Enhanced hydrolytic activity of Cu(II) and Zn(II) complexes in highly cross-linked polymers

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The chelate ligand tris[(1-vinylimidazol-2-yl)methyl]amine (5) was synthesized in five steps from commercially available starting materials. Upon reaction with $ZnCl_2$ or $CuCl_2$ in the presence of NH_4PF_6 , the complexes [Zn(5)Cl]PF₆ (6) and [Cu(5)Cl]PF₆ (7) were obtained. The structure of both complexes was determined by single-crystal X-ray crystallography. Immobilization of 6 and 7 was achieved by co-polymerization with ethylene glycol dimethacrylate. The supported complexes P6-Zn and P7-Cu were found to be efficient catalysts for the hydrolysis of bis(*p*-nitrophenyl)phosphate (BNPP) at 50 °C. At pH 9.5, the heterogeneous catalyst P7-Cu was 56 times more active than the homogeneous catalyst 7. Partitioning effects, which increase the local concentration of BNPP in the polymer, are shown to contribute to the enhanced activity of the immobilized catalyst.

Introduction

Transition-metal complexes with multidentate N-donor chelate ligands have been studied extensively as mimics for hydrolytic metalloenzymes.¹ Most efforts have focused on homogeneous, low molecular weight catalysts but immobilized metal complexes are increasingly being investigated as potential alternatives.^{2,3} Advantages of supported catalysts are the ease of separation and the possibility to recycle the catalyst as well as reduced problems with catalyst solubility and aggregation. The latter point is particularly evident for hydrolytically active Cu(II) complexes, which are known to form catalytically inactive hydroxy-bridged dimers $[L_nCu(\mu-OH)_2CuL_n]^{2+}$ (L_n = multidentate N-donor ligand).^{4,5} The supporting polymeric matrix may also be used to achieve some structural control over the first and/or second coordination sphere of the metal binding site using the technique of molecular imprinting.^{3,6}

In the following, we describe the synthesis and the characterization of immobilized Cu(II) and Zn(II) complexes. They were obtained by co-polymerization with ethylene glycol dimethacrylate (EGDMA) using a vinyl-substituted, tetradendate N-chelate ligand. In hydrolysis reactions of the activated phosphodiester bis(*p*-nitrophenyl)phosphate (BNPP), the polymeric catalysts were found to be up to 56 times more active than the corresponding homogeneous catalysts. Partitioning effects, which increase the local concentration of the substrate in the polymer, are shown to contribute to the enhanced activity of the immobilized catalyst.

Results and discussion

Synthesis of the polymerizable chelate ligand 5

For our investigations, we first synthesized the chelate ligand **5**. This ligand was chosen due to several reasons: (a) tetradendate polyamine ligands are known to form stable metal complexes in

a 1 : 1 ratio;⁷ (b) its nitrogen donors are of the imidazolyl type mimicking the histidine side chains found in the binding sites of many hydrolytic metalloenzymes; (c) it contains three vinyl groups and co-polymerization is expected to proceed with a high incorporation efficiency; (d) ligand **5** can be prepared easily in a few steps from commercially available starting materials, which allows to generate larger quantities.

The procedure for the synthesis of ligand **5** is outlined in Scheme 1. 1-Methylimidazole-2-carbaldehyde was known to be an excellent synthon for the preparation of polyimidazole ligands.^{8a,b,d} Consequently, we synthesized the corresponding polymerizable building block 1-vinylimidazole-2-carbaldehyde (1), which was then transformed to 1-vinylimidazole-2-carbaldehyde oxime (2) and reduced with zinc under alkaline conditions⁹ to obtain 1-vinylimidazole-2-methylamine (3). The Schiff-base intermediate of 1 and 3 was reduced *in situ* with NaBH₄ affording bis[(1-vinylimidazol-2-yl)methyl]amine (4). A reductive amination reaction with 1 and 4 gave the crude product 5. Purification of



Scheme 1 Synthesis of the polymerizable chelate ligand 5. *Reagents and conditions*: (i) *n*-BuLi, DMF, Et₂O, 75%; (ii) NH₂OH, EtOH–H₂O, 87%; (iii) Zn, NH₃aq, NH₄OAc, EtOH, 88%; (iv) NaBH₄, MeOH, 79%; (v) 1, NaBH₃CN, MeOH, 46%.

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ligand **5** was achieved by synthesizing the zinc- or copper-complex $[M(5)Cl]PF_6$ (M = Zn (6) or Cu (7)) (see below) followed by cleavage of the metal with HCl_{conc}. After adjusting the pH to ~14, the free base ligand was extracted with CHCl₃ to obtain the pure product in moderate yield.

The ¹H and ¹³C NMR spectra of **5** were in accordance with a C_3 symmetrical structure and showed similar chemical shifts as tris[(1-methylimidazol-2-yl)methyl]amine.¹⁰ A pronounced difference in chemical shift compared to the precursor **4** was found for the ¹H NMR signal of the CH=CH₂ vinyl protons of **5**, for which an upfield shift of 1.0 ppm was observed. This could be explained by ring current effects of the adjacent imidazole groups. Single crystals of ligand **5** were analyzed by X-ray diffraction. In the solid state, the ligand shows a concave, pseudo- C_3 symmetrical structure (Fig. 1). As indicated by the NMR spectra, the CH=CH₂ protons are in close proximity to the imidazole rings. The C–N(1) distances (1.492(3)–1.495(3) Å) and C–N(1)–C angles (111.8(2)–111.9(2)°) are comparable to what has been observed for other trisimidazole ligands.¹¹



Fig. 1 Graphical representation of the molecular structure of ligand 5 in the crystal.

