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$[Cu(Ph_2PCH_2CH_2PEt_2)_2]Cl$: A Chelated Copper(I) Complex with Tetrahedral Stereochemistry. Rate of Inversion Compared with Those of Isostructural Silver(I) and Gold(I) Complexes

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Received June 20, 1985

The air-stable, water-soluble complex $[Cu(Ph_2P(CH_2)_2PEt_2)_2]Cl$ has been isolated and characterized. This is a rare example of a tetrakis(tertiary phosphine) complex of copper(I) chloride. ^1H, ^{13}C, ^{31}P, and ^{65}Cu NMR studies together suggest that the complex has a tetrahedral coordination geometry with bis-chelated phosphine ligands, in dichloromethane and aqueous solutions. The temperature dependencies of the ^1H and ^{13}C NMR spectra are interpreted in terms of inversion at the tetrahedral copper(I) center via an intramolecular ring-opening mechanism. A similar dynamic ligand exchange is reported for the analogous complexes of silver(I) and gold(I). The rate of inversion of the metal center was found to increase in the order Cu(I) < Au(I) < Ag(I).

Introduction

(Tertiary phosphine)copper(I) halide complexes of the general formula $L_m(CuX)_n$ have been the subject of numerous crystallographic investigations, and a wide variety of coordination geometries and stereochemistries have been described. Complexes containing monodentate phosphines with m:n stoichiometries of 3:1, 2:1, 4:2, 3:2, 4:4, and 2:2 are known.[2-4] The variety of possible structures has been reviewed.[2] For bidentate phosphine ligands, complexes with P:Cu ratios of 3:1, 2:1, 4:3, and 1:1 have been isolated.[5-8] The polynuclear compounds contain both bridging and chelated bis(phosphine) ligands. There appear to be no reports, however, of 4:1 $L_m(CuX)_n$ complexes where X is halide for either mono(phosphine) or bidentate bis(phosphine) ligands (L).

Reactions in which such tetrakis(phosphine) complexes might be expected to be produced often seem to take a different course. For instance, $(PR_3)_3CuCl$ results from reactions of CuCl with 4 or more molar equiv of Ph_3P, Ph_2MeP, or $PhMe_2P$.[9] $[(Me_3P)_4Cu]Cl$ has been isolated from reactions of CuCl with a large excess of Me_3P, but the complex is highly unstable.[10] Similarly, a dimeric complex containing a bridging diphosphine and a 3:1 P:Cu ratio has been isolated from solutions containing CuCl and excess 1,2-bis(diphenylphosphino)ethane (dppe),[5] rather than the bis-chelated complex $[Cu(dppe)_2]Cl$. Furthermore, (tertiary phosphine)copper(I) halide complexes are involved in concentration- and temperature-dependent dissociative equilibria in solution.[9,11]

We have recently found that chelated, tetrahedral Au(I)[12,13] and Ag(I)[14] complexes with bidentate tertiary phosphine ligands exhibit greatly enhanced kinetic and thermodynamic stabilities with respect to similar complexes containing monodentate phosphine ligands. In this paper we report a rare example of a stable tertiary phosphine complex of copper(I) chloride with a 4:1 P:Cu ratio.

The bis-chelated complex $[Cu(eppe)_2]Cl$ (where eppe is $Ph_2P(CH_2)_2PEt_2$) is shown to adopt a tetrahedral coordination geometry in solution by multinuclear NMR experiments. The temperature dependence of the ^1H and ^{13}C NMR spectra enabled the energy barrier to inversion of the tetrahedral copper center to be studied. We also report studies of inversion of analogous Au(I) and Ag(I) $[M(eppe)_2]^+$ complexes.

Experimental Section

Materials. 1-(Diethylphosphino)-2-(diphenylphosphino)ethane (eppe) was purchased from Strem Chemicals Inc., and CuCl from Aldrich Chemical Co. Ltd.

Synthesis. Preparation of $[Cu(eppe)_2]Cl$. Eppe (0.54 g, 1.79 mmol) was dissolved in 10 mL of $CHCl_3$, and solid CuCl (0.081 g, 0.81 mmol) was added. After 2 h of stirring under a steady stream of N_2, all the solid had dissolved and an equal volume of hexane was added. A clear, oily residue formed on cooling the solution to 276 K for 24 h. The solvent was decanted off, and the oil was solidified by repeated trituration in ice-cold acetone (1 mL) and ice-cold hexane (1 mL). The yield of white solid, mp 112-115 °C, was 0.42 g (74%). Anal. Calcd for $C_{36}H_{48}ClCuP_4$: C, 61.44; H, 6.87; P, 17.61; Cl, 5.04. Found: C, 61.18; H, 6.77; P, 17.39; Cl, 5.52.

