DOI: 10.1002/ejic.200701103

Novel *N,N,O* Scorpionate Ligands and Transition Metal Complexes Thereof Suitable for Polymerisation

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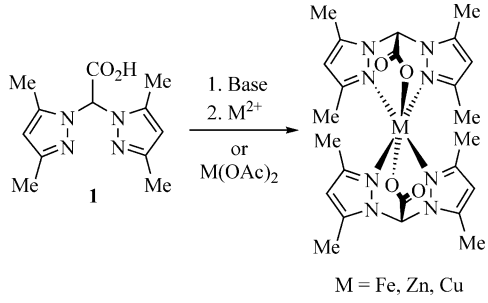
Dedicated to the memory of Professor Swiatoslaw Trofimenko

Keywords: Solid phase / Immobilisation / Polymerisation / Tripodal ligands / *N,N,O* ligands / Tricarbonyl complexes

Esterification of 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic acid (**2**) with methacryloyl chloride led to the new κ^3-*N,N,O* ligand 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-methacrylato-propionic acid (Hbdmpzmp) (**3**). The κ^3-*N,N,O* coordination as known from bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza, **1**) was proven by syntheses of the complexes [Mn(bdmpzmp)$(CO)_3$] (**4**) and [Re(bdmpzmp)$(CO)_3$] (**5**) and the single-crystal X-ray structure of **4**. The methacrylic ester functionality makes **3**, **4** and **5** suitable for polymerisation. Thus, copolymerisation of **3** with methyl methacrylate (MMA), a combination of MMA and ethylene glycol dimethacrylate (EGDMA) or pure EGDMA led to various solid phases (**P1a**–**P1c**, **P2**, **P3a**, **P3b**) with incorporated ligand. Polymer-bound manganese and rhenium tricarbonyl complexes could be obtained by copolymerisation of **4** and **5** with MMA as well as by a polymer analogous reaction of **P1a** with appropriate metal salts. In both cases, the facial tripodal binding behaviour was evidenced by IR spectra of the polymer supported transition metal complexes and the uptake of manganese was proven by AAS measurements. Reaction of the soluble deprotonated solid phase **P1a** with copper(II) chloride led to a deep-blue solid phase (**P-Cu-I**). The UV/Vis absorption maximum at 715 nm indicates the copper centres to act as crosslinking agent by a similar binding behaviour as in [Cu(bdmpza)$_2$]. In contrast, the heterogeneous reaction of **P1b** with copper(II) chloride formed a lime-green solid phase (**P-Cu-II**). The bathochromic shift of the absorption maximum by 78 nm suggests one-sided bound copper centres. EPR spectra do not show exchange narrowing between the copper centres indicating the metal centres to be far enough apart from each other to prevent magnetic interactions.

Introduction

Bis(pyrazol-1-yl)acetic acids, such as bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza, **1**) introduced 1999 by A. Otero,[1–4] are available in a broad variety of sterically less or stronger demanding, chiral and achiral ligands.[5–8] Complexes of these versatile *N,N,O* donor ligands with various transition metal complexes reveal their potential in coordination chemistry as scorpionate ligands closely related to hydrotris(pyrazol-1-yl)borate (Tp).[5,6,9,10] The *N,N,O* binding motif is of particular interest not only as tripodal ligand in organometallic and coordination chemistry but as mimic of the active site of enzymes with a 2-His-1-carboxylate motif as well.[6,11–13] Transition metal complexes of Hbdmpza with zinc and iron have proven to be good structural mimics for such metalloenzymes.[6,12] Due to their high binding affinity to metal centres, sterically non-demanding representatives of the bis(pyrazol-1-yl)acetic acids form bisligand complexes with the most bio-relevant transition metals, featuring octahedral coordination (Scheme 1).[6,14] Further reactions with additional ligands or potential substrates are therefore unfavourable.



Scheme 1.

The formation of bisligand complexes has been successfully prevented by the introduction of sterically more demanding substituents, such as *tert*-butyl, at the pyrazole rings as we reported on before.[6,12] This results in just one

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bound *N,N,O* ligand and various other ligands bound to the remaining free coordination sites. Nevertheless, this concept has not been extended to all bio-relevant transition metals, such as copper, so far, or leads to binuclear complexes. Furthermore, an influence of the sterically demanding substituents on the reactivity of the transition metal centre cannot be precluded.[12]

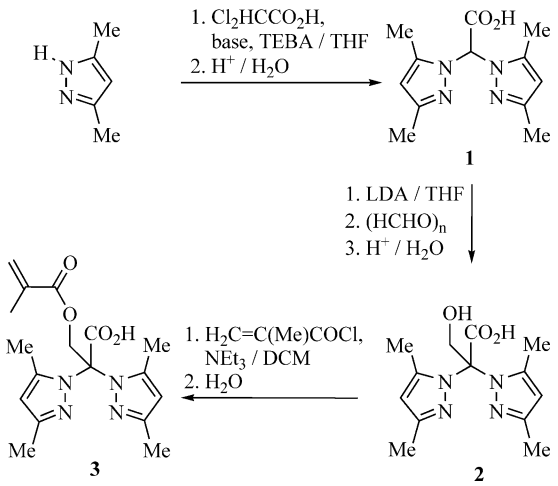
Recently, we have been successful in introducing linking groups such as allyl and hydroxymethyl to the bridging carbon atom of **1** suitable for solid-phase fixation of bis(3,5-dimethylpyrazol-1-yl)acids and manganese and rhenium tricarbonyl complexes thereof.[15] Solid-phase-grafted ligands are not only of interest due to the advantages of supported catalysts in potential applications,[16–19] but to prevent the formation of bisligand complexes without the need of sterically demanding substituents, as well. Polymerisation-active linking groups allow a cheaper synthesis and a more detailed control of the resulting solid than modifications of commercially available solid phases, concerning the degree of functionalisation and the structure of the surrounding solid phase.

Kunz and co-workers have presented polymers suitable for binding of the $M(CO)_3$ (M = Tc, Re) fragment particularly with regard to diagnostic nuclear medicine.[20] Recent works of Severin et al. show the potential of an immobilised copper complex of a multidentate N-donor ligand in catalytic ester hydrolysis,[21] while Heinze et al. have shown separated molybdenum centres on polymer support to be functional models for mononuclear molybdenum enzymes.[22]

Results and Discussion

Ligand Syntheses

As our recent investigations have shown, modification of **1** at the bridging carbon atom is a valuable way to stable and still κ^3-coordinating monoanionic *N,N,O* ligands with an additional linking group.[15] The hydroxymethyl linker in **2** is capable of further modification by esterification and therefore a convenient starting material to a polymerisation-active ligand (Scheme 2).[15]



Scheme 2.

Reaction of **2** with methacryloyl chloride in the presence of triethylamine at ambient temperature leads to the novel *N,N,O* ligand 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-methacrylatopropionic acid (Hbdmpzmp) (**3**) without forming polymerisation products during the conversion. The formation of **3** is clearly indicated by the ^1H and ^{13}C NMR spectra, revealing C_s symmetry in solution, showing a clear set of signals for the methacryl residue at δ = 1.86, 5.58 and 6.09 ppm in the ^1H NMR spectra. The molecular structure of **3**, as determined by X-ray crystallography, exhibits a hydrogen bond between the carboxylate donor and the pyrazole group [*d*(O1–N11) = 2.459(0) Å], which is in accordance with other bis(pyrazol-1-yl)acetic acids we reported on earlier (Figure 1).[15] An analogous reaction with acryloyl chloride at 4 °C forms the corresponding acrylic ester. Unfortunately, probably due to the high reactivity of the Michael acceptor, the acrylic ester could not be purified satisfactorily so far.

