Solid-State and Solution Structural Properties of Copper(I) Compounds with Bidentate Phosphane Ligands

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The copper(I) compounds [Cu(dppe)$_2$]X [X = BF$_4^-$, I$^-$; dppe = 1,2-bis(diphenylphosphanyl)ethane], [Cu(dppp)$_2$]X [X = BF$_4^-$, I$^-$; dppp = 1,3-bis(diphenylphosphanyl)propane], [Cu$_2$(dppe)$_3$I$_2$], and [Cu$_2$(dppe)$_2$I$_2$] have been prepared and their structural properties in solution and in the solid state have been determined. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra in solution [variable temperature and anion (I$^-$) concentrations] and analyses of solids (mass spectra, elemental analyses, and CPMAS ^{31}P-NMR spectra) are interpreted with equilibria in solution that involve two mono- and two dinuclear species. The structures of [Cu(dppe)$_2$]ClO$_4$, [Cu(dppp)$_2$]BF$_4$, and [Cu$_2$(dppe)$_3$I$_2$] · 2 CHCl$_3$ have been analyzed by X-ray crystallography. In all three structures the copper(I) center adopts a distorted tetrahedral geometry.

Introduction

Detailed structural studies and the understanding of solution equilibria and dynamics of copper(I) compounds of bidentate phosphanes are of importance due to their potential application as potent antitumor agents[1] and as free radical scavengers in industrial processes.[2][3] There are a number of published studies of solution equilibria and structures that involve copper(I) compounds with phosphane ligands with variable copper(I)-to-ligand ratios.[4] Similar equilibria have also been observed for silver(I) compounds of bidentate phosphane ligands.[5] Mononuclear[4e,4g,4i–4j,4l,4m,4p] and dinuclear phosphanecopper(I) compounds[4a–4d,4k,4n,4o,4q] with coordinated and bridging halide anions and with phosphane ligands in various coordination modes have been isolated and characterized. There is spectroscopic evidence that some of the structurally characterized solids lead to complex equilibria in solution. However, so far there is only relatively little thorough information on structures and dynamics in solution.[1,4f] Here we report our results from studies on the structural properties of copper(I) compounds of dppe and dppp in the solid state and in solution.

Results and Discussion

Syntheses and Properties of the Solids

Reaction of [Cu(CH$_3$CN)$_4$]BF$_4$ with dppe in CH$_2$Cl$_2$ in a 1:2 ratio yields [Cu(dppe)$_2$]BF$_4$ (**1**). [Cu(dppe)$_2$]I (**2**), [Cu$_2$(dppe)$_3$I$_2$] (**3**), and [Cu$_2$(dppe)$_2$I$_2$] (**4**) are prepared under similar conditions from CuI and dppe in CH$_2$Cl$_2$ or CHCl$_3$ (1:2, 2:3, and 1:1 Cu^I-to-ligand ratios). Reaction of dppp with [Cu(CH$_3$CN)$_4$]BF$_4$ and CuI in a 2:1 ratio in CH$_2$Cl$_2$ yields the compounds [Cu(dppp)$_2$]BF$_4$ (**5**) and [Cu(dppp)$_2$]I (**6**), respectively. X-ray quality crystals of **1** (as the perchlorate salt), **3** (with two disordered chloroform molecules in the lattice), and **5** were obtained by vapor diffusion of diethyl ether into a solution of the complexes in CH$_2$Cl$_2$ or CHCl$_3$. The solids were studied by X-ray diffractometry, mass spectrometry, elemental analysis, CPMAS ^{31}P-NMR and IR spectroscopy. ^{1}H, ^{13}C, and ^{31}P NMR was used to establish the solution structures of the compounds.

ORTEP[6] plots of the experimentally determined structures of [Cu(dppe)$_2$]ClO$_4$ (**1**), [Cu$_2$(dppe)$_3$I$_2$] (**3**), and [Cu(dppp)$_2$]BF$_4$ (**5**) are presented in Figure 1, and selected structural parameters are given in Table 1. As expected, the copper(I) center adopts a distorted tetrahedral geometry in these structures. The copper(I)−phosphane distances are in the range expected from other known structures[4b,4e,4g,4r] but there is a rather large variation in the individual distances, also within each complex. The degree of distortion from tetrahedral geometry depends primarily on the chelate ring size (dppe vs. dppp), with bite angles of the five-membered chelate rings of approximately 90° and bite angles of the six-membered rings of approximately 98°, and this leads to a flattening of the tetrahedral chromophores (deviation of the angles θ in Table 1 from 90°). All chelate rings are puckered, and the six-membered rings have the expected chair conformations.

There is no crystal structural analysis of [Cu$_2$(dppe)$_2$I$_2$] (**4**). The structural assignment given in Scheme 1 is based on the reported structures of [Cu$_2$(dppf)$_2$I$_2$][7] [dppf: 1,1′-bis(diphenylphosphanylferrocene)] and [Cu$_2$(PhPH$_2$)$_4$I$_2$][8] (PhPH$_2$: phenylphosphane). The signals in the CPMAS ^{31}P-NMR spectra of the copper(I) complexes are rather broad, due to distortion from tetrahedral symmetry, unresolved coupling to the copper nuclei, quadrupole interactions involving the copper centers and the presence of two isotopes (^{63}Cu, ^{65}Cu);[9] nevertheless, the observed spectra (see Table 2 for chemical shift data) are qualitatively in good agree-