Mass spectral analysis by fast atom bombardment (University of London Intercollegiate Research Service, VG Analytical ZAB-1F instrument) gave the parent ion at m/e 667 with the correct isotopic substitution pattern for $[Cu(Ph_2P(CH_2)_2PEt_2)_2]^+$ and a peak at m/e 365 corresponding to the loss of one $Ph_2P(CH_2)_2PEt_2$ ligand on fragmentation.

The conductivity of a 1.6 mM solution of the complex in CH_3CN was found to be 129 Ω^{-1} cm^2 mol^{-1}, a value within the expected range for a 1:1 electrolyte.

$[Au(eppe)_2]Cl$ was prepared as described elsewhere[13] and had a satisfactory elemental analysis. $[Ag(eppe)_2]NO_3$ was obtained as a white solid by dissolving $AgNO_3$ (0.031 g, 0.18 mmol) in a solution of eppe (0.11 g, 0.36 mmol) in $CHCl_3$ (10 mL). The solvent was then removed by lyophilization. The complex was fully characterized by ^{31}P and ^{109}Ag NMR as described previously.[14]

NMR Measurements. ^1H NMR spectra were recorded at 199.5 MHz and ^{13}C spectra at 50.1 MHz on a JEOL FX200 spectrometer and were referenced to Me_4Si.

^{31}P spectra were recorded on either a Bruker AM400 machine at 161.9 MHz or a Bruker WM250 instrument at 101.3 MHz in 10-mm tubes. H_3PO_4 (85% in D_2O) was used as an external chemical shift reference.

^{65}Cu NMR spectra were recorded on the Bruker AM400 spectrometer at 113.70 MHz using ca. 85 mM solutions in CD_2Cl_2 and 10-mm tubes. A 100-kHz sweep width was used, together with 1024 data points (acquisition time 0.0051 s), giving a digital resolution of 195 Hz/point.

Results and Discussion

An air-stable white solid was isolated from reactions of copper(I) chloride with a small molar excess of eppe in chloroform. Microanalytical and mass spectral data suggested that this was the bis-chelated complex $[Cu(Ph_2P(CH_2)_2PEt_2)_2]Cl$. Its conductivity in CH_3CN was consistent with formulation as an ionic

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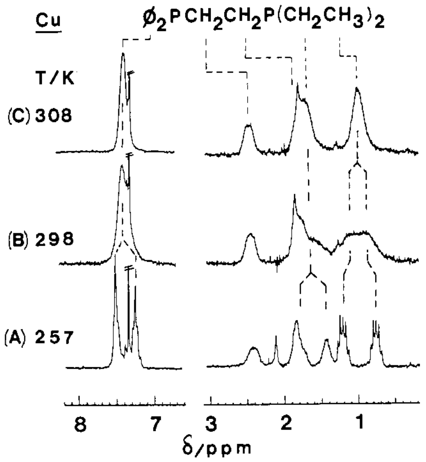

Figure 1. 200-MHz ^1H NMR spectra of $[Cu(eppe)_2]Cl$ in $CDCl_3$ at (A) 257, (B) 298, and (C) 308 K, showing, e.g. for the ethyl CH_3 protons near 1 ppm, slow exchange, coalescence, and relatively fast exchange, respectively, on the NMR time scale. The sharp peak at 257 K is assigned to H_2O. It shifts to low frequency with increasing temperature.

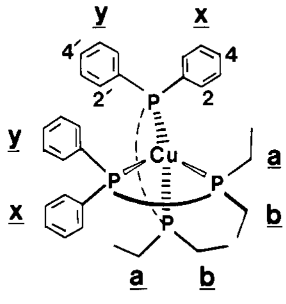

Figure 2. One of the enantiomers of $[Cu(eppe)_2]^+$, showing the two types of ethyl (a and b) and two types of phenyl (x and y) groups.

complex. The structure in solution was investigated in detail by multinuclear NMR studies.