Synthesis of the metal complexes 6 and 7

The transition-metal complexes 6 and 7 were prepared by mixing stoichiometric quantities of ligand 5 with the corresponding metal chloride in methanol (Scheme 2). The products precipitated upon addition of NH_4PF_6 to the reaction mixtures. Both complexes



Scheme 2 Synthesis of the transition-metal complexes 6 and 7.

were characterized by mass spectrometry, UV-Vis-near-IR spectroscopy, IR spectroscopy, elemental analyses and single-crystal X-ray crystallography (Fig. 2 and 3). In addition, complex **6** could be investigated in solution by NMR spectroscopy. The ¹H and ¹³C NMR spectra of **6** in CD₃CN exhibited only one set of signals in accordance with a C_3 symmetrical structure of the cation. It is interesting to note that the pronounced upfield shift, which was found for the ¹H NMR signal of the CH=CH₂ protons of ligand **5** (δ 6.08 ppm), was no longer observed for the Zn complex **6**



Fig. 2 Graphic representation of the molecular structure of the cation of complex 6 in the crystal. The counter anion is omitted for clarity. Selected bond lengths, distances (Å) and angles (°): Zn(1)-N(2) 2.0214(18), Zn(1)-N(4) 2.0227(18), Zn(1)-N(6) 2.0269(16), Zn(1)-Cl(1) 2.2625(5), $Zn(1) \cdots N(1) 2.5676(15)$; N(2)-Zn(1)-N(4) 110.68(7), N(2)-Zn(1)-N(6) 117.16(7), N(4)-Zn(1)-N(6) 106.85(7), N(2)-Zn(1)-Cl(1) 103.21(5), N(4)-Zn(1)-Cl(1) 111.56(5), N(6)-Zn(1)-Cl(1) 107.36(5).



Fig. 3 Graphic representation of the molecular structure of the cation of complex 7 in the crystal. The counter anion is omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.176(3), Cu(1)–N(2) 2.001(3), Cu(1)–N(4) 2.118(3), Cu(1)–N(6) 2.002(3), Cu(1)–Cl(1) 2.2367(11); N(2)–Cu(1)–N(6) 130.76(13), N(2)–Cu(1)–N(4) 110.90(12), N(6)–Cu(1)–N(4) 107.79(12), N(2)–Cu(1)–N(1) 79.00(12), N(6)–Cu(1)–N(1) 80.20(12), N(4)–Cu(1)–N(1) 78.35(11), N(2)–Cu(1)–Cl(1) 98.03(10), N(6)–Cu(1)–Cl(1) 100.29(9), N(4)–Cu(1)–Cl(1) 104.91(9), N(1)–Cu(1)–Cl(1) 176.28(8).

(δ 6.91 ppm). The coordination of **5** to Zn(II) prevents the orientation of the CH=CH₂ protons towards the aromatic imidazole groups.

UV-Vis-near-IR spectra of **6** and **7** have been recorded in acetonitrile. As expected, complex **6** showed no bands in the region from 250–1100 nm. Complex **7** displayed an intense band at 290 nm ($\varepsilon = 5.8 \times 10^3$ dm³ mol⁻¹ cm⁻¹) which can be assigned to intraligand and metal-to-ligand charge transfer (LMCT) transitions.¹² Furthermore, broad bands of low intensity were found at 816 nm ($\varepsilon = 87$ dm³ mol⁻¹ cm⁻¹) and at ~1100 nm ($\varepsilon \sim 100$ dm³ mol⁻¹ cm⁻¹) which is typical for a trigonal bipyramidal copper(II) complex.^{8,13}

The structures of the isomorphous complexes 6 and 7 in the crystal are depicted in Fig. 2 and 3. Both complexes contain mononuclear cations of the formula [M(5)Cl]⁺. Interesting differences, however, are observed for the distances of the metal atoms to the bridgehead sp^3 -nitrogen atom N(1) of the ligand. The value for the Zn complex 6 of Zn(1)-N(1) 2.5676(15) Å points to a very weak interaction and the overall geometry is best described as distorted tetrahedral (Fig. 2). This is in agreement with what has been observed for zinc complexes with tris(imidazolylmethyl)amine ligands.¹⁴ For the Cu complex 7, however, a value of Cu(1)–N(1) 2.176(3) Å is observed. The geometry of the latter is therefore best described as distorted trigonal bipyramidal (Fig. 3).^{8,13} The distances observed for the bonds between the metal ions and the imidazole nitrogen atoms N(2), N(4) and N(6) (M-N 2.001(3)-2.118(3) Å) or the chloro atoms (Zn(1)-Cl(1) 2.2625(5) Å; Cu(1)-Cl(1) 2.2367(11) Å) were all within the expected range.⁷

In anticipation of the hydrolysis studies, we have investigated the coordination chemistry of the Cu complex 7 with the substrate BNPP. Upon reaction of complex 7 with the silver salt of BNPP in acetonitrile followed by removal of AgCl, we were able to obtain complex 8 (Scheme 3).



Scheme 3 Synthesis of complex 8.

Complex 8 was comprehensively characterized including a single-crystal X-ray analysis (Fig. 4). The quality of the latter was unfortunately not very high due to the disordered p-nitrophenolate moieties and a discussion of bond lengths and angles is therefore not presented. From the data it is clear, however, that the BNPP

anion acts as a monodentate ligand and that the geometry of the Cu complex is similar to what has been found for the chloro

complex 7 (Fig. 3). It should be noted that 8 represents one of the



Fig. 4 Graphic representation of the molecular structure of the cation of complex 8 in the crystal. The hydrogen atoms, the counter anion and the solvent molecules are omitted for clarity. Only one orientation of the disordered p-nitrophenolate molecules is shown.

Immobilization of the metal complexes 6 and 7

Radical initiated (AIBN) co-polymerization of 6 and 7 (each 2.5 mol%) with the crosslinker EGDMA (97.5 mol%) in acetonitrile at 65 °C gave the insoluble polymers P6-Zn (colorless) and P7-Cu (pale green) in high yield (94 and 90%) (Scheme 4). The polymers were ground, washed with CH₃CN, and dried. The metal content was found to be 5.06 mg Zn/g polymer for P6-Zn and 3.22 mg Cu/g polymer for P7-Cu as determined by ICP-OES. These values corresponded to an incorporation rate of 65% in the case of P6-Zn and 42% for P7-Cu. The moderate incorporation rate suggests that some of the vinyl groups of the ligand were not polymerized. It was therefore expected that metal complexes with one, two and three connections to the polymer backbone can be found in the polymer. The attachment to the polymer backbone via one vinyl side chain as shown in Scheme 4 represents just one possible-but statistically very likely-situation. The complexes 6 and 7 showed a very different behavior in the polymerization process. While complex 6 co-polymerized with EGDMA in the typical fashion,¹⁶ the polymerization of 7 was slow and resulted in a glassy green co-polymer. An explanation for the different behavior could be that the Cu complex participates in atom transfer radical



Scheme 4 Synthesis of the zinc(II)- and copper(II)-containing polymers **P6-Zn** and **P7-Cu**. Complexes with a two- or threefold attachment to the polymer backbone are not shown.

few Cu(II)-BNPP complexes known so far.15

polymerization (ATRP) reactions. In fact, structurally related tripodal copper catalysts have been used for atom transfer radical polymerization reactions (ATRP).¹⁷

The BET surface area of **P6-Zn** was determined to be 429 m² g⁻¹ and that of **P7-Cu** 416 m² g⁻¹. These values are comparable to those observed for other highly cross-linked EGDMA polymers prepared with the porogen CH₃CN.¹⁸ Despite the similar surface area, the BET isotherms of the polymers **P6-Zn** and **P7-Cu** showed pronounced differences. While **P7-Cu** displayed a hysteresis indicating mesopores with an average pore diameter of 57 Å, **P6-Zn** showed no hysteresis at all indicating the absence of detectable mesopores.