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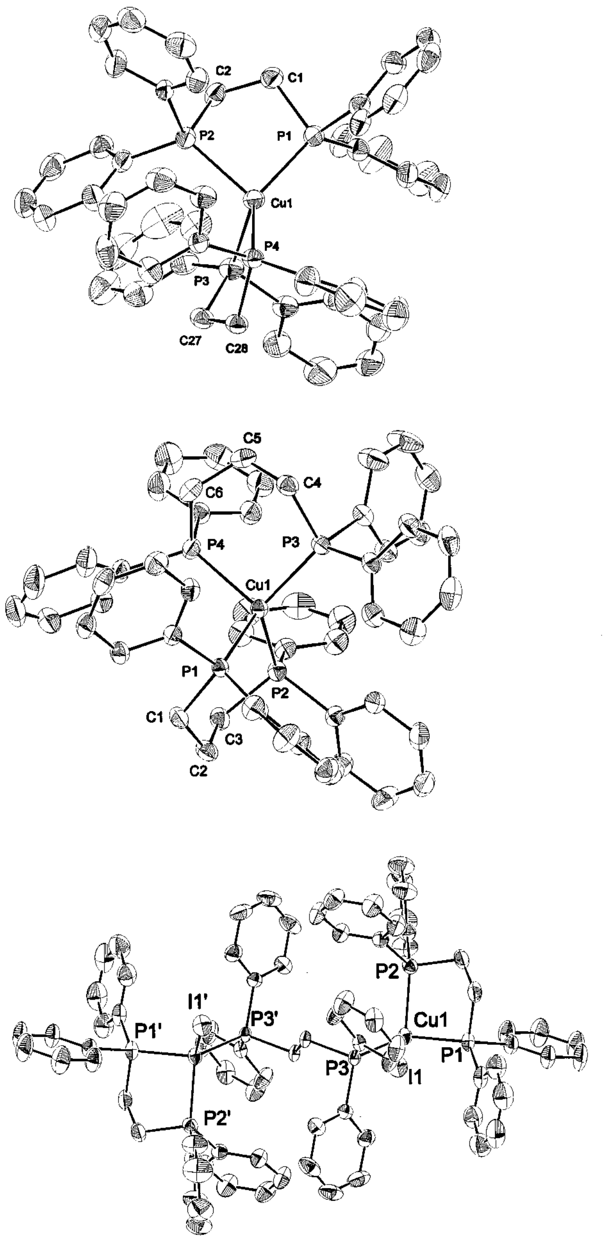


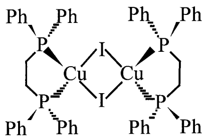
(1)

(5)

(3)

Figure 1. ORTEP[6] plots of the structures of the molecular cations of $[Cu(dppe)_2]ClO_4$ (**1**), $[Cu(dppp)_2]BF_4$ (**5**), and of the dinuclear compound $[Cu_2(dppe)_3I_2] \cdot 2\ CHCl_3$ (**3**)

ment with the X-ray structures of **1**, **3**, **5** (Figure 1), the putative structure of **4** (Scheme 1), published NMR data of $[CuP_4]^+$ and the structural assignments based on the solution NMR data (see below).



Scheme 1. Putative structure of $[Cu_2(dppe)_2I_2]$ (**4**) in solid state and in solution

Table 1. Selected structural parameters of $[Cu(dppe)_2]ClO_4$ (**1**), $[Cu(dppp)_2]BF_4$ (**5**), and $[Cu_2(dppe)_3I_2] \cdot 2\ CHCl_3$ (**3**)

Parameter	$[Cu(dppe)_2]ClO_4$	$[Cu(dppp)_2]BF_4$	$[Cu_2(dppe)_3I_2] \cdot 2\ CHCl_3$
Cu(1)−P(1)	2.259(2) Å	2.303(1) Å	2.315(2) Å
Cu(1)−P(2)	2.301(2) Å	2.298(1) Å	2.321(2) Å
Cu(1)−P(3)	2.300(2) Å	2.296(1) Å	2.273(2) Å
Cu(1)−P(4)	2.270(2) Å	2.317(1) Å	−
Cu(1)−I(1)	−	−	2.623(1) Å
P(1)−Cu(1)−P(2)	90.34(7)°	98.22(5)°	89.82(8)
P(1)−Cu(1)−P(3)	120.38(8)°	120.29(5)°	116.24(7)
P(2)−Cu(1)−P(3)	103.95(8)°	122.83(5)°	109.70(7)
P(3)−Cu(1)−P(4)	90.58(7)°	97.66(5)°	−
P(1)−Cu(1)−I(1)	−	−	113.88(6)
P(2)−Cu(1)−I(1)	−	−	116.29(6)
P(3)−Cu(1)−I(1)	−	−	109.79(5)
θ_1[a]	87.69°	81.44°	80.15°
θ_2[a]	74.43°	77.74°	76.79°

[a] Tetrahedral twist angles (tetrahedral, $\theta = 90°$; θ_2: planes involving the chelate rings).

Table 2. ^1H- and ^{31}P-NMR chemical shifts of Cu^I compounds of dppe and dppp

Compound	^1H NMR $\delta(CH_2)$ [ppm]	^{31}P NMR $\delta(P)$ [ppm]	CPMAS ^{31}P NMR $\delta(P)$ [ppm]
dppe	2.09	−12.47	−12.1
dppp	2.21; 1.58	−17.18; −17.26	−20.5; −24.4
$[Cu(dppe)_2]^+$	2.46	+7.5	+10.3
[Cu(dppe)(*P*-dppe)I]	−	−9.5	−
$[Cu_2(dppe)_3I_2]$	2.27	−5.0	−
$[Cu_2(dppe)_2I_2]$	2.56	−12.5	−20.0
$[Cu(dppp)_2]BF_4$	2.29; 1.62	−8.5	−10.1
$[Cu(dppp)_2]I$	2.28; 2.05; 1.64	−8.8; −17.5	−10.0