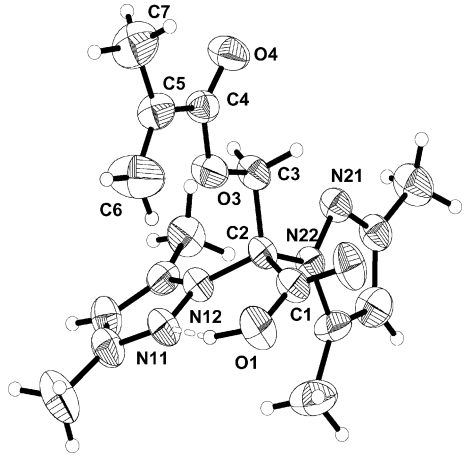


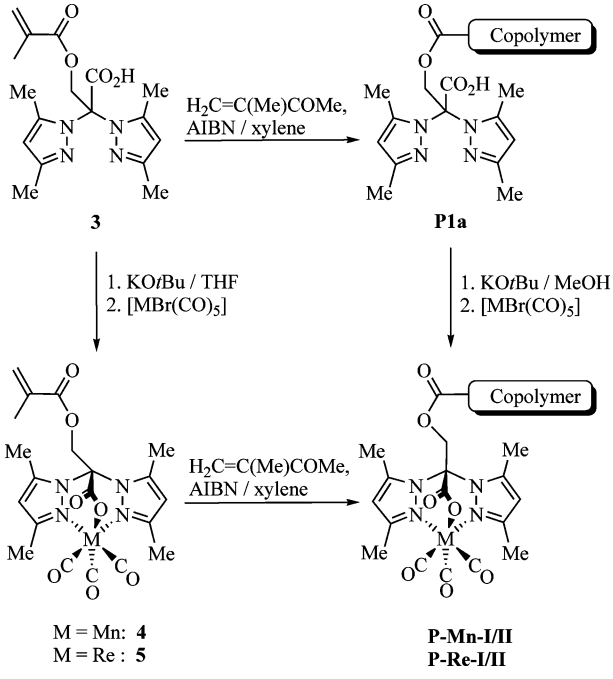
Figure 1. Molecular structure of 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-methacrylatopropionic acid (**3**); thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: *d*(C1–O1) = 1.291(4), *d*(C1–O2) = 1.213(5), *d*(O1–H1) = 1.11(6), *d*(N11–H1) = 1.42(5), *d*(C4–C5) = 1.491(6), *d*(C5–C6) = 1.362(6), ∠(O1,C1,O2) = 123.9(4), ∠(N12,C2,N22) = 108.1(3).

The radical polymerisation activity of methacrylate type double bonds is distinctly higher than that of acrylate type double bonds,[23–25] causing considerable impact on the polymer structure, if double bonds with diverse reactivity ratios are copolymerised.[25] A preferred statistical distribution of the incorporated ligand in the solid phase is achieved at similar reactivity ratios.[25] Therefore, the methacrylate type linker is the favoured linking group for the copolymerisation with methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA).

Manganese and Rhenium Complexes

To prove the tripodal binding behaviour and to achieve complexes suitable for the solid-phase fixation, the manganese and rhenium tricarbonyl complexes of **3** were synthesised following the general concept of reacting the potassium salt of the deprotonated ligand with $[MnBr(CO)_5]$ and

[$ReBr(CO)_5$], respectively (Scheme 3).[5] The reaction can be monitored by IR spectroscopy due to the intense characteristic signals of the carbonyl ligands. The formation of tricarbonyl complexes is clearly indicated by a single A′ and two close A′′ and A′ signals typical for unsymmetrical "piano stool" carbonyl complexes [**4**: $\tilde{\nu}$(CO) = 2034, 1940 and 1913 cm^{-1}; **5**: $\tilde{\nu}$(CO) = 2024, 1918 and 1894 cm^{-1}].[5] In comparison to [Mn(bdmpza)$(CO)_3$] and [Re(bdmpza)-$(CO)_3$] the complexes **4** and **5** show almost identical IR absorptions, proving the *N*,*N*,*O*-binding motif of ligand **3** and excluding a coordination of the methacryl linking group to the metal centre.[5] The IR signals at 1693 (**4**) and 1701 cm^{-1} (**5**) can be assigned to the asymmetric carboxylate vibration. The additional IR band at 1732 (**4**) and 1734 cm^{-1} (**5**) is induced by the asymmetrical carboxylate vibration of the methacryloyl ester. The ^{1}H NMR spectra of the manganese complex **4** shows only very weak and broad signals. Nevertheless the ^{13}C NMR spectra of **4** and **5** allow a clear assignment and a well-defined set of signals for the carbonyl ligands (**4**: 219.1 and 221.4 ppm, **5**: 194.6 and 195.6 ppm).



Scheme 3.

X-ray structure analysis of complex **4** unambiguously reveals the κ^3-*N*,*N*,*O* coordination (Figure 2). As we observed earlier for the related tripodal tricarbonyl complex [Mn(bdmpzap)$(CO)_3$] [bdmpzap = 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionate],[15] complex **4** crystallises in a chiral conformation with both possible enantiomers in the cell due to the space group $P2_1/a$. The methacryl linker is retained between the carboxylate and one pyrazole donor (Figure 2), thus breaking the C_s symmetry usually observed for tricarbonyl complexes bearing the bdmpza ligand such as [Mn(bdmpza)(CO_3)].[5] Similar to our recent report on [Re(bdmpzap)$(CO)_3$],[15] this chirality is not only observed in the X-ray structure analyses of **4**, but also in case of complex **5** in solution. This is indicated by an AB system in the ^{1}H NMR spectra of **5** for the -CH_2O- group at δ = 5.31 and 5.79 ppm, causing coupling between the diastereotopic protons and a set of two signals for each pyrazole carbon atom in the ^{13}C NMR spectrum. Broad signals in the ^{1}H NMR spectra do not allow to resolve the ^3J(H,H) coupling constants of the AB system. Thus a dynamic interconversion between the two enantiomers is assumed.

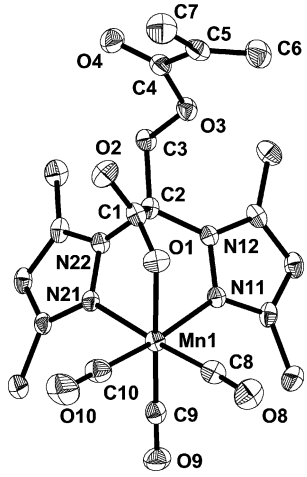


Figure 2. Molecular structure of [Mn(bdmpzmp)$(CO)_3$] (**4**); thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: *d*(C1–O1) = 1.260(3), *d*(C1–O2) = 1.222(3), *d*(Mn1–N11) = 2.0389(18), *d*(Mn1–N21) = 2.0806(18), *d*(Mn1–C8) = 1.809(2), *d*(Mn1–C9) = 1.796(2), *d*(Mn1–C10) = 1.804(2), *d*(Mn1–O1) = 2.0259(16), *d*(C8–O8) = 1.146(3), *d*(C9–O9) = 1.149(3), *d*(C10–O10) = 1.149(3), ∠(N21,Mn1,C8) = 177.12(9), ∠(N11,Mn1,C10) = 173.16(10), ∠(O1,Mn1,C9) = 178.57(9), ∠(N11,Mn1,O1) = 83.66(7), ∠(N21,Mn1,O1) = 87.60(7), ∠(N11,Mn1,N21) = 83.44(7), ∠(O2,C1,C2,C3) = 25.6(2).

It is noteworthy, that this effect is enhanced by a slightly bent [∠(O2–C1–C2–C3) = 25.6(2)°] carboxylate donor. This observation is in contrast to the almost linear coordination we observed in [Mn(bdmpza)(CO_3)] and [Mn-(bdmpzap)(CO_3)].[5,15] This might be explained by a steric interaction between the methacryl linker and the carboxylate donor.

Copolymers

Ligand **3** as well as the complexes **4** and **5** show a free methacryl linker which should provide polymerisation activity. To achieve the solid-phase fixation of **3** and complexes thereof, MMA and/or EGDMA are the preferred comonomers in radical induced polymerisation reactions due to their similar methacryl residues as mentioned above. While polymerisation with pure MMA leads to linear polymers, addition of EGDMA as crosslinking agent leads to a network structure (Scheme 3 and Figure 3).[25]

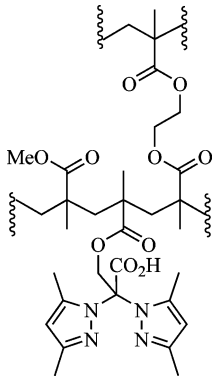


Figure 3. Possible formular structure of copolymers of **3** with MMA and/or EGDMA. Due to the free radical polymerisation, atactic arrangement has to be assumed.

