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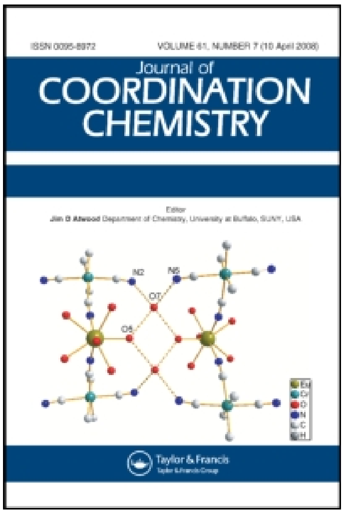

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A variable temperature ^{31}P NMR study of 9-30 atom macrocylic rings of silver(I) with long chain diphosphines

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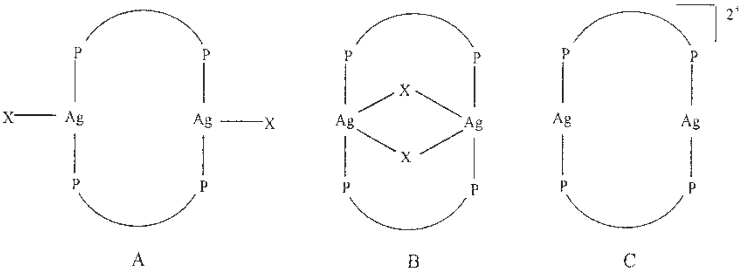
The coordination chemistry of equimolar amounts of silver(I) with the long chain diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (where $n = 6$, 8, 10, or 12) has been studied by variable temperature $^{31}P\{^1H\}$ NMR. In all cases two silver(I)/diphosphine complexes were observed in solution at ambient temperature with $^1J(^{107}Ag–P)$ values of ca 500 Hz indicating silver(I) coordinated to two phosphorus atoms in a linear mode. A van't Hoff study on the variable temperature $^{31}P\{^1H\}$ NMR data has been used to assign monomeric and dimeric species.

Keywords: Organophosphorus compounds; Nuclear magnetic resonance; Electrospray mass spectrometry; Ag(I) complexes

1. Introduction

The coordination chemistry of silver(I) with the flexible diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (where $n \leq 6$) mixed in equimolar amounts reveals the propensity of the ligands to bridge two Ag(I) centers giving a 2 : 2 macrocyclic ring. The macrocyclic ring complexes reported in the literature are illustrated below.



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The nature of the anion and the length of the methylene backbone play a significant role in determining the type of complex formed. DPPM ($Ph_2PCH_2PPh_2$) forms a complex of type **A** with the weakly coordinating anion NO_3^{1-} [1, 2]. The formation of complex type **A** and not type **B** with NO_3^{1-} has been explained as being due to the short span of the DPPM ligand [3]. A complex of type **A** was also reported for DPPM with the $PhCH_2CO_2^{1-}$ anion [4]. DPPP ($Ph_2P(CH_2)_3PPh_2$) and DPPB ($Ph_2P(CH_2)_4PPh_2$) form complexes of type **A** with NO_3^{1-} [5, 6]. In addition, the ligands DPPP and DPPB have been shown to form complexes of type **C** with the anion BF_4^{1-} [7, 8]. Again it could be argued here that the methylene backbone is too short to give a complex of type **B**. DPPPent ($Ph_2P(CH_2)_5PPh_2$) with the Cl^{1-} anion formed a dimeric complex of type **B**, $[Ag_2(\mu\text{-DPPPent})_2(\mu\text{-Cl})_2]$ [9]. The methylene backbone in DPPPent is long enough for the formation of the four-membered Ag_2Cl_2 core. DPPH ($Ph_2P(CH_2)_6PPh_2$) also forms a dimeric complex of type **B**, $[Ag_2(\mu\text{-DPPH})_2(\mu\text{-ClO}_4)_2]$ with ClO_4^{1-} [10]. It has been suggested that two (μ-ClO_4) in $[Ag_2(\mu\text{-DPPH})_2(\mu\text{-ClO}_4)_2]$ stabilize the 18-membered $[Ag_2(DPPH)_2]$ macrocycle [11].

Solution studies indicating the formation of complexes of type **C** have previously been reported for DPPM [12, 13], DPPE [13], and DPPP [13].

To our knowledge, there are no reports of the coordination chemistry of Ag(I) with the long methylene backbone ligands $Ph_2P(CH_2)_nPPh_2$ (where $n \geq 6$) mixed in equimolar quantities with a poorly coordinating anion which would preclude stabilization of the $\geq$18-membered $[Ag_2(\text{diphosphine})_2]$ core by the anion. Herein, we report an *in situ* $^{31}P\{^1H\}$ NMR solution study on the coordination chemistry of equimolar mixtures of $AgBF_4$ with the long backbone ligands $Ph_2P(CH_2)_6PPh_2$ (abbreviated DPPH), $Ph_2P(CH_2)_8PPh_2$ (DPPO), $Ph_2P(CH_2)_{10}PPh_2$ (DPPD), and $Ph_2P(CH_2)_{12}PPh_2$ (DPPDOD) and the application of van't Hoff analyses in assigning the solution species observed.