Hydrolysis reactions

0.07

0.06

0.05

0.04

0.03

0.02

0.01

0.00

0

50

p-Nitrophenolate Conc. / mM

To evaluate the catalytic activity of the complexes 6 and 7 and the corresponding polymers **P6-Zn** and **P7-Cu**, we investigated the hydrolysis of the activated phosphodiester bis(pnitrophenyl)phosphate (BNPP). This substrate is frequently used as a model for biologically relevant phosphodiesters such as DNA and RNA. Advantages and drawbacks of activated model substrates have been discussed by Breslow and Singh¹⁹ and Menger and Ladika.²⁰

The reactions were performed in buffered aqueous solution (H₂O–DMSO 95:5) at 50 ± 1 °C. In the case of the heterogeneous hydrolysis reactions, the amount of polymer that was employed corresponds to a metal ion concentration of 1.0 mM if the polymers would be completely soluble in the buffer. After an incubation time of 30 min, the reactions were initiated by addition of a freshly prepared stock solution of the substrate BNPP (final conc.: 5.0 mM). After a given time, the reaction tubes were centrifuged and the concentration of the product *p*-nitrophenolate in the clear supernatant was determined by UV/Vis spectroscopy at $\lambda = 400$ nm. The initial rate was determined by a plot of *p*-nitrophenolate concentration *vs*. time. The initial rate of the spontaneous hydrolysis was substracted.

The complexes 6 and 7 and their immobilized versions P6-Zn and P7-Cu displayed very different hydrolytic activities (Fig. 5).



150

200

Time / min

250

300

350

Whereas the initial rate of hydrolysis at pH 9.5 in the presence of the homogeneous Zn complex 6 was found to be 7.6 × 10^{-6} mM min⁻¹, a rate of 1.6×10^{-4} mM min⁻¹ was observed for reactions with the polymer P6-Zn. This corresponds to a rate enhancement of a factor of 21. An even more pronounced difference was found for the Cu complexes. The initial rates for reactions with 7 and P7-Cu were 2.7×10^{-5} and 1.5×10^{-3} mM min⁻¹, respectively. The immobilized Cu complex P7-Cu was thus 56 times more active than the homogeneous complex 7. Hydrolysis of the reaction product *p*-nitrophenyl phosphate (NPP) in the presence of P7-Cu was approximately two orders of magnitude slower than that of BNPP. For the experiments described above, consecutive hydrolysis reaction can therefore be neglected.

The hydrolysis of BNPP promoted by 7 and P7-Cu was investigated in more detail. The effect of pH on the hydrolytic activity was studied in the pH range 7.0–11.0. Stable complex formation for both compounds was confirmed by the absence of precipitation of metal hydroxide at high pH. The pH vs. initial rates profiles are shown in Fig. 6. For P7-Cu, a strong increase of the initial rates of nearly one order of magnitude was observed in the pH range 7.0–9.5. This pH dependency can be explained by the assumption that the deprotonation of a coordinated water molecule is necessary to generate the catalytically active species.²¹ The sigmoidal curve of P7-Cu was fitted with the Boltzmann model to give a kinetically determined pK_a value of 8.6 ± 0.1. A plot of the rate enhancements as a function of pH shows that the largest difference between homogeneous and heterogeneous catalysts are found at a pH of approximately 9.5 (Fig. 7).



Fig. 6 Plot of the initial rates of BNPP hydrolysis reactions mediated by 7 (\bigcirc) or **P7-Cu** (\bigcirc) as a function of pH. *Reaction conditions*: $[Cu^{2+}] = 1.0 \text{ mM}$, [BNPP] = 5.0 mM, H₂O–DMSO 95 : 5, 64 mM buffer, 50 \pm 1 °C. The following buffers were employed: HEPES (pH 7.0–8.0), CHES (pH 8.5–10.0), and CAPS (pH 10.5–11.0). The data points represent averaged values from two independent experiments; the errors are less than 4%. Dashed line represents a non-linear curve fit by the Boltzmann model with *R* >0.993.

The effect of temperature on the rate of the hydrolysis of BNPP was studied. Pseudo-first order rate constants were determined at four different temperatures in the range between 30 and 60 °C. Arrhenius parameters E_a and A were obtained from the plot of ln k_{obs} vs. 1/T (Fig. 8). The activation energy was found to

100



Fig. 7 Ratio of the initial rates of BNPP hydrolysis reactions mediated by 7 and **P7-Cu** as a function of pH. For the reaction conditions see Fig. 6.



Fig. 8 Plot of $\ln k_{obs}$ *vs.* 1/T for the **P7-Cu** mediated hydrolysis of BNPP. *Reaction conditions*: $[Cu^{2+}] = 1.0 \text{ mM}$, [BNPP] = 5.0 mM, H_2O –DMSO 95 : 5, 64 mM CHES buffer, pH 9.5, 30–60 °C. The data points represent averaged values from two independent experiments; the errors are less than 4%. Dashed line represents a linear regression with R > 0.998.

be $E_a = 65 \pm 2 \text{ kJ mol}^{-1}$, while the frequency factor A was $8.4 \pm 0.4 \times 10^6 \text{ min}^{-1}$. These values are similar to those obtained for a polymeric, EGDMA-based Cu(II) catalysts studied by the group of Verma.²ⁱ

P7-Cu was able to act as a true catalyst, as evidenced by the fact that *p*-nitrophenolate was observed in 53% yield after 96 h using a substrate to catalyst ratio of 5 : 1. For this reaction, it is likely that some hydrolysis of the reaction product NPP occurred concomitantly to the hydrolysis of BNPP.

To verify that immobilized copper complexes were responsible for catalysis and not a small amount of leached Cu^{2+} , we have performed "stop-experiments" in which the polymer was separated after 50 min by centrifugation and the isolated supernatant was monitored spectrophotometrically. The hydrolysis reaction of BNPP was slowed significantly by a factor of 290 (Fig. 9). The metal-free polymer **P7** showed no acceleration of the hydrolysis of BNPP at all.