Depending on the rate of crosslinking agent, low molecular weight, high molecular weight soluble polymers or intractable fully crosslinked networks may be achieved.[25] The latter is also formed by the polymerisation with pure EGDMA.[21] The results of the free radical induced polymerisation reactions of **3** in xylene at 80 °C with AIBN as radical initiator (**P1a**–**P1c**) at different monomer ratios of ligand **3** and MMA are shown in Table 1.

During the polymerisation, in the case of **P1a**–**P1c**, the PMMA like polymer remains in solution until it is precipitated in methanol. The elemental analysis verifies the incorporation of ligand **3** and allows to determine the amount of incorporated ligand **3**. Up to a monomer ratio of ca. 0.25 mmol/g of **3** the linker-modified ligand is well incorporated into the polymer, leading to polymers with up to 0.20 mmol/g of solid-phase-bound ligand. Higher monomer ratios of **3** do not lead to higher incorporation rates. This may be explained by a rather large steric demand of ligand **3**, causing two ligands too close to each other to be unfavourable.

Polymerisation in presence of 0.42 mmol EGDMA per gram of monomers, a crosslinker concentration at which high molecular weight soluble polymers are formed,[25] leads to the crosslinked polymer **P2** with a similar amount of incorporation. Copolymerisation of **3** with pure EGDMA in xylene or acetonitrile as porogene[21] leads to highly crosslinked polymers, cognizable by the white mass precipitating a few minutes after addition of the radical initiator and the apparent very low bulk density of the resulting polymer. The amount of incorporated ligand is determined to 0.15 mmol/g in xylene and 0.13 mmol/g in acetonitrile, respectively. The slightly lower incorporation compared to the polymerisation results with MMA is in accordance with the copolymerisation results of EGDMA with MMA, showing total monomer conversion of EGDMA, while unpolymerised MMA remains.[25]

Copolymerisation of the complexes **4** and **5** with MMA under the same conditions lead to a white (**P-Re-II**) or slightly brownish (**P-Mn-II**) powder into which the metal complexes have been incorporated according to the elemental analysis as well (Table 1). To further investigate the incorporated tricarbonyl complexes, IR spectra of the polymer samples were recorded (Figure 4).

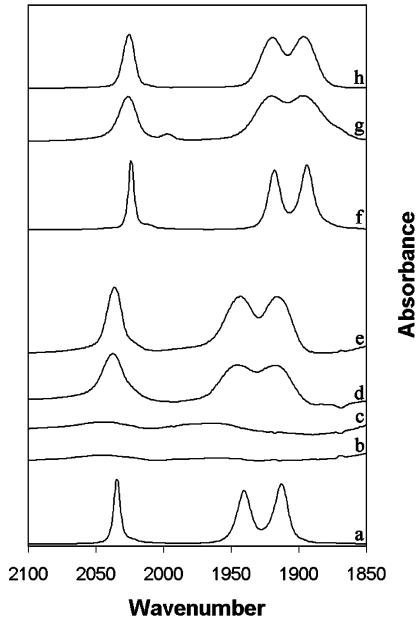


Figure 4. IR spectra of (a) [Mn(bdmpzap)$(CO)_3$] (THF), (b) the control experiment with PMMA and [MnBr$(CO)_5$] (nujol), (c) the control experiment with [Mn(bdmpzap)$(CO)_3$] (nujol), (d) the manganese tricarbonyl complex formed out of **P1a** and [MnBr$(CO)_5$] (**P-Mn-I**) (nujol), (e) the manganese tricarbonyl complex **2** copolymerised with MMA (**P-Mn-II**) (nujol), (f) [Re(bdmpzap)$(CO)_3$] (THF), (g) the rhenium tricarbonyl complex formed out of **P1a** and [ReBr$(CO)_5$] (**P-Re-I**) (nujol) and (h) the rhenium tricarbonyl complex **3** copolymerised with MMA (**P-Re-II**) (nujol).

The copolymers formed in presence of **4** (Figure 4, e) and **5** (Figure 4, h) both exhibit clear IR spectra showing up the characteristical IR absorptions of a tricarbonyl complex indicated by a single A′ (**P-Mn-II**: 2037 cm^{-1}, **P-Re-II**:

Table 1. Incorporation of functionalised ligand **3** and complexes **4** and **5**.

Monomers	Polymer	Ligand or complex/monomers [mmol/g]	% Nitrogen content	Ligand or complex/polymer [mmol/g]
MMA	**P1a**	0.26	1.13	0.20
MMA	**P1b**	0.14	0.54	0.10
MMA	**P1c**	0.48	1.19	0.21
MMA/EGDMA	**P2**	0.24	1.16	0.20
EGDMA (Xylene)	**P3a**	0.26	0.87	0.15
EGDMA (MeCN)	**P3b**	0.26	0.74	0.13
MMA	**P-Mn-II**	0.14	0.50	0.09
MMA	**P-Re-II**	0.13	0.77	0.14

2026 cm^{-1}) and two close A′′ and A′ vibrations (**P-Mn-II**: 1946, 1917 cm^{-1}, **P-Re-II**: 1921, 1897 cm^{-1}). A comparison to the IR spectra of the free complexes **4** and **5**, as described above, exhibits nearly identical location of these signals. A control experiment, the polymerisation of MMA in presence of the linker-free complex [Mn(bdmpzap)$(CO)_3$] shows no incorporation of the complex and consequently the absence of any carbonyl signals in the IR spectra.

Copolymerisation of the transition metal complexes **4** and **5** is only one possible reaction pathway to the incorporated tricarbonyl complexes. A different approach is the tricarbonyl complex formation on polymer, a so-called polymer analogous formation, by deprotonation of the incorporated ligand on the solid phase **P1a** and subsequent reaction with [$MnBr(CO)_5$] or [$ReBr(CO)_5$], respectively (Scheme 3). Deprotonation of **P1a** in methanol with equimolar amounts of KO*t*Bu leads to a clear solution of the potassium salt of **P1a**. Although the solubility of a linear polymer is not highly surprising, it is noteworthy that **P1a** in contrast to pure PMMA is dissolved by very polar solvents in the presence of base which may be explained by the polarity of a highly charged polymer chain as it is well-known for biopolymers such as DNA. Further reaction with [$MnBr(CO)_5$] and [$ReBr(CO)_5$] in methanol leads to the incorporated manganese and rhenium complexes **P-Mn-I** and **P-Re-I**, which precipitate slowly during the reaction. IR spectra again prove the formation of tricarbonyl complexes and the desired κ^3-*N*,*N*,*O* coordination of the solid-phase-bound ligand. The IR spectra are almost identical [**P-Mn-I**: 2038, 1947, 1918 cm^{-1} (Figure 4, d), **P-Re-I**: 2028, 1921, 1897 cm^{-1} (Figure 4, g)] to the solid phases **P-Mn-II** and **P-Re-II** obtained by copolymerisation of the polymerisation-active tricarbonyl complexes. The amount of manganese in **P-Mn-I** was determined by AAS to 0.083 mmol g^{-1}. This equals an occupancy of 42% of the existent binding sites of **P1a**.

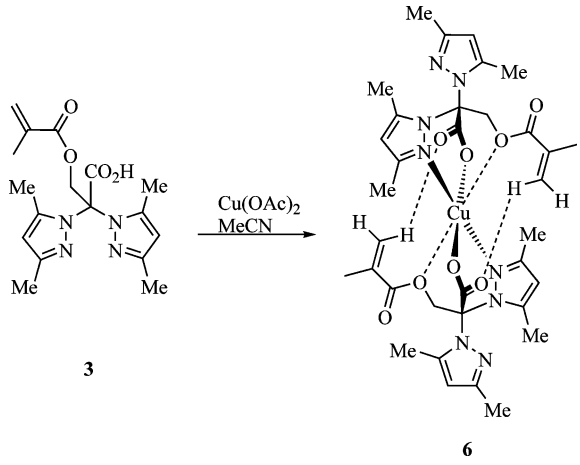
Blank experiments with a polymer formed by polymerisation of MMA in the presence of 2-bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionic acid instead of **3** and subsequent reaction with KO*t*Bu and [$MnBr(CO)_5$] lead to a white solid phase without any noticeable carbonyl vibrations (Figure 4, b).