2. Experimental section

2.1. *Materials*

All solvents were purchased from Fisher Scientific Company and purified prior to use by conventional methods. Silver(I) tetrafluoroborate was prepared as previously described [14]. The ligands $Ph_2P(CH_2)_6PPh_2$ (DPPH), $Ph_2P(CH_2)_8PPh_2$ (DPPO), $Ph_2P(CH_2)_{10}PPh_2$ (DPPD), and $Ph_2P(CH_2)_{12}PPh_2$ (DPPDOD), were synthesized with slight modifications and characterized as previously described [15, 16]. The modification involved increasing the length of the reaction time from 30 to 60 min upon addition of the appropriate α,ω-dibromo alkane and then slowly heating to 60°C for 60 min before isolation of the product. Yields 50–80%.

2.2. *Physical methods*

Proton NMR spectra were recorded on a Bruker AC 250 multinuclear spectrometer operating at 250 MHz. The phosphorus-31 NMR spectra were recorded on a Bruker AC 250 multinuclear spectrometer operating at 101 MHz and (for variable temperature studies) either a Bruker AM 400 multinuclear spectrometer operating at 162 MHz or a Bruker Avance 400 multinuclear spectrometer operating at 162 MHz. Tetramethylsilane (TMS) was used as an internal standard for proton NMR and

85% phosphoric acid was used as an external standard for the phosphorus NMR. $CDCl_3$ and d_6-acetone were used as internal lock solvents. Chemical shifts (δ) were reported in parts per million (ppm) with peaks downfield of the standard given positive values.

Electrospray mass spectra were recorded with a VG Trio 2000 quadrupole mass spectrometer. A syringe pump delivered the mobile phase to the vaporization nozzle of the electrospray ion source at a flow rate of $3\,\mu L\,min^{-1}$. Theoretical isotopic mass distributions were obtained with Isotope Pattern Calculator Version 1.6.6 [17]. Instrument settings were as follows: needle voltage, 3.4 kV; repeller voltage, 0.38 kV; sampling cone voltage 20–110 V; lens voltages, 63 and 12 V; and electrospray source temperature, 60°C [18].

The sample solutions were prepared by dissolving the appropriate molar ratios of $AgBF_4$ in acetone and the ligand in methylene chloride or acetone, depending on solubility, to give a 0.001 M solution. The solutions were then diluted 10 times with the appropriate mobile phase to give solutions that were 0.0001 M. A 50% : 50% acetonitrile–water mixture was used as the mobile phase for the majority of the complexes. However, the polar nature of the solvent mixture made it difficult to dissolve the longer diphosphines and their Ag(I) complexes. To increase the solubility of the ligands and their complexes a 100% acetonitrile solvent system was used. Similar results were observed in 100% acetonitrile and in the 50% : 50% acetonitrile–water solvent system.

2.3. *Variable-temperature $^{31}P\{^1H\}$ NMR studies*

Appropriate molar amounts of the ligands were dissolved in methylene chloride or acetone, depending on solubility, and added to an acetone solution of $AgBF_4$ to yield mixtures with ligand concentration, (C_L): Ag concentration, (C_M) of 1 to 1, having overall concentrations of 0.02–0.04 M. The solutions were run *in situ* at temperatures ranging from room temperature down to 225 K. Temperature calibration utilized methanol.

Calculation of the equilibrium constant at various temperatures for the equilibrium;

$$\left[Ag_2(P\,^\wedge P)_2\right]^{+2} \leftrightarrow 2\left[Ag(P\,^\wedge P)\right]^{+1} \quad \text{where } P\,^\wedge P = \text{DPPH, DPPO, DPPD, DPPDOD}$$

was performed using peak integrals. An example of the calculation of the equilibrium constant for the silver(I)-DPPO complexes at 298 K is shown below.

	Ag^{1+}	+ DPPO →	$[Ag_2(DPPO)_2]^{2+}$	+ $[Ag(DPPO)]^{1+}$
Start, moles	1.0×10^{-4}	1.0×10^{-4}	0	0
Equilibrium, %	P	0	51.9	48.1

Number of moles of $[Ag(DPPO)]^{1+}$ at equilibrium $= (0.481)(1.0\times10^{-4}) = 4.81\times10^{-5}$

Number of moles of $[Ag_2(DPPO)_2]^{2+}$ at equilibrium $= (0.519/2)(1.0\times10^{-4}) = 2.60\times10^{-5}$

Number of moles of Ag^{+1} at equilibrium $= 1.0\times10^{-4} - [(4.81\times10^{-5}) + 2(2.60\times10^{-5})] = 0$

Total volume of solution = 4.00 mL, thus
$[Ag(DPPO)]^{1+} = 1.20 \times 10^{-2}$ M
$[Ag_2(DPPO)_2]^{2+} = 6.50 \times 10^{-3}$ M
Given the equilibrium; $[Ag_2(DPPO)_2]^{2+} \leftrightarrow 2\ [Ag(DPPO)]^{1+}$

$$K = (1.20 \times 10^{-2})^2/(6.50 \times 10^{-3})$$

$$K = 2.22 \times 10^{-2}\ \mathrm{M}$$

3. Results and discussion

The equimolar $AgBF_4$/DPPH *in situ* mixture at room temperature gave a $^{31}P\{^1H\}$ NMR spectrum with a doublet of doublets with well-resolved $^{109/107}Ag$–^{31}P coupling at 10.9 ppm and 0.9 ppm with $^1J(^{107}Ag$–$^{31}P)$ values of 498 and 490 Hz, respectively figure 1. The coupling constant values are consistent with Ag(I) coordinated to two P atoms in a linear mode [19]. The chemical shifts are too far apart for the two doublets to represent two different conformers of the same silver–diphosphine complex, a phenomenon previously noted by Pryde *et al.* [20] and Hill *et al.* [15] with long-chain diphosphine complexes of Pt(II).

