Silver(I) Complex Formation with Phosphorus Donors in Propylene Carbonate: a Thermodynamic and Spectroscopic Investigation

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The thermodynamics of complex formation between silver(I) and PPh_3, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) has been investigated in propylene carbonate at 298 K and 0.1 mol dm^{-3} ionic strength (NEt_4ClO_4) by potentiometric and calorimetric techniques. Within the silver(I) concentration range investigated, PPh_3 forms three successive mononuclear complexes, dppm only polynuclear species, whereas mononuclear complexes, in addition to polynuclear ones, are formed by dppe and dppp. The thermodynamic data show that all complexes are stabilized by exothermic terms, the entropy changes being negative. In the mononuclear complexes, dppe and dppp act as chelating agents while in the very stable $[Ag_2L_2]^{2+}$ species all the diphosphines behave as bridging ligands. These conclusions have been confirmed by ^{31}P NMR studies on solutions of silver(I). Comparison of the thermodynamic data for formation of the silver(I) complexes with the same ligands in dimethyl sulfoxide (dmso) show that the complexes are considerably weaker in dmso, mainly reflecting the stronger solvation of Ag^+ in dmso with respect to propylene carbonate.

The chemistry of transition-metal complexes with phosphines[1] has been the subject of intensive study primarily because of their applications as hydrogenation catalysts[2] and, more recently, in biology and medicine as anticancer drugs.[3]

Previous studies[4] from this laboratory on the complexation of silver(I) with phosphorus-donor compounds of general formula $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–3) in dimethyl sulfoxide (dmso) showed that complexes are formed in which the diphosphines behave as chelating agents or bidentate bridging ligands and that electronic effects and steric factors play an important role both in the co-ordination behaviour of the diphosphines and in the thermodynamic stability of their complexes.

In the present paper we report the thermodynamics of silver(I) complexation, in the dipolar aprotic solvent propylene carbonate, with triphenylphosphine, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) possessing different basicities and steric properties. The primary aim was to study the influence of the solvent on the nature and thermodynamic stability of the species formed in solution, as the formation of metal complexes is much influenced by the solvation of the species involved.[5] Propylene carbonate was chosen as solvent since it has physicochemical properties similar to those of dmso but a smaller solvating ability toward monovalent metal cations, in particular toward silver(I).[5]

Experimental

Chemicals.—Anhydrous $AgClO_4$ was obtained by heating, under vacuum at 323 K and for several days, the solid obtained by crystallization from benzene of a $AgClO_4{\cdot}H_2O$ (Fluka puriss.) solution from which water had been previously removed by a Dean and Stark distilling receiver.[6] Propylene carbonate (Fluka > 99%) was distilled at reduced pressure from CaH_2. The middle 60% fraction was collected and redistilled under identical conditions.[7] The distillate was stored in a dark bottle in a dry-box. Stock solutions of silver(I) perchlorate were prepared from anhydrous $AgClO_4$ and freshly distilled propylene carbonate. The exact silver content of the solutions was determined by potentiometric titration with chloride. The phosphines, analytical grade products from Strem Chemicals, were recrystallized twice from CH_2Cl_2–EtOH. Their purity was checked by measuring melting points on a Buchi 512 apparatus and by ^{31}P-$\{^1H\}$ NMR spectroscopy. Propylene carbonate solutions of the phosphines were prepared by dissolving weighed amounts of the anhydrous compounds in freshly distilled solvent containing 0.1 mol dm^{-3} NEt_4ClO_4 as supporting electrolyte. To prevent oxidation to phosphine oxides, all these solutions were prepared afresh before each set of titrations in a glove-box under a nitrogen atmosphere. The water content of the solutions, typically 10–30 ppm, was determined by a Metrohm 684 KF coulometer. Infrared and ^{31}P NMR measurements revealed that no formation of phosphine oxides occurred within 24 h. Similar spectroscopic checks were also performed on each of the potentiometric and calorimetric titration mixtures. Again no phosphine oxidation was detected.