^1H and ^{13}C NMR. The ^1H NMR spectrum of $[Cu(Ph_2P(CH_2)_2PEt_2)_2]Cl$ (Figure 1) is consistent with a tetrahedral structure in solution. Tetrahedral bis-chelate complexes derived from unsymmetrical ligands are enantiomeric with absolute configurations Δ and Λ.[15] Both enantiomers of $[Cu(eppe)_2]Cl$ would be expeced to have identical ^1H NMR spectra arising from protons in two equally populated, nonequivalent environments (Figure 2). At low temperatures, two apparent five-line multiplets at 0.76 and 1.21 ppm were observed (the chemical shift of the CH_3 protons of the free ligand was 1.00 ppm, ambient temperature). When the temperature was raised, the methyl signals exhibited typical two-site chemical exchange behavior: they coalesced at high temperature to give a single methyl resonance with an averaged chemical shift of 0.98 ppm (Figure 1C). Similarly, two sets of resonances were observed for the ethyl CH_2 protons at low temperature with shifts of ca. 1.42 and 1.80 ppm (compared to 1.43 ppm for the free ligand). These coalesced to a single resonance at 1.68 ppm. The phenyl resonances also showed dynamic behavior. A single broad resonance at 7.36 ppm resolved into two distinct multiplets at low temperatures. The ^1H NMR results therefore indicated a low-energy barrier to racemization of the tetrahedral metal center.

$\{^1H\}^{13}C$ NMR spectra (Figure 3) provided further evidence for tetrahedral coordination. At 255 K, two sets of resonances of equal intensity were observed for each of the aromatic carbons C_2, C_3, and C_4 and for both ethyl carbons. As the temperature was raised, these resonances broadened and coalesced, so that by 309 K an averaged resonance was observed for each type of carbon. With the exception of C_4, all resonances for aromatic carbons exhibited ^{31}P–^{13}C spin–spin coupling and appeared as quasi triplets in the slow-exchange limits as a result of the second-order ^{13}C–^{31}P–CH_2–CH_2–^{31}P spin systems.[16] A similar pattern was observed for the CH_2 carbon atoms.

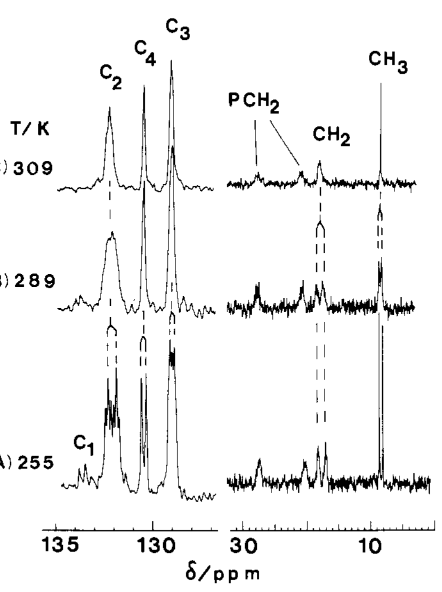

Figure 3. 50-MHz $\{^1H\}^{13}C$ NMR spectra of a 0.24 M solution of $[Cu(eppe)_2]Cl$ in $CDCl_3$ at (A) 255, (B) 289, and (C) 309 K, showing the transition from slow exchange at low temperature to fast exchange at high temperature. The multiplet splittings, e.g. for C_2, arise from ^{31}P couplings.

The chemical shift differences between resonances for the carbon nuclei in their two nonequivalent environments follow the order CH_2 (1.21) > CH_3 (0.67) > C_4 (0.35) > C_3 (0.23) > C_2 (0.19) > C_1 (0.0), where the figures in parentheses are the shift differences in ppm. The corresponding proton figures are CH_3 (0.45) > CH_2 (0.38) > phenyl (ca. 0.26).

The relative signs of these shift differences could not be determined since no connectivity between the phenyl and other resonances could be established. No NOE's on irradiation of ^1H NMR resonances were observed at 225 K.

