Bis-phosphonio-isophosphindolide Copper Complexes

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Phosphorus Heterocycles, Copper Complexes, Crystal Structure, 31P NMR Data

Bis-triphosphonylo-isophosphindolide salts 1[X] react with Cu(I)-halides CuX to give isolable products of composition [(I)CuX2]. X-ray crystal structure analyses confirmed that for X = Br, Cl dinuclear complexes [(μ-X)CuX2] with μ2:η1(P)-bridging cations 1 are formed, while for X = I a solid phase containing a salt [I]CuI6 and a complex [(I):CuI4] with a terminal μ1:η1(P)-coordinated ligand 1 was obtained. The bonding parameters in the two types of complexes suggest that 1 is a hybrid between a phosphonium cation and a phospholide anion whose π-system is less nucleophilic than the phosphorus lone-pair. 31P NMR studies revealed that in solution in all cases binuclear complexes [(I)Cu-X] are in dynamic equilibrium with small amounts of mononuclear species and free 1. The same equilibria were detected in the system 1[OTf]/CuOTf. NMR studies of ligand exchange reactions indicated that the stability of complexes [(I)CuX2] increases in the order X = OTf < I < Br, Cl, and titration of [(I)CuBr3] with Et4NBr allowed to determine the equilibrium constant of the complex formation reaction.

Introduction

Low coordinate phosphorus cations of the formula R2P+ have received much interest because of their capability to form transition metal complexes [1 - 3]. Among the different types [3] of such cations, bis-phosphonio-isophosphindolides like 1 [4] are unique because their low Lewis acidity allows the formation of stable complexes even with electrophilic metal centers such as univalent coinage metal cations [5 - 8]. As is exemplified by the reactivity of 1 towards Ag+ (Scheme 1) [8], these complexes include both mononuclear compounds (2) with μ1(P)- and dinuclear complexes (3) with μ2(P)-coordination of the ligand. With respect to its coordination properties, the cation 1 behaves thus as a hybrid between a phosphonium ion which occurs exclusively as a 2-electron donating ligand, and a (μ2,η)-P-coordinated phospholide anion [9] which acts as a 4-electron donor.

Examples of complexes of 1 with the lightest coinage metal, copper, are so far limited to a single compound, viz. the dinuclear complex 4 (Scheme 2) [6]. Unlike as in μ2-phospholide complexes, but in analogy to copper aryl compounds

Scheme 1. Bis-phosphonio-isophosphindolide silver complexes.

[10], the bonding in the Cu2P unit displays features of a 2-electron-3-center L(σ)->M bond which involves mainly the phosphorus lone-pair and is stabilized by secondary interactions between the metals and the ligand π-system [3, 6, 7]. The interesting features of this compound stimulated us to investigate the chemistry of copper complexes of 1 in more detail. In particular, we wished to find out how far the bonding situation and complex stability are controlled by the halide co-ligands, and if mononuclear

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copper complexes with similar composition as 2 could be obtained. The results of these studies are reported here.

**Results**

**Reactions**

Addition of solid CuX (X = Cl, Br, I) to solutions of the appropriate bis-phosphonio-isophosphindolide salt 1[X] (0.5 to 1 equiv.) in CH$_2$Cl$_2$/MeOH or CH$_2$Cl$_2$/EtOH produced yellow to orange reaction mixtures which contained according to $^{31}$P NMR spectroscopic assays dynamically exchanging equilibrium mixtures of free 1 and its copper complexes whose composition varied with stoichiometry and temperature. Isolable complexes precipitated as orange crystalline solids from d-$^2$C W M eO H after partial evaporation of the solvents and cooling. All products obtained by this procedure possess the analytical composition 1[X] x 2 CuX, regardless of the initial stoichiometry, and were further characterized by their mass spectra and $^{31}$P NMR spectra. In addition to 4, whose crystal structure had been reported previously [6], the analogous chloride and iodide complexes were also characterized by X-ray crystallography. Attempts to apply the same work-up procedure to CH$_2$Cl$_2$/EtOH solutions were successful only in the case of the reaction of 1[Cl] with CuCl; here, a small amount of yellow, crystalline material was obtained whose analytical data proved the presence of a mononuclear complex, (I)CuCl$_2$ [11].