These results prove the ability of the methacryl residue in **3**, **4** and **5** to act as a polymerisation active linking group and prove the tripodal coordination properties of the incorporated ligand.

Nevertheless, these experiments do not unambiguously prove that the incorporation of the *N*,*N*,*O* scorpionate ligand does prevent undesired reactions such as the formation of bisligand complexes, since the tricarbonyl complexes are usually obtained in solution without observable bisligand coordination. Therefore, we further investigated the coordination towards copper.

Copper Containing Complexes and Copolymers

Recent results by Reedijk et. al show Hbdmpza to react with copper(II) salts leading to the bisligand complex [Cu(bdmpza)$_2$] with tripodal κ^3-*N*,*N*,*O* coordination of both bdmpza ligands.[14] Similar reaction of **3** with copper(II) acetate in acetonitrile (Scheme 4) forms a light-violet powder characterised by the asymmetric carboxylate vibration at $\tilde{\nu}$ = 1682 cm^{-1} and a [MH^+] peak in the FAB mass spectra at *m*/*z* 755.



Scheme 4.

The additional IR band at $\tilde{\nu}$ = 1726 cm^{-1} is assigned to the asymmetrical carboxylate vibration of the methacryloyl ester. X-ray structure analysis of **6** confirms the formation of the bisligand complex [Cu(bdmpzmp)$_2$], but reveals a κ^2-*N*,*O* coordination of **3**, allowing a primary square-planar coordination of the copper centre (Figure 5). The free octahedral positions are occupied by the oxygen atoms O3 and O3a of the methacryl linker.

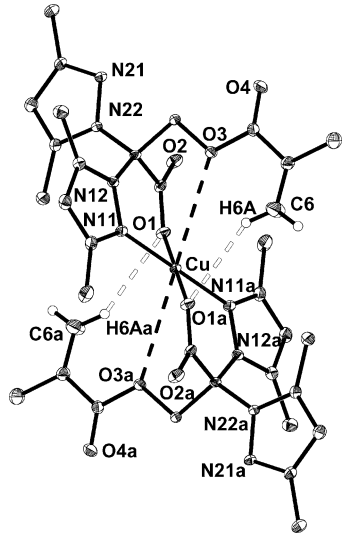
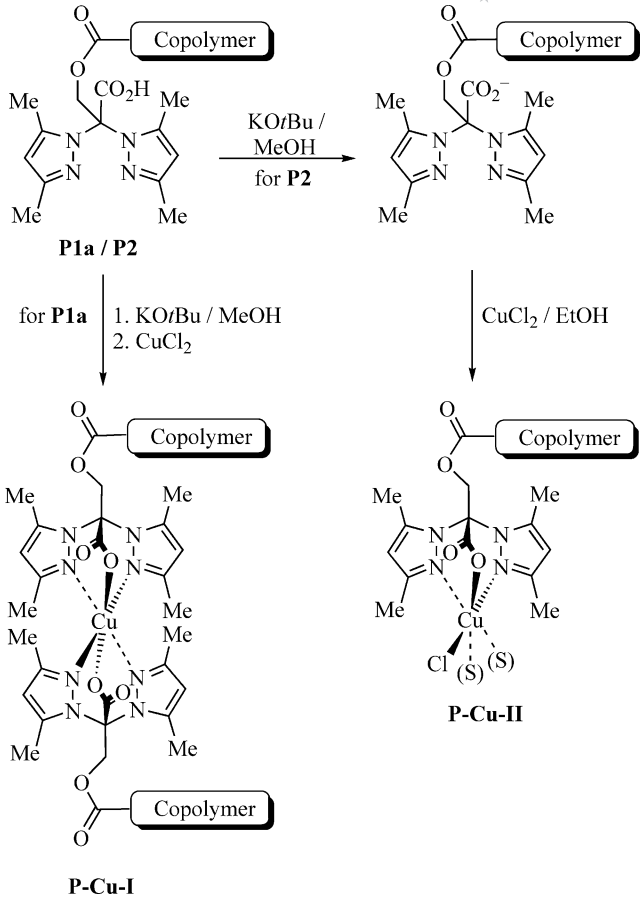


Figure 5. Molecular structure of [Cu(bdmpzmp)$_2$] (**6**); thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: *d*(O1–Cu) = 1.8938(15), *d*(N11–Cu) = 1.9906(17), *d*(H6A–Cu) = 2.94(3), *d*(H6A–O1a) = 2.75(3), *d*(H6A–O1) = 4.11(3), *d*(C5–C6) = 1.339(4), *d*(C5–C7) = 1.467(3), *d*(C5–C4) = 1.489(3), *d*(O3–H6A) = 2.48(3), *d*(O3–Cu) = 3.3695(15); ∠(N11,Cu,O1) = 87.98(7), ∠(N11,Cu,O1a) = 92.02(7), ∠(H6A,Cu,O1) = 114.8(6), ∠(H6A,Cu,O1a) = 65.2(6).

This may be explained by two synergetic effects. On the one hand the Jahn–Teller distortion which is clearly apparent in [Cu(bdmpza)$_2$] leads to an elongated Cu–N bond towards one of the pyrazole donors and therefore facilitates dissociation of one pyrazole donor.[14] Instead of the pyrazole N-donor O3 of the ester functionality seems to be involved in a weak σ donor interaction with *d*(O3–Cu) = 3.3695(15) Å. On the other hand, there is a weak intramolecular hydrogen bond (IMH type) from the olefinic hydrogen H6A to the O1a atom of the symmetry equivalent ligand. This is a well-known behaviour of hydrogen atoms positioned close to copper carboxylato complexes.[26] A rather similar example [Cu(Hceph)$_2$] has been discussed into details by Desiraju and Thakur.[26] Although the metal–hydrogen distance *d*(Cu–H6A) = 2.94(3) Å in **6** is longer than that of [Cu(Hceph)$_2$] [*d*(Cu–H) = 2.45 Å], the O···H hydrogen bridges are almost equal (**6**: *d*(O1a–H6A) = 2.75(3)) Å; [Cu(Hceph)$_2$]: *d*(O–H) = 2.73 Å)}.[26]

Polymerisation of MMA in the presence of **6** leads only to very small amounts of a blue-green glassy and viscous material with high nitrogen content indicating nearly no incorporation of MMA. Copper complexes are well-known to act as atom transfer radical polymerisation (ATRP) catalysts, monoanionic copper complexes with nitrogen and oxygen donors are even deliberately used in ATRP.[27,28] The exceptional polymerisation behaviour, not observed during the copolymerisation with any other metal complex, may therefore be explained by radical transfer to the redox-active paramagnetic copper centre inhibiting the classical radical induced polymerisation.

The syntheses of copper complexes of **3** incorporated in PMMA hence follow the procedure successfully applied in the syntheses of manganese and rhenium tricarbonyl complexes on polymer as described above, by first deprotonating the solid phase **P1a** containing incorporated ligand **3** with KO*t*Bu in methanol and subsequent reaction with the copper salt (Scheme 5). Addition of a solution of $CuCl_2$ in dry methanol to the clear solution of deprotonated **P1a** in methanol immediately causes precipitation of **P-Cu-I** as a blue, powdery mass. Thin-film UV/Vis spectra of **P-Cu-I** prove the incorporation of copper on the solid phase and show an absorption maximum at 715 nm, which is close to the absorption maximum of the complex [Cu(bdmpza)$_2$] (Figure 6, d).[14] Therefore, the formation of a bisligand complex on the solid phase appears likely and may also explain the immediate precipitation of **P-Cu-I** after addition of the copper salt. Thus the formation of the bisligand complex out of the dissolved polymer causes the transition metal unit to act as crosslinking agent, bridging two incorporated ligand residues and thus leading to a network structure. Although the coordination of the metal centre may not be elucidated in detail, the nearly identical UV/Vis spectra indicate a similar binding as reported by Reedijk et al.[14] for [Cu(bdmpza)$_2$]. The amount of incorporated copper is determined by AAS to 0.085 mmol g^{-1}. Assuming crosslinking this results in 85% of the binding sites occupied by copper atoms.



Scheme 5.

