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Thermodynamic and Spectroscopic Studies on Silver(I) Complex Formation with Phosphorus Multidentate Ligands in Dimethyl Sulfoxide

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Received November 14, 1989

The thermodynamic parameters of complexation of silver(I) with bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), bis(2-(diphenylphosphino)ethyl)phenylphosphine (etp), and tris(2-(diphenylphosphino)ethyl)phosphine (PP_3), have been determined by potentiometric and calorimetric techniques in dimethyl sulfoxide (DMSO). The measurements have been conducted at 25 °C and 0.1 M ionic strength (NEt_4ClO_4). Dppm forms only polynuclear species in solution. Mononuclear complexes, in addition to polynuclear species, are by contrast formed with all other ligands. All complexes are formed in strongly exothermic reactions while the entropy changes are negative. The thermodynamic data indicate that, in the mononuclear complexes with silver(I), the ligands act as chelating agents. Very stable complexes of the type M_2L_2 are formed by dppm, dppe, and dppp: in these complexes, the diphosphines act as bridging ligands. Structural studies of solutions of silver(I) by means of ^{31}P NMR technique confirm the conclusions drawn from the thermodynamic data about the nature and structure of the complexes formed in solution. Comparisons of the thermodynamic data relative to formation of silver(I) complexes with analogous ligands coordinating via nitrogen show that the silver(I) complexes with phosphorus donor ligands are far more stable than with nitrogen donor ligands.

Introduction

Ligands coordinating via donor atoms of the nitrogen group are well recognized for their ability to form strong complexes with soft acceptors.[2] Among these types of ligands, the simple triphenyl derivatives Ph_3X (X = N, P, As, Sb, Bi) offer the interesting opportunity to study a set of ligands of the same general class possessing different affinities toward soft acceptors such as the monovalent metal ions copper(I), silver(I), and gold(I). Because of the very low solubility of these compounds in water, the thermodynamics of complex formation between metal ions and these ligands cannot be investigated in aqueous solution, unless sulfonate groups are introduced in the aromatic rings to make them soluble in water.[3] Thus thermodynamic measurements with such ligands have been performed in non-aqueous solvents where both the ligands and the complexes formed are readily soluble. Studies of thermodynamics of complex formation of copper(I)[4] and silver(I)[5] with these ligands have been carried out in dimethyl sulfoxide (DMSO) and for silver(I)[6] and gold(I)[7] also in pyridine. The aim of these investigations was mainly to ascertain the affinity sequence displayed by the monovalent d^{10} acceptors copper(I), silver(I), and gold(I) for ligands coordinating via donor atoms of the nitrogen group.

No equilibrium studies in solution have so far been reported for the complexation of these acceptors with phosphorus multidentate ligands whereas data are available on the thermodynamics of silver(I) complex formation with nitrogen multidentate ligands in DMSO.[8,9] Considerably more attention has been by contrast devoted to the preparation and structural characterization of silver(I) complexes with mono- and multidentate phosphorus ligands.[10-16] ^{31}P NMR spectroscopy in addition to X-ray diffraction methods have been widely used to determine ligand electronic effects and steric factors involving these complexes.

In this paper we report the thermodynamic functions $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the complex formation of silver(I) with some polyphosphines in DMSO. The ligands investigated were as follows: bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,3-bis(diphenylphosphino)propane (dppp) of general formula $Ph_2P(CH_2)_nPPh_2$ (n = 1–3). In addition the two ligands bis(2-(diphenylphosphino)ethyl)phenylphosphine (etp) and tris(2-(diphenylphosphino)ethyl)phosphine (PP_3), a ter- and a tetradentate ligand, were also studied.

The aim of this work was first to obtain some information on the nature and thermodynamic stability of the species formed in DMSO solution between silver(I) and ligands possessing different steric properties and basicities and then to compare the data obtained with those previously reported for analogous silver(I) complexes with nitrogen donor ligands also in DMSO.