Treatment of 1[OTf] (OTf = triflate) with one or two equivalents of CuOTf \times 0.5 C$_6$H$_6$ afforded yellow solutions whose $^{31}$P NMR spectra indicated the formation of similar equilibria as in the reactions with copper halides. No crystalline complexes could be isolated in this case.

**Crystal structures**

Crystals of the reaction product of 1[Cl] and CuCl are composed of discrete binuclear complexes 5 whose key feature is a planar, four membered ring consisting of the P$^2_2$-atom of a $\mu_2$-coordinated cation 1, a $\mu$-chlorine, and two trigonal planar Cu-atoms (Fig. 1). The Cu(2) atom is found in a split position which suggests that the crystal contains two different molecules 5a,b in a ratio of approx. 83:17 whose bonding parameters are similar enough to prevent the resolution of positional differences for further atoms [12]. Even if on the whole the constitution of the major component 5a resembles that of 4 [6], the metal coordination spheres in both species display some notable differences (see below).

The corresponding reaction product of 1[I] with CuI can be considered as a solid phase consisting of a 1:1 mixture of an ionic component (I)$_2$[Cu$_4$I$_6$] and a neutral tetranuclear complex [(I)Cu$_2$I($\mu$-I)$_2$]$_2$ (6) (Fig. 2). The latter can be formally described in terms of a central planar [Cu$_3$I$_4$]$^2$ moiety whose terminal halogens are further coordinated to the metal atoms of cationic [(I)CuI]$^+$ fragments.
Fig. 2. ORTEP view (50% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of complex 6 in crystalline \( \{[\text{ICu}_{4}]_{2} \times 6 \times 1.5 \text{CH}_{2}\text{Cl}_{2}\} \). Selected bond distances [Å]: Cu(1)-I(1) 2.501(2), Cu(1)-I(2) 2.573(2), Cu(1)-P(1) 2.199(2), Cu(2)-I(1) 2.520(2), Cu(2)-I(3) 2.572(2), Cu(2)-I(3A) 2.557(2), P(1)-C(1) 1.733(7), P(1)-C(9) 1.719(7), P(2)-C(2) 1.751(7), P(3)-C(9) 1.746(7), C(2)-C(3) 1.441(10), C(3)-C(4) 1.390(10), C(3)-C(8) 1.404(10), C(4)-C(5) 1.378(12), C(5)-C(6) 1.368(12), C(6)-C(7) 1.406(10), C(7)-C(8) 1.440(10), C(8)-C(9) 1.440(10); bond angles [°]: P(1)-Cu(1)-I(1) 123.5(1), P(1)-Cu(1)-I(2) 119.2(1), I(1)-Cu(1)-I(2) 117.3(1), I(3)-Cu(2)-I(3A) 115.8(1), I(2)-Cu(2)-I(3) 121.5(1), I(2)-Cu(2)-I(3A) 122.4(1), C(2)-P(1)-C(9) 93.0(3), C(2)-P(1)-Cu(1) 132.2(3), C(9)-P(1)-Cu(1) 134.5(2), Cu(1)-I(2)-Cu(1) 102.8(1), Cu(2)-I(3)-Cu(2A) 64.2(1).

All copper atoms exhibit planar coordination geometries, and the whole complex displays crystallographic C\(_1\)-symmetry. The bonding parameters in the central \( \{[\text{ICu}(\mu-I)]_{2} \}\) moiety differ little from those found for \( \{[\text{ICuL}_{4}]_{2} \}^{2-} \) anions [13, 14] The exocyclic Cu(1)-I(2) (2.573(2) Å) and the endocyclic Cu-I bonds (2.557(2), 2.572(2) Å) are similar and distinctly longer than the bond to the terminal iodide (Cu(1)-I(1) 2.501(2) Å). The \( [\text{CuI}_{4}]^{2-} \) anions in the same structure appear as a distorted cubic array of Cu atoms where each face of the cube is topped by an iodine atom, and each metal site has an occupancy of 0.5. An arrangement of this type represents a typical feature in crystal structures of salts with \( [\text{CuI}_{4}]^{2-} \) anions (X = Br, I) [15] and can be rationalized in terms of an orientational disorder of particles which consist of a tetrahedral Cu\(_4\)-core with edge-bridging \( \mu^2\)-iodide ligands (a representation showing the two possible anion orientations is depicted in Fig. 3).