It is apparent from space-filling models of the complex that severe steric interactions exist in tetrahedral complexes of this type. This suggests that intramolecular rearrangements by ring-opening mechanisms may be favorable. It is clear from the space-filling model that each of the two ethyls (a and b) or two phenyls (x and y) are in distinct magnetic environments; see Figure 2. Ethyls of type a lie over phenyl rings of type x, whereas ethyls of type b lie close to other ethyl groups of type b. In the model, the two phenyl rings of type y lie close and face to face. We assume that the two environments observed in the slow-exchange limit of ^1H and ^{13}C NMR spectra correspond to phenyl rings of type x and y and to ethyls of type a and b, respectively. It is reasonable to assume that the chemical shifts are influenced to a large extent by the ring currents of the phenyl groups. Since only four sets of ^{13}C NMR signals are seen for each phenyl ring, the rings must be flipping rapidly on the NMR time scale; this would be facilitated by epimerization via a ring-opening mechanism.

^{31}P and ^{65}Cu NMR.[17] The 101-MHz $\{^1H\}^{31}P$ NMR spectrum of $[Cu(eppe)_2]Cl$ in CD_2Cl_2 (Figure 4) consisted of two broad peaks at 183 K with a separation of 525 Hz. Each peak appeared to have an asymmetrical line shape, suggesting that unresolved fine structure was present. However, the solution could not be cooled further without freezing. As the temperature was raised, the peaks broadened further, and at ambient temperature (293 K) a single, very broad resonance with a chemical shift of ca. 8 ppm was observed.

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(17) The more abundant isotope ^{63}Cu is generally selected for NMR experiments. ^{65}Cu was chosen here because of its smaller quadrupole moment and, consequently, the possibility of obtaining sharper resonances. The relaxation times of either isotope are usually short enough to allow rapid pulsing, and so spectra can be obtained in a reasonable time.

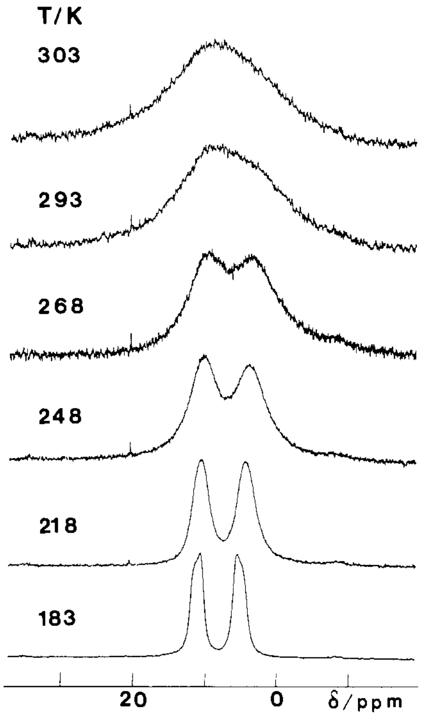

Figure 4. 101-MHz $\{^1H\}^{31}P$ NMR spectra of $[Cu(eppe)_2]Cl$ in CD_2Cl_2 at various temperatures.

It seems unlikely that the splitting into two broad signals at low temperature is a result of $^{63/65}Cu$–^{31}P spin–spin coupling. This has been observed only for highly symmetrical $[Cu(PR_3)_4]^+$ complexes,[18-20] such as $[Cu(P(OMe)_3)_4]BF_4$. In these, there is a spherical charge distribution at $^{63/65}Cu$. The electric field gradients are therefore very small, relaxation via the quadrupolar mechanism is relatively ineffective, and two overlapping 1:1:1:1 quartets are observed. In the less symmetrical complex studied here there is likely to be a more significant quadrupolar contribution to copper relaxation.

The splittings in the low-temperature ^{31}P NMR spectrum probably arise from the ^{31}P AA′BB′ spin system. This was substantiated by higher frequency (162 MHz) measurements. The separation of the two broad peaks at 183 K was 5.3 ppm: the same as that at 101 MHz. This suggests that it is related to the chemical shift difference between phosphorus nuclei, perhaps the Ph_2P and Et_2P groups of the ligand. For the free eppe ligand, the value of $\delta(^{31}P(Ph_2)) - \delta(^{31}P(Et_2))$ is 5.6 ppm. The ^{31}P NMR spectrum of the Ag(I) complex also exhibited a marked temperature dependence. The spectra at various temperatures were too complicated to analyze fully, but the shift difference $\delta(^{31}P(Ph_2)) - \delta(^{31}P(Et_2))$ was estimated to be ca. 1.0 ppm from the slow-exchange spectrum at 223 K.[14] Curiously, the 24.2-MHz $\{^1H\}^{31}P$ spectrum of $[Au(eppe)_2]Cl$ in $CDCl_3$ consisted of a sharp ($\Delta\nu_2$ = 6 Hz) singlet resonance at 18.8 ppm, which did not broaden significantly on cooling the solution to 213 K. This was assumed to arise as a consequence of very small values for $\delta(^{31}P(Ph_2)) - \delta(^{31}P(Et_2))$ ($<<$1.0 ppm) and J(AB) ($<$10 Hz).[13]