The stabilities of the complexes have been determined by potentiometry by means of the silver electrode, and the heats of formation of the complexes, by calorimetry. The thermodynamic data were combined, when possible, with $^{31}P\{^1H\}$ NMR studies in order to gain information on the bonding mode and structural aspects of the complexes formed.

The potentiometric and the calorimetric measurements have been performed at 25 °C in the ionic medium used previously for the silver(I)–polyamine systems, viz. 0.1 M tetraethylammonium perchlorate. The ^{31}P NMR studies were performed in the range 308–183 K.

Experimental Section

Chemicals. The solutions of silver(I) perchlorate in DMSO were prepared and standardized as described elsewhere.[8] The tetraethylammonium perchlorate and the DMSO solvent were treated as described previously.[8,9] The ligands were commercial products of analytical grade (Strem Chemicals) and were recrystallized twice from CH_2Cl_2–EtOH. Their purity was checked by measuring melting points on a Buchi 512 apparatus. Solutions of the ligands were prepared by weighing known amounts of the anhydrous phosphines in freshly distilled DMSO. In order to prevent the oxidation of the ligands to phosphine oxides, all the ligand solutions were prepared afresh before each set of titrations, in a dried glovebox under nitrogen atmosphere. The diphosphine solutions

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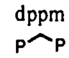
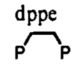
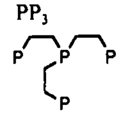
Table I. Overall Stability Constants and Thermodynamic Functions for Ag(I)–Phosphine Systems[a] in DMSO at 25 °C and I = 0.1 mol dm^{-3}

		log β	$-\Delta G°$	$-\Delta H°$	$-\Delta S°$
PPh_3[b]	ML	6.58	37.6	51.8	48
	ML_2	10.73	61.3	89.9	96
	ML_3	13.17	75.2	126.2	171
dppm	M_2L	12.46 (5)	71.1 (3)	107 (6)	120 (21)
	M_2L_2	22.75 (6)	129.8 (4)	188 (4)	195 (15)
	M_2L_3	25.57 (21)	146 (1)	261 (6)	386 (23)
dppe	ML	7.73 (5)	44.1 (3)	87 (6)	144 (21)
	ML_2	13.91 (5)	79.4 (3)	149 (2)	233 (8)
	M_2L	11.91 (5)	68.0 (3)	110 (2)	141 (7)
	M_2L_2	18.28 (9)	104.3 (6)	186 (10)	274 (36)
dppp	ML	8.65 (5)	49.4 (3)	95 (5)	153 (18)
	ML_2	14.39 (7)	82.1 (4)	162 (2)	268 (8)
	M_2L	12.37 (4)	70.6 (2)	115 (2)	149 (7)
	M_2L_2	20.13 (9)	114.9 (5)	195 (7)	269 (25)
etp	ML	11.69 (7)	66.7 (4)	109 (2)	142 (8)
	ML_2	16.69 (14)	95.3 (8)	159 (2)	214 (9)
	M_2L	15.45 (16)	88.2 (9)	135 (3)	157 (13)
	M_2L_3	32.01 (17)	182.7 (9)	291 (6)	364 (23)
PP_3	ML	13.29 (6)	75.9 (3)	140 (4)	215 (14)
	ML_2	16.25 (28)	93 (1)	173 (9)	268 (34)
	M_2L	17.88 (9)	102.0 (5)	166 (3)	215 (11)

[a] $\Delta G°$ and $\Delta H°$ in kJ mol^{-1}; $\Delta S°$ in J K^{-1} mol^{-1}. Figures in parentheses correspond to three standard deviations. The substituents at trivalent phosphorus are phenyl groups. [b] Reference 5.

were stable for about a week while the etp and PP_3 solutions were stable for only about 24 h, as checked by IR and ^{31}P NMR measurements. Spectroscopic measurements were also performed after each potentiometric and calorimetric titration: no formation of phosphine oxide could be detected.