While the metric parameters of the individual free and coordinated cations 1 in the above structures differ only insignificantly and agree all closely with reported data [5 - 8, 16], their coordination modes reveal some flexibility. The planar geometry of phosphorus in the tetranuclear complex 6 (sum of valence angles 359.6°, Fig. 4a) is similar as in phosphinenium complexes [1 - 3], but the P-Cu bonds (2.199(2) Å) are slightly longer than in the phosphane complex \([\text{Cy}_3\text{P}]_{2}\text{Cu}_2(\mu-\text{Cl})_2\] (2.18 Å [17]) and fail thus to show the expected [3] bond shortening. Similar features had also been noted for gold and silver complexes of 1 [5, 8]. Unlike the irregular T-shaped metal coordination geometry in 2 [8], all bond angles at Cu(1) lie in a narrow range of 120 ± 3°.

Very similar metric parameters as for 6 are found for the Cu(1) atom in 5a,b (Fig. 4b, Cu(1)-P 2.2014(13) Å, sum of bond angles at P(1) 358°). In contrast, the environment of the second Cu atom is notably different and appears distorted T-shaped (Cu(2) in 5a), or nearly linear (Cu(2A) in 5b), respectively. Most characteristic are the elongation of the Cu(2)/Cu(2A)-P(1) distance (2.483(9)/2.86(2) Å) and the opening of the Cl(1)-Cu(2)/Cu(2A)-Cl(2) angle (141.94(4)/172.2(2)°) opposite to this bond. Considering that the bonds from the \( \mu^-\)Cl ligand to Cu(2)/Cu(2A) (2.221(6)/2.052(11) Å) are shorter than to Cu(1) (2.310(2) Å), the molecular structure of the complex resembles a contact ion.
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Fig. 4. Comparison of the phosphorus and copper coordination environments (ORTEP view, 50% probability ellipsoids) in 6 (a) 5a,b (b), and 4 (c) [4]. Bond distances [Å] and angles [°] for 4 (from ref. [4]): Cu(1)-Br(1) 2.262(2), Cu(1)-Br(2) 2.289(2), Cu(2)-Br(2) 2.371(1), Cu(2)-Br(3) 2.351(1), P(1)-Cu(2) 2.255(2), P(2)-Cu(2) 2.265(2), P(1)-Cu(1) 1.07(1), P(1)-Cu(1)-Br(3) 116.2(1), P(1)-Cu(1)-Br(1) 136.7(1), P(1)-Cu(1)-Br(2) 114.4(1), P(1)-Cu(2)-Br(2) 137.9(1), Br(1)-Cu(2)-Br(3) 127.7(1).

pair of phosphonium-like [(I)CuCl]⁺ and [Cu’Cl₂]⁻ fragments which are held together by Cu-Cl- and weaker Cu’-P-donor/acceptor interactions.

The same basic features as described above had also been noted in the molecular structure of 4 [6], however, the inequivalence of the two P-Cu bond distances was in this case less pronounced (P(1)-Cu(1) 2.255(2), P(1)-Cu(2) 2.351(1) A), and the distorted T-shaped coordination geometries of both metals were more similar (Fig. 4c).

NMR spectroscopic investigations

Low temperature 31P NMR spectra (-90°C, CH₂Cl₂) of 4, 5 displayed AX₂ patterns with chemical shifts and couplings (Table I) comparable to those of a μ-(CF₂CO₂)-μ-bis-phosphonio-isophosphindolide silver complex [8]. The signals of the endocyclic phosphorus atoms broadened and eventually disappeared when the temperature was raised, while the resonances of the PP₃ moieties remained sharp, but displayed an increase of Jpp. Similar effects have also been noted for silver complexes of 1 [8] and indicate the onset of dissociation of the complex and concomitant dynamic exchange between coordinated and free ligands.

Attempts to dissolve the copper iodide complex lead to precipitation of a small amount of CuI. 31P NMR spectra (-90 °C) of the supernatant solutions displayed AX₂ patterns attributable to a binuclear complex [(I)Cu₂Br₃] (7) and an additional doublet with similar parameters (δ31P 15.55, Jpp = 90 Hz) as the highfield doublet of 1. Both signal patterns coalesced when the temperature was increased. The multiplicity of the additional signal may be rationalized in terms of the AX₂ part of a second AX₃ system whose A-part evades detection due to severe dynamic exchange broadening; by analogy to silver complexes of 1 [8], we explain this signal as the averaged resonance of a rapidly exchanging mixture of free 1 and a mononuclear copper complex (presumably of composition (I)CuCl) which are both formed by partial dissociation of 7.