The majority of the reactive metal sites of **P7-Cu** are in the interior of the polymeric particles. To verify that diffusional processes were not rate limiting, we have carried out a reaction without stirring. The initial rate for the BNPP hydrolysis slowed



Fig. 9 Plot of *p*-nitrophenolate concentration *vs*. time for the **P7-Cu** mediated hydrolysis of BNPP. *Reaction conditions*: $[Cu^{2+}] = 1.0 \text{ mM}$, [BNPP] = 5.0 mM, H_2O –DMSO 95 : 5, 64 mM CHES buffer, pH 9.5, 50 ± 1 °C. The data points represent averaged values from two independent experiments; the errors are less than 1%. Dashed lines represent least-squares linear regressions with *R* >0.999.

down by only 13% to 1.3×10^{-3} mM min⁻¹. A variation of the stirring speed had a negligible influence on the initial hydrolysis rates as long as the polymer particles were homogeneously suspended in the solution. Furthermore, we investigated the BNPP hydrolysis using polymers with a different average particle size (>100 and 25–50 µm). The initial rates were similar within a 10% error. These experiments suggested that the observed reaction rates were not affected by diffusional processes to a significant extent.

As described above, the polymers P6-Zn and P7-Cu showed a similar surface area but a different pore structure. We were interested whether this difference in polymer morphology had an effect on the hydrolysis reactions. Therefore, we exchanged Zn(II) in P6-Zn for Cu(II). This was accomplished by treating P6-Zn with HCl (~20%), followed by neutralization with NaOH (1 M) and re-metalation with CuCl₂ in methanol to give P6-Cu. The metal content of the polymers was determined by ICP-OES. In the exchange process, 96% of the zinc ions were cleaved off and 97% of the free binding sites were re-occupied by Cu(II) indicating a facile access to the binding sites. Polymer P6-Cu was then tested for its ability to promote the hydrolysis of BNPP. An initial rate of 1.6×10^{-3} mM min⁻¹ was determined for **P6-Cu**, which is very similar to what was found for **P7-Cu** (1.5×10^{-3} mM min⁻¹). This data showed that the different pore structure of P6-Zn and P7-Cu was not responsible for the differences in catalytic activity but rather the nature of the metal ion.

Partitioning studies

Recent studies have shown that highly cross-linked EGDMA polymers can act as potent sorbents for organic compounds dissolved in fluorous solvents.²² The consequence of such a partitioning is a high local concentration within the pores of the polymer. This leads to the possibility that the activity of a catalyst embedded in such a support may be enhanced by a favorable substrate concentration gradient. Investigations with immobilized Rh catalysts have confirmed that rate enhancements due to partitioning can indeed occur.²³ Chang and co-workers have demonstrated that similar effects can be observed for reactions performed in aqueous solutions.^{2c,e}

The partitioning of BNPP into the EGDMA polymers used in this study could strongly affect the hydrolysis kinetics. We therefore investigated the adsorption of the substrate BNPP and the hydrolysis product *p*-nitrophenolate using a metal-free polymer **P8**, which was obtained by homo-polymerization of EGDMA with CH₃CN as the porogen. The amount of **P8** was varied in the range that was used for hydrolysis reactions (0–215 mg). After an equilibration time of 30 min²⁴ in a buffered aqueous solution of BNPP, the polymer was separated by centrifugation and the UV-Vis spectrum of the supernatant was recorded (Fig. 10). The difference in BNPP concentration before and after addition of the polymer **P8** was calculated from the absorption at $\lambda = 288$ nm ($\varepsilon =$ 17.8×10^3 dm³ mol⁻¹ cm⁻¹).



Fig. 10 UV-Vis spectra of BNPP solutions after addition of different amounts of **P8** (0, 24.0, 59.2, 98.6, 146 and 215 mg). The polymer was removed by centrifugation and an aliquot of the supernatant was diluted 75 times prior to the measurements. *Conditions*: $V_{\text{total}} = 3.0 \text{ mL}$, [BNPP] = 5.0 mM, H₂O–DMSO 95 : 5, 64 mM CHES buffer, pH 9.5, 50 ± 1 °C.

The BNPP concentration in solution decreased significantly upon addition of **P8**. This demonstrates that BNPP is strongly adsorbed to the EGDMA polymer. In a typical hydrolysis reaction, 59.2 mg of **P7-Cu** were employed (V = 3.0 mL). The experiments with **P8** show that approximately 30% of the total BNPP partitions into the polymeric matrix under those conditions (Fig. 11). As a consequence, a very high local concentration of BNPP is found within the pores of the polymer. The increased local concentration is likely to be an important factor for the superior hydrolytic activity of the polymers **P6-Zn** and **P7-Cu** as compared to the homogeneous catalysts **6** and **7**.

The hydrolysis product *p*-nitrophenolate was also adsorbed to the polymer. The uptake of *p*-nitrophenolate by the polymer **P8** was determined for solutions with an initial *p*-nitrophenolate concentration of 0.1 mM. This corresponds to a reaction progress of 2%. 16% of the *p*-nitrophenolate was absorbed by 59.2 mg of **P8**. These results show that the partitioning of *p*-nitrophenolate is relatively low under the conditions employed in the kinetic studies.

Conclusion

Highly cross-linked organic polymers are increasingly being used as supports for immobilized transition-metal catalysts.²⁵ These materials display a number of favorable characteristics. When



Fig. 11 BNPP-uptake by the polymer **P8** as a function of the amount of polymer added. The content of BNPP in the polymer was calculated from the UV-Vis data as described in the text. For conditions see Fig. 10. The data points represent averaged values from two independent experiments; the errors are less than 1%.