Potentiometric Measurements. The potentiometric data were obtained by means of the galvanic cell

$^{(-)}Ag$	C_M mmol dm^{-3} $AgClO_4$ C_L mmol dm^{-3} L I=0.1 mol dm^{-3}	NEt_4ClO_4 0.1 mol dm^{-3}	$AgClO_4$ 0.1 mol dm^{-3}	$Ag^{(+)}$

L = phosphorus multidentate ligand

For the emf measurements a PHM 84 Radiometer was used, equipped with a Metrohm EA 282/2 silver electrode as a working electrode and a Metrohm 440 silver electrode as a reference. Stable readings were usually obtained within 5 min in the most favorable cases and within 20 min in the least favorable ones. Ingold vessels with outer jackets were used for the titrations. The temperature of the solutions was kept at 25.0 ± 0.1 °C by means of water circulating in the outer jackets. Solutions of silver(I) perchlorate of concentration 2 ≤ C^0_M ≤ 10 mmol dm^{-3} were titrated with solutions of dppm, dppe, and dppp of concentration 10 ≤ C^0_L ≤ 50 mmol dm^{-3}. As the solubilities of etp and PP_3 did not exceed 7 mmol dm^{-3} at 25 °C, in addition to titrations where C^0_M was ca. 2 and 6 mmol dm^{-3}, respectively, back-titrations were also run where silver(I) perchlorate solutions of concentration C^0_M = 50 mmol dm^{-3} were added to ligand solutions of concentration C^0_L about 7 mmol dm^{-3}. All titrations were carried out at least in duplicate. The reproducibility was better than 0.2 mV for low values of C_L/C_M and better than 0.4 mV for higher ones. The electrode couple was periodically checked in the range $10^{-5} \leq [Ag^+] \leq 10^{-2}$ M. No significant deviations from Nernst's law were found. The stability constants were calculated, from the emfs measured, by the computer program Superquad.[17] Several hypotheses about the chemical species formed in solution were considered. The best fit of experimental data was obtained by assuming that in the equilibrium mixture of the various systems the complexes reported in Table I were present.

Calorimetric Measurements. A Tronac Model 450 calorimeter interfaced with a North Star-Horizon computer was used. All the experiments were carried out at 25.000 ± 0.001 °C. The heats of formation of the silver(I) complexes with dppm, dppe, and dppp were determined by adding ligand solutions (50 mmol dm^{-3}) to metal solutions (2 ≤ C^0_M ≤ 10 mmol dm^{-3}) under the same conditions of ionic strength as those used in the potentiometric study. As the solubilities of etp and PP_3 in DMSO did not allow us to reach high C_L/C_M ratios (see Figure 3b), as in the potentiometry, back-titrations were also run for all system. In these cases, metal solutions (20 ≤ C^0_M ≤ 50 mmol dm^{-3}) were added to ligand solutions of about 7 mmol dm^{-3}. For each system direct and reverse calorimetric titrations superimposed. Each titration was repeated at least twice. The heats of dilution for silver(I) and ligand solutions were also determined. These were so small, however, that no corrections were necessary. The enthalpy changes were calculated by means of the least-squares program Letagrop-Kalle.[18]