Evidence for the dissociation of the binuclear complexes 4, 5, 7 was likewise obtained from 31P NMR studies of mixtures with excessive 1[X] or tetraalkylammonium halides. Spectra of solutions containing 4, 5, and additional 1[X], displayed at -70 °C besides the signals of the binuclear complexes a second AX₂ pattern whose δ31P and Jpp values were similar, but not identical, to those of free 1. The observations that δ31P(A) varied with changing ratio of the reactants and further the P(A)-multiplet broadened and eventually disappeared at lower temperatures (-100 °C) lead to assign this resonance, as above, as a dynamic averaging of the signals of a mononuclear complex and free 1.

In order to elucidate the dissociation process in more detail, reactions of [(I)Cu₂X₃] with Et₄NX were carried out in the form of titrations. For X = Br, exchange between the binuclear complex and other phosphorus containing components was sufficiently slow below -60 °C to allow 31P NMR spectroscopic monitoring of the variation in the molar fraction.

<table>
<thead>
<tr>
<th>δ31P (ppm)</th>
<th>δ31P(A) (ppm)</th>
<th>2Jpp (Hz)</th>
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<tr>
<td>4</td>
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Table I. 31P-NMR data (-100 °C in CH₂Cl₂) of copper complexes of 1; δ [ppm], J [Hz]. P⁺ and P⁻ denote the phosphorus nuclei in A2X spin systems.

a Not observed due to excessive linewidth or insufficient signal-to-noise ratio; b at -105 °C.
Fig. 5. Representation of the variation of the molar fraction $\chi(4)$ at $-62^\circ$C with the degree of titration $\tau$ during the titration of 4 with Et$_4$NBr. Diamonds and errorbars denote experimental values and their estimated errors. The solid curve represents the result of a fit on the basis of the reaction model in Scheme 3 which yielded the value of the overall equilibrium constant as $K = 1.5(4) \times 10^2$.

Scheme 3. Representation of the reaction sequence describing the stepwise dissociation of dinuclear complexes [(1)Cu$X_3$], and definition of the appropriate equilibrium constants:

\[
\begin{align*}
[(1)CuX_3] + X & \rightleftharpoons [(1)CuX_2] + CuX_2^- \quad K_1 \quad (1) \\
[(1)CuX_3] & \rightleftharpoons (1)CuX_2 + CuX_2^- \quad K_2 \quad (2) \\
[(1)CuX_3] + X & \rightleftharpoons (1)CuX_2 + 2 CuX_2^- \quad K_1 \times K_2 = K
\end{align*}
\]

$\chi(4)$ during the titration (Fig. 5); for $X = Cl$, I this approach failed because of insufficient retardation of exchange even at $-100^\circ$C, or the formation of precipitates. If we assume that in the presence of excess $X^-$ all higher copper halide aggregates are converted into $[CuX_2^-]$ [18], and that the mononuclear intermediate has indeed the composition [(1)Cu$X_3$] as was suggested by the above mentioned isolation of a CuCl-complex of this composition, the reaction can be formulated as the two step sequence shown in Scheme 3. A fit of the values of $\chi(4)$ determined at $-62^\circ$C (Fig. 5) yielded the product of equilibrium constants $K = K_1 \times K_2 = 1.5(4) \times 10^2$. Since the available spectra did not permit explicit determination of the molar fractions of [(1)Cu$X_2$] or 1, respectively, evaluation of $K_1$, $K_2$ was not feasible.

In order to trace down the influence of the bridging halides on the complex stabilities, we studied also the product distribution in ligand scrambling reactions between complexes with unlike halides. Mixed species [(1)Cu$XX'$$_2$] were characterized in situ by 1D and 2D $^{31}$P NMR studies in the slow exchange regime below $-60^\circ$C, and relevant data are listed in Table I. Even if for the mixed complexes two isomeric forms can be conceived, in all cases only a single set of signals was observed. Inspection of the $^{31}$P NMR spectra of individual reaction mixtures revealed that in the case of $X_0$, $X' = Cl$, Br the dinuclear species [(1)Cu$Br_rCl_{1-x}$] ($n = 0 - 3$) were the only detectable products. Accordingly, the scrambling reaction may be expressed in terms of the equations shown in Scheme 4. Computation of the equilibrium constants from the relative signal intensities yielded $K_{3,1} = K_{3,2} = 3.7(2)$ which is close to the statistical value of $K_{3,1} = K_{3,2} = 3$.