Equilibria in Solution

dppe Compounds

A broad signal at $\delta = 2.46$ is observed in the ^1H-NMR spectrum of $[Cu(dppe)_2]BF_4$ (**1**) in CD_2Cl_2. It is assigned to the methylene protons of the coordinated dppe ligands. The line broadening suggests unresolved ^{31}P-^1H coupling (relevant chemical shift data are assembled in Table 2). The ^{31}P-NMR spectrum of **1** in CD_2Cl_2 consists of a very broad signal centered at $\delta = +7.5$. It is assigned to the four phosphorus atoms coordinated to the copper(I) center. Lowering of the temperature leads to a significant decrease of $\Delta\nu_{1/2}$ (2500 Hz at 298 K vs. 250 Hz at 193 K) and a small upfield shift ($\Delta\delta \approx 0.9$) of this signal. This variation as a function of temperature is similar to that reported for $[Cu(dppey)_2]^+$ [4p] [dppey = *cis*-bis(diphenylphosphanyl)ethene] and consistent with the line shapes that have been calculated for fast quadrupolar relaxation[10] of a CuP_4 complex. No splitting is observed over the whole temperature range and the ^{31}P-NMR chemical shifts in the solid state and in solution are similar (Table 2). This suggests that only one species is present in solution, that is, the structure of **1** (see Figure 1) is conserved.

The high-field region of the ^{1}H-NMR spectrum of [Cu(dppe)$_2$]I (**2**) is presented in Figure 2. There are three broad signals at $\delta = 2.56$, 2.46, and 2.26, the latter is split into two signals at $\delta = 2.27$ and 2.24. Three broad resonances at $\delta \approx +7.5$, -5, and -12.5 are observed in the ^{31}P-NMR spectrum of **2** (Figure 3a). The signals at $\delta = 2.46$ (^{1}H NMR) and $+7.5$ (^{31}P NMR) are due to the molecular cation observed in the solids of **1** and **2**, that is, to the structure that is conserved from the solid state; the other signals must be due to other species in solution, which is indicative of a chemical exchange process.

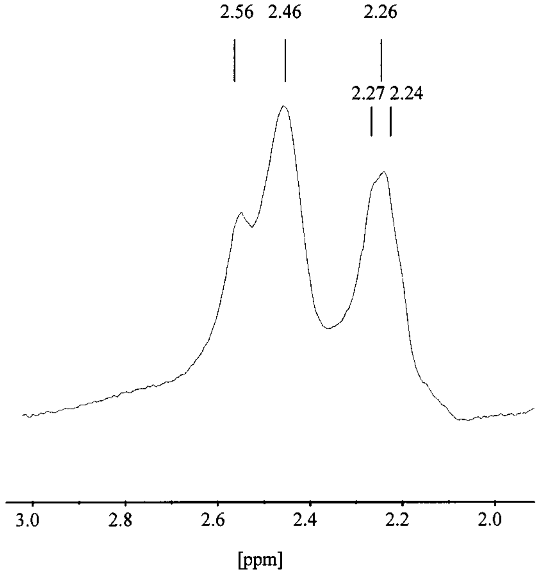


Figure 2. ^{1}H-NMR spectrum (200 MHz) of [Cu(dppe)$_2$]I (**2**) (298 K; CDCl$_3$)

From variable-temperature ^{31}P-NMR spectra of **2** (Figure 3) it emerges that (i) there is a significant decrease in the line width and a small upfield shift of the signal at $\delta = +7.5$, assigned to [Cu(dppe)$_2$]$^+$ (see above); (ii) there is an additional multiplet at $\delta = -9.5$ which has maximum relative intensity around 240 K; (iii) at lower temperatures the relative intensity of the signal at $\delta = +7.5$ increases. The multiplet at $\delta = -9.5$ is tentatively assigned to a mononuclear intermediate with one bidentate and one monodentate dppe ligand, that is, a species that results from substitution of one phosphane donor by I$^-$. This is consistent with the chemical shift data (see below and Table 2), the concentration profile (relative intensities, see Figure 3 and above) and the NMR titration experiments (see below).

There is a broad signal at $\delta = 2.56$ in the ^{1}H-NMR spectrum of **4** (see Table 2). This is assigned to the methylene protons of the bidentate dppe ligands. A broad resonance at approximately $\delta = -12.5$ (close to that of the metal-free ligand) is observed in the corresponding ^{31}P-NMR spectrum. A similar observation was made in NMR studies of [Cu$_2$(dppf)$_2$I$_2$], which was characterized by an X-ray crystal structure.[7] Addition of metal-free dppe to a solution of **4** in CDCl$_3$ leads to additional signals at $\delta = 2.27$ and -5 in the ^{1}H- and ^{31}P-NMR spectra, respectively (Figure 4). These new signals are tentatively assigned to a species with two chelated and one bridging phosphane ligand (Scheme 2). Further addition of dppe leads to decreasing intensity of the signal at $\delta = 2.56$ (^{1}H NMR), a sharpening of the signal at $\delta = -12.5$ (^{31}P NMR) and two additional signals at $\delta = 2.46$ (^{1}H NMR) and $\delta = +7.5$ (^{31}P NMR). That is, addition of dppe to [Cu$_2$(dppe)$_2$I$_2$] produces [Cu(dppe)$_2$]$^+$ via [Cu$_2$(dppe)$_3$I$_2$].

