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Synthesis and Transition Metal Complexes of Novel *N*,*N*,*O* Scorpionate Ligands Suitable for Solid Phase Immobilisation

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Introduction of an allyl or a hydroxymethyl group to bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1**) at the bridging carbon atom leads to the new tripodal *N*,*N*,*O* ligands 2,2-bis(3,5-dimethylpyrazol-1-yl)pent-4-enoic acid (Hbdmpzpen) (**2**) and 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic acid (Hbdmpzhp) (**3**). These ligands exhibit similar chemical behaviour to that of **1**, but they have the additional possibility to be immobilised to a solid phase. Esterification of the hydroxymethyl linker of **3** yields 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionic acid (Hbdmpzap) (**4**). The molecular structures of **2**, **3** and **4** all exhibit intramolecular hydrogen bridges. Introduction of a hydroxymethyl group to methyl bis(3,5-dimethylpyrazol-1-yl)acetate (**5**) yields methyl 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionate (Mebdmpzhp) (**6**), which can be immobilised on Merrifield polymer to yield modified resin **P**-**6**. To investigate the reactivity of these new ligands, manganese and rhenium complexes of **2**, **3** and **4** have been studied. The molecular structures of the two manganese complexes [Mn(bdmpzpen)(CO)$_3$] (**7**) and [Mn(bdmpzap)(CO)$_3$] (**8**) have been confirmed by single-crystal X-ray structure determination. Saponification of polymer resin **P**-**6** and subsequent reaction with [ReBr(CO)$_5$] yields rhenium tricarbonyl complexes anchored on Merrifield polymer (**P**-Re). Solid phase immobilisation of the [Mn(bdmpzpen)(CO)$_3$] (**7**) and [Re(bdmpzpen)(CO)$_3$] (**9**) complexes on 3-mercaptopropyl functionalised silica is initialised by AIBN. The tripodal coordination of manganese and rhenium in these functionalised Merrifield resins (**P**-Re) and silica (**S**-Mn, **S**-Re) is proven by a single A$_1$ and two E signals in the IR spectra that are typical for unsymmetrical "piano stool" type carbonyl complexes.

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Introduction

Bis(pyrazol-1-yl)acetic acids have proved to be a versatile class of *N*,*N*,*O* ligands, structurally related to the well-known hydrotris(pyrazol-1-yl)borate (Tp). Different synthetic routes for achiral, chiral and enantiopure bis(pyrazol-1-yl)acetic acids have been developed since their introduction to coordination chemistry in 1999 by A. Otero.[1,2] A broad spectrum of transition metal complexes bearing these ligands revealed their behaviour as weak electron-donating ligands in inorganic chemistry,[2a,2c] which often behave almost identically to Tp ligands. Typical examples are the manganese and rhenium tricarbonyl complexes [Mn(bdmpza)(CO)$_3$] and [Re(bdmpza)(CO)$_3$] [bdmpza: bis(3,5-dimethylpyrazol-1-yl)acetate].[2a] Furthermore, model complexes with iron(II) and zinc(II) show their potential to mimic the active site of metalloenzymes with a 2-His-1-carboxylate motif.[2b,2e–2g]

Fixation of these ligands on a solid phase is of particular interest, especially with regard to the potential use as catalysts with easy work up or to achieve dedicated structural environments with sterically less hindered ligands. Most methods used for immobilisation of ligands or transition metal complexes introduce a linker group to the ligand which connects the ligand through stable covalent bonds to the solid material.[3] Isolated double bonds as in allyl or acryl groups open up a broad field of methods available to immobilise the ligand.[4,5] Common examples are copolymerisation, metathesis reactions and especially radical-induced carbon–sulfur bond formations.[5] Recent investigations on structurally related bis(oxazoline) ligands have shown the feasibility of immobilising such ligands while maintaining catalytic activity of the resulting immobilised complexes.[5b] Alternatively, a hydroxymethyl linker would allow solid phase fixation by esterification or ether synthesis.