In reactions where $X$, $X' = Cl$, I or Br, I, formation of considerable amounts of free 1 and mononuclear complexes together with precipitation of CuX was observed. Among the dinuclear compounds, 4 and 5 were detected as the major species beside small amounts of mixed halide complexes, while 7 was not observed at all.

The $^{31}$P NMR spectra of reactions of 1[OTf] with CuOTf at $-100^\circ$C revealed the presence of equilibria between free 1 and three distinguishable complexes. As in the system 1[OTf]/AgOTf [8], the relative concentrations of the individual products varied strongly with the stoichiometry of the reactants. Based on the analysis of these variations and on a comparison of the observed chemical shifts with those of silver or gold complexes of 1 [5, 8], the new products were assigned to one mono- and two distinguishable dinuclear complexes, respectively (Table I).
Discussion

The results of the spectroscopic studies reveal in all reactions of \(1[X]\) with copper salts \(CuX\) the same dynamic equilibria between \(1\) and kinetically labile mono- and dinuclear complexes with \(\mu_1, \eta^1\)-P- and \(\mu_2, \eta^1\)-P-coordinated cations. At low temperatures and in the presence of an excess of \(Cu^+\) ions, the dinuclear complexes \([(1)Cu_2X_3]\) constituted the most abundant phosphorus containing components. For \(X = Cl, Br\), these species precipitated as the least soluble components from the mixtures and could thus be isolated and structurally characterized. The isolation of a product with a different composition for \(X = I\) suggests that in this case precipitation of a mixture of the minor equilibrium components had occurred.

Even if evaluation of individual complex stability constants was not feasible, the results of the spectroscopic studies suggest that all complexes are also thermodynamically not very stable and undergo in solution partial dissociation with cleavage of \(1\). The relative stabilities of mono- and dinuclear complexes depend on the nature of \(X\), with the preference to form dinuclear species increasing in the order \(X = OTf < I < Br \approx Cl\). A low proficiency of OTf\(^-\) to adopt a \(\eta^2\)-bridging coordination had also been noted for the silver complex \([3]\). The presence of an excess of \(Cu^+\) ions, the dinuclear complexes \][(1)Cu_2X_3]\] have similar thermodynamic stabilities as the corresponding homoleptic compounds. The observation of only a single isomer for each mixed species suggests a “symmetric” constitution with the unique halide in the bridging position, even if this cannot be finally proven from the available data.

The bonding between the \(\eta^1\)-coordinated cation \(1\) and a single \(Cu^+\) (\(d^{10}\)) in \(6\) can be pictured as a superposition of a dative \(P\rightarrow Cu\ \sigma\) and a retrodative \(Cu\rightarrow P\ \pi\)-bonding contribution \([3]\). However, since \(1\) is a weaker electrophile than an aminophosphonium ion \([3, 4]\) and exhibits further an additional occupied \(\pi\)-orbital of high energy which may interact repulsively with filled metal d-orbitals, the back donation and thus the formal double bond character is lowered \([3]\) and the bonding situation resembles more closely that of a phosphane or phospholide ligand. This explains why the P-Cu bond distance in \(6\) is close to that of phosphane complexes (vide supra), whereas P-M bonds in aminophosphonium complexes are normally 4 - 10% shorter than in comparable phosphane complexes \([3]\).

Even if the individual Cu-P bonds in \(4\) and \(5a\) differ substantially, the mean Cu-P distances are similar \((2.34 \text{ Å in } 5a, 2.30 \text{ Å in } 4)\) and match those of electron deficient bonds in \(\mu_3\)-phosphido copper complexes \((2.32 - 2.36 \text{ Å})\) \([20]\), and the intra-ligand P-C bonds in both compounds compare to those in free \(1\). Whereas these features suggested for \(4\) a description of the phosphorus-metal bonding with a dominant 3-center-2-electron \(P(lone-pair)\rightarrow Cu_2\ \sigma\)-bond and weaker \(P(\pi)\rightarrow Cu/Cu\rightarrow P(\pi^*)\) interactions \([6]\), the higher asymmetry of the Cu-P core in \(5a\) (see Fig. 3b,c) implies a description of the shorter P(1)-Cu(1) bond of \(5a\) in the same way as in \(6\), while the P(1)-Cu(2) bond may be described assuming dative and retrodative interactions which involve both \(\pi\)-orbitals on the side of the ligand. The observed bond lengths suggest that the \(\pi\)-nucleophilicity of \(1\) is significantly weaker than that of the phosphorus lone pair or the \(\pi\)-electron system of a phospholide anion, presumably due to hyperconjugative interaction with the \(\text{P}_3\text{P}^*\) groups.