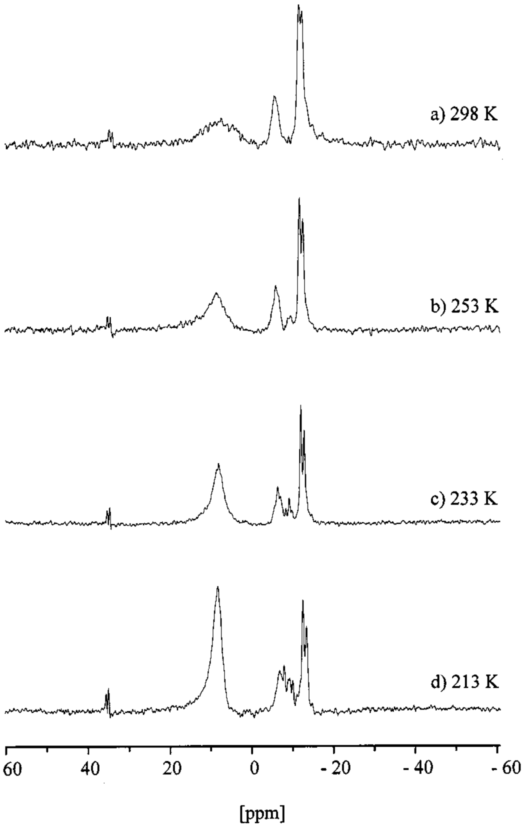
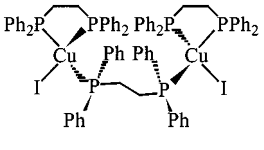


Figure 3. Temperature-dependent ^{31}P-NMR spectra (81 MHz) of [Cu(dppe)$_2$]I (**2**) (CDCl$_3$; 85% H$_3$PO$_4$)



Scheme 2. Solution structure of [Cu$_2$(dppe)$_3$I$_2$] based on ^{1}H- and ^{31}P-NMR spectroscopy

In a similar experiment ^{1}H- and ^{31}P-NMR spectra of [Cu$_2$(dppe)$_3$I$_2$] (**3**) were measured in dependence of the concentration of added dppe. The two signals in the ^{1}H-NMR spectrum of **3** at $\delta = 2.46$ and 2.27 are assigned to the complexes [Cu(dppe)$_2$]I and [Cu$_2$(dppe)$_3$I$_2$], respectively. In the ^{31}P-NMR spectra there are signals at $\delta = +7.5$ and -5.0, respectively. Addition of excess dppe results in the disappearance of the resonances at $\delta = 2.27$ (^{1}H NMR) and -5.0 (^{31}P NMR). That is, as expected, the equilibrium is shifted towards [Cu(dppe)$_2$]$^+$. Hence, the signals at $\delta =$

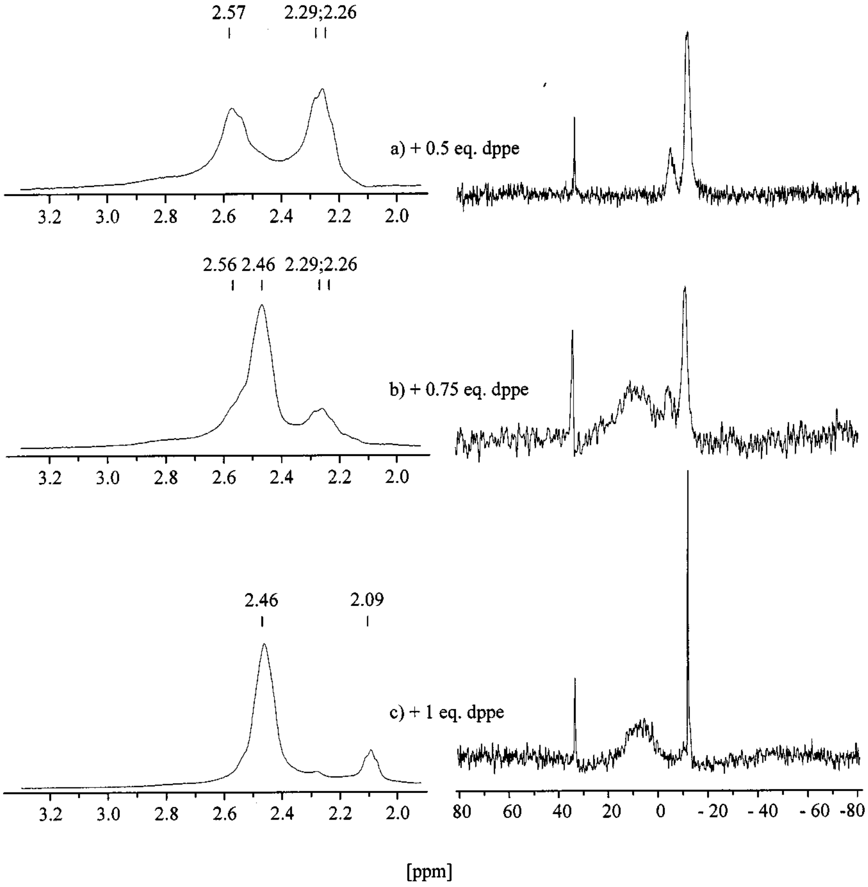


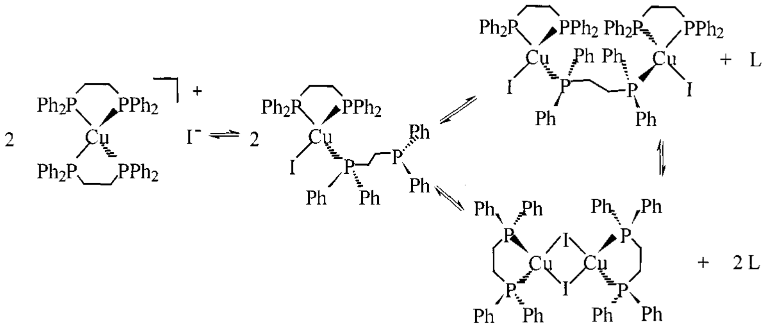
Figure 4. ^{1}H- and ^{31}P-NMR spectra (200 MHz, 81 MHz) of [$Cu_2(dppe)_2I_2$] (**4**) with different concentrations of added ligand [$CDCl_3$; 298 K; a small amount of impurity at $\delta(^{31}P) \approx 33$ is due to phosphane oxide]

2.27 (^{1}H NMR) and −5.0 (^{31}P NMR) are assigned to the same compound, that is, to [$Cu_2(dppe)_3I_2$].