We have not attempted to simulate the spectrum for two overlapping XAA′BB′ spin systems (where X is ^{63}Cu or ^{65}Cu, $I = {}^3/_2$). However, Marker and Gunter[18] have calcuated ^{31}P NMR line shapes for CuP_4 complexes with varying copper quadrupolar relaxation rates. Quadrupolar relaxation rates increase with increasing solvent viscosity (confirmed by ^{65}Cu NMR; vide infra), and so multiplets that arise through coupling to $^{63/65}Cu$ would be expected to broaden with decreasing temperature. The reverse was observed in ^{31}P NMR spectra of $[Cu(eppe)_2]Cl$ (Figure 4).

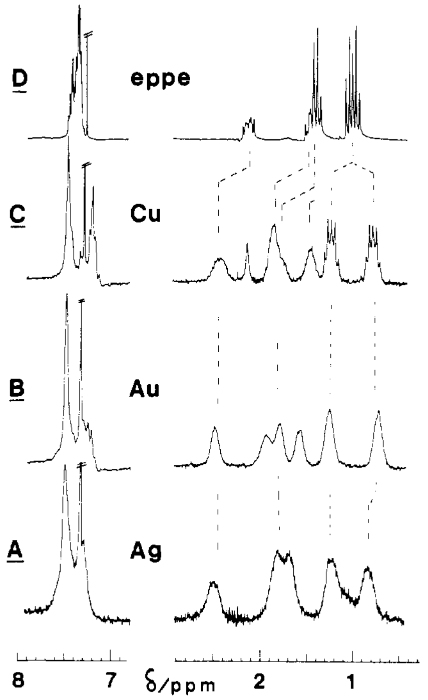

Figure 5. 200-MHz ^1H NMR spectra of 12 mM solutions of $[M(eppe)_2]^+$ complexes in $CDCl_3$ compared to that of the ligand itself: (A) $[Ag(eppe)_2]NO_3$ at 211 K; (B) $[Au(eppe)_2]Cl$ at 214 K; (C) $[Cu(eppe)_2]Cl$ at 257 K; (D) free eppe at 273 K. The slow-exchange region was not observed above the freezing point of the solvent for the Au(I) and Ag(I) complexes.

This again suggests that the spliting is a result of the second-order AA′BB′ ^{31}P spin system in this complex, possibly broadened by residual $^{63/65}Cu$ coupling.

^{65}Cu NMR studies were in accord with these suggestions and gave support for a proposed tetrahedral coordination geometry for the complex. At 300 K, a very broad ^{65}Cu NMR resonance ($\Delta\nu_{1/2}$ = 5000 Hz) was observed for $[Cu(eppe)_2]Cl$ in CD_2Cl_2. At lower temperatures the resonance broadened further, and at 183 K no resonance was detectable. The resonance frequency of the ^{65}Cu signal at 300 K was 28 407 886 ± 50 Hz (on a scale that places the ^1H frequency of tetramethylsilane at exactly 100 MHz), which corresponds to a ^{63}Cu frequency of 26 519 492 ± 47 Hz. This shift is 70 ppm to high frequency of the ^{63}Cu resonance of $[Cu(P(OMe)_3)_4]ClO_4$[19] and is in accord with previous observations that Cu(I) phosphine complexes have chemical shifts to higher frequency of resonances of phosphite complexes.[20]

Inversion of Cu(I), Ag(I), and Au(I). The chemical exchange processes observed in the ^1H and ^{13}C NMR spectra of $[Cu(eppe)_2]Cl$ are explicable if inversion of a tetrahedral Cu(I) center occurs. An approximate exchange rate of ca. 63 s^{-1} was calculated[21] from the coalescence temperature of the ^{13}C methyl singlets, corresponding to a free energy of activation of 62 ± 8 kJ mol^{-1} at 294 K.