In addition to confirming the view of bis-phosphonio-isophosphindolides as hybrids between phosphonium cations and phospholide anions, the structural features of complexes \(4, 5\) underline the importance of the \(\mu\)-halide for the stability of dinuclear aggregates. A concise analysis of the interplay in the bonding of the two different bridging ligands is objects by the limited number of com-
pounds; nonetheless, comparison of the molecular structures of 4, 5 with that of the silver complex 3 [8] suggests that absence of additional bridging ligands and low donating power of the co-ligands favor a more symmetric $\mu_2$-coordination of 1 with shorter P-M bonds, which may be interpreted as an enhanced participation of $\pi$-electrons in metal bonding.

**Experimental Section**

**General remarks:** All manipulations were carried out under dry argon. Solvents were dried by using standard procedures. Copper salts were commercially available and were dried in vacuo prior to use. The salts I[X] were prepared as described [4, 16, 21]. NMR spectra: Bruker AMX 300 (1H: 300 MHz, 31P 121.5 MHz, chemical shifts referenced to ext. TMS or 85% H3PO4). NMR data of copper complexes were obtained from spectra recorded between -70 and -100 °C in the slow exchange regime. Where necessary, signal assignments were derived from 2D-Soft-Cosy spectra recorded via selective excitation of the signals of the coordinated phosphorus nuclei with gaussian shaped pulses. Quantitative analysis was performed via integration of suitable 'H signals. - MS: Kratos Concept. Elemental analyses: Heraeus CHNO-Rapid.

**Preparation of Complex 4:** A mixture of 1[Br] (2.00 g, 2.72 mmol) and CuBr (0.39 g, 2.72 mmol) was treated with 50 ml of CH3OH, and the resulting suspension was stirred at 20 °C for 6 h. CH2Cl2 (20 ml) was then added, and the mixture was refluxed until the yellow precipitate had dissolved. Cooling to -30 °C produced yellow crystals which were collected by filtration and dried in vacuo. Yield 1.13 g (70% with respect to CuBr), m. p. 191 °C.

C44H34C12Cu,P3 (889.1)

Calcd C 59.44 H 3.85%, Found C 58.6 H 3.9%.

1H NMR (30 °C, CDCl3); δ = 7.84 - 7.53 (m, 30 H, C6H5), 6.95 - 6.81 (m, 4 H, C6H4), – (+)-FAB-MS: m/z (%) = 888 (11, [1(Cu2Cl3)]+), 853 (44, [1(Cu2Cl2)]+), 753 (80, [1(CuCl)]+, 717 (29, [1(Cu)]+, 655 (100, 1+) – UV/VIS (BaSO4): $\lambda_{max}$ = 425, 381 nm.

(b) A suspension of 1[Cl] (3.50 g, 5.06 mmol) and CuCl (0.50 g, 5.06 mmol) in 50 ml of CH3OH was stirred for 6 h at ambient temperature. The formed precipitate was filtered off and recrystallized at -30 °C from CH2OH/CH2Cl2 (1:1) to give 1.5 g (37%) of yellow crystals of [1(CuCl)] (11), m. p. 280 °C (dec).

C44H34Cl2Cu,P3 (811.4)

Calcd C 65.51 H 4.29%, Found C 65.00 H 4.38%.

1H NMR (CDCl3); δ = 7.75 - 7.55 (m, 30 H, C6H5), 7.00 - 6.89 (m, 4 H, C6H4).

**Reaction of 1[Br] with copper(I) iodide:** A suspension of 1[Br] (3.00 g, 3.83 mmol) and CuI (0.73 g, 3.83 mmol) in 50 ml of CH2Cl2/CH3OH (3:2) was stirred for 12 h at ambient temperature. The yellow precipitate was filtered off and dried in vacuo. Since no uniform elemental analysis could be obtained, the material was assumed to be an inhomogeneous mixture and was discarded. Prolonged storage of the mother liquid at -20 °C produced further 0.52 g (22% with respect to CuI) of orange crystals of m. p. 235 °C (dec.) and analytical composition with BaSO4.