To prevent formation of solid-phase bisligand complexes, a different synthetic route was established. After deprotonating polymer **P2** (which contains a similar amount of ligand as **P1a**, but was polymerised in the presence of the cross-linking agent EGDMA) in methanol, the solvent was removed in vacuo. The resulting powdery potassium-salt of **P2** was treated heterogeneously with small amounts of a solution of $CuCl_2$ in ethanol (Scheme 5). The polymer immediately turns green and **P-Cu-II** is obtained as a lime-green powder. Again, UV/Vis spectra prove the binding of copper onto the solid phase but show a significant bathochromic shift of the absorption maximum by 78 nm to 793 nm (Figure 6, e). This considerable shift indicates a different coordination of the copper centre, presumably arranged by at least one nitrogen and one oxygen donor of the incorporated ligand, one chloro ligand and potential further coordinated solvent molecules (Scheme 5). These results do not allow to distinguish between a possible tetragonal coordination with one solvent molecule and κ^2-*N,O* coordination or a possible octahedral coordination with an additional solvent molecule and κ^3-*N,N,O* coordination of the ligand. AAS measurements reveal a copper content of 0.093 mmol g^{-1}, i.e. 47% of incorporated ligands bound to copper. Hence, it is likely, that the rigid and undissolved solid phase was not capable of bisligand complex formation but formation of one-sided bound copper centres.

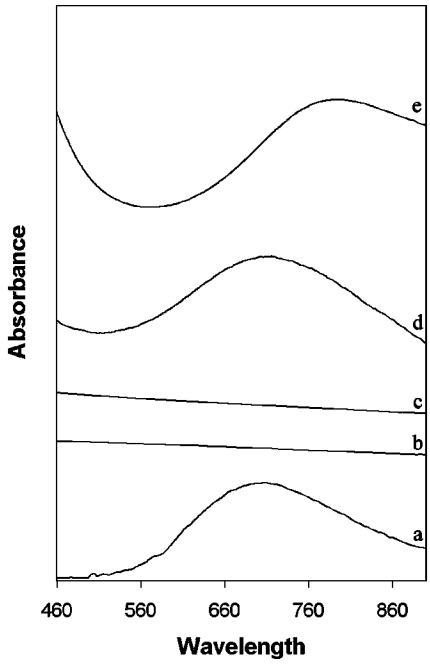


Figure 6. UV/Vis spectra of (a) $[Cu(bdmpza)_2]$ in methanol (b) the control experiment of PMMA treated with KO*t*Bu and subsequent $CuCl_2$ (polymer film) (c) the control experiment of PMMA treated with KO*t*Bu and after removal of the solvent subsequent treatment with a solution of $CuCl_2$ (polymer film) (d) **P-Cu-I** formed by the reaction of **P1a** with KO*t*Bu and subsequent addition of $CuCl_2$ to the polymer solution (polymer film) (e) **P-Cu-II** formed by the reaction of **P2** with KO*t*Bu and after removal of the solvent heterogeneous reaction with a solution of $CuCl_2$ (polymer film). In (b)-(e) a pure PMMA film was used as background.

To gather further information about the copper centres grafted onto the MMA carrier material, EPR spectra of **P-Cu-I** and **P-Cu-II** were recorded. The EPR spectra of pure $[Cu(bdmpza)_2]$, as published by Reedijk, exhibits no resolution of $g_\parallel$, $g_\perp$ or $A_\parallel$, which is explained by exchange narrowing due to the close distance of the copper ions in the lattice.[14] In contrast, the EPR spectra of **P-Cu-I** and **P-Cu-II** clearly show three $A_\parallel$ signals. The values of $A_\parallel$ are measured to $A_\parallel$ = 13.1 mT (**P-Cu-I**, $g_\parallel$ = 2.313 mT, $g_\perp$ = 2.059 mT) and $A_\parallel$ = 13.1 mT (**P-Cu-2**, $g_\parallel$ = 2.307, $g_\perp$ = 2.096 mT). This is in the range of typical values for a tetragonal copper centre and is in accordance with a possibly elongated octahedral geometry.[14] The values are close to those of diamagnetic diluted $[Cu(bdmpza)_2]$.[14] Additional hyperfine splitting with ^{14}N, which would possibly allow to differentiate between **P-Cu-I** and **P-Cu-II**, could not be observed, maybe due to limited resolution and line broadening of the solid-phase EPR spectra. Nevertheless, the observed hyperfine splitting with ^{63}Cu and ^{65}Cu allows to estimate the distance between the copper centres to at least 10 Å, which is in accordance with isolated copper centres on the solid phase without the possibility of interactions between the metal centres.

Conclusions

Esterification of 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic acid (**2**) with methacryloyl chloride leads to the new polymerisation-active ligand 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-methacrylatopropionic acid (**3**). The κ^3-*N*,*N*,*O* coordination of this ligand could be demonstrated by the syntheses of the corresponding manganese and rhenium tricarbonyl complexes. Ligand **3** as well as these complexes **4** and **5** show polymerisation activity and could successfully be copolymerised with methyl methacrylate (MMA). Polymerisation in presence of supplemental crosslinker ethylene glycol dimethacrylate (EGDMA) allows further control of the structure of the solid phase. The amount of incorporation was monitored by elemental analysis and the maintenance of the tripodal *N*,*N*,*O* coordination upon solid-phase fixation was proven by polymer IR spectra. Furthermore, the solid phases obtained by copolymerisation of the ligand **3** are able to provide monoanionic tripodal binding sites, as proven by the syntheses of the manganese and rhenium tricarbonyl complexes with polymer analogous reactions of the solid phase with $[MnBr(CO)_5]$ and $[ReBr(CO)_5]$, respectively.

Reaction of the incorporated ligand with copper(II) chloride results in two different copper-containing solid phases depending on the reaction conditions. Reaction of copper(II) with a deprotonated dissolved solid phase without EGDMA probably leads to crosslinking via the copper centres by the formation of bisligand complexes as supposed by the polymer film UV/Vis spectra. Heterogeneous reaction of a crosslinked deprotonated solid phase with copper(II) leads to distinctly different UV/Vis spectra, assuming one-sided bound copper(II). In both cases, AAS spectra prove the admission of copper and EPR spectra reveal the distance between the supported copper centres to be large enough to suppress interactions of the metal centres among each other.

Experimental Section

General Remarks: All operations were carried out under an inert gas atmosphere by using conventional Schlenk techniques. Solvents were freshly distilled and degassed prior to use from appropriate drying agents. The yields refer to analytically pure substances and were not optimised. IR spectra: Varian Excalibur FTS-3500 FT-IR spectrometer in CaF_2 cuvets (0.2 mm) or in Nujol. UV/Vis: Varian Cary 50. ^1H, ^{13}C and 2D NMR spectra: Bruker DPX300, δ values relative to TMS or the deuterated solvent. EPR spectroscopy: JEOL JES-FA 200, internal ^{55}Mn standard. Mass spectra: Jeol JMS-700 using FAB technique with NBA as matrix. Elemental analysis: Euro EA 3000 (Euro Vector) and EA 1108 (Carlo–Erba) ($\sigma \pm 1\%$ of the measured content). AAS: Perkin–Elmer 5100PC F-AAS with AS-90 sample automation, acetylene/air flame (Cu: 0.9 L min^{-1} acetylene/9.9 L min^{-1} air; Mn: 2.0 L min^{-1} acetylene/8.1 L min^{-1} air), method: standard addition. A Bruker-Nonius Kappa-CCD and an Enraf–Nonius CAD4 Mach3 were used for X-ray structure determination. Methyl methacrylate and EGDMA were extracted with diluted NaOH three times, dried with Na_2SO_4, distilled and stored at –30 °C. All other chemicals were used as purchased without further purification. 2-Bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic acid (**2**), 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionic acid (Hbdmpzap) and $[Mn(bdmpzap)(CO)_3]$ were synthesised as described earlier.[15] $[Cu(bdmpza)_2]$,

[$ReBr(CO)_5$] and [$MnBr(CO)_5$] were synthesised according to literature.[14,29,30]

