $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 1, 2$) showed one phosphorus resonance, with both $J(^{103}\text{Rh}-^{31}\text{P})$ and $J(^{199}\text{Hg}-^{31}\text{P})$. This points to equivalent P-atoms, all *cis* to Hg. The ^{13}C NMR spectrum for $\text{L} = (\text{Ph}_2\text{P})_2\text{CH}_2$ showed the presence of two sets of phenyl groups (Table VIII) pointing to different environments for the phenyl groups on each side of the P_4Rh plane as a result of the presence of Cl and HgCl.

The ^{31}P NMR spectrum of the reaction product from $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2]\text{BF}_4$ and HgCl_2 showed many peaks, most probably doublets with coupling constants ranging from 70 to 80 Hz. Complete interpretation of the spectrum was not possible, but more than one compound may be present as a result of different orientations of the methyl-substituted ligand.

$[\text{RhL}_2\text{O}_2](\text{BF}_4)$. The oxygen adducts $[\text{RhL}_2\text{O}_2](\text{BF}_4)$ $\text{L} = (\text{Ph}_2\text{P})_2\text{CHMe}$, $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 1, 2, 3$) exhibited quartets of triplets, *i.e.* an $\text{AA}'\text{BB}'\text{X}$ pattern. Baird *et al.* explained such a pattern for $[\text{Rh}\{(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_2\text{O}_2\}]\text{Cl}$ with a stereochemically rigid trigonal bipyramidal structure [36]. This is in line with the X-ray analysis of $[\text{Rh}\{(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_2\text{O}_2\}](\text{PF}_6)$ [12].

For the O_2 adduct $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{O}_2](\text{BF}_4)$ the AB part for only one $\text{AA}'\text{BB}'\text{X}$ spin system is observed. This points to the presence of a single isomeric structure in which two sets of two equal phosphorous atoms are present. This requires that in the trigonal bipyramidal structure the ligands are arranged with both their methyl groups pointing inwards or outwards (Fig. 9).

One of the main decomposition products of $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{O}_2](\text{BF}_4)$ in CDCl_3 showed a very similar $\text{AA}'\text{BB}'\text{X}$ ^{31}P NMR pattern (-25.8δ , $J^{103}(\text{Rh}-^{31}\text{P})$ 95 Hz, -43.3δ , $J(^{103}\text{Rh}-^{31}\text{P})$ 75 Hz, $J(^{31}\text{P}-^{31}\text{P})$ 31 Hz). Furthermore, the IR spectrum

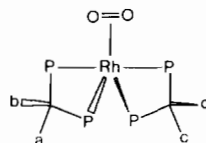


Fig. 9. Schematic representation of $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHR}\}_2\text{O}_2]\cdot\text{BF}_4$.

showed two absorptions in the $\nu(\text{O}-\text{O})$ region. These features may be an indication for the presence of two different coordination modes for O_2 , but further study is necessary for a reliable conclusion.

Stability of the mononuclear rhodium compounds

The present results support previous observations about the influence of the ring size of the chelating ligands on the stability of the complexes formed. As was already known $[\text{RhL}_2\text{O}_2]\text{X}$ is much more stable with $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ than $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ [37, 38]. The $(\text{Ph}_2\text{P})_2\text{CH}_2$ compound has intermediate stability. The chelating ring size also influences the relative stability of several isomers: the *cis* isomer of $[\text{RhL}_2\text{HCl}]\text{X}$ is more stable than *trans* for $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$, whereas for $\text{L} = (\text{Ph}_2\text{P})_2\text{CH}_2$ the converse is true.

The present results clearly indicate that substituents on that chelate ring also influence the relative stability of the complexes and the formation of isomers. $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2](\text{BF}_4)$ is air sensitive in the solid state. In contrast, $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2](\text{BF}_4)$ is stable in air for weeks once isolated. Both compounds decompose in CHCl_3 . The oxygen adduct $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CHMe}\}_2\text{O}_2](\text{BF}_4)$ is also much more stable than $[\text{Rh}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_2\text{O}_2](\text{BF}_4)$. The latter compound decomposes slowly in CHCl_3 solution within one day. From these results it seems that methyl substitution in $(\text{Ph}_2\text{P})_2\text{CH}_2$ has a stabilizing effect on the complexes formed.

Conclusions

The present results show that the type of complexes formed with the multidentate phosphines $(\text{Ph}_2\text{P})_2\text{CHR}$ depend on the metal and its co-ligands, *e.g.* mono-bridged di- and tri-nuclear silver carboxylates; double bridged dinuclear silver tetrafluoroborates; double bridged dinuclear rhodium carbonyls and double chelated mononuclear anionic rhodium compounds.

Methyl substituents on the methylene carbon atom of $(\text{Ph}_2\text{P})_2\text{CH}_2$ have a stabilizing effect on the complexes formed and, furthermore, for compounds with two $(\text{Ph}_2\text{P})_2\text{CHMe}$ ligands various isomers are possible in theory. In practice the number of such isomers and their relative abundance varies with the metal and its coordination geometry. These results

can be interpreted by puckering of the metal–phosphine unit, creating inequivalent methylene positions.

Acknowledgements

We thank Mr. H. Nijon for experimental assistance and Mr. J. M. Ernsting for recording the ^{31}P NMR spectra. Prof. Dr. K. Vrieze is thanked for his stimulating interest.

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