Results and Discussion

We found bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) (**1**) to be a convenient starting material for linker modified ligands, which is accessible from dibromo- or dichloroacetic acid in a one-step synthesis.[2a,2b] Deprotonation of the remaining hydrogen at the bridging carbon atom in **1** with excess LDA in THF at –80 °C and subse-

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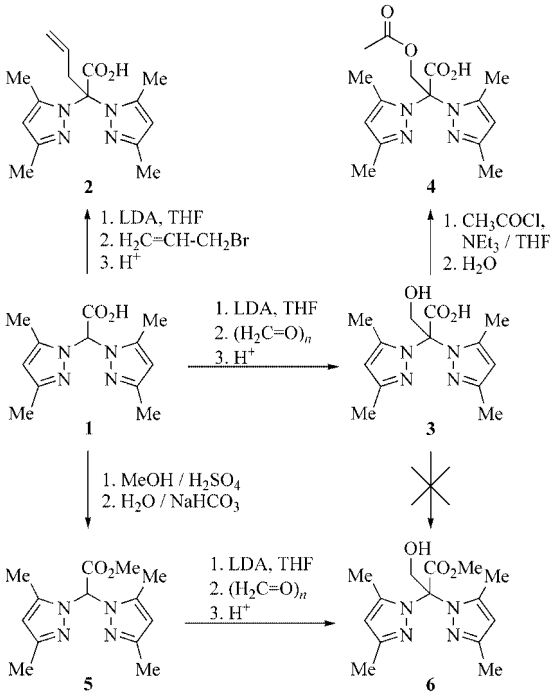
quent alkylation with allyl bromide leads to 2,2-bis(3,5-dimethylpyrazol-1-yl)pent-4-enoic acid (Hbdmpzpen) (**2**) (Scheme 1). Similar modifications of tris(pyrazolyl)methane ligands with various bases such as *n*BuLi or LiN[Si(CH$_3$)$_3$]$_2$ have been reported recently by D. L. Reger et al.[6]



Scheme 1.

Despite heating under reflux, no reaction of the deprotonated carboxylate group with allyl bromide is observed, although this is a well-known reaction, for example in the case of fluoroacetic acid.[7] Thus, the asymmetric carboxylate IR band (THF) is found at 1729 cm^{-1}. The molecular structure of **2** (Figure 1) was determined by X-ray crystallography, which revealed an intramolecular hydrogen bridge [d(O1–N11) = 2.504(2) Å] between the carboxylate and the pyrazolyl group. The ^{1}H and ^{13}C NMR spectroscopic data of resulting ligand **2** are almost identical to those of **1**, except for the lack of a ^{1}H NMR resonance of the bridging CH group and the additional allyl resonances. This is consistent with a C_s symmetry in solution.

A quite similar reaction with paraformaldehyde instead of allyl bromide yields 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic acid (Hbdmpzhp) (**3**) (Scheme 1).

Again, the result of an X-ray structure determination of **3** exhibits an intramolecular hydrogen bond [d(O3–N21) = 2.715(3) Å], in this case between the hydroxy and the pyrazolyl group (Figure 2).

According to the NMR spectroscopic data, the molecular structure exhibits C_s symmetry in solution as well. The IR band (KBr) at 1752 cm^{-1} is assigned to the carboxylate signal. In solution, two IR bands occur for the carboxylate group (THF, 1750 and 1716 cm^{-1}), which indicates that there is hydrogen bonding between the carboxylate group and the OH-linker.

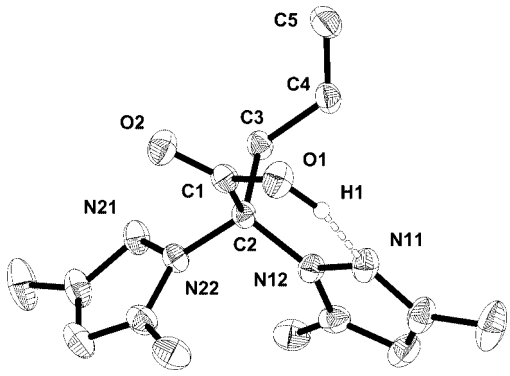


Figure 1. Molecular structure of 2,2-bis(3,5-dimethylpyrazol-1-yl)-pent-4-enoic acid (**2**); thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: d(C1–O1) = 1.3194(18), d(C1–O2) = 1.2058(17), d(O1–N11) = 2.504(2), ∠(N12,C2,N22)=108.09(11).