The equimolar $AgBF_4$/diphosphine *in situ* mixtures for DPPO, DPPD, and DPPDOD at room temperature showed $^{31}P\{^1H\}$ NMR spectra with the same general feature of two doublets with well-resolved $^{109/107}Ag$–^{31}P coupling. The $AgBF_4$/DPPO *in situ* mixture showed a well-resolved doublet at 10.8 ppm with a $^1J(^{107}Ag$–$^{31}P)$ of 499 Hz. The second doublet appeared upfield at 9.5 ppm with a $^1J(^{107}Ag$–$^{31}P)$ of 503 Hz. The $AgBF_4$/DPPD *in situ* mixture showed a well-resolved doublet at 12.8 ppm with a $^1J(^{107}Ag$–$^{31}P)$ of 507 Hz. The second doublet does not show the resolved $^{109/107}Ag$–^{31}P coupling and appears upfield at 11.0 ppm with a $^1J(Ag$–$^{31}P)$ value of 508 Hz. The $AgBF_4$/DPPDOD *in situ* mixture showed a well-resolved doublet at 12.2 ppm with a $^1J(^{107}Ag$–$^{31}P)$ of 503 Hz with the second doublet appearing

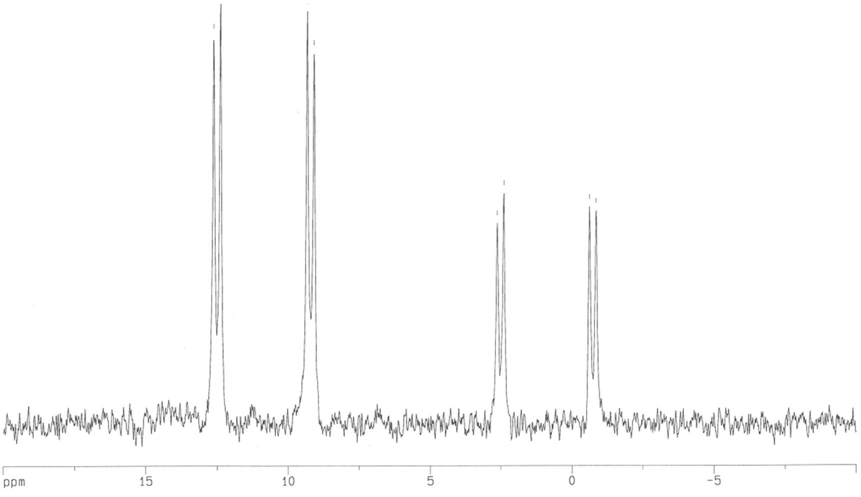

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of an equimolar $AgBF_4$/DPPH *in situ* mixture at 298 K.

Table 1. Summary of the $^{31}P\{^1H\}$ NMR data for the equimolar $AgBF_4$/diphosphine *in situ* mixtures at 298 K.

$AgBF_4$/Diphosphine	δ of doublet, ppm	$^1J(^{107}Ag–P)$, Hz	% Total P
DPPH	10.9	498	65.7
	0.9	490	34.3
DPPO	10.8	499	48.1
	9.5	503	51.9
DPPD	12.8	507	68.7
	11.0	508[a]	31.3
DPPDOD	12.2	503	70.5
	10.9	498	29.5

[a] ^1J ($^{107/109}$Ag–P) coupling not resolved.

upfield at 10.9 ppm with a $^1J(^{107}Ag–^{31}P)$ of 498 Hz. Table 1 summarizes the room temperature $^{31}P\{^1H\}$ NMR observations for the equimolar $AgBF_4$/diphosphine *in situ* mixtures.