Synthesis of 2,2-Bis(3,5-dimethylpyrazol-1-yl)-3-methacrylatopropionic Acid (3): To a solution of Hbdmpzhp (**2**) (1.00 g, 3.60 mmol) in dichloromethane (100 mL) is added an excess of NEt_3 (4.00 mL, 2.92 g, 28.9 mmol). Then methacryloyl chloride (870 μL, 940 mg, 9.00 mmol) is subjoined dropwise under continuous stirring. The mixture is stirred for 2 d. Water (20 mL) is added slowly and the two-phased mixture is vigorously stirred for three hours. The solvents are removed in vacuo. The slurry residue is dissolved in water, acidified with diluted HCl (pH 2) and extracted with diethyl ether (4 × 200 mL). The combined organic layers are dried (Na_2SO_4) and concentrated under reduced pressure to obtain an oily residue of **3**. After recrystallisation from acetone, **3** was afforded in colourless blocks suitable for X-ray structure determination. Yield 723 mg (2.09 mmol, 58%); m.p. 128–131 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.75 (s, 6 H, C^5-CH_3), 1.86 (dd, $^4J_{H,H}$ = –1.8, $^4J_{H,H}$ = –0.9 Hz, 3 H, =C-CH_3), 2.25 (s, 6 H, C^3-CH_3), 5.38 (s, 2 H, OCO-CH_2), 5.58 (qd, $^4J_{H,H}$ = –1.8, $^2J_{H,H}$ = 1.7 Hz, 1 H, *cis* H_2C=CMe), 5.94 (s, 2 H, H_{pz}), 6.09 (dq, $^4J_{H,H}$ = –0.9, $^2J_{H,H}$ = 1.7 Hz, 1 H, *trans* H_2C=CMe) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz, 25 °C): δ = 10.6 (C^5-CH_3), 13.1 (C^3-CH_3), 18.0 (=C-CH_3), 67.1 (-CH_2-O), 78.3 (C_{bridge}), 108.8 (C_{pz}-H), 126.9 (H_2C=), 135.1 (=CMe-), 142.0 (C^5_{pz}), 147.2 (C^3_{pz}), 165.6 (-CO_2CH_2-), 168.0 (CO_2H) ppm. IR (THF): $\tilde{\nu}$ = 1750 (sh, CO_2H), 1733 (s, CO_2R), 1563 (w, C=N) cm^{-1}. FAB-MS: *m*/*z* (%) = 369 (7) [M + Na^+], 347 (3) [MH^+], 302 (6) [MH^+ – CO_2H], 217 (Me)CO_2], (100) [MH^+ – CO_2H – H_2C=C. $C_{17}H_{22}N_4O_4$ (346.38 g/mol): calcd. C 58.95, H 6.40, N 16.17; found C 58.96, H 6.56, N 16.50%.

Synthesis of [Mn(bdmpzmp)(CO)$_3$] (4): Hbdmpzmp (**3**) (590 mg, 1.70 mmol) in dry THF (30 mL) is deprotonated with KO*t*Bu (191 mg, 1.70 mmol) and the reaction mixture is stirred at ambient temperature for 30 min. The complex [$MnBr(CO)_5$] (468 mg, 1.70 mmol) is added, the reaction mixture is heated under reflux and controlled by IR on a regular basis. After 12 h the reaction is completed and the solvent is removed in vacuo. The yellow residue is washed with water (5 × 10 mL), diethyl ether (5 × 10 mL) and dried in vacuo to yield **4** as a light yellow powder. Crystals suitable for X-ray structure determination were obtained from a solution of **4** in benzene layered with *n*-hexane. Yield 530 mg (1.09 mmol, 64%); m.p. 197–199 °C (dec.). ^{1}H NMR: not resolved due to very broad signals. ^{13}C NMR ($CDCl_3$, 75.5 MHz, 25 °C): δ = 14.1 (C^5-CH_3), 14.5 (C^3-CH_3), 17.2 (=C-CH_3), 60.4 (-CH_2-O-), 80.2 (C_{bridge}), 111.0 (C_{pz}-H), 143.8 (C_{pz}), 152.9 (C_{pz}), 219.1 (C=O), 221.4 (C=O) ppm. IR (THF): $\tilde{\nu}$ = 2034 (s, C=O), 1940 (s, C=O), 1913 (s, C=O), 1732 (m, CO_2R), 1693 (m, CO_2^-), 1562 (w, C=N) cm^{-1}. FAB-MS: *m*/*z* (%) = 485 (10) [MH^+], 356 (60) [MH^+ – CO_2 – H_2C=C(Me)CO_2]. $C_{20}H_{21}N_4O_7Mn$ (484.34 g mol^{-1}): calcd. C 49.60, H 4.37, N 11.57; found C 49.69, H 4.68, N 11.27%.

Synthesis of [Re(bdmpzmp)(CO)$_3$] (5): Hbdmpzmp (**3**) (414 mg, 1.19 mmol) in dry THF (40 mL) is deprotonated with KO*t*Bu (134 mg, 1.19 mmol) and the reaction mixture is stirred at ambient temperature for 30 min. The complex [$ReBr(CO)_5$] (485 mg, 1.19 mmol) is added, the reaction mixture is heated under reflux and controlled by IR on a regular basis. After 16 h the reaction is completed and the solvent is removed in vacuo. The white residue is washed with water (5 × 10 mL), diethyl ether (5 × 10 mL) and dried in vacuo to yield **6** as a light grey powder. Yield 408 mg (0.660 mmol, 55%); m.p. 201–203 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.91 (s, 3 H, =C-CH_3), 2.53 (br., 12 H, C^3-CH_3 and C^5-CH_3), 5.31 and 5.79 (AB system, br., coupling not resolved, 2 H, -CH_2-O), 5.63 (br., 1 H, *cis* H_2C=CMe), 6.06 (br., 3 H, *trans* H_2C=CMe- and C_{pz}-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 12.5 (C^5_{pz}-CH_3), 14.3 (C^3_{pz}-CH_3), 15.4 (=C-CH_3), 60.5 (-CH_2-O-), 81.9 (C_{bridge}), 110.7 and 111.0 (2 × C_{pz}-H), 126.8 (H_2C=), 133.9 (=CMe-), 141.3 and 143.2 (2 × C^5_{pz}), 153.2 and 154.2 (2 × C^3_{pz}), 162.3 (-CO_2CH_2-), 164.9 (CO_2^-), 194.6 (C=O), 195.6 (C=O) ppm. IR (THF): $\tilde{\nu}$ = 2024 (s, C=O), 1918 (s, C=O), 1894 (s, C=O), 1734 (m, CO_2R), 1701 (m, CO_2^-), 1559 (w, C=N) cm^{-1}. FAB-MS: *m*/*z* (%) = 617 (16) [MH^+], 487 (100) [M^+ – CO_2 – H_2C=C(Me)CO_2]. $C_{20}H_{21}N_4O_7Re$ (615.61 g mol^{-1}): calcd. C 39.02, H 3.44, N 9.10; found C 39.46, H 3.51, N 8.94%.

Synthesis of [Cu(bdmpzmp)$_2$] (6): To Hbdmpzmp (**3**) (300 mg, 866 μmol) in dry acetonitrile (25 mL) copper(II) acetate monohydrate (45.0 mg, 225 μmol) is added and the reaction mixture is stirred at ambient temperature for 4 h. The violet residue is filtered off and washed with water (5 × 5 mL) and diethyl ether (5 × 5 mL) and dried in vacuo to yield **6** as a light violet powder. Crystals suitable for X-ray structure determination were obtained from a solution of **6** in dichloromethane layered with *n*-hexane. Yield 136 mg (0.180 mmol, 79%); m.p. 135–136 °C. IR (KBr): $\tilde{\nu}$ = 1726 (m, CO_2R), 1682 (s, CO_2^-), 1558 (w, C=N) cm^{-1}. FAB-MS: *m*/*z* (%) = 776 (2) [M + Na^+], 755 (2) [MH^+], 709 (1) [MH^+ – CO_2], 623 (2) [M^+ – CO_2 – H_2C=C(Me)CO_2], 279 (100) [MH^+ – $C_{17}H_{22}N_4O_4$ – CO_2 – H_2C=C(Me)CO_2]. $C_{34}H_{42}N_8O_8Cu$ (754.29 g mol^{-1}): calcd. C 54.14, H 5.61, N 14.86; found C 54.34, H 5.61, N 14.83%.

General Procedure for the Copolymerisation of 2: To a solution of the comonomers in dry xylene (10 mL) **2** is added whilst stirring and the solution is heated to 80 °C. After addition of azobisisobutyronitrile (20.0 mg, 0.121 mmol) the mixture is stirred for 2 h under a nitrogen atmosphere.