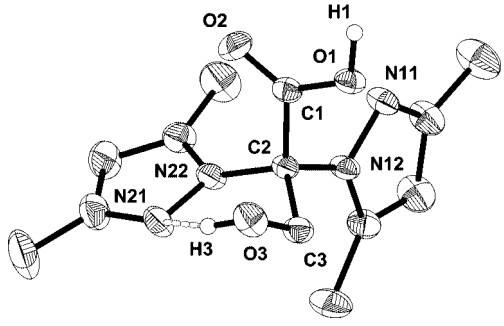


Figure 2. Molecular structure of 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic acid (**3**); thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: d(C1–O1) = 1.320(3), d(C1–O2) = 1.201(3), d(C3–O3) = 1.414(3), d(O3–N21) = 2.715(3), ∠(N12,C2,N22) = 109.6(2).

Because the linker groups are introduced at the bridging carbon atom, this concept may be extended to homochiral bis(pyrazol-1-yl)acetic acids, which we reported on recently,[2h,2i] without breaking the chirality or chiral induction.

Besides direct solid phase fixation, the functional OH-group of **3** may be used for further modifications. Possible applications would be linking biomolecules by esterification or the addition of new linking groups. Esterification with acetyl chloride at the OH-linker (Scheme 1) leads to **4** and provides a heteroscorpionate ligand with the protected OH-linker.

The intramolecular hydrogen group is found in the X-ray structure, too, [d(O1–N21) = 2.478(3) Å] between the carboxylic acid and the pyrazole nitrogen (Figure 3).

On the other hand, ligand **3** may be modified at the carboxylate donor instead of the OH-linker. This is necessary depending on the applied procedure of solid phase fixation (see below) to prevent the carboxylate donor from acting as a linking group. Although the most obvious protecting group is methyl ester **6** (Scheme 1), direct esterification of **5** results in 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-ethanol caused by decarboxylation. Therefore, methyl ester **6** is synthesised by esterification of **1** in a first step and subsequent

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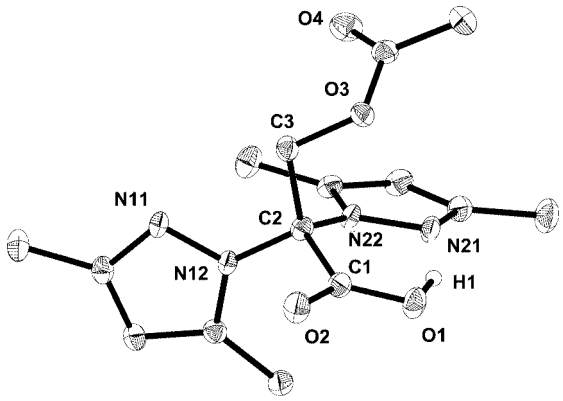
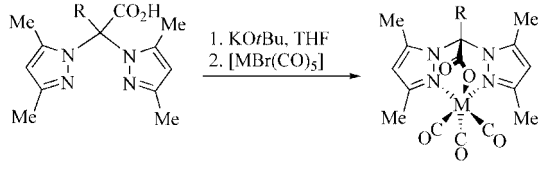


Figure 3. Molecular structure of 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionic acid (**4**); thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: d(C1–O1) = 1.306(3), d(C1–O2) = 1.203(3), d(O1–N21) = 2.478(3), ∠(N12,C2,N22)=108.72(18).

reaction of **5** with LDA and paraformaldehyde to **6** (Scheme 1).