C44H34Cl2Cu,P3 (840.2)

Calcd C 42.34 H 2.89%, Found C 43.2 H 3.1%.

1H NMR (CDCl3); δ = 7.83 - 7.54 (m, 30 H, C6H5), 6.88 - 6.79 (m, 4 H, C6H4). - UV/VIS (BaSO4): $\lambda_{max}$ = 435, 383 nm.

**Reaction of 1[OTf] with copper(I) triflate:** Mixtures of 1[OTf] (0.87 g, 1.00 mmol) with 1 or 2 equivs. of CuOTf × 0.5 C6H6 were dissolved in CH2Cl2. The resulting solutions were characterized by low temperature 31P NMR spectra.

**Titration of 4 with Et3NBr:** Twelve samples were prepared by combining 1.00 ml of a CH2Cl2 solution containing 4 (1.0 × 10⁻² mol L⁻¹) and Et3NBr (2.0 × 10⁻³ mol L⁻¹, to prevent precipitation of CuBr), with 0.00 to 1.10 ml of a 1.0 × 10⁻² molar solution of Et3NBr in
CH₂Cl₂, and filling up with CH₂Cl₂ to a total volume of 2.1 ml. The samples were transferred to NMR tubes and analyzed by ³¹P NMR spectroscopy at -62 °C. Values of the molar fraction χ(4) were calculated from the integrals of the signals of PPh₃-groups. The value of the equilibrium constant K = 1.5(4) × 10² (see Scheme 5) was obtained from a fit of the experimental values in a plot of (χ(4) vs. the degree of titration τ. The fit function χcalc(τ) was determined by solving nonlinearly [23] the equation K = (c(4) c(Br⁻))/(c(1) c²(CuCl₂⁻)) under the constraints imposed by mass and charge balance for c(4), and substituting further χ(4) = c(4)/c₀ where c₀ denotes the initial concentration of the copper complex.

X-ray crystallographic study of 5 at 203(2) K: Single crystals of composition C₄₄H₄₄Cl₂Cu₂P₃ × 1.5 CH₂Cl₂ × 2.5 CH₃OH were obtained as yellow needles from CH₂Cl₂/CH₃OH (1:1) at ~20 °C. M = 1076.5, triclinic, space group Pī (No. 2): a = 12.302(3), b = 12.768(2), c = 16.814(4) Å, α = 82.34(1)°, β = 92.99(1)°, γ = 76.96(1)°, V = 2451.2(9) Å³, Z = 2, ρcalc = 1.475 Mg m⁻³, F(000) = 2492, μ(Mo-Kα) = 3.16 mm⁻¹. 17157 reflections (16754 independent reflections, Rint = 0.080) were collected on a Nicolet R3m diffractometer (Mo-Kα radiation, graphite monochromator, ω scans) in the range 3 ≤ 2θ ≤ 50° (−15 ≤ h ≤ 15, −16 ≤ k ≤ 16, 0 ≤ l ≤ 30). Of these, 16752 were used for structure solution (direct methods) and refinement (full-matrix least-squares on F², 991 parameters, 36 restraints, non hydrogen atoms anisotropic, hydrogens with a “riding” model); wR₂ = 0.182, R₁ (1 > 2σ(1)) = 0.060. A semi-empirical absorption correction from ψ-scans was applied (min./max. transmission 0.848/0.973). The four copper atoms in the [Cu₂I₄]²⁻ anion were disordered.

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-134157 (5) and CCDC-100993 ([{1}₂[Cu₂I₄] × 6 × 1.5 CH₂Cl₂]). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223) 336-033, email: teched@ccdc.cam.ac.uk).

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[11] Single crystal X-ray diffractometry produced a data set which could be solved and served to confirm the molecular constitution, but could not be successfully refined; N. Korber, unpublished results.
[12] In order to verify that the disorder is not an artifact of the crystal structure analysis we studied several crystals of 5 all of which displayed the same behavior.
[23] The procedure for the iterative numeric solution of the underlying equation systems has been described in: M. Binnewies, Chemische Gleichgewichte, Wiley-VCH, Weinheim (1996).