Potentiometric Measurements.—The experimental data employed for the determination of the stability constants of the silver–phosphine complexes were the equilibrium concentrations of the silver(I) ion which were obtained from potentiometric measurements. The potentiometric apparatus and other experimental details were described previously.[8] Titrations were performed at 298 K of solutions of silver(I) perchlorate of concentration $2 < c_M^0 < 10$ mmol dm^{-3} with solutions of the phosphine concerned of concentration 20 <

Table 1 Overall stability constants and thermodynamic functions for silver(I)–phosphine systems* in propylene carbonate at 298 K and $I = 0.1$ mol dm^{-3}

L	Complex	log β_j	$-\Delta G_{\beta j}^{\ominus}$	$-\Delta H_{\beta j}^{\ominus}$	$-\Delta S_{\beta j}^{\ominus}$
PPh_3	$[AgL]^+$	9.95(3)	56.8(2)	70.5(7)	46
	$[AgL_2]^+$	17.17(3)	98.0(2)	122.3(6)	82
	$[AgL_3]^+$	21.41(4)	122.2(3)	167(2)	150
dppm	$[Ag_2L]^{2+}$	16.68(15)	95.2(9)	139(2)	147
	$[Ag_2L_2]^{2+}$	29.50(16)	168.4(9)	249(2)	270
	$[Ag_2L_3]^{2+}$	35.01(12)	199.8(7)	310(3)	370
dppe	$[AgL]^+$	13.75(24)	78(1)	114(1)	121
	$[AgL_2]^+$	21.94(15)	125.2(9)	173(2)	160
	$[Ag_2L]^{2+}$	18.01(9)	102.8(5)	144(5)	138
	$[Ag_2L_2]^{2+}$	30.63(21)	175(1)	233(5)	194
dppp	$[AgL]^+$	14.1(4)	80(1)	120(9)	134
	$[AgL_2]^+$	21.83(15)	124.6(9)	198(2)	246
	$[Ag_2L]^{2+}$	18.15(12)	103.6(7)	147(2)	146
	$[Ag_2L_2]^{2+}$	32.63(21)	186(1)	253(2)	225

* $\Delta G_{\beta j}^{\ominus}$ and $\Delta H_{\beta j}^{\ominus}$ in kJ mol^{-1}, $\Delta S_{\beta j}^{\ominus}$ in J K^{-1} mol^{-1}. Figures in parentheses correspond to three standard deviations.

$c_L^0 < 70$ mmol dm^{-3} using at least three different initial silver(I) concentrations. Each titration was carried out in duplicate in 0.1 mol dm^{-3} NEt_4ClO_4. The electrode couple was periodically checked in solutions containing only silver(I) perchlorate: in the range $10^{-5} < [Ag^+] < 10^{-2}$ mol dm^{-3}, the electromotive force values varied with the metal-ion concentration according to Nernst's law. The computer program SUPERQUAD[9] was used for the calculation of stability constants, giving the best fit of the experimental data.

Calorimetric Measurements.—A Tronac model 87-558 precision calorimeter was employed to measure the reaction heats at 298 K. The titration and calibration procedures were similar to those previously described.[10–12] In particular, the titrations were performed by adding phosphine solutions of concentration c_L^0 at a constant rate (0.2116 cm^3 min^{-1}) to 20 cm^3 of silver(I) solutions of $2 < [Ag^+] < 10$ mmol dm^{-3}. Each titration was repeated at least twice. The heats of dilution, determined in separate runs were negligible in the concentration ranges of silver(I) and phosphines used. The enthalpy changes for the systems were calculated using the least-squares program LETAGROP KALLE.[13]

^{31}P NMR Measurements.—The $^{31}P-\{^1H\}$ NMR spectra were recorded between 228 and 298 K on a Bruker AC 200 F spectrometer equipped with a VT 1000 variable-temperature probe operating at 81.02 MHz in the Fourier-transform mode while locked on the ^2H resonance of deuteriated acetone; 5 mm tube samples with an internal 2 mm capillary containing the deuteriated solvent were used. The chemical shifts are reported with respect to 85% H_3PO_4. A shift to low field is indicated by a positive sign. Measurements were performed for 10^{-2} mol dm^{-3} Ag^+ solutions, where the ratio $R = c_L/c_M$ varied in the range 0.2–3.0 : 1. All the solutions were prepared afresh by dissolving in propylene carbonate the anhydrous $AgClO_4$ and anhydrous phosphines in the required ratios. The NMR spectral simulations were performed on an Aspect 3000 computer using the program PANIC.[14]

Results

The overall stability constants obtained from the potentiometric measurements are listed in Table 1 with the limits of error indicated. Fig. 1 shows the distribution of silver(I) between the different complexes at varying phosphine concentrations.

