At 35 °C, as seen in Figure 1, k_W for dimethyl sulfoxide shows no maximum, only a decrease in slope; at 60 °C the maximum has become quite pronounced and has broadened.

The least-squares values of the enthalpies and entropies of activation listed in Table V were calculated for each solvent mixture by using eq 17, where k_B is the Boltzmann constant and the other symbols have their usual meaning. Several rate constant

$$\ln\frac{k_i}{T_i} = \ln\frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT_i} \qquad (17)$$

determinations were made at each temperature in each solvent mixture. The enthalpy of activation, $\Delta H_W^\ddagger$, for k_W clearly shows a dependence on solvent composition. It is at a maximum at $X_S = X_W = 0.5$ and decreases with approach to either neat solvent. Johnson and King[28] reported a qualitatively similar trend for $k_0 = k_W + k_S$ for dimethyl sulfoxide mole fractions less than 0.5 (temperature data for mole fractions greater than 0.5 were not reported) in water–dimethyl sulfoxide mixtures. Since k_W contributes to k_0 much more importantly than k_S in this composition range, it is highly probable that the two sulfoxide systems are again showing similar behavior. The enthalpy of activation, $\Delta H_S^\ddagger$, for k_S shows a dependence on solvent composition also with a maximum at $X_S = 0.2$. The activation parameters listed in Table V can be used to calculate k_S and k_W values for each solvent mixture at 29.9, 38.5, and 50.5 °C. The ratios k_S/k_W of these values can be then compared to the spectrophotometrically determined $[Co(NH_3)_5Sol^{3+}]/[Co(NH_3)_5)OH_2^{3+}]$ ratios. When this is done, satisfactory agreement is obtained between the two sets of Q values.

The first-order rate constant k_W for either sulfoxide complex, $Co(NH_3)_5Sol^{3+}$, reacting with water is a function of the solvent composition but it is *not a function of any integral power of the mole fraction or activity of either solvent; instead* k_W *is proportional to the first power of* n_W/n_0 as the ratio was determined from the water proton line broadenings in $Cr(NH_3)_5(OS(CH)_2)_3^+$ solutions. The least-squares linear equations are

$$\log (10^5 k_W) = (1.11 \pm 0.05) + (0.92 \pm 0.02) \log (n_W/n_0)$$

for the water–dimethyl sulfoxide system and

$$\log (10^5 k_W) = (1.01 \pm 0.03) + (0.91 \pm 0.03) \log (n_W/n_0)$$

for the water–tetramethylene sulfoxide system.

The first-order rate constants k_S for sulfoxide replacing water in $Co(NH_3)_5OH_2^{3+}$ are also a function of solvent composition but are not a function of any integral power of the mole fraction or activity of either solvent in the binary mixture. Instead they are dependent on the second power of n_D/n_0 as determined from the dimethyl sulfoxide proton line broadenings for $Cr(NH_3)_5OH_2^{3+}$ solutions. The least-squares linear equations are

$$\log (10^5 k_S) = (0.332 \pm 0.017) + (1.95 \pm 0.08) \log (n_D/n_0)$$

for water–dimethyl sulfoxide systems and

$$\log (10^5 k_s) = (0.371 \pm 0.017) + (1.98 \pm 0.07) \log (n_D/n_0)$$

for water–tetramethylene sulfoxide systems.

The specific rate of the reverse reaction in eq 13 is proportional to the probability that there is a water molecule in the solvation shell of $Co(NH_3)_5Sol^{3+}$. This is strong evidence that the substitution reaction has an I_d mechanism because the water molecule must be in the solvation shell around $Co(NH_3)_5Sol^{3+}$ when the transition state is reached or substitution will not occur. Also it is strongly indicated that one water molecule is a stoichiometric component of the activated complex and is most probably the one entering (leaving) the first coordination shell in the solvent interchange. In an analogous fashion the specific rate of the forward reaction in eq 13 is proportional to the square of the probability that there is a sulfoxide molecule in the solvation shell of $Co(NH_3)_5OH_2^{3+}$. Thus two sulfoxide molecules appear to be stoichiometric components of the activated complex. One molecule presumably is the entering (leaving) molecule in the solvent-interchange reaction and the second performs some necessary function such as interacting with one or the other of the entering (leaving) ligand molecules or perhaps both in turn. Thus preferential solvation studies can provide information that brings meaning to an otherwise rather meaningless dependence of rate constants and overall equilibrium constants on solvent composition.