The resulting polymer solution in xylene is slowly poured into a mixture of methanol (300 mL) and diluted HCl (3 mL), immediately precipitating the polymer as a bright white solid. The residue is filtered off and washed severely with methanol and the remaining polymer is dried in vacuo. The content of ligand in the polymer is determined by elemental analysis.

P1a: Following the general procedure using destabilised methyl methacrylate (1.08 mL, 1.00 g, 9.99 mmol) and **2** (100 mg, 0.288 mmol). Incorporation: 0.20 mmol g^{-1}.

P1b: Following the general procedure using destabilised methyl methacrylate (1.08 mL, 1.00 g, 9.99 mmol) and **2** (50.0 mg, 0.144 mmol). Incorporation: 0.10 mmol g^{-1}.

P1c: Following the general procedure using destabilised methyl methacrylate (1.08 mL, 1.00 g, 9.99 mmol) and **2** (200 mg, 0.576 mmol). Incorporation: 0.21 mmol g^{-1}.

The blank experiment uses 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionic acid (92.3 mg, 0.288 mmol), following the general procedure.

P2: Following the general procedure using destabilised methyl methacrylate (1.08 mL, 1.00 g, 9.99 mmol), ethylene glycol dimethacrylate (95.0 μL, 100 mg, 0.50 mmol) and **2** (100.0 mg, 0.288 mmol). Incorporation: 0.20 mmol g^{-1}.

P3a: Following the general procedure using ethylene glycol dimethacrylate (950 μL, 1.00 g, 5.04 mmol) and **2** (100 mg, 0.288 mmol). Due to the high amount of cross-linking agent, the polymer precipitates during the polymerisation, and therefore is ground and added to a mixture of methanol (300 mL) and diluted HCl (3 mL) prior to washing with methanol. Incorporation: 0.15 mmol g^{-1}.

P3b: Following the general procedure using ethylene glycol dimethacrylate (950 μL, 1.00 g, 5.04 mmol) and **2** (100 mg, 0.288 mmol)

in acetonitrile instead of xylene. Due to the high amount of crosslinking agent, the polymer precipitates during the polymerisation, and therefore is ground and added to a mixture of methanol (300 mL) and diluted HCl (3 mL) prior to washing with methanol. Incorporation: 0.13 mmol g^{-1}. The blank experiment uses 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionic acid (92.3 mg, 0.288 mmol), following the same procedure.

Copolymerisation of MMA with 4 (P-Mn-II): To a solution of destabilised methyl methacrylate (1.08 mL, 1.00 g, 9.99 mmol) in dry xylene (10 mL) ligand **3** (69.7 mg, 0.144 mmol) is added whilst stirring and the suspension is heated to 80 °C. After addition of azobisisobutyronitrile (20.0 mg, 0.121 mmol) the mixture is stirred for 2 h under a nitrogen atmosphere. The resulting polymer solution in xylene is slowly filtered through a syringe microfilter and dropped into methanol (300 mL), immediately precipitating the polymer as a very light yellow solid. The residue is filtered off and washed severely with methanol. The remaining polymer is dried in vacuo. The content of complex in the polymer is determined by elemental analysis to 0.09 mmol g^{-1}. IR (nujol): $\tilde{\nu}$ = 2037 (s, C=O), 1946 (s, C=O), 1917 (s, C=O) cm^{-1}. The blank experiment uses [Mn(bdmpzap)(CO)$_3$] (66.0 mg, 0.144 mmol), following the same procedure.

Copolymerisation of MMA with 5 (P-Re-II): To a solution of destabilised methyl methacrylate (1.08 mL, 1.00 g, 9.99 mmol) in dry xylene (10 mL) complex **4** (88.7 mg, 0.144 mmol) is added whilst stirring and the suspension is heated to 80 °C. After addition of azobisisobutyronitrile (20.0 mg, 0.121 mmol) the mixture is stirred for 2 h under a nitrogen atmosphere. The resulting polymer solution in xylene is slowly filtered through a syringe microfilter and dropped into methanol (300 mL), immediately precipitating the polymer as a white solid. The residue is filtered off and washed severely with methanol and the remaining polymer is dried in vacuo. The content of complex in the polymer is determined by elemental analysis to 0.14 mmol g^{-1}. IR (nujol): $\tilde{\nu}$ = 2026 (s, C=O), 1921 (s, C=O), 1897 (s, C=O) cm^{-1}.

Immobilisation of Mn on P1a (P-Mn-I): To a suspension of **P1a** (150 mg, loading 0.20 mmol g^{-1}, 1.00 equiv.) in dry methanol (20 mL) KO*t*Bu (3.37 mg, 30.0 μmol) is added and the suspension is stirred at 50 °C under a nitrogen atmosphere. The polymer dissolves completely and after 2 h [MnBr(CO)$_5$] (8.25 mg, 30.0 μmol) is added and the solution is stirred for 3 d at 50 °C. After several hours, **P-Mn-I** starts to precipitate as a yellowish slurry. The mixture is cooled down to room temperature, the precipitate is filtered off, washed with methanol and water and dried in vacuo resulting in **P-Mn-I** as a yellow powder. The content of manganese in the polymer is determined by AAS to 0.083 mmol g^{-1}. IR (nujol): $\tilde{\nu}$ = 2038 (s, C=O), 1947 (s, C=O), 1918 (s, C=O) cm^{-1}. The blank experiment uses pure PMMA (150 mg) as obtained by the control experiment of **P1a**, following the same procedure.

Immobilisation of Re on P1a (P-Re-I): To a suspension of **P1a** (150 mg, loading 0.20 mmol g^{-1}, 1.00 equiv.) in dry methanol (20 mL) KO*t*Bu (3.37 mg, 30.0 μmol) is added and the suspension is stirred at 50 °C under a nitrogen atmosphere. The polymer dissolves completely and after 2 h [ReBr(CO)$_5$] (12.2 mg, 30.0 μmol) is added and the solution is stirred for 3 d at 50 °C. After several hours, **P-Re-I** starts to precipitate as a white slurry. The mixture is cooled down to room temperature, the precipitate is filtered off, washed with methanol and water and dried in vacuo resulting in

Table 2. Details of the structure determination for **3**, **4** and **6**.

	3	**4**	**6**
Empirical formula	$C_{17}H_{22}N_4O_4$	$C_{20}H_{21}MnN_4O_7$	$C_{34}H_{42}CuN_8O_8$
Formula mass	346.39	484.35	754.3
Crystal colour/habit	colourless block	yellow plate	blue prism
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/a$	$P2_1/c$
a [Å]	8.676(2)	12.1154(7)	8.8422(7)
b [Å]	12.749(4)	15.3039(8)	12.1958(7)
c [Å]	16.865(4)	12.5755(13)	16.7929(7)
α [°]	90.00	90.00	90.00
β [°]	103.50(3)	116.975(6)	103.152(5)
γ [°]	90.00	90.00	90.00
V [Å^3]	1814.9(8)	2078.0(3)	1763.41(19)
θ [°]	2.02–24.11	3.22–27.5	2.9–28.49
h	–9 to 9	–15 to 15	–11 to 11
k	–14 to 0	–19 to 19	–16 to 16
l	0 to 19	–16 to 16	–22 to 22
F(000)	736	1000	790
Z	4	4	2
μ (Mo-K_α) [mm^{-1}]	0.092	0.687	0.682
Crystal size [mm]	0.38 × 0.3 × 0.3	0.32 × 0.16 × 0.023	0.21 × 0.16 × 0.10
$D_{calcd.}$ [g cm^{-3}], T [K]	1.268, 250	1.548, 150	1.421, 150
Reflections collected	2985	45570	46808
Independent reflections	2876	4762	4449
Observed reflections ($I > 2\sigma I$)	1471	3510	3563
Parameter	229	289	238
Weight parameter a	0.0812	0.0381	0.0681
Weight parameter b	0	1.4923	0.8610
R_1 (obsd.)	0.0597	0.0388	0.0441
R_1 (overall)	0.1776	0.0662	0.0624
wR_2 (obsd.)	0.1378	0.0825	0.1136
wR_2 (overall)	0.1736	0.0912	0.1222
Diff. peak/hole [e/Å^3]	–0.255/0.25	–0.393/0.359	–0.373/1.000

P-Re-I as a white powder. IR (nujol): $\tilde{\nu}$ = 2028 (s, C=O), 1921 (s, C=O), 1897 (s, C=O) cm^{-1}.