As in dmso,[15] the potentiometric data for the Ag^+–PPh_3 system are consistent with the consecutive formation of mononuclear complexes, $[AgL_j]^+$ (j = 1–3). Co-ordination of a fourth phosphine could not be detected in solution from the potentiometric data as a solid of composition $[Ag(PPh_3)_4]ClO_4$, as determined by elemental analysis, precipitated at a ligand-to-metal ratio higher than 3 : 1.

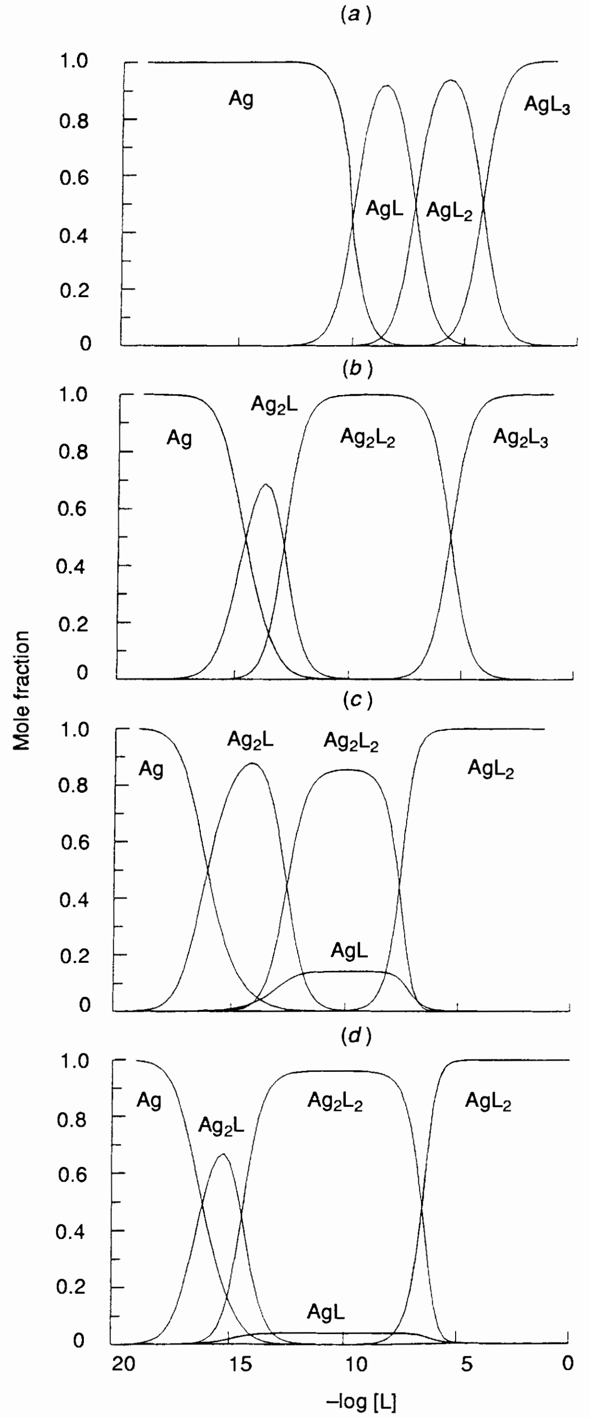


Fig. 1 Distribution curves for the silver(I)–phosphine systems in propylene carbonate at $c_M^0 = 10.0$ mmol dm^{-3}: (*a*) PPh_3, (*b*) dppm, (*c*) dppe and (*d*) dppp

For dppm no mononuclear complexes, $[AgL]^+$ and $[AgL_2]^+$, could be detected in appreciable amount, while such complexes are formed both by dppe and dppp: $[AgL_2]^+$ is the most stable species in solution at high dppe and dppp concentration; $[AgL]^+$ is only a minor species under our experimental conditions.