Supplementary Material Available: Tables showing the molar extinction coefficients for $Co(NH_3)_5OH_2^{3+}$ and for $Co(NH_3)_5(OS(CH_2)_4)^{3+}$ in water–tetramethylene sulfoxide systems at 29.9, 38.5, and 50.5 °C (2 pages). Ordering information is given on any current masthead page.

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Stable, Chelated, Tetrahedral Silver(I) Complexes with Bidentate Phosphine Ligands. A Novel Application of INEPT to $^{109}Ag\{^{31}P\}$ NMR

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Received February 12, 1985

By the use of $^{109}Ag\{^{31}P\}$ INEPT pulse sequences, ^{109}Ag NMR spectra with good signal-to-noise ratios were obtained from bisphosphine complexes in relatively dilute solutions (e.g. 65 mM) in short times (1 h). They substantiated the existence of stable, chelated complexes of the type $[Ag(L_2)_2]NO_3$, where L_2 is $Ph_2PCH_2CH_2PPh_2$ (dppe), $Et_2PCH_2CH_2PPh_2$ (eppe), $Et_2PCH_2CH_2PEt_2$ (depe), $Ph_2PCH{=}CHPPh_2$ (dppey), and $Ph_2P(CH_2)_3PPh_2$ (dppp). Some of these complexes were isolated and further characterized. The difficulties of interpreting the $^{109}Ag\{^{31}P\}$ INEPT spectra arising from the second-order spin system of the eppe complex are discussed and clarified by the use of similar DEPT experiments.

Introduction

Tetrakis complexes of the group 1B (11[21]) metal ions Cu(I), Ag(I), and Au(I) containing monodentate phosphines are usually considered to be of low thermodynamic stability and high kinetic lability.[2]

However, we have recently shown that such four-coordinate Au(I) complexes containing bidentate bis(tertiary phosphines)

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(1) (a) Birkbeck College. (b) Bruker Spectrospin.

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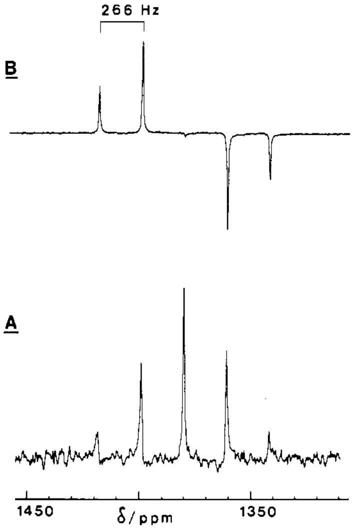

Figure 1. ^{109}Ag NMR spectra of 0.6 M [Ag(dppe)$_2$]NO$_3$ in CDCl$_3$ at 300 K: (A) normal, single-pulse acquisition (12 111 pulses, 2-s delay, 50° pulse); (B) ^{109}Ag{^{31}P} INEPT (2048 repetitions of the pulse sequence, τ = 0.93 ms).

exhibit greatly enhanced stability both in the solid state and in solution.[3] We now report similar studies of Ag(I) complexes.

The ^{31}P NMR studies reported by Muetterties and Alegranti[4] demonstrate the kinetic lability of phosphines in [Ag(PR$_3$)$_4$]$^+$ complexes: Ag–P spin–spin coupling is seen only at temperatures below −70 °C. If weakly coordinating anions are used, a range of tetrakis(phosphine) and tetrakis(phosphite) Ag(I) salts can be isolated. Previous investigations of bidentate bisphosphine Ag(I) complexes have been much less extensive;[5–7] no studies that might confirm the existence of chelated four-coordinate complexes in solution have been reported.