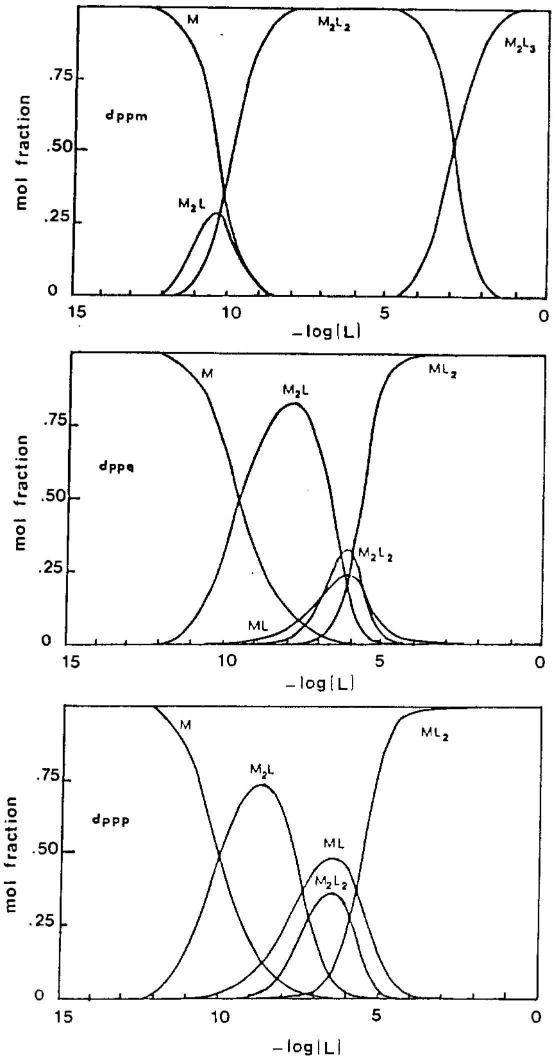


Figure 1. Distribution curves for the silver(I)–diphosphine systems at C^0_M = 5.0 mmol dm^{-3}.

^{31}P NMR Measurements. $^{31}P\{^1H\}$ NMR spectra were recorded on a Brucker WP 80 spectrometer equipped with a VT-100 variable-temperature accessory operating at 32.41 MHz in the FT mode while locked on the ^2H resonance of a deuterated solvent. In this work, 10-mm-tube samples with internal 5-mm-tube references were used. The chemical shifts are reported with respect to 85% H_3PO_4. A positive sign indicates a shift to low field of resonance. The spectra were measured in DMSO at 308 K and in CH_2Cl_2 between 308 and 183 K. For silver(I)–dppm, –dppe, and –dppp systems, measurements were performed where the ratio C_L/C_M was ranging between 0.2 and 2. All the solutions were prepared by dissolving anhydrous $AgClO_4$ and anhydrous ligands in the required ratios.

Results and Discussion

The overall stability constants for the silver(I) complexes with the ligands studied in this work are listed in Table I with the limits of error indicated. The distribution curves of the various silver(I)

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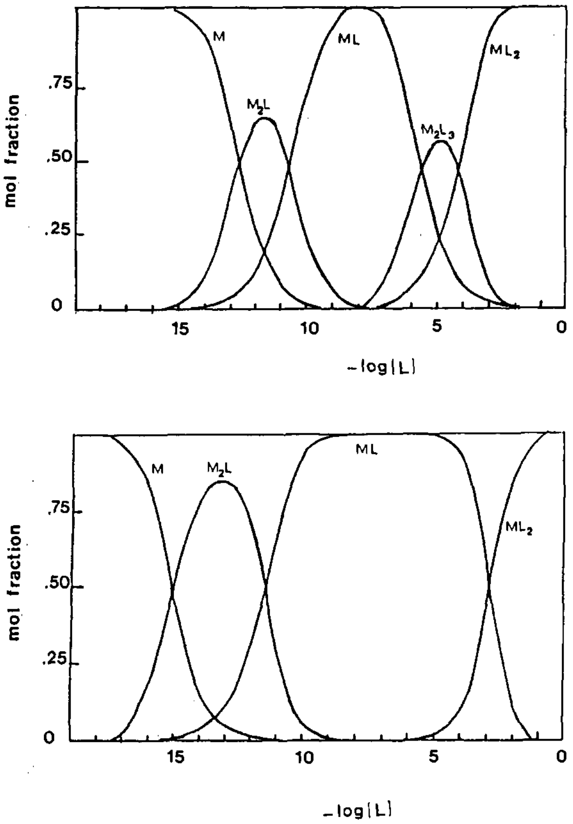


Figure 2. Distribution curves for the silver(I)-polyphosphine systems at C^0_M = 2.0 mmol dm^{-3}.