Common to all the diphosphines is the formation of polynuclear complexes. In particular the dinuclear complexes

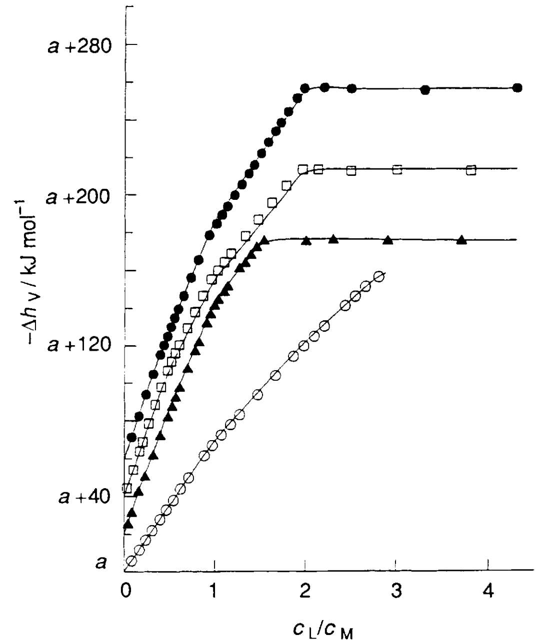


Fig. 2 The total molar enthalpy changes, Δh_v, as a function of $R = c_L/c_M$ for silver(I)–phosphine systems in propylene carbonate at c_M^0 = 5.0 mmol dm^{-3}. (○) PPh$_3$, $a = 0$, (□) dppm, $a = -20$; (▲) dppe, $a = -40$; (●) dppp, $a = -60$. The solid lines have been calculated from the values of β_j and ΔH_j° in Table 1

Table 2 ^{31}P NMR data

Ligand	R^a	T/K	δ	$^1J(^{31}P-^{107}Ag)^b$/Hz
PPh$_3$	0.5	228	≈14	≈725
	2.0	228	12.2	497
	3.0	228	9.7	319
dppm^c	0.3	228	11.6	725^{d,e}
	1.0	298	11.5	504^{d,f}
dppe	0.2	228	≈13	≈740
	1.0	228	≈7	≈550
			≈9	≈550
	2.0	298	3.7	231
dppp	0.2	228	≈9	≈740
	1.0	298	8.9	510
	2.0	298	−4.7	220

[a] $R = c_L/c_M$. [b] $^1J(^{31}P-^{109}Ag) = 1.15 \times {}^1J(^{31}P-^{107}Ag)$. [c] The spectrum at R = 0.3:1 is the AA′ part of an AA′XX′ spin system, that at R = 1.0:1 is the AA′A″A‴ part of an AA′A″A‴XX′ spin system. [d] Value from computer simulation of the experimental spectrum; accuracy in coupling constants not better than ±0.5 Hz. [e] Additional calculated parameters: $^1J(^{31}P-^{109}Ag) = 833$, $^2J(P-CH_2-P') = 159.1$, $^3J(^{31}P-^{107}Ag) = -6.2$, $^3J(^{31}P-^{109}Ag) = -8.3$ Hz. [f] Additional calculated parameters: $^1J(^{31}P-^{109}Ag) = 580$, $^2J(P-CH_2-P') = 136.0$, $^3J(^{31}P-^{107}Ag) = -0.4$, $^3J(^{31}P-^{109}Ag) = -1.2$, $^2J(P-^{107}Ag-P') = 302.4$, $^2J(P-^{109}Ag-P') = 300.1$ Hz.

$[Ag_2L]^{2+}$ and $[Ag_2L_2]^{2+}$ are formed and are predominant over a wide range of phosphine concentration, $[Ag_2L]^{2+}$ being prevalent at the beginning of the titrations when the metal-to-ligand ratios are still large. For dppm the best fit of the experimental data was obtained when, in addition to the species $[Ag_2L]^{2+}$ and $[Ag_2L_2]^{2+}$, a complex of composition $[Ag_2L_3]^{2+}$ was taken into account at high free phosphine concentrations. No trace of any mononuclear complex beyond the second one was observed for any of the systems investigated.

The assumptions about the species formed in solution, made on the basis of the potentiometric data, are confirmed by the calorimetric measurements. Typical calorimetric titrations are shown in Fig. 2 where the total molar enthalpy changes, Δh_v, are shown as a function of the ratio $R = c_L/c_M$ for the different phosphines. The values of Δh_v were obtained by dividing the total heats of reaction, q_i, measured at each titration point by the number of moles of metal ion in solution.