^{107}Ag and ^{109}Ag are both spin-$^1/_2$ nuclei with high natural abundances of 51% and 49%, respectively. They might appear to be attractive for NMR studies, but very few reports of their use have appeared.[8] This is because of their poor sensitivities (3.4×10^{-5} and 4.9×10^{-5}, respectively, relative to ^{1}H), due to low gyromagnetic ratios, and very long spin–lattice relaxation times (T_1). Colquhoun and McFarlane[9] have studied trends in ^{107}Ag shielding in phosphite complexes using a ^{31}P{^{107}Ag,^{1}H} triple-resonance technique. It has recently been shown that if resolved ^{1}H–^{109}Ag scalar coupling is present then ^{109}Ag NMR spectra are easily recorded via the INEPT (insensitive nuclei enhancement via polarization transfer) method.[10–12] Such couplings are very rare and indeed are not observed for the bis(phosphine) complexes considered here. However, phosphorus-irradiation INEPT experiments have been successfully applied to the observation of ^{103}Rh, ^{183}W, and ^{57}Fe,[13] and we have therefore sought to extend the INEPT experiment to the ^{109}Ag{^{31}P} system. The isolation of several stable, tetrahedral bisphosphine Ag(I) complexes containing five- or six-membered chelate rings is also reported.

Table I. NMR Chemical Shifts and Coupling Constants for Tetrahedral Silver(I) Bisphosphine Complexes[f]

	δ		−*J*/Hz[a]	
complex	^{31}P	^{109}Ag	^{107}Ag–^{31}P	^{109}Ag–^{31}P
[Ag(dppe)$_2$]NO$_3$	4.4	1378	231	266
[Ag(depe)$_2$]NO$_3$	1.3	*d*	226	260
[Ag(eppe)$_2$]NO$_3$[c]	−2.3	1432	*d*	290, 232
[Ag(dppey)$_2$]NO$_3$	1.5	1413[b]	235	271
[Ag(dppp)$_2$]NO$_3$	−5.2	1468[b]	220[b,e]	253[b,e]

[a] ±1 Hz; note that coupling constants are negative. [b] Solvent 10% H$_2$O/90% 1:1 acetone–acetone-d_6. [c] 223 K. [d] Not measured. [e] Not resolved in CDCl$_3$. [f] In CDCl$_3$ at 300 K, unless otherwise stated.

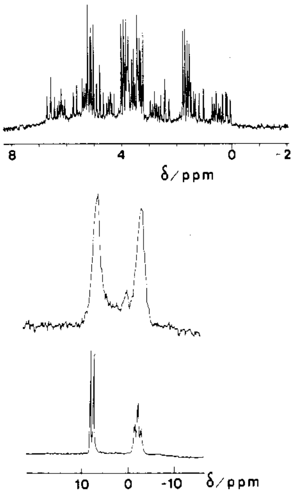

Figure 2. ^{31}P{^{1}H} NMR spectra of 65 mM [Ag(eppe)$_2$]NO$_3$ in CDCl$_3$: (A) 24 MHz at 223 K; (B) 24 MHz at 302 K; (C) 121 MHz at 223 K.

Abbreviations for Ligands

dppe = (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$
depe = Et$_2$PCH$_2$CH$_2$PEt$_2$
eppe = Et$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$
dppey = *cis*-(C$_6$H$_5$)$_2$PCH═CHP(C$_6$H$_5$)$_2$
dppp = (C$_6$H$_5$)$_2$PCH$_2$CH$_2$CH$_2$P(C$_6$H$_5$)$_2$

Experimental Section

Materials. 1,2-Bis(diphenylphosphino)ethane (dppe), 1,2-bis(diethylphosphino)ethane (depe), 1,3-bis(diphenylphosphino)propane (dppp), *cis*-1,2-bis(diphenylphosphino)ethylene (dppey), and 1-(diethylphosphino)-2-(diphenylphosphino)ethane (eppe) were purchased from Strem Chemicals and silver nitrate and acetate from Johnson Matthey Ltd.