To study the potential of these new ligands, **2**, **3**, **4** and **6**, in coordination chemistry and to examine their chemical behaviour, tricarbonyl complexes with manganese and rhenium were synthesised. The general synthesis of such tricarbonyl metal complexes starts from $[MnBr(CO)_5]$ and $[ReBr(CO)_5]$, respectively, and leads after reaction with potassium bis(pyrazol-1-yl)carboxylates to the corresponding tricarbonyl complexes.[2a]

To verify tripodal binding of the solid-bound ligand, manganese and rhenium complexes of ligand **4**, which bears the acetyl protected OH-linker, were synthesised accordingly (Scheme 2). The protected OH linker in **4** acts as model for the solid phase bound ligand.



Scheme 2.

In contrast to **3**, ligand **4** reacts with the metal carbonyls as it is well known for the heteroscorpionate ligand Hbdmpza.[2a] This is also observed with allyl-functionalised ligand **2** (Scheme 2).

The formation of tricarbonyl complexes **7** to **10** can be monitored by IR spectroscopy during the reaction. The presence of the tricarbonyl complexes is indicated by a single A_1 and two E signals typical for unsymmetrical "piano stool" type carbonyl complexes[2a] [**7**: $\tilde{\nu}$(CO) = 2033, 1939 and 1911 cm^{-1}; **9**: $\tilde{\nu}$(CO) = 2023, 1915 and 1892 cm^{-1}; **8**: $\tilde{\nu}$(CO) = 2034, 1940 and 1913 cm^{-1}; **10**: $\tilde{\nu}$(CO) = 2024, 1918 and 1894 cm^{-1}]. These IR absorptions are in good agreement with those of the complexes $[M(bdmpza)(CO)_3]$ (M = Mn, Re) we reported on earlier and prove the desired κ^3-*N,N,O* coordination of the ligands.[2a] The IR bands at 1687 (**7**), 1697 (**9**), 1692 (**8**) and 1702 (**10**) cm^{-1} are assigned to the asymmetric carboxylate vibration $\tilde{\nu}_{asym}(CO_2^-)$. Complexes **8** and **10** show an additional IR signal at 1761 and 1762 cm^{-1}, respectively, which was assigned to the asymmetric carboxylate vibration in the acetyl residue. The complexes are also confirmed by the $[M + H]^+$ peaks in the FAB and FD mass spectra. In the case of **7**, in accordance with $[Mn(bdmpza)(CO)_3]$, the ^1H NMR spectra consists of broad signals without clear couplings. Nevertheless, the signals can be assigned unambiguously. Also the ^1H and ^{13}C NMR spectra of **9** show a clear set of signals for the coordinated bdmpzpen ligand. The carboxylate group shows a ^{13}C NMR resonance at δ = 164.5 ppm. Two ^{13}C NMR resonances are observed for the carbonyl ligands of complexes **7** and **9** (**7**: 220.6 ppm, 222.4 ppm, **9**: 195.7 ppm, 196.0 ppm).

Finally, X-ray structure analyses of **7** (Figure 4) and **8** (Figure 5) doubtless reveal the κ^3-*N,N,O* coordination of tripodal *N,N,O* ligands **2** and **4**. Complex **8** crystallised in a chiral conformation with the acetyl protected linker group positioned between one pyrazole donor and the carboxylate donor (Figure 5 and Scheme 3). Both possible enantiomers are found in the cell because of the space group P-1.

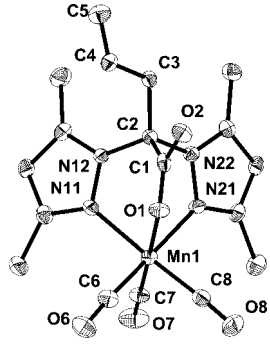


Figure 4. Molecular structure of $[Mn(bdmpzpen)(CO)_3]$ (**7**); thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: d(C1–O1) = 1.266(5), d(C1–O2) = 1.233(4), d(Mn1–N11) = 2.049(3), d(Mn1–N21) = 2.090(3), d(Mn1–O1) = 1.993(3), d(Mn1–C6) = 1.813(4), d(Mn1–C7) = 1.805(4), d(Mn1–C8) = 1.817(4), d(C6–O6) = 1.153(5), d(C7–O7) = 1.149(5), d(C8–O8) = 1.149(5), ∠(N11,Mn1,C8) = 175.15(16), ∠(N21,Mn1,C6) = 176.41(15), ∠(O1,Mn1,C7) = 175.61(14), ∠(N11,Mn1,O1) = 83.72(12), ∠(N21,Mn1,O1) = 85.02(12), ∠(N21,Mn1,C7) = 91.77(15), ∠(N11,Mn1,C7) = 93.09(16), ∠(N11,Mn1,N21) = 86.22(12).