The room temperature $^{31}P\{^1H\}$ NMR spectra of the Ag–diphosphine complexes suggest two distinct complexes which have been assigned to the *trans*-spanning chelated monomer $[Ag(Ph_2P(CH_2)_nPPh_2)]^{1+}$ and the *trans*-macrocyclic bridged dimer $[Ag_2(Ph_2P(CH_2)_nPPh_2)_2]^{2+}$. The reasons for the monomer/dimer thesis are several. The flexible diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, 2, or 3) are known for their propensity, when mixed in equimolar amounts, to form the dimeric or 2 : 2 macrocyclic ring with Ag(I) [1–5, 11–13] supporting the presence of the dimer. Furthermore, $[Ag_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)_2X_2]$ ($n = 5$ or 6), have been reported in the solid-state [9, 10]. In both cases the macrocyclic ring is stabilized by anions also bridging the silver ions, i.e., $[Ag_2(\mu\text{-}Ph_2P(CH_2)_5PPh_2)_2(\mu\text{-}Cl)_2]$ and $[Ag_2(\mu\text{-}Ph_2P(CH_2)_6PPh_2)_2(\mu\text{-}ClO_4)_2]$. Tetrafluoroborate, BF_4^{1-}, however, is a poor nucleophile and does not bridge the silver ions to offer the dimer stability. In the absence of the extra stability conferred by silver bridging anions the $\geq$18-membered macrocyclic dimeric rings are prone to fragmenting to give two monomeric rings, resulting in an equilibrium between the two species. Secondly, the ligands $Ph_2P(CH_2)_nPPh_2$ (where $n \geq 6$) have a methylene backbone chain long and flexible enough to *trans*-chelate a Ag(I) ion. Indeed, the first example of a metal complex with a *trans*-chelating diphosphine ligand had a C_5 methylene backbone [21]. The *trans*-spanning chelate $[Ag(\eta^2\text{-POOP})]BF_4$ [22, 23] where POOP is 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, i.e., the DPPO ligand with the methylene groups at positions 3 and 6 replaced by oxygen is known. Diphosphine ligands with rigid backbone chains have widely been reported in the literature to complex Ag(I) and form a monomer [24]. These observations support the presence of a monomeric Ag(I)–diphosphine complex. Thirdly, the presence of Ag–diphosphine monomer and dimer present in equilibrium in solution is not unprecedented. Del Zotto *et al.* [25] proposed a $[Ag(DPPE)]^{1+}$/$[Ag_2(DPPE)_2]^{2+}$ equilibrium in solution at lower temperatures after observing two species in the ^{31}P NMR both with J(Ag–P) values of ca 550 Hz. Finally, it has been noted that diphosphines alone with Ag(I) tend to form chelate complexes and other ring structures and not polymeric complexes [26]. Furthermore, the formation of a polymeric species should have led to poor solubility of the mixtures, a phenomenon not observed. These observations support our contention that no polymeric complexes were formed.

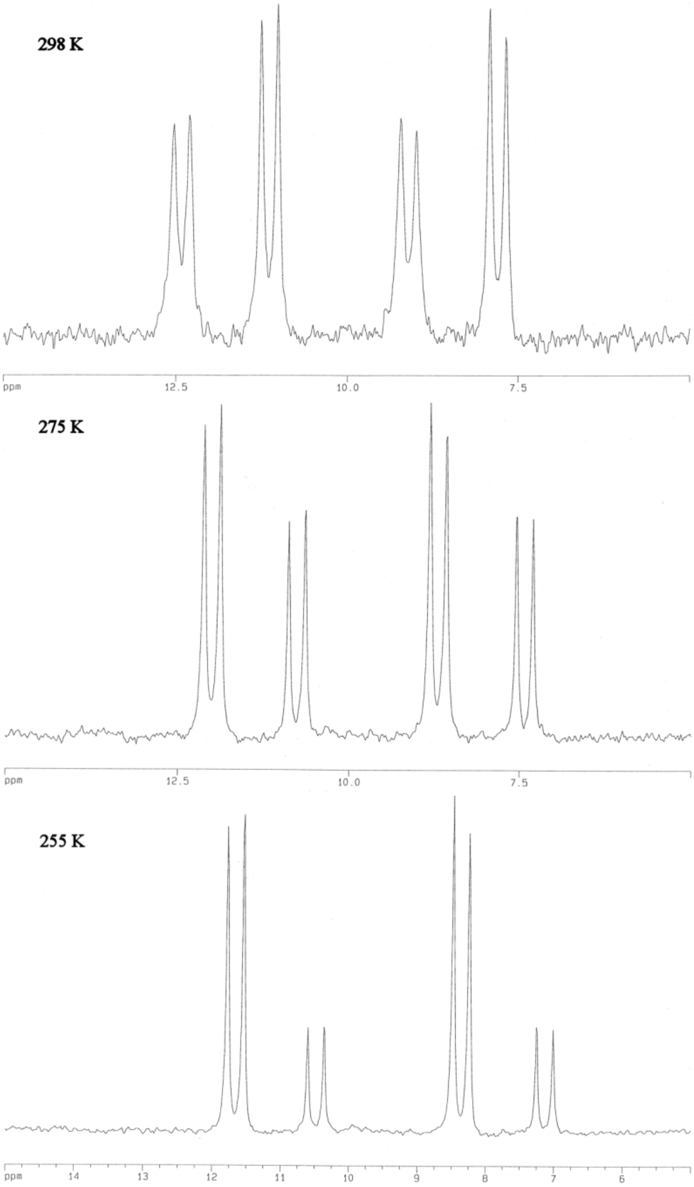

Figure 2. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of DPPO : $AgBF_4$ ($C_L/C_M = 1.0$).

The equilibrium below is thus proposed to exist in these *in situ* mixtures:

$$\left[Ag_2(\mu - Ph_2P(CH_2)_nPPh_2)_2\right]^{2+} \longleftrightarrow 2\left[Ag(\eta^2 - Ph_2P(CH_2)_nPPh_2)\right]^{1+}$$

The *in situ* mixtures were further studied by variable temperature $^{31}P\{^{1}H\}$ NMR in an effort to study the equilibrium between monomeric and dimeric species and assign

Table 2. van't Hoff analysis data from the variable temperature ^{31}P NMR for the equimolar *in situ* Ag(I)/DPPO mixture for the equilibrium $[Ag_2(DPPO)_2]^{2+} \leftrightarrow 2[Ag(DPPO)]^{1+}$.