Preparations. [Ag(dppe)$_2$]NO$_3$. Dppe (0.5 g, 1.25 mmol) was dissolved in acetone (25 mL) and AgNO$_3$ (0.1 g, 0.6 mmol) in H$_2$O (1 mL) added. After 30 min the volume of the clear colorless solution was reduced to 10 mL. The product was precipitated by the addition of H$_2$O (50 mL), recrystallized from acetone-H$_2$O, washed with H$_2$O, and dried in vacuo: yield of white needles 0.52 g (90%); mp 225–230 °C. Anal. Calcd for C$_{52}$H$_{48}$AgNO$_3$P$_4$: C, 64.61; H, 5.00; N, 1.45; P, 12.82. Found: C, 63.90; H, 5.05; N, 1.51; P, 13.30.

[Ag(depe)$_2$]NO$_3$. AgNO$_3$ (0.21 g, 1.22 mmol) suspended in a solution of depe (0.51 g, 2.45 mmol) in CHCl$_3$ (5 mL) rapidly dissolved, and the resulting solution was stirred for 30 min. The solvent was removed by rotary evaporation and the oily residue solidified by repeated scratching with diethyl ether and hexane: yield of white solid product 0.5 g (70%); mp 104–114 °C. Anal. Calcd for C$_{20}$H$_{48}$AgNO$_3$P$_4$: C, 41.25; H, 8.31; N, 2.41; P, 21.27. Found: C, 39.44; H, 7.88; N, 2.40; P, 31.53.

The following compounds were obtained from solutions used for NMR measurements.

[Ag(dppey)$_2$]NO$_3$. Dppey (0.35 g, 0.89 mmol) was suspended in acetone (50% d_6) (2 mL), and a solution of AgNO$_3$ (0.07 g, 0.41 mmol) in H$_2$O (0.2 mL) was added. After gentle shaking, the solid dissolved to give a pale yellow solution, and when the mixture was allowed to stand at ambient temperature, the product crystallized as white needles; mp 239–244 °C. Anal. Calcd for C$_{52}$H$_{44}$AgNO$_3$P$_4$: C, 64.87; H, 4.61; N, 1.45; P, 12.87. Found: C, 63.71; H, 4.95; N, 1.43; P, 11.87.

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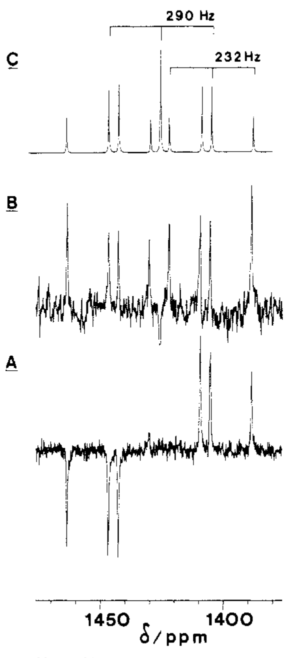

Figure 3. 13.97-MHz $^{109}Ag\{^{31}P\}$ spectra of 65 mM $[Ag(eppe)_2]NO_3$ in $CDCl_3$ at 223 K: (A) INEPT spectrum (3107 repetitions of the pulse sequence, τ = 0.90 ms); (B) DEPT spectrum (4000 repetitions of the pulse sequence, τ = 1.75 ms, θ = 22 μs); (C) spectrum of the X region (simulated AA′BB′X spectrum obtained with $\Delta\nu$(P–P) = 150 Hz, ^3J(P–P) = 10 Hz, ^2J(P–P) = 50 Hz, and $^1J(^{109}Ag–^{31}P)$ = −290 and −232 Hz).