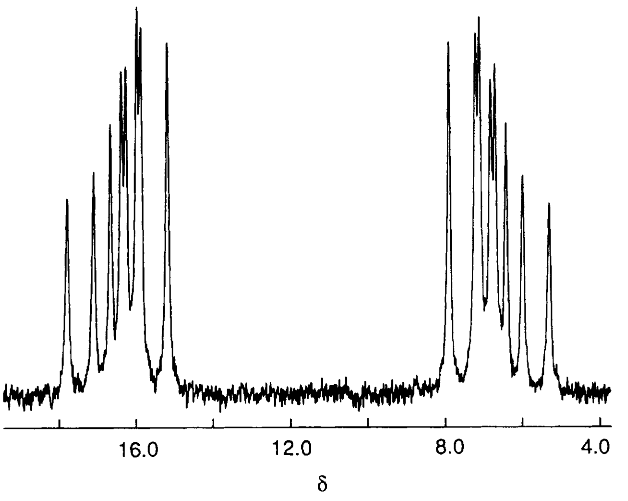


Fig. 3 The ^{31}P-{^{1}H} NMR spectrum obtained at 228 K for the Ag–dppm system at R = 0.3:1. The complex $[Ag_2(dppm)]^{2+}$ is the species present in solution

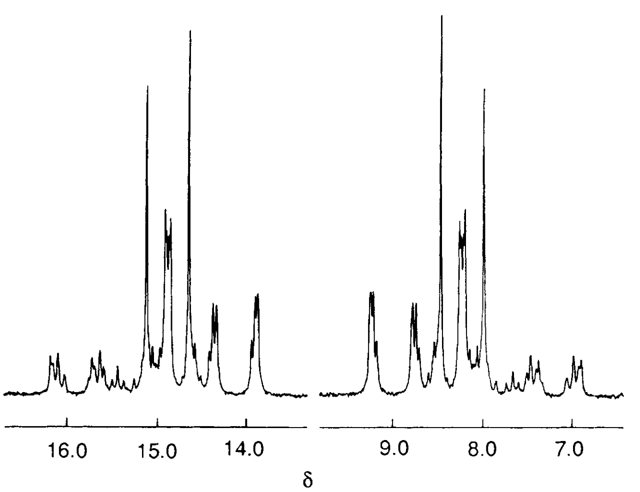


Fig. 4 The ^{31}P-{^{1}H} NMR spectrum obtained at 298 K for the Ag–dppm system at R = 1.0:1. The complex $[Ag_2(dppm)_2]^{2+}$ is the species present in solution

Owing to the formation of solid $[Ag(PPh_3)_4]ClO_4$ no data concerning the interaction of PPh$_3$ with silver(I) at R > 3:1 could be obtained. The curve for dppm shows that a sharp change of slope occurs at R = 1.5:1 and that at higher R values no more heat is evolved. The enthalpy data for dppe and dppp, very similar in profile, show a change of slope at R = 0.5, 1 and 2:1 respectively. In this case, no thermal effects were observed for R > 2:1. These trends are all in line with the formation of complexes having stoichiometries consistent with the potentiometric results.

Computer minimization of the differences among calculated and observed Δh_v values gave the overall enthalpy changes for formation of the silver(I) complexes. These values, together with the corresponding calculated free energy and entropy changes, are summarized in Table 1.

In Table 2 the most significant NMR results are collected, while the experimental spectra for $[Ag_2(dppm)]^{2+}$ at 228 and $[Ag_2(dppm)_2]^{2+}$ at 298 K are shown in Fig. 3 and 4 respectively.