The observations from temperature-dependent and ligand-concentration-dependent ^{1}H-NMR and ^{31}P-NMR data, and observations based on the solid-state samples are assembled in Scheme 3. The mononuclear compound [$Cu(dppe)_2$]I is in equilibrium with the putative intermediate [Cu(dppe)(*P*-dppe)I], which only is observed at low temperature. Dissociation of one or two ligand molecules leads to the dinuclear compounds [$Cu_2(dppe)_3I_2$] and [$Cu_2(dppe)_2I_2$], respectively, which have been observed in the solid.

dppp Compounds

Two broad signals for [$Cu(dppp)_2$]BF_4 (**5**) with an intensity ratio of 2:1 are observed in the ^{1}H-NMR spectrum at δ = 2.29 and 1.62 (methylene groups of the coordinated dppp ligands). A broad signal at δ = −8.5 (upfield shift of approximately 8.7 ppm with respect to the metal-free ligand) is observed in the ^{31}P-NMR spectrum of **5** in CD_2Cl_2. This is assigned to the four coordinated phosphorus atoms. The ^{31}P-chemical shifts in the solid state and in solution are similar (see Table 2) and thus the structure of **5** (see Figure 1) is conserved in solution.



Scheme 3. Proposal for the solution equilibria of copper(I) compounds of dppe with two mono- and two dinuclear species

In the high-field region of the ^{1}H-NMR spectrum of [Cu(dppp)$_2$]I (**6**) in CD_2Cl_2 there are multiplets at δ = 2.28 and 1.64 and some signals of lower intensity at δ = 2.05. The ^{31}P-NMR spectrum has a broad signal at δ = −8.80 and a signal at −17.5. The low-intensity signals in the ^{1}H- and ^{31}P-NMR spectra of **6** suggest that chemical exchange processes, similar to those of [Cu(dppe)$_2$]I, take place. Unfortunately, the proximity of the ^{31}P-NMR signals, due to the smaller chemical shift of the six-membered ring bisphosphane compounds, makes an identification of intermediate compounds in the region between δ = −8 and −17.5 difficult. Thus, a thorough investigation of the solution equilibrium was not appropriate.

The low-temperature ^{31}P-NMR spectrum of [Cu(dppp)$_2$]BF$_4$ (**5**) in CD_2Cl_2 (Figure 5) has features that are significantly different from those of [Cu(dppe)$_2$]BF$_4$ (**1**) (see Table 2). Below 213 K the signal at δ = −8.5 splits into two signals (δ = −5.84 and −10.36 at 193 K). The iodine salt **6** in CD_2Cl_2 leads to identical spectroscopic results; the signal at δ = −17.5 (room temperature) disappears at low temperature (193 K). An interpretation of these observations emerges from temperature-dependent ^{1}H-NMR spectroscopy. The two signals at δ = 2.29 and 1.62 (CD_2Cl_2, 298 K), assigned to the methylene protons of **5**, are split into five signals at δ = 2.85, 2.53, 2.20, 1.47, and 0.88 (CD_2Cl_2, 193 K) with an intensity ratio of 1:1:2:1:1. The ^{13}C-NMR spectrum (CD_2Cl_2, 193 K) has three signals at δ = 26.97, 25.91, and 16.62. These may be assigned to the three chemically and magnetically nonequivalent methylene groups of the six-membered ring in a frozen chair conformation. This is in agreement with the two signals in the ^{31}P-NMR spectrum, and these may be assigned to the two nonequivalent phosphorus atoms of the bidentate ligand. This interpretation is also supported by the [^{13}C-^{1}H] spectrum of **5** in CD_2Cl_2.

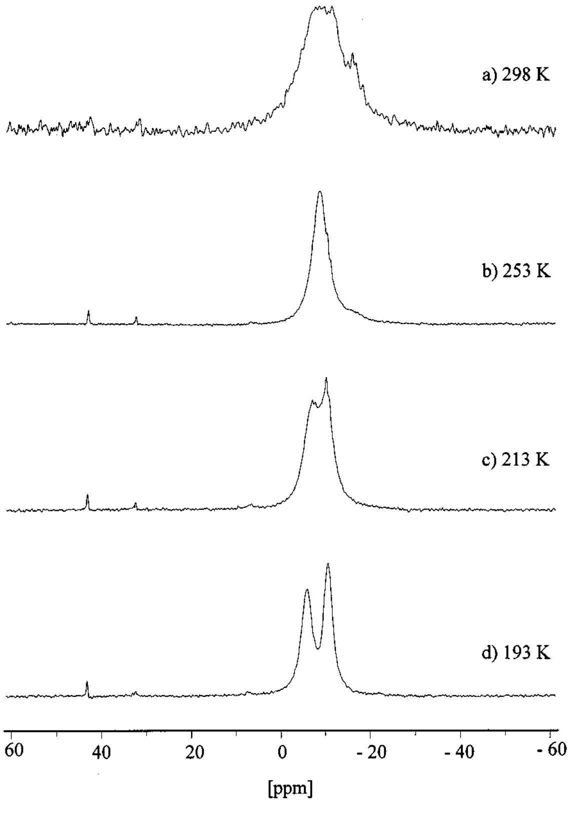


Figure 5. Temperature-dependent ^{31}P-NMR spectra (81 MHz) of [Cu(dppp)$_2$]BF$_4$ (**5**) (CD_2Cl_2; 85% H_3PO_4)

Experimental Section

Materials: 1,2-Bis(diphenylphosphanyl)ethane (dppe) and 1,3-bis(diphenylphosphanyl)propane (dppp) were purchased from Aldrich; CuI was obtained from Fluka and $Cu(BF_4)_2 \cdot x\ H_2O$ from ABCR Chemicals.