Thus, the coordination of the new ligands is not hindered by the additional linker groups at the bridging carbon atom. Coordination of the linker to the metal centre instead of the carboxylate donor does not take place in the case of **2**. The position of the allyl group in **7** (Figure 3), as well as of the acetyl group in **8**, indicate its ability to act as a linking group to solid phase. The agreement of the bond lengths and angles of **7** and **8** with those of the previously reported $[Mn(bdmpza)(CO)_3]$[2a] implies similar ligand properties of **2**, **3** and **4** in comparison to those of **1**.

Both complexes $[Mn(bdmpzap)(CO)_3]$ (**8**) and $[Re(bdmpzap)(CO)_3]$ (**10**) exhibit an AB system in the ^1H NMR spectrum for the -CH_2O- protons because of the chi-

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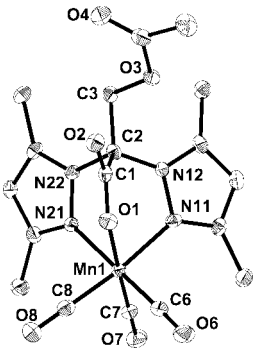


Figure 5. Molecular structure of [Mn(bdmpzap)$(CO)_3$] (**8**); thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: d(C1–O1) = 1.263(4), d(C1–O2) = 1.226(4), d(Mn1–N11) = 2.037(3), d(Mn1–N21) = 2.060(3), d(Mn1–O1) = 1.999(3), d(Mn1–C6) = 1.809(4), d(Mn1–C7) = 1.786(4), d(Mn1–C8) = 1.808(5), d(C6–O6) = 1.150(4), d(C7–O7) = 1.157(5), d(C8–O8) = 1.152(5), ∠(N11,Mn1,C8) = 173.26(16), ∠(N21,Mn1,C6) = 176.70(17), ∠(O1,Mn1,C7) = 177.21(15), ∠(N11,Mn1,O1) = 84.22(11), ∠(N21,Mn1,O1) = 86.51(11), ∠(N21,Mn1,C7) = 92.22(15) ∠(N11,Mn1,C7) = 93.19(16), ∠(N11,Mn1,N21) = 84.39(12).

Scheme 3. Dynamic interconversion of the two enantiomers of complexes **8** and **10**. The Newman projection shows the view along the C3–C2 axis. The numbering was carried out according to Figure 5.

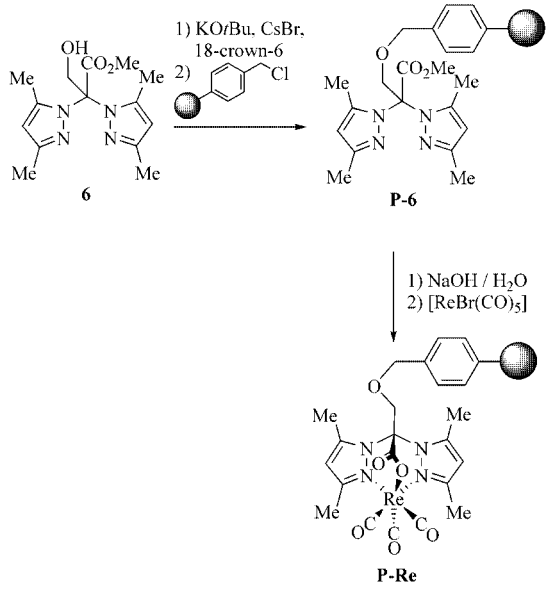
rality described above. These AB systems, as well as the signals of the two methyl groups, are rather broad due to a dynamic interconversion of the two possible enantiomers (Scheme 3). This dynamic interconversion might also explain why rather weak ^{13}C NMR spectroscopic data were obtained for manganese and rhenium complexes **8** and **10**.