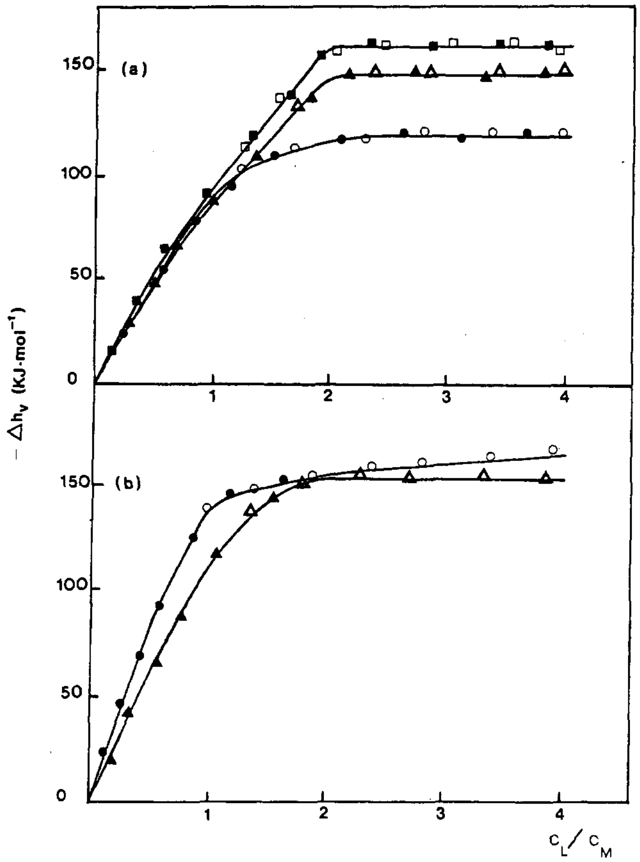
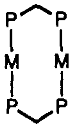


Figure 3. Total molar enthalpy changes per mole of metal ion as a function of C_L/C_M for silver(I)-polyphosphine systems: (a) (●) dppm, (▲) dppe, and (■) dppp at C^0_M = 5.0 mmol dm^{-3}; (b) (▲) etp and (●) PP_3 at C^0_M = 2.0 mmol dm^{-3}. Open symbols refer to back-titrations. The solid lines have been calculated from the values of β and $\Delta H°$ reported in Table I.

complexes at varying ligand concentrations are reported in Figures 1 and 2.

For dppm no mononuclear complexes, ML and ML_2, could be detected in appreciable amount. For all the diphosphines, the polynuclear species are predominant in a wide range of ligand concentration whereas the ML complexes are only minor species. These complexes are by contrast important species for etp and PP_3. A common feature of all the systems is the formation in appreciable amount of the dinuclear species M_2L, which are formed at the beginning of the titrations when the metal–ligand ratios are still fairly large, whereas very stable complexes of the type M_2L_2 are formed only by the diphosphines and a complex of composition M_2L_3 had to be introduced in order to fit the experimental data for dppm and etp. No formation of complexes beyond the second one was observed in any of the systems investigated. In Figure 3 the heat evolved per mole of silver(I), Δh_v, obtained directly from the calorimetric measurements, is plotted as a function of the ratio C_L/C_M. From the experimental data, the overall enthalpy changes for the silver(I) complex formation have been obtained. The corresponding values, together with the calculated free energy and entropy changes, are summarized in Table I. For comparison in the same table have also been entered the stability constants and the thermodynamic functions for the complex formation of silver(I) with the unidentate ligand triphenylphosphine, PPh_3, determined under the same experimental conditions, viz. 25 °C and I = 0.1 mol dm^{-3}.[5]

As mentioned above, there is no evidence for formation of mononuclear species of silver(I) with dppm. Given the nature of the ligand, this is somehow to be expected: dppm is in fact a bidentate ligand in which the donor atoms are separated by only one methylene group, and therefore the formation of mononuclear species would give rise to highly strained four-membered chelate rings. The constraint imposed by the ligand therefore favors the formation of polynuclear species. This is in accordance with the tendency of dppm to act as a bridging ligand:[10] this is further supported by the fact that, in the solid state, the (bis(diphenylphopshine)methane)silver compound $[Ag_2(dppm)_2(NO_3)_2]$, has been prepared and characterized by IR, NMR, and X-ray techniques.[13] The molecule has been found to contain a $[Ag_2(dppm)_2]^{2+}$ core structure with the two silver atoms bridged by the two dppm ligands to give a eight-membered ring (I).