Measurements: ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra at 200.13 or 300.13, 50.32 or 75.47, and 81.03 or 121.5 MHz, respectively, were measured with a Bruker AS 200 or a Bruker WH300 instrument with dichloromethane or chloroform as internal reference. H_3PO_4 (85%) was used as external reference for ^{31}P-NMR spectra. The ^{1}H-COSY and [^{13}C-^{1}H] spectra at 500.13 and 125.77 MHz were obtained with a Bruker Advance 500 instrument. − Infrared spectra (KBr pellets) were measured with a Perkin-Elmer 16PC FT-IR instrument. − Elemental analyses were obtained from the microanalytical laboratory of the chemical institutes of the University of Heidelberg. − Mass spectra (FAB or FD) were measured with a Finnigan 8400 (nitrobenzyl alcohol matrix) or a Jeol JMS-700 instrument.

Syntheses: All manipulations were carried out under Ar, using standard Schlenk techniques. CH_2Cl_2, $CHCl_3$, and diethyl ether were degassed by bubbling Ar through the solutions for 20 min. [Cu(CH$_3$CN)$_4$]BF$_4$ was prepared as reported in the literature.[11]

[Cu(dppe)$_2$]BF$_4$·0.5 H$_2$O (1): [Cu(CH$_3$CN)$_4$]BF$_4$ (0.395 g, 1.26 mmol) was dissolved in CH_2Cl_2 (4 mL). The ligand dppe (1 g, 2.51 mmol) in CH_2Cl_2 (6 mL) was added (15 min) and the solution was stirred for 15 min at room temperature. After removing approximately 6 mL of the solvent and adding diethyl ether (10 mL), the solution was kept at −15°C over night. The resulting white precipitate was filtered off, recrystallized from methanol/water, and dried in vacuo. Yield (recrystallized): 0.63 g (0.66 mmol; 52%). − $C_{52}H_{48}BCuF_4P_4 \cdot 0.5\ H_2O$ (956.2): calcd. C 65.32, H 5.16, P 12.96; found C 65.43, H 5.13, P 13.03. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3050 (m, C_{ar}−H), 2918 (m, CH_2) 1482 (m, C_{ar}=C_{ar}), 1434 (s, P−Ph), 1054 (s, BF_4^-), 740, 694 (s, C_{ar}−H, 5 H neighboring). − MS (FAB); *m/z* (%): 859 (100) [M − BF$_4$], 646 (7) [M − BF$_4$ − CH$_2$CH$_2$PPh$_2$], 461 (98) [M − BF$_4$ − CH$_2$CH$_2$PPh$_2$ − PPh$_2$].

[Cu(dppe)$_2$]I·0.5 H$_2$O (2): A solution of dppe (1 g, 2.51 mmol) in $CHCl_3$ (6 mL) was slowly added to a suspension of CuI (0.239 g, 1.26 mmol) in $CHCl_3$ (2 mL). After stirring for 45 min, a pale yellow solution was obtained. The volume was reduced to 2 mL and diethyl ether was carefully added, until a white solid started to precipitate. After keeping at −15°C over night, the white precipitate was filtered off, recrystallized from methanol/water, and dried in vacuo. Yield (recrystallized): 0.43 g (0.43 mmol; 34%). − $C_{52}H_{48}CuIP_4 \cdot 0.5\ H_2O$ (996.3): calcd. C 62.69, H 4.96, P 12.44; found C 62.42, H 4.97, P 12.33. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3044 (m, C_{ar}−H), 2924 (m, CH_2) 1480 (m, C_{ar}=C_{ar}), 1432 (s, P−Ph), 740, 700 (s, C_{ar}−H, 5 H neighboring).

[Cu$_2$(dppe)$_3$I$_2$] (3): A solution of dppe (1 g, 2.51 mmol) in CH_2Cl_2 (2 mL) was added to a suspension of CuI (0.319 g, 1.67 mmol) in CH_2Cl_2 (8 mL). The resulting colorless solution was stirred for 15 min, when a white solid started to precipitate. After storage at

Table 3. Crystallographic data for $[Cu(dppe)_2]ClO_4$ (**1**), $[Cu_2(dppe)_3I_2]\cdot 2\ CHCl_3$ (**3**), and $[Cu(dppp)_2]BF_4$ (**5**)[13]

Empirical formula	$C_{52}H_{48}ClCuO_4P_4$	$C_{80}H_{74}Cl_6Cu_2I_2P_6$	$C_{54}H_{52}BCuF_4P_4$
Formula mass	959.8	1814.9	975.3
Crystal dimensions [mm]	0.60 × 0.50 × 0.50	0.95 × 0.45 × 0.30	0.60 × 0.55 × 0.40
Crystal system	monoclinic	triclinic	monoclinic
a [Å]	12.169(3)	11.828(4)	17.432(3)
b [Å]	40.640(9)	12.341(7)	15.273(3)
c [Å]	19.738(5)	15.691(8)	18.209(4)
α [°]	90	77.03(5)	90
β [°]	97.25(2)	71.64(3)	99.86(2)
γ [°]	90	67.47(4)	90
V [Å^{-3}]	9683.3(40)	1993.8(17)	4776.3(16)
Space group	$P2_1/c$	$P-1$	$P2_1/c$
Z	8	2	4
Calcd. density [g cm^{-3}]	1.317	1.511	1.356
Absorption coeff. [mm^{-1}]	0.682	1.671	0.644
$F(000)$	3984	910	2024
θ range [°]	1.69−22.50	1.80−28.81	1.75−25.00
Radiation (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
$R1$[a] [$I > 2\sigma(I)$]	0.062	0.072	0.061
$wR2$[b] (all data)	0.158	0.186	0.151
No. of reflections			
Measured	13116	10401	8702
Unique	12449 [R(int) = 0.032]	10400 [R(int) = 0.023]	8411 [R(int) = 0.060]
Obsd. [$I > 2\sigma(I)$]	8133	6652	6067
No. of variables	1150	444	782
Goodness of fit on F^2	1.131	1.057	1.063