Species (assigned $\delta(^{31}P)$, ppm)[a]	% Total P in species assigned $\delta(^{31}P) = 10.8$	% Total P in species assigned $\delta(^{31}P) = 9.5$	ln *K*	1/*T* (1/K)
$[Ag_2(DPPO)_2]^{2+}$ (10.8)	51.9	48.1	−3.81	0.0034
	62.1	37.9	−4.46	0.0036
$[Ag(DPPO)]^{1+}$ (9.5)	67.9	32.1	−4.88	0.0038
	75.4	24.6	−5.52	0.0039
	79.7	20.3	−5.96	0.0041
	86.6	13.4	−6.87	0.0043
	90.2	9.8	−7.54	0.0044
$[Ag(DPPO)]^{1+}$ (10.8)	51.9	48.1	−3.58	0.0034
	62.1	37.9	−2.98	0.0036
$[Ag_2(DPPO)_2]^{2+}$ (9.5)	67.9	32.1	−2.64	0.0038
	75.4	24.6	−2.15	0.0039
	79.7	20.3	−1.95	0.0041
	86.6	13.4	−1.27	0.0043
	90.2	9.8	−0.88	0.0044

[a] $\delta(^{31}P)$ values at 298 K.

the monomer and dimer. The thermodynamic parameter ΔS was estimated for the equilibrium. An assignment of the monomeric and dimeric species was made, and the equilibrium constants, *K*, calculated at various temperatures from the peak integrals as described in the experimental section. A plot of ln *K* *versus* $1/T$ has a slope of ΔH/R and an intercept of ΔS/R. The assignment of the monomeric and dimeric species that gave a positive value of ΔS was taken as correct. Figure 2 shows the variable temperature $^{31}P\{^1H\}$ NMR spectra for the equimolar $AgBF_4$/DPPO *in situ* mixture. Table 2 shows the data from the variable temperature $^{31}P\{^1H\}$ NMR studies utilized for the van't Hoff analyses. Figure 3 shows the ln *K* *versus* $1/T$ plots from the data for each of the two possible monomer/dimer chemical shift assignments for the $AgBF_4$/DPPO *in situ* mixture. Table 3 lists the van't Hoff analyses data for the monomer/dimer that gave a positive value of ΔS for the equilibrium:

$$[Ag_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)_2]^{2+} \leftrightarrow 2[Ag(\eta^2\text{-}Ph_2P(CH_2)_nPPh_2)]^{1+}$$

Note that the δ value for the dimers is more or less constant at about 10.9 ppm. In the monomeric species there is a relatively large variation ranging from −1.7 to 12.8 ppm with the general trend being a downfield shift with increasing ligand methylene backbone length. The Ag(I)/DPPH and Ag(I)/DPPO *in situ* mixtures showed only two species over the temperature range studied, giving a perfect mass balance for *K* value determinations. The Ag(I)/DPPD mixture was unique in that the species assigned as the dimer at room temperature showed a doublet with the $^1J(^{109/107}Ag–^{31}P)$ coupling not resolved. This implies exchange at this higher temperature with some species other than the monomer which showed the well-resolved $^1J(^{109/107}Ag–^{31}P)$ coupling at this temperature. The Ag(I)/DPPD and Ag(I)/DPPDOD *in situ* mixtures showed small amounts of a one-coordinate Ag(I)–diphosphine complex (i.e., $^1J(Ag–P) = ca$ 750 Hz) [27, 28], $[Ag_2(\mu\text{-diphosphine})]^{2+}$, at a lowered temperature (9.5 and 7.5% of total P,