prepared in the presence of a porogen, highly cross-linked polymers typically show a high surface area between 50 and 500 $m^2 g^{-1}$.¹⁸ This ensures efficient access to the reactive sites within the polymer. Catalytic transformations are thus not restricted to sites on the outer surface of the polymer particle. The permanent pore structure of highly cross-linked polymers allows the use of polar and nonpolar solvents for catalysis. This is in contrast to lightly cross-linked supports such as Merrifield resins, for which swelling in an appropriate solvent is necessary for access to the interior volume.²⁶ A further advantage of highly crosslinked supports is the possibility to create site-isolated metal sites, which can be of importance if the catalysts suffer from selfdeactivation.²⁷ Finally, these polymers may act as potent sorbents for organic molecules, which may lead to favorable concentration gradients during catalysis. All these factors are of relevance for the immobilized catalysts P6-Zn and P7-Cu described in this study. The polymers show surface areas of >400 m² g⁻¹ and the accessibility of the active sites is indeed very good as demonstrated by the nearly quantitative metal exchange reaction which was used to make P6-Cu. The partitioning studies show that the substrate BNPP is strongly adsorbed to the EGDMA polymer. This leads to a high local concentration of BNPP within the polymeric matrix, which facilitates its hydrolysis. It should be noted that so far there are only a few studies, which have addressed partitioning effects as a means to increase the catalytic efficiency of poly-EGDMA-based catalysts.^{2c,e,23} The data presented above clearly highlights the importance and the potential of such effects. A high local concentration of the substrate BNPP is unlikely to be the only reason for the superior catalytic performance of the immobilized catalysts. Otherwise, similar rate enhancements compared to their homogeneous counterparts would have been observed for P6-Zn and P7-Cu. In particular the heterogeneous catalyst P7-Cu is expected to benefit from site isolation effects since homogeneous Cu(II) catalysts have repeatedly been reported to partially deactivate via $[L_nCu(\mu-OH)_2CuL_n]^{2+}$ dimer formation.⁴ Several mechanistic studies suggest that for the phosphodiester hydrolysis with mononuclear Cu(II) or Zn(II) complexes, an intramolecular attack a metal-bound hydroxyide to a coordinated substrate is the crucial step.¹ A similar mechanism is like to account for the hydrolytic activity of **P6-Zn** and **P7-Cu** and the isolation of the BNPP complex **8** supports this assumption.

Experimental

General

All reagents and solvents used were commercially available and were used as received. Sodium bis(*p*-nitrophenyl)phosphate (BNPP) was purchased from Sigma-Aldrich. [AgBNPP] was obtained as a pale yellow precipitate by reaction of BNPP with AgNO₃ in H₂O–MeOH. Polymerizations were performed in a glovebox under an atmosphere of dinitrogen containing less than 1 ppm of oxygen and water. Prior to utilization, 2,2'azobisisobutyronitrile (AIBN) was recrystallized from MeOH and EGDMA was washed with NaOH (1 M) and saturated NaCl_{aq}, dried over Na₂SO₄ and distilled.

Instrumentation

The ¹H and ¹³C NMR spectra were recorded on a Bruker Advance DPX 400 using the residual protonated solvents as internal standards. All spectra were recorded at room temperature. The mass spectra were measured with the following instruments: Shimadzu Axima CRFplus spectrometer (MALDI-TOF; α-cyano-4hydroxycinnamic acid matrix), MicroMass Q-Tof Ultima spectrometer (ESI), and Varian 1200L spectrometer (EI). The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. The UV-Vis-near-IR spectra and hydrolysis kinetics were recorded on a Perkin-Elmer Lambda 35 spectrometer. The elemental analyses (Zn and Cu) were obtained by inductively coupled plasma atomic emission spectroscopy (ICP-OES) on a Perkin-Elmer ICP-OES 2000 DV instrument. The pH measurements were carried out with a Metrohm 692 pH/ion meter. The BET measurements were carried out by Quantachrome GmbH, Odelzhausen. Dinitrogen adsorption/desorption measurements were performed on a Quantchrome Autosorb-3 instrument at 77.4 K. Prior to the measurements, the samples were dried under vacuum at 100 °C for 2 h. All fitting procedures were effected by the Levenberg-Marquardt algorithm with Origin 7.0 from OriginLab Corporation.

Synthesis

1-Vinylimidazole-2-carbaldehyde (1). *n*-Butyllithium in hexane (1.6 M, 68.0 mL, 108 mmol) was added slowly to a solution of 1-vinylimidazole (9.06 mL, 100 mmol) in diethyl ether (200 mL) at -30 °C. The deep red solution turned to yellow after complete addition and was allowed to stir at -30 °C for 90 min. Dimethylformamide (7.76 mL, 100 mmol) was quickly added and the resulting beige suspension was stirred overnight at room temperature. The reaction was quenched by adding cautiously 50 mL of water followed by the careful addition of 70 mL of HCl_{aq} 12%. The layers were separated and the organic phase was washed with HCl_{aq} 12% (3 × 50 mL). The combined aqueous phases were saturated with potassium carbonate and extracted with chloroform (5 × 50 mL). The organic phase was dried over mgSO₄·2H₂O, filtered and concentrated under reduced pressure. The resulting brown solution was finally evaporated in vacuum at room temperature. The resulting brown residue was sublimed twice (50 °C, 60 mbar, air cooling). A colorless crystalline solid was obtained (yield: 9.15 g, 75%); v_{max}/cm^{-1} 1673vs (CO) and 1640vs (CH=CH₂); $\delta_{\rm H}$ (400 MHz; CDCl₃) 5.10 (1 H, d, ³J 8, CH=CH₂), 5.40 (1 H, d, ³J 16, CH=CH₂), 7.32 (1 H, s, H_{Im}), 7.52 (1 H, s, H_{Im}), 7.93 (1 H, dd, ³J_E 16, ³J_Z 8, CH=CH₂) and 9.85 (1 H, s, CHO); $\delta_{\rm C}$ (101 MHz; CDCl₃) 105.38 (CH=CH₂), 120.85, 129.85, 132.29, 142.44 and 182.32 (CHO); m/z (MALDI-TOF) 123.06 (100%, M + H⁺).

1-Vinylimidazole-2-carbaldehyde oxime (2). Hydroxylamine hydrochloride (3.66 g, 52.7 mmol) and sodium carbonate (2.79 g, 26.3 mmol) were dissolved in water (50 mL). The solution was placed in an ice-bath and 1-vinylimidazole-2-carbaldehyde (6.43 g, 52.7 mmol) dissolved in ethanol (25 mL) was added dropwise. The resulting white suspension was stirred for 90 min at 0 °C. The product was filtered off, washed with 75 mL of cold EtOH–H₂O (1 : 2) and dried in vacuum. A white crystalline powder was obtained (yield: 6.27 g, 87%); v_{max}/cm^{-1} 2738, 2678, 2614s (CHNOH) and 1640vs (CH=CH₂); $\delta_{\rm H}$ (400 MHz; MeOD) 4.99 (1 H, d, ³J 8, CH=CH₂), 5.47 (1 H, d, ³J 16, CH=CH₂), 7.10 (1 H, s, H_{Im}), 7.62 (1 H, s, H_{Im}), 7.80 (1 H, dd, ³J_E 16, ³J_z 8, CH=CH₂) and 8.09 (1 H, s, CHNOH); $\delta_{\rm C}$ (101 MHz; MeOD) 104.12 (CH=CH₂), 119.66, 130.43, 131.79, 141.49 and 141.59 (CHNOH); m/z (MALDI-TOF) 138.07 (100%, M + H⁺).