I

We believe that this structure is retained in solution: the resulting planar M_2P_4 structure on the other hand is in line with the tendency of silver(I) to coordinate linearly.[19]

The complex formation between silver(I) and all the phosphines always results in being enthalpy controlled: both the enthalpy and the entropy changes are in fact negative. The stability constants of ML complexes with the diphosphines are all much larger than those for the silver(I) complexes with the unidentate ligand triphenylphosphine. Also, the enthalpy and entropy changes are respectively more exothermic and more negative for the silver(I)–diphosphine systems. This indicates that the ligands act as chelating agents.

The thermodynamic functions, relative to the second step of complexation with these ligands, show that the second ligand also acts as a chelating agent. These complexes have a tetrahedral configuration in solution as confirmed by ^{31}P NMR spectroscopy (see below).

The silver(I) complexes formed with dppp are somewhat stronger than those with dppe, that is the six-membered chelate

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Table II. Overall Stability Constants and Thermodynamic Functions for Silver(I)–Phosphine and –Amine Systems in DMSO at 25 °C and I = 0.1 mol dm^{-3}[a]

	dppe	en[b]	dppp	tn[b]	etp	dien[b]	PP_3	tren[c]
log β_{11}	7.73	5.34	8.65	5.9	11.69	7.46	13.29	9.43
log β_{12}	13.91	9.50	14.39		16.69	10.20	16.25	11.2
log β_{21}	11.91		12.37	8.06	15.45		17.88	11.53
log β_{22}	18.28		20.13	14.4				
log β_{23}					32.01			
$-\Delta G°_{11}$	44.1	30.5	49.4	34	66.7	42.6	75.9	53.0
$-\Delta G°_{12}$	79.4	54.2	82.1		95.3	58.2	93	65.6
$-\Delta G°_{21}$	68.0		70.6	46.0	88.2		102.0	67.3
$-\Delta G°_{22}$	104.3		114.9	82				
$-\Delta G°_{23}$					182.7			
$-\Delta H°_{11}$	87	63	95	80.8	109	78.2	140	90
$-\Delta H°_{12}$	149	85	162		159	94	173	97
$-\Delta H°_{21}$	110		115	71.6	135		166	95
$-\Delta H°_{22}$	186		195	146.8				
$-\Delta H°_{23}$					291			
$-\Delta S°_{11}$	144	109	153	157	142	119	215	124
$-\Delta S°_{12}$	233	103	268		214	120	268	103
$-\Delta S°_{21}$	141		149	86	157		215	91
$-\Delta S°_{22}$	274		269	217				
$-\Delta S°_{23}$					364			

[a] $\Delta G°_{ij}$ and $\Delta H°_{ij}$ in kJ mol^{-1}; $\Delta S°_{ij}$ in J K^{-1} mol^{-1}. The log β_{ij} values refer to the reaction $iM^+ + jL \rightleftharpoons M_iL_j^{i+}$. [b] Reference 9. [c] Unpublished results. (tren = tris(2-aminoethyl)amine).

ring has more stability than the five-membered one. The same trend had already been found for the complex formation of silver(I) with the polyamines 1,2-diaminoethane (en) and 1,3-diaminopropane (tn) in DMSO.[9] As the stabilities of chelate complexes are mostly controlled by the strain in the chelate rings, some strain is evidently present within the five-membered chelate ring formed by dppe which, in addition to the higher basicity of dppp with respect to dppe, accounts for the higher stability of the silver(I) complexes with the former ligand.

It is reasonable to suppose that the dimeric species Ag_2L_2 formed by dppe and dppp with silver(I) have the same core structure as $[Ag_2(dppm)_2]^{2+}$. As before, the stability of the silver(I) complex with dppp is somewhat higher than with dppe. The same factors seen above are probably at play also in the formation of these complexes.