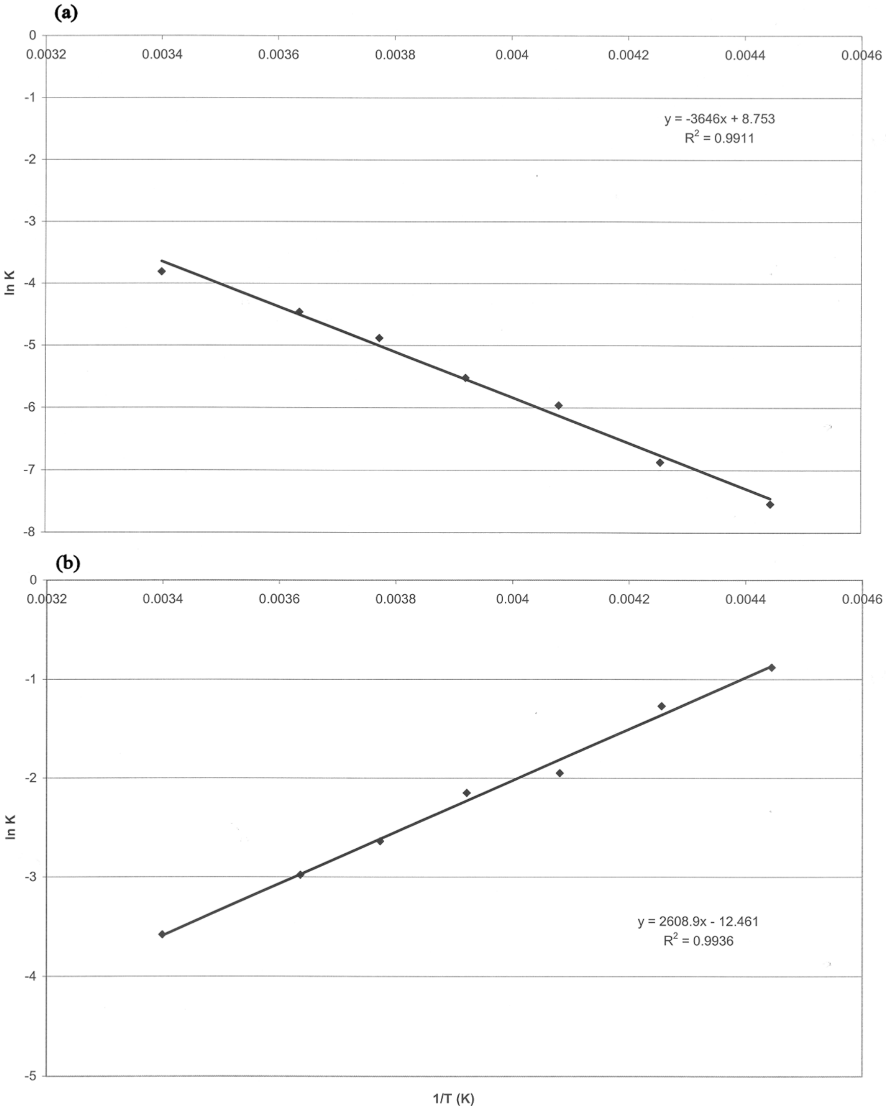

Figure 3. (a) Plot of ln *K* *vs.* $1/T$ for the equilibrium $[Ag_2(DPPDOD)_2]^{2+} \leftrightarrow 2[Ag(DPPDOD)]^{1+}$. (b) Plot of ln *K* *vs.* $1/T$ for the equilibrium $2[Ag(DPPDOD)]^{1+} \leftrightarrow [Ag_2(DPPDOD)_2]^{2+}$.

respectively at 225 K). At the lower temperatures, i.e., <255 K, all of the Ag(I) and phosphorus is accounted for by mass balance when the small amounts of $[Ag_2(\mu\text{-diphosphine})]^{2+}$ are considered. This suggests that the van't Hoff plots for Ag(I) with DPPD and DPPDOD may include error greater than those observed for the DPPH and DPPO mixtures in spite of the R^2 numbers of >0.95 obtained. The ΔH values obtained ranged from 12.9 to 30.3 kJ mol^{-1} while the ΔS values ranged from 22.3 to 72.8 J mol^{-1} K^{-1}. The equilibrium as written is thus slightly endothermic. From table 3 it is noted that in all the Ag(I)/diphosphine *in situ* mixtures studied, as the temperature decreases, the value of *K* decreases implying the

Table 3. van't Hoff analysis data from ^{31}P NMR for equimolar *in situ* silver(I)/diphosphine mixtures for the equilibrium, $[Ag_2(Ph_2P(CH_2)_nPPh_2)_2]^{2+} \leftrightarrow 2\ [Ag(Ph_2P(CH_2)_nPPh_2)]^{1+}$.

Ag(I)/Ligand	Species assignment[a] (δ, ppm)	ln K	$1/T$ (1/K)	ΔH[b] (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
DPPH	$[Ag_2(DPPH)_2]^{2+}$ (10.9)	−4.72	0.0034	26.5 ± 1.0	50.2 ± 4.1
		−5.61	0.0036		
	$[Ag(DPPH)]^{1+}$ (−1.7)	−5.94	0.0038		
		−6.44	0.0039		
		−7.00	0.0041		
		−7.72	0.0043		
		−7.93	0.0044		
DPPO	$[Ag_2(DPPO)_2]^{2+}$ (10.8)	−3.81	0.0034	30.3 ± 1.9	72.8 ± 7.5
		−4.46	0.0036		
	$[Ag(DPPO)]^{1+}$ (9.5)	−4.88	0.0038		
		−5.52	0.0039		
		−5.96	0.0041		
		−6.87	0.0043		
		−7.54	0.0044		
DPPD	$[Ag(DPPD)]^{1+}$ (12.8)	−2.59	0.0034	12.9 ± 0.7	22.3 ± 2.8
		−2.91	0.0036		
	$[Ag_2(DPPD)_2]^{2+}$ (11.0)	−3.15	0.0038		
		−3.47	0.0039		
		−3.68	0.0041		
		−3.88	0.0043		
		−4.19	0.0044		
DPPDOD	$[Ag(DPPOD)]^{1+}$ (12.2)	−3.13	0.0036	20.8 ± 3.1	51.3 ± 12.6
		−2.97	0.0038		
	$[Ag_2(DPPOD)_2]^{2+}$ (10.9)	−3.69	0.0039		
		−4.01	0.0041		
		−4.47	0.0043		
		−4.97	0.0044		

[a] Chemical shift values at 298 K.