$[Ag(dppp)_2]NO_3$. Dppp (0.29 g, 0.7 mmol) was dissolved in acetone (50% d_6) (2 mL), and a solution of $AgNO_3$ (0.06 g, 0.35 mmol) in H_2O (0.2 mL) was added with stirring. White crystals formed from the clear solution when it was allowed to stand overnight at ambient temperature; mp 213–218 °C. Anal. Calcd for $C_{54}H_{52}AgNO_3P_4$: C, 65.20; H, 5.27; N, 1.41; P, 12.45. Found: C, 63.23; H, 5.12; N, 1.55; P, 12.13.

The depe, dppey, and dppp complexes were all found to have slightly low carbon analyses. The reason for this was not investigated further since the analyses of the other elements were satisfactory and the NMR data were consistent with the proposed formulas.

NMR Measurements. ^{31}P NMR spectra at 24.15 and 121.50 MHz were recorded on JEOL FX60 and Bruker AM300 spectrometers, respectively. ^{109}Ag spectra at 13.97 MHz were recorded on a Bruker AM300 spectrometer equipped with a multinuclear accessory and a low-frequency-range 10-mm probe head fitted with a ^{31}P decoupling channel. The ^{31}P frequency was synthesized and amplified as previously described.[13]

$^{109}Ag\{^{31}P\}$ INEPT spectra were recorded with use of the following pulse sequence:[14] $[90°_x(^{31}P)–\tau–\{180°_x(^{31}P), 180°_x(^{109}Ag)\}–\tau–\{90°_y(^{31}P), 90°_x(^{109}Ag)\}]$–FID with $\tau = 1/4\{^1J(^{109}Ag–^{31}P)\}$. The 90° pulse for ^{31}P was 65 μs and for ^{109}Ag was 27.5 μs. A relaxation delay of between 1 and 5 s was introduced between repeats of the sequence of pulses. Spectra with reasonable signal-to-noise ratios were obtained from 0.2–0.06 M solutions in 1000–3000 repetitions of the pulse sequence. The pulse sequence for $^{109}Ag\{^{31}P\}$ DEPT spectra was as follows:[15] $[90°_x(^{31}P)–\tau–\{180°_x(^{31}P), 90°_x(^{109}Ag)\}–\tau–\{\theta°_y(^{31}P), 180°_x(^{109}Ag)\}–\tau]$–FID, where $\tau = 1/2\{^1J(^{109}Ag–^{31}P)\}$ and θ corresponds to $0.166\{180°(^{31}P)\}$ = 22 μs. A 1-s relaxation delay was introduced between repetitions of the sequence. Single-pulse ^{109}Ag NMR spectra were recorded with 15-μs (50°) pulses, with frequency width 3000 or 4000 Hz, acquisition time 0.512 or 0.684 s, respectively, 2-s relaxation delays, and quadrature detection. About 10 000–20 000 pulses were required to obtain spectra with reasonable signal-to-noise ratios.

NMR tubes 10 mm in diameter containing about 2 mL of solution were used. The solvent was usually $CDCl_3$, although the spectra of $[Ag(dppp)_2]NO_3$ and $[Ag(dppey)_2]NO_3$ were recorded in a mixture of acetone–acetone-d_6–H_2O in the ratio 1:1:0.1 v/v. Spectra were obtained at 300 K unless otherwise stated. The chemical shift references (both external) were 4 M $AgNO_3$ in D_2O for ^{109}Ag and H_3PO_4–D_2O (85:15 v/v) for ^{31}P. The high-frequency-positive sign convention is used.