(3). 1-Vinylimidazole-2-1-Vinylimidazole-2-methylamine carbaldehyde oxime (6.86 g, 50.0 mmol), ammonium acetate (8.34 g, 108 mmol), concentrated aqueous ammonia (150 mL, 2.58 mol) and ethanol (200 mL) were heated at 85 °C under reflux. After 5 min, zinc powder (13.8 g, 211 mmol) was added in portions over a period of 20 min. Heating was continued for 3 h. The excess of zinc was removed by filtration and the ethanol was evaporated. A solution of sodium hydroxide (42.8 g, 1.07 mol) in water (200 mL) was added, initially producing a white precipitate which redissolved nearly as the remainder of the sodium hydroxide solution was added. The colorless solution was extracted with CH_2Cl_2 (5 × 50 mL). The organic phase was dried over mgSO₄·2H₂O and concentrated to yield a light yellow oil (yield: 5.36 g, 87%). Contamination of bis[(1vinylimidazol-2-yl)methyl]amine (\sim 6%) was evidenced by ¹H and ¹³C NMR spectroscopy; v_{max}/cm^{-1} 3358, 3275w (NH₂) and 1645vs $(CH=CH_2)$; δ_H (400 MHz; CDCl₃) 3.92 (2 H, s, CH₂), 4.86 (1 H, d, ³J 8, CH=CH₂), 5.18 (1 H, d, ³J 16, CH=CH₂), 6.93 (1 H, s, H_{Im}), 6.98 (1 H, dd, ${}^{3}J_{E}$ 16, ${}^{3}J_{Z}$ 8, CH=CH₂) and 7.05 (1 H, s, H_{Im}); δ_{C} (101 MHz; CDCl₃) 38.68 (CH₂), 102.18 (CH=CH₂), 115.83, 128.26, 128.37 and 148.12; m/z (MALDI-TOF) 124.10 $(100\%, M + H^+).$

Bis[(1-vinylimidazol-2-yl)methyl]amine (4). 1-Vinylimidazole-2carbaldehyde (4.09 g, 33.2 mmol) and 1-vinylimidazole-2carbaldehyde (4.05 g, 33.2 mmol) were dissolved in methanol (150 mL) and stirred overnight at room temperature. Sodium borohydride (1.26 g, 33.2 mmol) was carefully added in portions at 0 °C and the yellow solution was further stirred for 3 h at room temperature. After evaporating the solvent, water (150 mL) was added. The solution was extracted with CHCl₃ (3 × 40 mL) and dried over mgSO₄·2H₂O. The solvent was removed and a yellow oil was obtained (yield: 6.01 g, 79%); v_{max} /cm⁻¹ 2891, 2820w (NH) and 1645vs (CH=CH₂); $\delta_{\rm H}$ (400 MHz; CDCl₃) 3.93 (4 H, s, CH₂), 4.86 (2 H, d, ${}^{3}J$ 8, CH=CH₂), 5.21 (2 H, d, ${}^{3}J$ 16, CH=CH₂), 6.98 (2 H, s, H_{Im}), 7.08 (2 H, dd, ${}^{3}J_{E}$ 16, ${}^{3}J_{Z}$ 8, CH=CH₂) and 7.20 (2 H, s, H_{Im}); δ_{C} (101 MHz; CDCl₃) 44.91 (CH₂), 101.98 (CH=CH₂), 116.00, 128.43, 128.97 and 145.44; *m/z* (EI) 108 (80%), 122 (50) and 230 (100, M + H⁺).

Tris[(1-vinylimidazol-2-yl)methyl]amine (5). A solution of bis[(1-vinylimidazol-2-yl)methyl]amine (4.92 g, 21.5 mmol), 1vinylimidazole-2-carbaldehyde (3.93 g, 32.2 mmol) and glacial acetic acid (6.3 mL, 110 mmol) in methanol (450 mL) was stirred overnight at room temperature. NaBH₃CN (3.78 g, 60.2 mmol) was added in portions and the reaction mixture was stirred for further 7 h. The reaction was quenched by adjusting the pH to 2.0 by careful addition of concentrated HCl. A white precipitate was formed which was filtered off. After reduction to a volume of 10 mL, water (100 mL) was added. The aqueous solution was washed with diethyl ether $(3 \times 40 \text{ mL})$. Then the pH was adjusted to about 8 by addition of Na_2CO_3 . The resulting yellow precipitate was extracted with CHCl₃ (3 \times 50 mL) and the organic phase was dried over mgSO₄ \cdot 2H₂O. The solvent was evaporated and the residue was dried in a vacuum. The crude product (4.96 g) could be purified by first synthesizing the corresponding zinc- or copper-complex 6 or 7 followed by removal of the metal with HCl 37%. After adjusting the pH to \sim 14, the white precipitate was extracted with CHCl₃ and dried over $mgSO_4 \cdot 2H_2O$. The solvent was evaporated and a white solid was obtained (yield: 3.28 g, 46%). The product was recrystallized from toluene (Found: C, 64.29; H, 6.54; N, 29.65. C₁₈H₂₁N₇ requires C, 64.46; H, 6.31; N, 29.23%); v_{max} /cm⁻¹ 1643vs (CH=CH₂); δ_{H} (400 MHz; CDCl₃) 3.81 (6 H, s, CH₂), 4.56 (3 H, d, ³J 8, CH=CH₂), 5.04 (3 H, d, ³J 16, CH=CH₂), $6.08 (3 \text{ H}, \text{dd}, {}^{3}J_{E} 16, {}^{3}J_{Z} 8, \text{CH}=\text{CH}_{2}), 7.01 (3 \text{ H}, \text{s}, \text{H}_{Im}) \text{ and } 7.19 (3 \text{ H}, \text{s}, \text{H}_{Im})$ H, s, H_{Im}); $\delta_{\rm C}$ (101 MHz; CDCl₃) 48.88 (CH₂), 101.81 (CH=*C*H₂), 115.96, 128.42, 128.71 and 144.50; m/z (MALDI-TOF): 336.30 $(100\%, M + H^+).$