[b] van't Hoff analyses R^2 values for the equimolar Ag(1)/DPPH, Ag(1)/DPPO, Ag(1)/DPPD and Ag(I)/DPPDOD mixtures are 0.9889, 0.9911, 0.9945 and 0.9556, respectively.

Table 4. Ring contributions to the ^{31}P NMR chemical shifts in the monomers.

Ligand	Free ligand[a] (δ, ppm)	Monomer[b] (δ, ppm)	ΔC[c] (ppm)	ΔR[d] (ppm)
DPPH	−16.0	0.9	16.9	−9.9
DPPO	−15.4	9.5	24.9	−1.9
DPPD	−16.0	12.8	28.8	+2.0
DPPDOD	−15.6	12.2	27.8	+1.0

[a] Relative to 85% H_3PO_4. [b] Relative to 85% H_3PO_4. [c] Coordination shift. $\Delta C = \delta$ complex $- \delta$ ligand. [d] Ring contribution to the chemical shift. $\Delta R = \Delta C - [\delta\, Ag(Ph_2PBu)_2 - \delta\, Ph_2PBu]$.

concentration of dimer increases (the exothermic direction) while that of the monomer decreases. The dimeric species is more stable at the lowered temperatures. The K values range from 10^{-2} to 10^{-4} implying that the equilibrium lies to the left, is enthalpically driven, and the dimeric species is favoured in all cases. Further, examination of the K values reveals that as the methylene backbone chain increases in length the relative amounts of the monomer at equilibrium increase.

Tables 4 and 5 list the coordination shifts, Δ, and the ring contribution, ΔR, of the dimeric and monomeric complexes. ΔR has been defined by Hill *et al.* [15]

Table 5. Ring contributions to the ^{31}P NMR chemical shifts in the dimers.

Ligand	Free ligand[a] (δ, ppm)	Dimer[b] (δ, ppm)	ΔC^{c} (ppm)	ΔR^{d} (ppm)
DPPH	−16.0	10.9	26.9	+0.1
DPPO	−15.4	10.8	26.2	−0.6
DPPD	−16.0	11.0	27.0	+0.2
DPPDOD	−15.6	10.9	26.5	−0.3

[a] Relative to 85% H_3PO_4. [b] Relative to 85% H_3PO_4. [c] Coordination shift. $\Delta C = \delta$ complex $- \delta$ ligand.
[d] Ring contribution to the chemical shift. $\Delta R = \Delta C - [\delta\, Ag(Ph_2PBu)_2 - \delta\, Ph_2PBu]$.

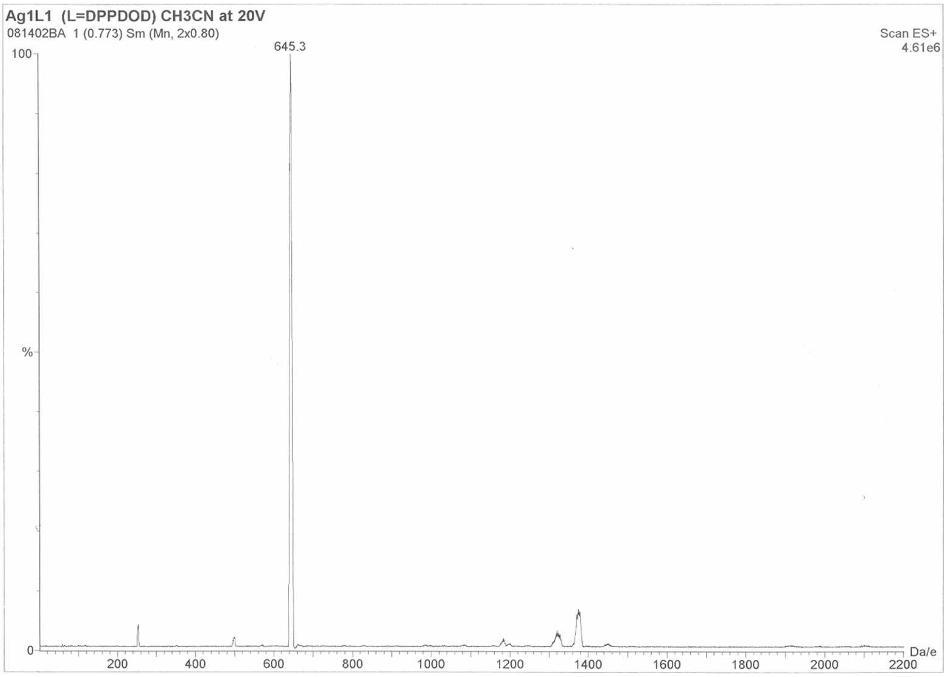

Figure 4. Electrospray mass spectrum of DPPDOD : $AgBF_4$ ($C_L/C_M = 1.0$) at a cone voltage of 20 V.

as the difference between the coordination shift of the diphosphine complex and the coordination shift of a similar bis(monophosphine) complex. That work involved square-planar platinum(II)–diphosphine complexes and the ΔR in the *trans*-spanning ligand monomeric complexes was determined to be a measure of ring strain. Here, ΔR is defined similarly with $[Ag\{(n\text{-}Bu)Ph_2P\}_2]^{1+}$ as the linear bis(monophosphine) complex. Examination of the data in table 4 reveals ΔR is approximately zero for all the dimers, i.e., there is almost no variation in the value of ΔR in the dimers. From table 5 it is clear for the monomeric complexes that ring strain is highest for DPPH with less ring strain in the DPPO, DPPD, and DPPDOD cases. This results from the increased ease of *trans*-spanning Ag(I) by the longer backbone chain ligands.