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $wR2 = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

−15°C over night, the product was filtered off, recrystallized from methanol/water, and dried in vacuo. Yield (recrystallized): 0.8 g (0.51 mmol; 61%). − $C_{78}H_{72}Cu_2I_2P_6$ (1576.2): calcd. C 59.43, H 4.60, P 11.80; found C 59.72, H 4.77, P 11.63. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3046 (m, $C_{ar}-H$), 2902 (w, CH_2) 1482 (s, $C_{ar}=C_{ar}$), 1432 (s, P−Ph), 747, 705 (s, $C_{ar}-H$, 5 H neighboring). − MS (FD); m/z (%): 1449 (5) [M − I, $^{63/65}$Cu], 1051 (17) [M − I − $Ph_2PCH_2CH_2PPh_2$, $^{63/65}$Cu], 859 (100) [M − I − $Ph_2PCH_2CH_2PPh_2$ − CuI, $^{63/65}$Cu], 461 (5) [M − I − $Ph_2PCH_2CH_2PPh_2$ − CuI − $Ph_2PCH_2CH_2$ − PPh_2, $^{63/65}$Cu].

$[Cu_2(dppe)_2I_2]\cdot 0.2\ CH_2Cl_2$ (4): A suspension of CuI (0.239 g, 1.26 mmol) in CH_2Cl_2 (2 mL) was treated with a solution of dppe (0.5 g, 1.26 mmol) in CH_2Cl_2 (3 mL). After addition of $CHCl_3$ (5 mL) and stirring for 30 min at room temperature, diethyl ether was layered onto the colorless solution, which was kept over night at −15°C. The white precipitate was filtered off, washed with cold diethyl ether, and dried in vacuo. Yield: 0.85 g (0.72 mmol; 57%). − $C_{52}H_{48}Cu_2I_2P_4\cdot 0.2\ CH_2Cl_2$ (1194.7): calcd. C 53.03, H 4.11, P 10.52; found C 51.94, H 4.06, P 10.22. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3043 (m, $C_{ar}-H$), 2924 (m, CH_2) 1481 (m, $C_{ar}=C_{ar}$), 1432 (s, P−Ph), 1096 (s, $C_{ar}=C_{ar}$), 739, 692 (s, $C_{ar}-H$, 5 H neighboring). − MS (FAB); m/z (%): 1051 (6) [M − I, $^{63/65}$Cu], 859 (100) [M − I − CuI], 653 (39) [M − I − $Ph_2PCH_2CH_2PPh_2$, $^{63/65}$Cu], 461 (70) [M − I − CuI − $Ph_2PCH_2CH_2PPh_2$].

$[Cu(dppp)_2]BF_4$ (5): A pale yellow solution of dppp (1 g, 2.43 mmol) in CH_2Cl_2 (5 mL) was slowly added to a solution of $[Cu(CH_3CN)_4]BF_4$ (0.382 g, 1.21 mmol) in CH_2Cl_2 (4 mL). After stirring for 15 min, the volume was reduced to 5 mL and diethyl ether was layered onto the solution. The resulting gum was solidified by scratching in ice-cold CH_2Cl_2, recrystallized from methanol/water, and dried in vacuo. Yield (recrystallized): 0.91 g, (0.93 mmol; 77%). − $C_{54}H_{52}BCuF_4P_4$ (975.3): calcd. C 66.50, H 5.37, P 12.70; found C 66.03, H 5.34, P 12.61. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3064 (m, $C_{ar}-H$), 2929 (m, CH_2) 1498 (m, $C_{ar}=C_{ar}$), 1439 (s, P−Ph), 1067 (s, BF_4^-), 746, 704 (s, $C_{ar}-H$, 5 H neighboring). − MS (FAB); m/z (%): 887 (51) [M − BF_4], 475 (100) [M − BF_4 − $Ph_2P(CH_2)_3PPh_2$].

$[Cu(dppp)_2]I\cdot 0.5\ H_2O$ (6): A white suspension of CuI (0.231 g, 1.21 mmol) in CH_2Cl_2 (2 mL) was added to a solution of dppp (1 g, 2.43 mmol) in CH_2Cl_2 (6 mL). After stirring for 15 min, a colorless solution was obtained. Addition of diethyl ether and storage at −15°C over night resulted in a white precipitate, which was filtered off, recrystallized from methanol/water, and dried in vacuo. Yield (recrystallized): 1.03 g (1.00 mmol; 83%). − $C_{54}H_{52}CuIP_4\cdot 0.5\ H_2O$ (1824.3): calcd. C 63.32, H 5.21, P 12.09; found C 63.24, H 5.14, P 12.12. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3047 (m, $C_{ar}-H$), 2912 (m, CH_2) 1489 (m, $C_{ar}=C_{ar}$), 1439 (s, P−Ph), 746, 699 (s, $C_{ar}-H$, 5 H neighboring).