Results

Titrations of Ag(I) acetate (chosen in preference to $AgNO_3$ because of its greater solubility in $CDCl_3$) with dppe were carried out. At a AgOAc:dppe ratio of 2:1 and a temperature of 300 K, a broad ^{31}P resonance was observed, which was resolved into a complex multiplet at 221 K with a chemical shift of 3.3 ppm. This was interpretable as three overlapping AA′XX′ spin systems arising from the three possible combinations of the two spin-$^1/_2$ Ag isotopes in the binuclear complex AcOAg(μ-dppe)AgOAc. The spectrum was analogous to that described for AcOAg(μ-dppm)AgOAc by van der Ploeg and van Koten.[5] The following coupling constants were derived by spectral simulation: $^1J(^{109}Ag–^{31}P)$ = −757 Hz, $^1J(^{107}Ag–^{31}P)$ = −657 Hz, $^5J(^{109}Ag–^{31}P)$ = +7 Hz, $^5J(^{107}Ag–^{31}P)$ = +10 Hz, and $^3J(^{31}P–^{31}P)$ = +46 Hz.

At a 1:1 ratio of AgOAc:dppe, again only one broad resonance was observed at ambient temperature, and although this split into two broad peaks at 220 K, no $^{107/109}Ag–^{31}P$ couplings were resolved.

In contrast, solutions containing an AgOAc:dppe ratio of 1:2 gave a sharp ^{31}P spectrum at 300 K consisting of two overlapping doublets with approximately equal chemical shifts and an intensity ratio of 51:49, which is the ratio of ^{107}Ag:^{109}Ag isotopes in natural abundance. The ratio of the coupling constants $^1J(^{107}Ag–^{31}P)/^1J(^{109}Ag–^{31}P)$ was 0.869 (the expected ratio of the respective nuclear magnetic moments of the two Ag isotopes). A 1:2 complex was subsequently isolated as the nitrate salt (see Experimental Section). Addition of excess dppe to a solution of this complex in $CDCl_3$ caused a slight broadening of the ^{31}P multiplet resonances and the appearance of a slightly broadened resonance for free dppe indicative of the relatively slow exchange on the NMR time scale (<400 s^{-1}) between free and bound dppe.

Since $[Ag(dppe)_2]NO_3$ exhibited well-resolved $^{109}Ag–^{31}P$ coupling (266 Hz, see Table I), an attempt was made to observe ^{109}Ag NMR resonances via a $^{109}Ag\{^{31}P\}$ INEPT experiment. The resulting spectrum is shown in Figure 1B. The "two-up"–"two-down" appearance is characteristic of the A part of an AX_4 spin system. The components of the 1:4:6:4:1 quintet are perturbed by the pulse sequences so that the inner and outer pairs of transitions are of opposite phase, and the middle transition, which has no J dependence, is nulled.

A ^{109}Ag NMR spectrum of the same complex taken with use of normal, single-pulse accumulation is shown in Figure 1A. The considerable improvement in signal-to-noise ratio for the INEPT spectrum, the result of only 2048 scans compared to 12 111 for the normal spectrum, is apparent.

The ^{109}Ag NMR results therefore suggest that a chelated $[Ag(dppe)_2]^+$ species exists in solution. Similar $^{109}Ag\{^{31}P\}$ INEPT NMR spectra were obtained for $[Ag(dppp)_2]NO_3$ and $[Ag(dppey)_2]NO_3$. The chemical shifts and coupling constants are given in Table I.

Attempts to determine the structure of $[Ag(eppe)_2]NO_3$ in solution by $^{31}P\{^1H\}$ NMR alone presented particular problems. The 24-MHz spectrum at ambient temperature (Figure 2B) appeared to consist of two broad unresolved resonances with a separation of 223 Hz, a value close to that expected for a $^1J(^{109}Ag–^{31}P)$ spin–spin coupling constant in a tetrahedral complex. When the solution was cooled to 223 K, a well-resolved asymmetrical multiplet pattern was observed (Figure 2A). At higher frequency, 121 MHz, the complexity of the spectrum increased dramatically (Figure 2C). The $^{109}Ag\{^{31}P\}$ INEPT spectrum, on the other hand (Figure 3A), appeared to be interpretable as the X part of an AA′BB′X spin system (vide infra). Again a spectrum with a good signal-to-noise ratio was obtained relatively quickly. The interpretation of this INEPT spectrum was aided by a $^{109}Ag\{^{31}P\}$ DEPT (distortionless enhancement by polarization transfer) experiment.[15]