[Zn(5)Cl]PF₆ (6). Anhydrous ZnCl₂ (89.7 mg, 659 μmol) was added to a solution of tris[(1-vinylimidazol-2-yl)methyl]amine (221 mg, 659 μmol) in methanol (12 mL). After 15 min, NH₄PF₆ (107 mg, 659 μmol) was added and a white precipitate was formed immediately. The product was isolated, washed with methanol, and dried in a vacuum (yield: 324 mg, 85%). Crystals were obtained by slow diffusion of diethyl ether into a CH₃CN solution of complex **6** (Found: C, 37.09; H, 3.91; N, 17.08. C₁₈H₂₁ClF₆N₇PZn requires C, 37.20; H, 3.64; N, 16.87%); v_{max} /cm⁻¹ 1651vs (CH=CH₂) and 833vs (PF₆⁻); $\delta_{\rm H}$ (400 MHz; CD₃CN) 4.25 (6 H, s, CH₂), 5.20 (3 H, d, ³*J* 8, CH=CH₂), 5.50 (3 H, d, ³*J* 16, CH=CH₂), 6.91 (3 H, dd, ³*J* _E 16, ³*J*_z 8, *CH*=CH₂), 7.19 (3 H, s, H_{Im}) and 7.50 (3 H, s, H_{Im}); $\delta_{\rm C}$ (101 MHz; CD₃CN) 53.08 (CH₂), 107.96 (CH=CH₂), 120.07, 126.81, 128.36 and 147.63; *m/z* (ESI-TOF) 434.07 (100%, M – PF₆⁻).

[Cu(5)Cl]PF₆ (7). Anhydrous CuCl₂ (88.6 mg, 659 μ mol) was added to a solution of tris[(1-vinylimidazol-2-yl)methyl]amine (221 mg, 659 μ mol) in methanol (12 mL). After 15 min, NH₄PF₆ (107 mg, 659 μ mol) was added and a pale green precipitate was formed immediately. The product was isolated, washed with methanol, and dried in a vacuum (yield: 286 mg, 75%). Crystals were obtained by slow diffusion of diethyl ether into a CH₃CN solution of complex 7 (Found: C, 37.14; H, 3.92; N

17.08. $C_{18}H_{21}ClCuF_6N_7P$ requires C, 37.32; H, 3.65; N, 16.92%); v_{max}/cm^{-1} 1652vs (*C*H=*C*H₂) and 832vs (PF₆⁻); $\lambda_{max}(CH_3CN)/nm$ 290 (ε/dm^3 mol⁻¹ cm⁻¹ 5.79 × 10³), 816 (87) and ~1100 (~100); m/z (ESI-TOF) 398.32 (100%, M - Cl - PF₆⁻) and 433.06 (47, M - PF₆⁻).

[Cu(5)BNPP]PF₆ (8). [AgBNPP] (45.1 mg, 101 µmol) in 3 mL of CH₃CN was added to a solution of complex **7** (58.5 mg, 101 µmol) in CH₃CN (3 mL) in the dark. After 15 min, the AgCl precipitate was removed by centrifugation. Pale green crystals were obtained by slow diffusion of diethyl ether into a CH₃CN solution of complex **8** (Found: C, 40.63; H, 3.56; N, 14.33. C₃₀H₂₉CuF₆N₉O₈P₂ requires C, 40.80; H, 3.31; N, 14.27%); ν_{max}/cm^{-1} 1650vs (*C*H=*C*H₂), 1089vs (P=O) and 830vs (PF₆⁻); λ_{max} (CH₃CN)/nm 285 (ε /dm³ mol⁻¹ cm⁻¹ 2.31 × 10⁴) and 1023 (114); *m/z* (ESI-TOF) 738.01 (100%, M – PF₆⁻).

Polymer P6-Zn. Complex **6** (244 mg, 419 µmol), EGDMA (3.24 g, 16.4 mmol), and AIBN (70.0 mg, 426 µmol) were dissolved in CH₃CN (3.36 mL) and heated for 24 h at 65 °C in a closed screw cap vial. The colorless, insoluble polymer was isolated, ground in a mortar, and washed with CH₃CN (5 × 80 mL). After drying in vacuum, a white powder was obtained (yield: 3.28 g, 94%); v_{max}/cm^{-1} 1722vs (EGDMA) and 844m (PF₆⁻); ICP-OES: 5.06 mg of Zn/g of polymer; BET surface area: 429 m² g⁻¹; average pore diameter: not determined.

Polymer P7-Cu. Complex 7 (243 mg, 419 µmol), EGDMA (3.24 g, 16.4 mmol), and AIBN (70.0 mg, 426 µmol) were dissolved in CH₃CN (3.36 mL) and heated for 24 h at 65 °C in a closed screw cap vial. The pale green, glassy, insoluble polymer was isolated, ground in a mortar, and washed with CH₃CN (5 × 80 mL). After drying in vacuum, a pale green powder was obtained (yield: 3.14 g, 90%); v_{max} /cm⁻¹ 1721vs (EGDMA) and 844m (PF₆⁻); ICP-OES: 3.22 mg of Cu/g of polymer; BET surface area: 416 m² g⁻¹; average pore diameter: 57 Å.

Polymer P6-Cu. The polymer **P6-Zn** (600 mg) was suspended in HCl (20 mL, 20%) for 30 min at room temperature. Subsequently, it was washed with water (3 × 20 mL), with NaOH_{aq} (2 × 40 mL, 1 M), and with MeOH (4 × 40 mL). Metalation of **P6** (580 mg) was achieved by mixing a solution of CuCl₂ in MeOH (40 mL, 0.5 M) with the polymer for 20 min. The resulting green polymer **P6-Cu** was washed with MeOH until the reaction with dithiooxamide was negative (5 × 40 mL) and then it was dried in a vacuum (yield: 523 mg); v_{max}/cm^{-1} 1722vs (EGDMA); ICP-OES: 0.19 mg of Zn/g of polymer, 5.21 mg of Cu/g of polymer.

Polymer P8. EGDMA (3.24 g, 16.4 mmol), and AIBN (70.0 mg, 426 µmol) were dissolved in CH₃CN (3.5 mL) and heated for 24 h at 65 °C in a closed screw cap vial. The white, insoluble polymer was isolated, ground in a mortar, and washed with CH₃CN (5×80 mL). After drying in vacuum, a white powder was obtained (yield: 3.03 g, 94%); v_{max} /cm⁻¹ 1722vs (EGDMA).