Discussion

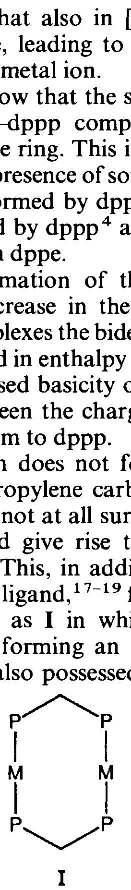
The silver(I) complexes studied in this work are all strongly enthalpy stabilized as a consequence of the formation of strong covalent Ag–P bonds and the weak solvation of both silver(I) and phosphines in propylene carbonate.[5] The decrease in the stepwise enthalpy changes pertaining to the formation of successive $[Ag(PPh_3)_n]^+$ (n = 1–3) complexes ($\Delta H^{\circ} = -70.5$, $\Delta H_2^{\circ} = -51.8$ and $\Delta H_3^{\circ} = -44.7$ kJ mol^{-1}, respectively) reflects the progressive weakening of the silver–phosphorus bonds as more phosphines are co-ordinated to the metal ion. The entropy changes for the different steps are all negative indicating that no extensive desolvation takes place at any step of complexation. The same trend was found in dmso.[15]

The $[AgL]^+$ complexes of dppe and dppp are considerably more stable than the corresponding PPh_3 complex. Further, their enthalpies of formation [much of the same order of magnitude as the enthalpy of formation of the bis(triphenylphosphine) complex] and their entropies of formation are respectively more exothermic and more negative than the corresponding ΔH_1° and ΔS_1° of silver(I) complexes with the unidentate phosphine. This indicates formation of silver(I) chelate complexes in which both phosphorus atoms of dppe and dppp are co-ordinated. Thermodynamic and ^{31}P NMR data (see below) show that also in $[AgL_2]^+$ complexes the phosphines are bidentate, leading to a presumed tetrahedral configuration around the metal ion.

The data in Table 1 show that the stabilities of the 1:1 and 1:2 silver(I)–dppe and –dppp complexes increase with increasing size of the chelate ring. This is likely the result of two concomitant factors: the presence of some strain within the five-membered chelate ring formed by dppe as compared with the six-membered one formed by dppp[4] and the higher basicity[16] of dppp as compared with dppe.

The enthalpies of formation of the dinuclear $[Ag_2L]^{2+}$ complexes, $-\Delta H_{\beta j}^{\circ}$, decrease in the order dppp > dppe > dppm. Since in these complexes the bidentate phosphines bridge two silver atoms, the trend in enthalpy values may be explained as due both to the increased basicity of the ligands and to the decreased repulsion between the charged centres as the chain length increases from dppm to dppp.

The diphosphine dppm does not form mononuclear complexes with silver(I) in propylene carbonate or in dmso.[4] As already observed,[4] this is not at all surprising as the formation of such complexes would give rise to highly strained four-membered chelate rings. This, in addition to the tendency of dppm to act as a bridging ligand,[17–19] favours the formation of polynuclear species such as **I** in which two metal ions are bridged by two ligands, forming an eight-membered chelate ring.[19] This structure is also possessed by the dimeric species $[Ag_2(dppm)_2]^{2+}$ in propylene carbonate solution, as confirmed by ^{31}P NMR data which also seem to indicate (see below) that the dimeric species $[Ag_2L_2]^{2+}$ formed by dppe and dppp have the same core structure as that of $[Ag_2(dppm)_2]^{2+}$.



I

A comparison of the thermodynamic functions for the silver(I) complexes studied in this work with those previously determined for the same systems in dmso[4,15] shows that the complexes are considerably weaker in dmso and that the large difference in the stabilities between the two solvents is due to the enthalpy terms, as the entropy contributions do not differ very much in the two solvents. The lower stability of the complexes in dmso and the trend in the thermodynamic functions are undoubtedly due to the stronger solvation of Ag^+ in dmso, as evidenced by the very endothermic heat of transfer for Ag^+ between dmso and propylene carbonate, $\Delta H_{tr} = 37.3$ kJ mol^{-1}.[5]

The stronger donating properties of dmso mean also a large increase in the heat of desolvation of the metal ion in this solvent and, consequently, less exothermic values of the heats of formation of the complexes in dmso. As mentioned above, the entropy contributions are negative, and therefore unfavourable to complex formation in both solvents. The trend observed is that expected given the weak solvation of both the metal ion and phosphines in propylene carbonate.[5]