Structure Determinations: Intensity-measurement data were obtained with a Syntex R3 diffractometer, using Mo-K_α radiation and operating in the ω-scan mode at room temperature. Data were corrected for Lp and absorption effects (ψ scan). The structures were solved by direct methods (SHELXS 86[12a]) and refined by full-matrix least-squares methods based on F^2 (SHELXL 97[12b]), using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions, but their parameters were not refined. The $CHCl_3$ solvent molecules in $[Cu_2(dppe)_3I_2]\cdot 2\ CHCl_3$ and the BF_4^- anion in $[Cu(dppp)_2]BF_4$ are disordered. The crystallographic data for $[Cu(dppe)_2]ClO_4$, $[Cu_2(dppe)_3I_2]\cdot 2\ CHCl_3$ and $[Cu(dppp)_2]BF_4$ are summarized in Table 3.

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[1] [1a] S. J. Berners-Price, R. K. Johnson, C. K. Mirabelli, L. F. Faucette, F. L. McCabe, P. J. Sadler, *Inorg. Chem.* **1987**, *26*, 3383 − [1b] S. J. Berners-Price, C. Brevard, A. Pagelot, P. J. Sadler, *Inorg. Chem.* **1986**, *25*, 596.

[2] [2a] H. L. Finkbeiner, A. S. Hay, D. M. White, *Polymerization Processes* (Eds.: C. E. Schildknecht, I. Skeist), Wiley-Interscience, New York, **1977**, p. 537 – [2b] G. W. Parshall, *Homogeneous Catalysis*, Wiley-Interscience, New York, **1980**, p. 113 – [2c] P. M. Henry, *Adv. Organomet. Chem.* **1975**, *13*, 363 – [2d] E. W. Stern, *Catal. Rev.* **1968**, *1*, 74.

[3] [3a] M. Freiberg, D. Meyerstein, *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1825 – [3b] M. Freiberg, W. A. Mulac, K. H. Schmidt, D. Meyerstein, *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1838 – [3c] H. Cohen, D. Meyerstein, *Inorg. Chem.* **1986**, *25*, 1506 – [3d] S. Goldstein, G. Czapski, H. Cohen, D. Meyerstein, *Inorg. Chem.* **1992**, *31*, 2439 – [3e] N. Navon, G. Golub, H. Cohen, D. Meyerstein, *Organometallics* **1995**, *14*, 5670.

[4] [4a] V. G. Albano, P. L. Bellon, G. Ciani, M. Manassero, *J. Chem. Soc., Dalton Trans.* **1972**, 171 – [4b] V. G. Albano, P. L. Bellon, G. Ciani, *J. Chem. Soc., Dalton Trans.* **1972**, 1938 – [4c] A. Camus, G. Nardin, L. Randaccio, *Inorg. Chim. Acta* **1975**, *12*, 23 – [4d] P. G. Eller, G. J. Kubas, R. R. Ryan, *Inorg. Chem.* **1977**, *16*, 2454 – [4e] P. Leoni, M. Pasquali, C. A. Ghilardi, *J. Chem. Soc., Chem. Commun.* **1983**, 240 – [4f] D. J. Fife, W. M. Moore, K. W. Morse, *Inorg. Chem.* **1984**, *23*, 1684 – [4g] G. Doyle, K. A. Eriksen, D. Van Engen, *J. Am. Chem. Soc.* **1985**, *107*, 7914 – [4h] P. F. Barron, J. C. Dyason, P. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, A. H. White, *J. Chem. Soc., Dalton Trans.* **1987**, 1099 – [4i] S. J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* **1988**, *66*, 2194 – [4j] D. F. Dempsey, G. S. Girolami, *Organometallics* **1988**, *7*, 1208 – [4k] G. A. Bowmaker, A. Camus, P. C. Healy, B. W. Skelton, A. H. White, *Inorg. Chem.* **1989**, *28*, 3883 – [4l] G. A. Bowmaker, P. C. Healy, L. M. Engelhardt, J. D. Kildea, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1990**, *43*, 1697 – [4m] D. J. Darensbourg, C. C. Chao, J. H. Reibenspies, C. J. Bischoff, *Inorg. Chem.* **1990**, *29*, 2153 – [4n] R. D. Hart, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1991**, *44*, 919 – [4o] B. Mohr, E. E. Brooks, N. Rath, E. Deutsch, *Inorg. Chem.* **1991**, *30*, 4541 – [4p] S. J. Berners-Price, L. A. Colquhoun, P. C. Healy, K. A. Byriel, J. V. Hanna, *J. Chem. Soc., Dalton Trans.* **1992**, 3357 – [4q] G. A. Bowmaker, R. D. Hart, B. E. Jones, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1995**, 3063 – [4r] S. Kitagawa, M. Kondo, S. Katawa, S. Wada, M. Maekawa, M. Munakata, *Inorg. Chem.* **1995**, *34*, 1455.

[5] S. J. Berners-Price, R. J. Brown, P. A. Harvey, P. C. Healey, G. A. Koutsantonis, *J. Chem. Soc., Dalton Trans.* **1998**, 1743.

[6] C. K. Johnson, *ORTEP, A Thermal Ellipsoid Plotting Program*, Oak Ridge National Laboratory, Tennessee, U.S.A., **1965**.

[7] S. P. Neo, Z. Y. Zhou, T. C. W. Mak, T. S. A. Hor, *J. Chem. Soc., Dalton Trans.* **1994**, 3451.

[8] R. J. Batchelor, T. Birchall, R. Faggiani, *Can. J. Chem.* **1985**, *63*, 928.

[9] E. M. Menger, W. S. Veeman, *J. Magn. Reson.* **1982**, *46*, 257.

[10] A. Marker, M. J. Gunter, *J. Magn. Reson.* **1982**, *47*, 118.

[11] G. J. Kubas, *Inorg. Synth.* **1979**, *19*, 90.

[12] [12a] G. M. Sheldrick, *SHELXS 86*, University of Göttingen, **1986** – [12b] G. M. Sheldrick, *SHELXL 97*, University of Göttingen, **1997**.

[13] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-114482 (**3**), -114483 (**1**), -114484 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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