Kinetic investigations

The hydrolysis of BNPP was carried out in 64 mM buffered aqueous solution (HEPES, CHES, and CAPS) at 50 \pm 1 °C. In the case of heterogeneous hydrolysis the amount of polymer corresponds to a metal ion concentration of 1.0 mM if the polymers would be completely soluble in the buffer. The crystalline

complexes 6 and 7 were dissolved in DMSO and diluted (\times 20) with aqueous buffer solution. After an incubation time of 30 min, the reactions were initiated by addition of a freshly prepared stock solution of the substrate (final concentration: 5.0 mM). After a given time, the reaction tubes were centrifuged for 1 min and the absorbance A of the clear supernatant was determined by UV/Vis at $\lambda = 400$ nm. For the determination of initial rates, the concentration of the hydrolysis product, p-nitrophenolate anion, was calculated from the absorbance A and the extinction coefficient ($\varepsilon = 18.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) by correction for the degree of ionization of *p*-nitrophenol (p K_a 6.87) at 50 ± 1 °C. The $pK_a = 7.15$ at 25 °C was corrected by van't Hoff reaction isobar. Initial rates were obtained by linear least-squares regression (R >0.998) from a plot of concentration of hydrolysis product against time. Reactions were monitored to less than 2% conversion of substrate to product. The buffers were HEPES (pH 7.0-8.0), CHES (pH 8.5-10.0), and CAPS (pH 10.5-11.0) and the pH remained constant within the error range after the experiment. Correction of spontaneous hydrolysis was effected across the pH range studied (7.0-11.0).

The Arrhenius parameters for **P7-Cu** were obtained by measuring the initial rates at 30, 40, 50 and 60 °C. Pseudo-first-order rate constants were calculated by using the following formula: initial rate = k_{obs} [BNPP]. These data were plotted as $\ln k_{obs}$ against 1/T and fitted to $\ln k_{obs} = \ln A + E_a/(RT)$. Linear least-squares regression gave the Arrhenius parameters E_a and A.

Partitioning studies

The uptake of the substrate BNPP and the hydrolysis product *p*nitrophenolate was determined by the difference in concentration before and after addition of the polymer **P8** after an equilibration time of 30 min in buffer solution at 50 ± 1 °C: ([S]_{ini} – [S]_{final})/[S]_{ini}. The substrate concentrations were calculated from the absorbance *A* and the extinction coefficients (BNPP at $\lambda_{max} = 288$ nm: $\varepsilon =$ 17.8×10^3 dm³ mol⁻¹ cm⁻¹, *p*-nitrophenolate at $\lambda_{max} = 400$ nm: $\varepsilon = 18.7 \times 10^3$ dm³ mol⁻¹ cm⁻¹). Conditions: $V_{total} = 3.0$ mL, [BNPP]_{ini} = 5.0 mM, [*p*-nitrophenolate]_{ini} = 0.1 mM, H₂O–DMSO 95 : 5, 64 mM CHES buffer, pH 9.5, 50 ± 1 °C.

Elemental analysis of polymers (ICP-OES)

A suspension of the respective polymer (\sim 80 mg) was heated in concentrated sulfuric acid (3 mL) at 140 °C for 2 h in a volumetric flask (25.0 mL). Hydrogen peroxide (30%, 1.0–1.5 mL) was added, and the colorless solution was heated for 12 h at 140 °C. The resulting clear solution was diluted to 25.0 mL with nitric acid (2%, aqueous) and analyzed by ICP-OES. Every analysis including sample preparation was done in duplicates and the error was less than 1.5%.

Crystallographic investigations

Data collection for the compounds **5–8** was performed at 140(2) K using Mo-K α radiation on a four-circle kappa goniometer with an Oxford Diffraction KM4 Sapphire CCD. Cell refinement and data reduction has been carried out with the aid of CrysAlis RED 1.7.1 β release.²⁸ A semiempirical absorption correction (MULTI-SCAN)²⁹ has been applied to the data sets of the compounds **6** and **7**. All structures were refined using the full-matrix least-

squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model". Structure refinement and geometrical calculations were carried out on all structures with SHELXTL 5.1.³⁰

Crystal data for 5. $C_{18}H_{21}N_7 \cdot 2H_2O$, M = 371.45, triclinic, space group $P\overline{1}$, a = 8.7133(17), b = 10.2885(18), c = 12.011(2) Å, a = 94.105(15), $\beta = 94.136(17)$, $\gamma = 103.709(16)^\circ$, U = 1038.9(3) Å³, T = 140(2) K, Z = 2, $D_c = 1.187$ g cm⁻³, μ (Mo-K α) = 0.082 mm⁻¹, 6178 reflections measured, 3200 unique ($R_{int} = 0.0576$) which were used in all calculations. The final $wR(F^2)$ was 0.1434 (all data).

Crystal data for 6. $C_{18}H_{21}ClF_6N_7PZn$, M = 581.21, monoclinic, space group I2/a, a = 13.8886(4), b = 24.7471(11), c = 14.5306(8) Å, $\beta = 108.775(4)^\circ$, U = 4728.5(4) Å³, T = 140(2) K, Z = 8, $D_c = 1.633$ g cm⁻³, μ (Mo-K α) = 1.288 mm⁻¹, 13843 reflections measured, 3773 unique ($R_{int} = 0.0243$) which were used in all calculations. The final $wR(F^2)$ was 0.0749 (all data).

Crystal data for 7. $C_{18}H_{21}ClCuF_6N_7P$, M = 579.38, monoclinic, space group I2/a, a = 13.5389(9), b = 24.865(2), c = 14.5342(11) Å, $\beta = 108.009(6)^\circ$, U = 4653.1(6) Å³, T = 140(2) K, Z = 8, $D_c = 1.654$ g cm⁻³, μ (Mo-K α) = 1.192 mm⁻¹, 13536 reflections measured, 3895 unique ($R_{int} = 0.0697$) which were used in all calculations. The final $wR(F^2)$ was 0.1135 (all data).

Crystal data for 8. $C_{30}H_{29}CuF_6N_9O_8P_2\cdot 0.5C_4H_{10}O, M =$ 920.16, triclinic, space group $P\overline{1}, a = 8.5886(16), b = 13.3393(19), c = 17.721(3) Å, a = 101.074(12), \beta = 96.831(14), \gamma = 92.850(13)^\circ, U = 1972.8(5) Å^3, T = 140(2) K, Z = 2, D_c = 1.549 g cm^{-3}, \mu(Mo-Ka) = 0.725 mm^{-1}, 11660$ reflections measured, 6067 unique ($R_{int} = 0.1171$) which were used in all calculations. The final $wR(F^2)$ was 0.3275 (all data).

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605676h

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