^{31}P *NMR Studies*.—In order to get more information on structural aspects of the species in solution, variable-temperature $^{31}P-\{^1H\}$ NMR measurements were made on solutions containing silver(I) and the phosphine in appropriate ratios. Generally, the ligand-to-silver ratios, $R = c_L/c_M$, were varied from 0.2 to 3.0:1 depending on the species to be studied in each system, while the temperature range explored, owing to the melting point of propylene carbonate, was limited to 298–228 K. A peculiar characteristic of the ^{31}P NMR spectra of silver(I) complexes containing magnetically equivalent phosphorus atoms is the doublet of doublets arising from coupling of the P atom to each of the spin $I = \frac{1}{2}$ silver isotopes (^{107}Ag and ^{109}Ag with 51.82 and 48.18% natural abundance, respectively). The ratio of the coupling constants $J(^{31}P-^{109}Ag)/J(^{31}P-^{107}Ag)$ is 1.15:1, which corresponds to the ratio of the nuclear magnetic moments of the silver isotopes.

The Ag–PPh_3 system was investigated for R = 0.5, 2.0 and 3.0:1. The spectra were found to be temperature dependent for each value of R. At the highest temperature only one singlet was observed, which can be ascribed to a process involving dissociation of the Ag–P bonds.[20] The singlet was split at lower temperatures and a more or less resolved doublet of doublets was obtained only at 228 K.

At R = 0.5:1 the process involving dissociation of the Ag–P bonds is operative even at 228 K. The separation between the two broad resonances (centred at *ca*. δ 14) in the spectrum at 228 K (*ca*. 780 Hz)* is however indicative of the existence in solution of a prevalent species in which the silver ion co-ordinates one phosphorus atom only, as found for complexes with tertiary phosphines,[21,22] phospholes[23,24] or hybrid P–N type compounds.[25]

At R = 2.0 and 3.0:1 the slow-exchange limit spectra showing a doublet of doublets [δ 12.2, $J(^{31}P-^{107}Ag)$ = 497; δ 9.7, $J(^{31}P-^{107}Ag)$ = 319 Hz respectively] were obtained at 228 K. The coupling constant values agree well with literature data concerning compounds where two[21–25] or three[22–24] phosphorus atoms respectively are co-ordinated to silver ion.

Both the regular shift toward lower fields of the phosphorus resonance and the decreasing $J(^{31}P-^{107}Ag)$ values on increasing ligand-to-metal ratio observed in the above spectra fit well with the thermodynamic results which indicate the presence in solution of the species $[AgL]^+$, $[AgL_2]^+$ and $[AgL_3]^+$ for R = 0.5, 2.0 and 3.0:1 respectively.

$^{31}P-\{^1H\}$ NMR spectra for the Ag–dppm system were collected at R = 0.3, 1.0, 1.5 and 2.0:1. At R = 0.3:1 the spectrum run at 298 K shows two very broad signals centred at about δ 11. The spectra run at lower temperatures show separation into distinct broad signals, which eventually sharpened, at 228 K, into a resolved symmetric multiplet centred at δ 11.6 (Fig. 3). The low-temperature limiting spectrum has been reproduced by computer simulation assuming an AA'XX' spin system for an Ag–P–P–Ag core. The complexity of the spectral pattern arises from the three statistical combinations of the silver isotopes with two strongly coupled phosphorus atoms. The calculated spectral parameters (Table 2), with a $^1J(^{31}P-^{107}Ag)$ value typical of complexes in which the silver ion co-ordinates one P atom only,[20–25] were in accord with an $[Ag_2L]^{2+}$ structure in which dppm bridges two

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* This value may be roughly interpreted as the average of the $^{31}P-^{107,109}Ag$ coupling constants, which therefore can be estimated as *ca*. 725 and 835 Hz, respectively.

silver ions. The same structure has been suggested for the carboxylato complexes $[Ag_2(O_2CR)_2(dppm)]$ (R = Me,[17] Et, Pr^i or Ph[18]), for which the slow-exchange limit spectra were obtained at *ca.* 223 K in dichloromethane or chloroform solutions.