As for etp and PP_3, the thermodynamic functions suggest that these ligands act as ter- and tetradentate, giving rise to two and three fused five-membered chelate rings, respectively, with a tetrahedral configuration around the metal ion. Most likely a rearrangement of the ligands occurs when the 1:2 complexes are formed. The huge value of the ratio K_1/K_2 (5×10^6 for etp and 2×10^{10} for PP_3) and the very low value of $-\Delta H°_2$ as compared with $-\Delta H°_1$ for the two systems seem to indicate that in the complex $[Ag(etp)_2]^+$ both ligands act as bidentate while in the complex $[Ag(PP_3)_2]^+$ probably one ligand acts as terdentate and the second one as unidentate.

In Table II are reported the free energy, enthalpy, and entropy changes for the silver(I) complexes with some of the ligands investigated here and for comparison the thermodynamic functions of complex formation between silver(I) and analogous ligands coordinating via nitrogen. The polyphosphines form with silver(I) a larger number of species than the polyamines. In particular, polynuclear species are formed by silver(I) with all the phosphines but only with tn and tren among the amines.

Moreover, the enthalpy changes relative to silver(I) complex formation with phosphorus donor ligands are much more negative than with N-donor ligands, reflecting a stronger covalency of the bond Ag–P as compared to Ag–N.

In order to get further useful information on the coordination geometry of the different species formed by silver(I) with these ligands, variable-temperature $^{31}P\{^1H\}$ NMR measurements were also run for the easily soluble diphosphine complexes. In the case of silver(I)–dppm system, ^{31}P NMR spectra were collected for solutions where R = C_L/C_M was varied between 0.2 and 1.5: a broad band was always observed in DMSO at 308 K. As far as silver(I)–dppe and –dppp systems were concerned, broad signals were also obtained in DMSO at 308 K, for solutions where $R < 2$, reasonably due to a rapid phosphorus exchange.

These exchange processes might be possibly frozen out by lowering the sample temperature, provided that a suitable solvent could be found. Unfortunately, in dichloromethane and other solvents (or solvent mixtures) with which low temperatures could be reached, it was not possible to investigate the above-mentioned solutions of silver(I)–dppm ($0.2 < R \leq 1.5$), –dppe, and –dppp ($0.2 < R < 2$), because of the formation of precipitates.

On the other hand useful data were obtained from the spectra collected when $R = 2$ for silver(I)–dppe and –dppp systems at 308 K in dmso and at lower temperatures in CH_2Cl_2.

Within the temperature range investigated in CH_2Cl_2 (308–183 K), no significant variations, with respect to DMSO, were observed in the spectra, a part from the obvious slight variation in δ values, thus indicating that the same static situation (only ML_2 complexes are present) exists in DMSO at 308 K and in CH_2Cl_2 at 183 K.

In both solvents, the spectra for silver(I)–dppe and –dppp systems recorded at various temperatures consist of two doublets due to spin–spin coupling of equivalent P atoms to $^{107-109}Ag$: natural abundance silver consists in fact of two isotopes having spin $^1/_2$, ^{107}Ag (51% abundance) and ^{109}Ag (49% abundance). In DMSO these two doublets were centered at δ = 3.56 and δ = −4.79, respectively.

$J(^{107}Ag–P)$ values were 232 and 220 Hz for silver(I)–dppe and –dppp systems respectively, which are in good agreement with the observed 227 Hz value for sp^3 silver coordination, as found for AgL_4 complex, where L = tri-*p*-tolylphosphine.[20] In addition, also Socol and Verkade[15] found for AgL_4 tetrahedral complexes (L = monophosphines) $J(^{107}Ag–P)$ values between 212 and 230 Hz. Our results thus agree with the hypothesis that in these ML_2 complexes both ligands behave as bidentate according to what is suggested by thermodynamic data.

Acknowledgment. We thank P. Polese for experimental assistance.

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