In DEPT, a pulse of length θ, applied to the sensitive nucleus (^{31}P), is incorporated into the sequence (see Experimental Section) and, generally, multiplets with enhanced intensity but without phase distortion are obtained. The $^{109}Ag\{^{31}P\}$ DEPT spectrum shown in Figure 3B was obtained by application of a 22-μs θ pulse. This value was calculated by using the relationship $\theta = \pi J\Delta$, where

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Δ is the refocusing time in a refocused INEPT sequence, with the assumption of a first-order AX_4 spin system for which the ideal Δ value is $0.1666/J$.[16] The choice of the delay between pulses (τ, 1.75 ms) corresponded to an estimated $^1J(^{109}Ag-^{31}P)$ value of 286 Hz ($\tau = 1/2J$). The spectrum was simulated as the X part of an AA'BB'X spin system, and $^1J(^{31}P-^{109}Ag)$ coupling constants of −232 and −290 Hz were obtained. Variations in the choice of $^2J(^{31}P-^{31}P)$, $^3J(^{31}P-^{31}P)$, and $\nu(^{31}PPh_2) - \nu(^{31}PEt_2)$ caused little change in the appearance of the simulated spectrum, but a good fit was obtained with values of 50, 10, and 150 Hz, respectively. With use of these values, and the calculated $^1J(^{107}Ag-^{31}P)$ coupling constants, a ^{31}P NMR spectrum similar to the experimental spectrum shown in Figure 2C was simulated. The fit was not exact and the parameters were not refined since they were not expected to provide further insight into the structure of the complex.

Discussion

The ^{109}Ag NMR studies described here provide convincing evidence for the existence of four-coordinate, tetrahedral bisphosphine silver(I) complexes in solution. Complexes with five- and six-membered chelate rings exhibit remarkably enhanced kinetic and thermodynamic stability when compared to similar Ag(I) complexes of monodentate phosphines. The rate of Ag–P bond rupture in $[Ag(P(p\text{-tol})_3)_4]^+$, for example, has been reported to be $>2000\ s^{-1}$ at 313 K,[4] whereas in the complexes described here, which contain chelate rings, the rates are <ca. 220 s^{-1}.

Comparatively little use has been made of ^{109}Ag (or ^{107}Ag) NMR in structural studies of silver complexes in solution. The sensitivity is low, and relaxation rates are often unfavorable (very slow).[8] However, we have demonstrated here that greatly enhanced sensitivities can be obtained via $^{109}Ag\{^{31}P\}$ INEPT NMR experiments and that spectra from second-order spin systems can be interpreted. ^{109}Ag INEPT NMR spectra with good signal-to-noise ratios were obtained in under 1 h of acquisition time at Ag(I) concentrations as low as 65 mM. The repetition time of the INEPT pulse sequence is governed by the ^{31}P and not the ^{109}Ag spin–lattice relaxation time (T_1). The theoretical maximum enhancement of the intensity of ^{109}Ag resonances is 8.70, $\gamma(^{31}P)/\gamma(^{109}Ag)$.[13]

The ^{109}Ag chemical shifts observed here are at the high-frequency end of the currently known ^{109}Ag shift range.[17] This strong deshielding is presumably a reflection of the good π-acceptor properties of the bisphosphine ligands. Within the series, the relative shieldings are expected to parallel the s character of the Ag–P bonds. Tolman has proposed[19] that steric rather than electronic effects of phosphine ligands dominate the differences in stability of metal–phosphine complexes. By this argument, increasing the cone angle of the ligand results in a decrease in the s character of the phosphorus lone pair. Thus in our series dppp has the largest cone angle and $[Ag(dppp)_2]^+$ would be expected to have the highest frequency ^{109}Ag chemical shift—as is observed.