Similar dynamic NMR behavior was observed for analogous Ag(I) and Au(I) $[M(eppe)_2]^+$ complexes. For $[Ag(eppe)_2]NO_3$ in $CDCl_3$, at temperatures above ca. 235 K, only one set of proton NMR resonances was observed for both the ethyl and phenyl groups. As the temperature was lowered, these broadened and appeared to split into two sets of resonances of equal intensity. However, at the lowest temperature studied (211 K) the resonances were still broadened, suggesting that the slow-exchange limit had

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[21] Full line-shape analyses of the ^1H NMR spectra at various temperatures were not attempted in view of the complicated ^1H–^{31}P and ^1H–^1H spin–spin couplings present. Most of the ^{13}C NMR resonances are also second-order multiplets due to ^{31}P coupling. Sharp singlets were obtained for the CH_3 carbons, but the chemical shift differences at 50 MHz were small, and coalescence and narrowing occurred over a temperature range of only 5 °C. This was too small to enable meaningful activation parameters to be derived especially in view of the relatively poor temperature control in the probe (±1 °C).

Table I. ^{1}H NMR Data for Cu(I), Ag(I), and Au(I) Complexes of Eppe[a] in the Slow- (or Near-Slow-) Exchange and Fast-Exchange Regions

	δ						
	eppe	$[Au(eppe)_2]Cl$		$[Ag(eppe)_2]NO_3$		$[Cu(eppe)_2]Cl$	
assgnt	273 K	214 K	292 K	211 K[g]	290 K	257 K	308 K
CH_3[b]	1.00	0.69[d] 1.21	0.94	0.82[e] 1.20	1.00	0.76[f] 1.21	0.98
CH_3CH_2	1.43[c]	1.54 1.90	1.74[c]	2.70[c]	2.70[c]	1.42 1.80	1.68
Et_2PCH_2	1.43[c]	1.75	1.75[c]	2.70[c]	2.70[c]	1.76	1.76
Ph_2PCH_2	2.10	2.44	2.44	2.46	2.46	2.40	2.40
phenyl	7.37	7.22 7.46	7.32	7.36	7.36	7.20 7.46	7.36

[a] 12 mM solutions in $CDCl_3$. [b] Second-order multiplets. [c] Overlapping multiplets for bridge and ethyl CH_2 protons. [d] Coalescence at 257 K. [e] Coalescence at ca. 225 K. [f] Coalescence at 298 K. [g] Slow-exchange region is below the freezing point of the solvent.

Table II. ^{13}C NMR Data for $[M(eppe)_2]Cl$ Complexes (0.24 M Solutions in $CDCl_3$)

	δ			
	$[Cu(eppe)_2]Cl$		$[Au(eppe)_2]Cl$	
assgnt	223 K	308 K	214 K	290 K
phenyl				
C_1[a]	133.18	h	134.30	134.06
C_2[a]	132.10 131.81	132.22[d]	132.23[c] 131.82[c]	132.18[b]
C_3[a]	129.00 128.77	129.06[b]	128.80[c]	128.95
C_4[b]	130.55 130.20	130.47	130.41[c]	130.46
Ph_2PCH_2[a]	27.38	27.38	30.79	30.26
Et_2PCH_2[a]	20.09	20.76	22.70	23.40
CH_3CH_2[a]	18.19 16.98	17.87[e]	21.80 20.17	21.31
CH_3[b]	8.70 8.03	8.35[f]	9.27 8.44	8.71[g]

[a] Quasi-triplet arising from ^{13}C PP′ spin system (see text). [b] Singlet. [c] Separate resonances not fully resolved—slow-exchange region is below 214 K. [d] Coalescence at 287 K. [e] Coalescence at 297 K. [f] Coalescence at 294 K. [g] Coalescence at 245 K. [h] Not resolved.

not been reached (Figure 5A). Similarly, for $[Au(eppe)_2]Cl$ one set of proton NMR resonances was observed at 298 K and these split into two sets as the temperature was lowered. The slow-exchange region had not been reached at 214 K so that the resonances were slightly broadened and multiplet structure was not resolved, (Figure 5B).

The coalescence temperatures for the methyl proton resonances of the Cu(I), Ag(I), and Au(I) $[M(eppe)_2]^+$ complexes were estimated to be 298, 225, and 257 K, respectively, for 12 mM solutions in $CDCl_3$. Therefore, the rate of inversion of the metal center increases in the order Cu(I) < Au(I) < Ag(I).