4. *ESMS*

The electrospray mass spectra of the $Ag(I)/Ph_2P(CH_2)_nPPh_2$ *in situ* mixtures showed the same general features. The base peak was comprised predominantly

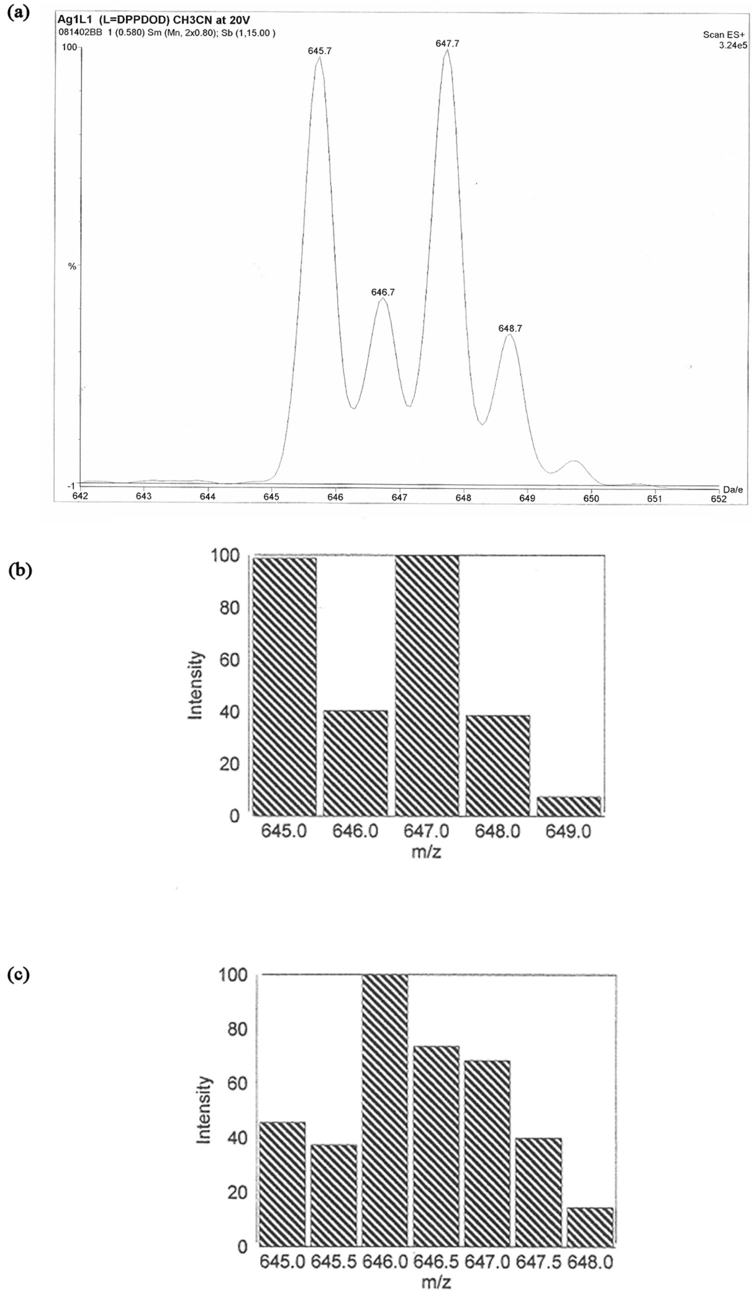

Figure 5. (a) Observed isotopic pattern for DPPDOD : AgBF$_4$ ($C_L/C_M = 1.0$). (b) Calculated isotopic pattern for [Ag(DPPDOD)]$^{1+}$. (c) Calculated isotopic pattern for [Ag$_2$(DPPDOD)$_2$]$^{2+}$.

of [Ag(Ph$_2$P(CH$_2$)$_n$PPh$_2$)]$^{1+}$ with some minor amounts of [Ag$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_2$]$^{2+}$ and a minor peak in the DPPH and DPPDOD cases for the ion pair [Ag$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_2$BF$_4$]$^{1+}$. Figure 4 shows the electrospray mass spectrum for the equimolar AgBF$_4$/DPPDOD *in situ* mixture at a cone voltage of 20 V.

The base peaks' $[Ag(Ph_2P(CH_2)_nPPh_2)]^{1+}/[Ag_2(Ph_2P(CH_2)_nPPh_2)_2]^{2+}$ composition was verified by increasing the cone voltage and observing the $[Ag(Ph_2P(CH_2)_nPPh_2)]^{1+}/[Ag_2(Ph_2P(CH_2)_nPPh_2)_2]^{2+}$ isotopic pattern. As shown in figure 5, the pattern tends to be closer to the theoretical patterns for $[Ag(Ph_2P(CH_2)_nPPh_2)]^{1+}$. The monomer/dimer phenomenon in an electrospray mass spectrometric peak has been reported in the literature [14, 29].

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