The temperature dependence of the ^{31}P NMR spectrum of $[Ag(eppe)_2]NO_3$ indicated that a dynamic chemical exchange process was occurring in solution, and this has been confirmed by ^1H NMR measurements.[18] However, detailed analyses of the ^{31}P NMR spectra at various temperatures are hampered by the complicated nature of the spin system involved. The two $^1J(^{31}P-^{109}Ag)$ couplings of −290 and −232 Hz corresponding to silver couplings to the Ph_2P and Et_2P phosphorus atoms cannot be unambiguously assigned, but it is intriguing that they are approximately 30 Hz lower and higher, respectively, than the values observed for the related complexes containing symmetrical bis(phosphine) ligands, $[Ag(dppe)_2]NO_3$ and $[Ag(depe)_2]NO_3$ (see Table I). This implies a relative weakening of two of the Ag–P bonds (either Ph_2P or Et_2P) and relative strengthening of the others. This would probably facilitate an intramolecular exchange process involving ring opening. It is notable that the $^1J(^{31}P-^{109}Ag)$ couplings observed for the dppey and dppp complexes are respectively higher and lower than those of dppe and depe complexes. The stabilities of the chelate rings might be expected to follow the order dppey > dppe, depe > dppp on the basis of rigidity and ring size. The low value of $^1J(^{31}P-^{109}Ag)$ for $[Ag(dppp)_2]^+$ is consistent with Tolman's arguments[19] since the ligand has the largest cone angle in the series studied here.

Even at very low temperature in the slow-exchange region and at high field, the ^{31}P NMR spectrum of $[Ag(eppe)_2]NO_3$ exhibits remarkable complexity. This is a consequence of the similar frequency difference between the chemical shifts of the nonequivalent phosphines (Ph_2P and Et_2P) and the $^1J(^{31}P-^{107/109}Ag)$ coupling constants. ^{109}Ag NMR was therefore attractive because the spectrum was not complicated by transitions involving ^{107}Ag and because the appearance of the X part of an AA'BBX spin system usually shows little dependence on the J(A–B) coupling constants.[20] The major drawbacks of ^{109}Ag NMR, viz. low sensitivity and long relaxation times, were largely overcome by the use of the $^{109}Ag\{^{31}P\}$ INEPT experiments. However, the resultant spectra, although showing good signal-to-noise ratios, exhibited phase and intensity distortions such that it was not possible to make an unambiguous assignment of the spin system involved. There appear to be no previous reports of the analyses of INEPT spectra from second-order spin systems, and this is not a trivial problem. Clearly the choice of τ (ideally $1/4J$) will affect the intensities of the signals in the INEPT spectrum, and in the present case, an average of the two $^1J(^{31}P-^{109}Ag)$ couplings was chosen. DEPT experiments are commonly used to overcome the problem of phase distortions. In the present case two of the central transitions that were missing from the INEPT spectrum reappeared in the DEPT spectrum and so did the third, although as only a weak central line and with inverted phase. It is perhaps not surprising that some distortions are still present in the DEPT spectrum since the chosen value of τ (ideally $1/2J$) corresponded to a guessed average J value of 286 Hz. Secondly, the value of the pulse θ assumed that the spin system was first order, AX_4. It is evident that future experiments of this type will be profitable in studies of a wide range of spin-$^1/_2$ metal–phosphine complexes. It should be possible to optimize the conditions of the pulse sequences to minimize phase and intensity distortions arising from second-order spin systems.

Acknowledgment. We thank Smith Kline and French Laboratories (Philadelphia), the SERC, the MRC, and University of London Intercollegiate Research Service for their support for this work.

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(21) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)