The behavior of the ^{13}C NMR resonances of $[Au(eppe)_2]Cl$ with temperature resembled that described above for Cu(I), except that the coalescence temperatures were lower (as for ^{1}H NMR). The ^{13}C NMR spectrum of the Ag(I) complex was not studied. All the ^{1}H and ^{13}C NMR data are listed in Tables I and II.

In previous reports the rates of inversion of tetrahedral bis-chelated compounds of d^{10} metal ions have increased with increasing metal ion radius,[15] and so it seems likely that different mechanisms may operate, at least to some extent, within the eppe series. Plausible mechanisms for inversion are (i) an intramolecular mechanism, with breakage of one or more M–P bonds, (ii) a twist motion involving a planar transition state, and (iii) an intermolecular pathway involving ligand exchange and a bimolecular transition state.[15]

A mechanism involving a planar transition state is highly unlikely for the d^{10} metal ions, since a large free energy difference would be expected to exist between tetrahedral and planar forms. Intermolecular pathways also seem unlikely since the rate of exchange would be expected to increase with increasing concentration. For $[Au(eppe)_2]Cl$ the rate of exchange showed no concentration dependence: the coalescence temperature of the methyl proton NMR resonances was 257 K for both 12 mM and 0.23 M solutions in $CDCl_3$. For $[Cu(eppe)_2]Cl$, the exchange rate was found to be slower at higher concentrations: the coalescence temperature of a 0.24 M solution of the compex was higher than that of a 12 mM solution. Mechanisms involving Cl$^-$ displacement of one of the phosphine ligand cannot be ruled out. Chloride bridges are common for other Cu(I) phosphine complexes in solution.[9,11]

The rates of inversion of both the Cu(I) and Au(I) $[M(eppe)_2]Cl$ complexes were found to be solvent-dependent, being higher in $CDCl_3$ than in D_2O solutions. Such a solvent dependence might be expected for an intramolecular exchange mechanism, involving the breaking of at least one M–P bond. Ring opening would be expected to be a highly favorable process in view of the severe steric interactions observed in space-filling models of the tetrahedral complexes. We have recently reported detailed ^{31}P and ^{109}Ag NMR studies of the Ag(I) complex $[Ag(eppe)_2]NO_3$.[14] The observation of two markedly different $^1J(^{109}Ag-^{31}P)$ coupling constants (−290 and −232 Hz), corresponding to silver couplings to the Ph_2P and Et_2P phosphorus atoms, implied a relative weakening of two of the Ag–P bonds (either Ph_2P or Et_2P) and a relative strengthening of the others. This distortion from tetrahedral geometry would be expected to facilitate a bond-breaking mechanism. A similar dissociative mechanism for the inversion process was suggested in a recent report of the racemization of bis-chelated Au(I) compexes with achiral phosphine ligands.[22]

Conclusion

An air-stable, water-soluble, bis-chelated complex of copper(I) chloride can be isolated in good yield from reactions with eppe. This is a rare example of a stable tertiary phosphine complex of a copper(I) halide with a 1:4 Cu:P ratio. Tetrahedral coordination in solution was shown to persist by ^{1}H, ^{13}C, ^{31}P and ^{65}Cu NMR spectroscopy.

The high stability of the complex in solution with no evidence of significant dissociation, or equilibria with coordinately unsaturated species, makes it highly suitable as a starting material for synthetic and other reactivity studies that require a Cu(I) starting material, especially those in aqueous media. The remarkably high stability of chelated bis(phosphine) complexes compared to mono(phosphine) analogues appears to be paralleled in copper(I), silver(I),[14] and gold(I)[12] chemistry. However, the low-energy barriers to racemization of the chiral, tetrahedral metal centers in $[M(eppe)_2]^+$ complexes observed here are consistent with the occurrence in solution of intramolecular inversion processes involving facile breaking of at least one M–P bond. In this respect the kinetic stability of the Cu(I) complex is higher than that of the Ag(I) or Au(I) complex.

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

Registry No. $[Au(eppe)_2]Cl$, 100082-39-1; $[Ag(eppe)_2]NO_3$, 99128-40-2; $[Cu(eppe)_2]Cl$, 100082-38-0; ^{65}Cu, 14119-06-3; ^{13}C, 14762-74-4.

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