Immobilisation of Cu on P1a (P-Cu-I): To a suspension of **P1a** (150 mg, loading 0.20 mmol g^{-1}, 1.00 equiv.) in dry methanol (20 mL) KO*t*Bu (3.37 mg, 30.0 μmol) is added and the suspension is stirred at 50 °C under a nitrogen atmosphere. The polymer dissolves completely and after 2 h a solution of excess $CuCl_2$ (10.0 mg, 74.4 μmol) in dry methanol (1 mL) is added. **P-Cu-I** immediately precipitates as a blue solid. The precipitate is filtered off, washed severely with dry methanol and dried in vacuo resulting in **P-Cu-I** as a blue powder. The content of copper in the polymer is determined by AAS to 0.085 mmol g^{-1}. UV: λ_{max} = 715 nm. The blank experiment uses pure PMMA (150 mg) as obtained by the control experiment of **P1a**, following the same procedure.

Immobilisation of Cu on P2 (P-Cu-II): To a suspension of **P2** (150 mg, loading 0.20 mmol g^{-1}, 1.00 equiv.) in dry methanol (20 mL) KO*t*Bu (3.37 mg, 30.0 mmol) is added and the suspension is stirred at 50 °C under a nitrogen atmosphere. The polymer dissolves completely and after 2 h the solvent is removed in vacuo. To the white powdery residue a solution of excess $CuCl_2$ (10.0 mg, 74.4 μmol) in dry ethanol (1 mL) is added. The residue immediately turns green. It is severely washed with dry ethanol and dried in vacuo resulting in **P-Cu-II** as a lime green powder. The content of copper in the polymer is determined by AAS to 0.093 mmol g^{-1}. UV: λ_{max} = 793 nm. The blank experiment uses pure PMMA/EGDMA copolymer (150 mg).

X-ray Structure Determinations: Single crystals of **3**, **4** and **6** were mounted with Paratone-N or glue on a glass fibre. A Bruker-Nonius Kappa-CCD and an Enraf–Nonius CAD4 Mach3 diffractometer were used for data collection. The structures were solved by using direct methods and refined with full-matrix least-squares against F^2 {Siemens SHELX-97}.[31] A weighting scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2Fc^2 + \max(F_o^2,0)]/3$. Most hydrogen atoms were included in their calculated positions and refined in a riding model. The proton of the carboxylic acid **3** was found and its coordinates were refined freely. All details and parameters of the measurements are summarised in Table 2. The structure pictures were prepared with the program Diamond 2.1e.[32]

CCDC-661578 (for **3**), -661579 (for **4**) and -661580 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ESR spectra of [Cu(bdmpza)$_2$], **P-Cu-I** and **P-Cu-II**.

Acknowledgments

Generous financial support by the Deutsche Forschungsgemeinschaft (DFG) (SFB 583) is gratefully acknowledged. We thank Dr. F. Heinemann for collecting two X-ray datasets and Mr. J. Schmidt for AAS measurements.

[1] A. Otero, J. Fernández-Baeza, J. Tejeda, A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, A. Lara-Sánchez, M. Fernández-López, M. Lanfranchi, M. A. Pellinghelli, *J. Chem. Soc. Dalton Trans.* **1999**, 3537–3539.
[2] A. Otero, J. Fernández-Baeza, J. Tejeda, A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, A. Lara-Sánchez, M. Fernández-López, *J. Chem. Soc. Dalton Trans.* **2000**, 2367–2374.
[3] A. Otero, J. Fernández-Baeza, A. Antiñolo, F. Carrillo-Hermosilla, J. Tejeda, E. Díez-Barra, A. Lara-Sánchez, L. Sánchez-Barba, I. López-Solera, M. R. Ribeiro, J. M. Campos, *Organometallics* **2001**, *20*, 2428–2439.
[4] A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L. Sánchez-Barba, M. T. Expósito, A. M. Rodríguez, *Dalton Trans.* **2003**, 1614–1619.
[5] N. Burzlaff, I. Hegelmann, B. Weibert, *J. Organomet. Chem.* **2001**, *626*, 16–23.
[6] A. Beck, B. Weibert, N. Burzlaff, *Eur. J. Inorg. Chem.* **2001**, 521–527.
[7] I. Hegelmann, N. Burzlaff, *Eur. J. Inorg. Chem.* **2003**, 409–411.
[8] L. Peters, N. Burzlaff, *Polyhedron* **2004**, *23*, 245–251.
[9] N. Burzlaff, I. Hegelmann, *Inorg. Chim. Acta* **2002**, *329*, 147–150.
[10] A. López-Hernández, R. Müller, H. Kopf, N. Burzlaff, *Eur. J. Inorg. Chem.* **2002**, 671–677.
[11] I. Hegelmann, A. Beck, C. Eichhorn, B. Weibert, N. Burzlaff, *Eur. J. Inorg. Chem.* **2003**, 339–347.
[12] A. Beck, A. Barth, E. Hübner, N. Burzlaff, *Inorg. Chem.* **2003**, *42*, 7182–7188.
[13] R. Müller, E. Hübner, N. Burzlaff, *Eur. J. Inorg. Chem.* **2004**, 2151–2159.
[14] B. Kozlevčar, P. Gamez, R. de Gelder, W. L. Driessen, J. Reedijk, *Eur. J. Inorg. Chem.* **2003**, 47–50.
[15] E. Hübner, T. Haas, N. Burzlaff, *Eur. J. Inorg. Chem.* **2006**, 4989–4997.
[16] M. Tada, Y. Iwasawa, *Chem. Commun.* **2006**, 2833–2844.
[17] B. M. L. Dioos, I. F. J. Vankelecom, P. A. Jacobs, *Adv. Synth. Catal.* **2006**, *348*, 1413–1446.
[18] M. I. Burguete, J. M. Fraile, J. I. García, E. García-Verdugo, C. I. Herrerías, S. V. Luis, J. A. Mayoral, *J. Org. Chem.* **2001**, *66*, 8893–8901.
[19] R. A. Findeis, L. H. Gade, *Dalton Trans.* **2003**, 249–254.
[20] P. C. Kunz, N. E. Brückmann, B. Spingler, *Eur. J. Inorg. Chem.* **2007**, 394–399.
[21] A. Schiller, R. Scopelliti, K. Severin, *Dalton Trans.* **2006**, 3858–3867.
[22] K. Heinze, A. Fischer, *Eur. J. Inorg. Chem.* **2007**, 1020–1026.
[23] M. Shima, A. Kotera, *J. Polym. Sci., Part A Polym. Chem.* **1963**, 1115–1121.
[24] E. L. Madruga, M. F. García, *Macromol. Chem. Phys.* **1996**, *197*, 1185–1191.
[25] A. K. Ho, I. Iin, P. A. Gurr, M. F. Mills, G. G. Qiao, *Polymer* **2005**, *46*, 6727–6735.
[26] T. S. Thakur, G. R. Desiraju, *Chem. Commun.* **2006**, 552–554.
[27] Y. Inoue, K. Matyjaszewski, *Macromolecules* **2004**, *37*, 4014–4021.
[28] J. M. Goodwin, M. M. Olmstead, T. E. Patten, *J. Am. Chem. Soc.* **2004**, *126*, 14352–14353.
[29] D. Vitali, F. Calderazzo, *Gazz. Chim. Ital.* **1972**, *102*, 586–596.
[30] W. Abel, G. Wilkinson, *J. Chem. Soc.* **1959**, 1501–1505.
[31] G. M. Sheldrick, *SHELX-97*, Programs for Crystal Structure Analysis, University of Göttingen, Göttingen (Germany), **1997**.
[32] K. Brandenburg, M. Berndt, Diamond – Visual Crystal Structure Information System, Crystal Impact GbR, Bonn (Germany), **1999**. For Software Review see: W. T. Pennington, *J. Appl. Crystallogr.* **1999**, *32*, 1028–1029.

Received: October 12, 2007
Published Online: January 22, 2008