At $R = 1.0:1$ a slow-exchange limit spectrum was obtained even at 298 K (Fig. 4). The very complicated symmetric pattern (at least 64 lines are detectable) arises from the three statistical combinations of the silver isotopes with phosphorus atoms strongly coupled through both the metal ion $[^2J(^{31}P\text{-}Ag\text{-}^{31}P')]$ and the CH_2 group $[^2J(^{31}P\text{-}CH_2\text{-}^{31}P')]$, in the eight-membered annular structure **I**. The ^{31}P NMR spectrum was considered to be the AA′A″A‴ part of an AA′A″A‴XX′ spin system. The calculated spectral parameters (Table 2) agree with those reported by van der Ploeg and van Koten[18] for the complex $[Ag_2(dppm)_2][BF_4]_2$ in dichloromethane solution at low temperature, even if no $^2J(^{31}P\text{-}Ag\text{-}^{31}P')$ was reported by those authors. Computer simulation of the ^{31}P NMR spectrum of the two isomers of the complex $[Au_2(Ph_2PCH_2CH_2PEt_2)_2]Cl_2$, which possess a similar annular core structure,[26] gave $^2J(^{31}P\text{-}Au\text{-}^{31}P')$ values close to those obtained for our system. An eight-membered annular structure has been suggested to exist also in an acetonitrile solution of the complex $[Ag_2(dppm)_2][NO_3]_2$, on the basis of the virtual quintet observed in the ^1H NMR spectrum.[19]

At $R = 1.5$ and $2.0:1$ unresolved broad bands were obtained throughout the temperature range investigated (298–228 K). The spectral pattern was about the same for the two R values, a symmetric multiline system centred at *ca.* δ 5. At the highest R value an additional broad signal at *ca.* δ −20 was detected, indicative of free phosphine involved in a dynamic process. These results agree with thermodynamic data, which exclude the presence of $[AgL_2]^+$ derivatives for the Ag–dppm system (see above).

The Ag–dppe and –dppp systems were investigated at $R = 0.2$, 1.0 and $2.0:1$. At $R = 0.2:1$ the spectra at 298 K showed a broad band at δ 13.4 for dppe and δ 9.3 for dppp. A splitting of the singlet was observed on lowering the temperature, but even at 228 K the signals were rather broad. Nevertheless, the separation between the bands [*ca.* 790 Hz for both systems, estimated $J(^{31}P\text{-}^{107}Ag)$ and $J(^{31}P\text{-}^{109}Ag)$ *ca.* 740 and 850 Hz respectively: for these calculated values see the footnote for the $Ag\text{-}PPh_3$ system when $R = 0.5:1$] is consistent with the existence in solution of a species in which the silver ion co-ordinates one phosphorus atom only. In accordance with thermodynamic data, we can conclude that for both systems this complex can be formulated as the dinuclear bridged $[Ag_2L]^{2+}$.

At $R = 1.0:1$ for the Ag–dppe system, even at the lowest temperature available (228 K) the spectrum consists of two couples of incompletely resolved signals in *ca.* 1:6 intensity ratio (δ ≈9 and ≈7, respectively). This spectral pattern likely indicates that at least two species are present in equilibrium: Fig. 1 shows in fact that about 15% $[AgL]^+$ and 85% $[Ag_2L_2]^{2+}$ are present. The separation between each couple of signals can be roughly evaluated as 550 Hz, thus indicating that two phosphorus atoms are co-ordinated to the silver(I) ion in both complexes.[21–25]

At $R = 1.0:1$ for the Ag–dppp system the spectrum at 298 K shows a well shaped doublet of doublets [δ 8.9, $J(^{31}P\text{-}^{107}Ag) = 510$ Hz]. This is in accord with the presence of a species where the silver ion co-ordinates two phosphorus atoms.[21–25] The thermodynamic results indicate that, in addition to the main species $[Ag_2L_2]^{2+}$, $[AgL]^+$ is present in about 4% of the total silver(I) concentration (see Fig. 1). Such a species, which should give a four-line spectrum, was not evidenced under our NMR experimental conditions, given its very low concentration.

Finally, at $R = 2.0:1$ the typical doublet of doublets expected for the slow-exchange limit spectrum was obtained in the whole temperature range investigated both for the Ag–dppe and –dppp systems (δ 3.7 and −4.7). The $J(^{31}P\text{-}^{107}Ag)$ values of 231 and 220 Hz respectively were in good agreement with those previously reported for species in which four P atoms are bonded to one silver ion in a tetrahedral configuration.[22–24]

These results confirm what is suggested by the thermodynamic data, *i.e.* that in $[AgL_2]^+$ complexes, as well as in $[AgL]^+$, both dppe and dppp behave as bidentate ligands.

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