In the case of OH-functionalised ligand **3**, the IR spectra of the manganese and the rhenium compounds indicate the formation of at least two species because several bands for the CO signals appear. This is backed by NMR spectra, which shows more than one set of signals for the methyl groups of the pyrazole donors. Furthermore, the NMR signals are broadened and especially the carboxylate group is not clearly visible in the IR spectra. Although we could not solve this problem in detail, this might indicate a dynamic equilibrium in which either the carboxylate donor or the hydroxo linker coordinates towards the metal centre. A related dynamic behaviour was reported recently by W. Kläui and coworkers.[8] After binding the hydroxymethyl linker to solid phase, this part of the molecule will presumably act no longer as a donor towards the metal centre as shown in complex **8**. Thus, this behaviour will not interfere with the future use of ligands **3** or **6** as a solid-bound *N*,*N*,*O* ligand.

Solid Phase Binding

The purpose of our efforts, as mentioned above, is to bind monoanionic *N*,*N*,*O* ligands to various solid phases. This solid phase fixation of the ligands and their complexes should strongly affect their chemical properties. For instance, the formation of bisligand complexes [ML_2] as well as the autoxidation or dimerisation of complexes should be prevented.

Chloromethylated resin, so called Merrifield polymer, is one of the most popular solid phase supports. Thus, we used this resin in our first attempt to bind linker modified bis(pyrazol-1-yl)acetic acids to a solid phase. Primarily, Merrifield polymer was designed to bind carboxylic acids. Thus, we had to use the ester methyl 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionate (**6**) instead of the 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic acid (**3**). Fixation on the resin is achieved by nucleophilic substitution of the benzylic chlorine for the deprotonated OH-linker of **6** (Scheme 4). The best result was obtained by using a mixture of KO*t*Bu, 18-crown-6 and CsBr in this reaction. To verify the functionalisation of the polymer, elemental analyses of solid phase samples were accomplished. Determination of the nitrogen content does not only prove the binding of ligand **6** to the solid phase, but also enables the calculation of the degree of functionalisation (Table 1). Usually, an occupancy of more than 20% of the theoretical sites was achieved. Subsequent saponification of functionalised Merrifield resin **P-6** with H_2O/NaOH/THF leads to the targeted monoanionic *N*,*N*,*O* functionalised solid phase. Further reaction with [$ReBr(CO)_5$] afforded polymer mounted tricarbonyl rhenium complex **P**-Re (Scheme 4). A similar reaction with [$MnBr(CO)_5$] has not been successful so far.



Scheme 4.

The IR spectra of **P**-Re exhibits a single A_1 and two E signals [$\tilde{\nu}$(CO) = 2022, 1915 and 1890 cm^{-1}] (Figure 6c). The location of these signals is almost identical to those of the complex [Re(bdmpzap)$(CO)_3$] (**10**) (Figure 6a) which we described above. An additional signal at 1964 cm^{-1} is caused by the Merrifield polymer (Figure 6b and Fig-

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Table 1. Occupancy of the functionalised solid phases **P-6**, **S-2**, **S**-Mn and **S**-Re.

Solid phase	Linker [mmol g^{-1}]	Functionalised solid phase	Nitrogen content [%]	Ligand/ complex [mmol g^{-1}]	Occupancy of sites [%]
Merrifield polymer	1.1	**P-6**	1.26	0.23	21
Mercaptopropyl silica	0.98	**S-2**	0.97	0.17	18
Mercaptopropyl silica[a]	0.98	**S**-Mn	0.20	0.036	4
Mercaptopropyl silica[b]	0.98	**S**-Mn-II	0.35	0.063	6
Mercaptopropyl silica[a]	0.98	**S**-Re	0.23	0.041	4
Mercaptopropyl silica[b]	0.98	**S**-Re-II	0.44	0.078	8

[a] After 8 h. [b] After 48 h.

ure 6c). A control experiment with unfunctionalised methyl bis(3,5-dimethylpyrazol-1-yl)acetate (**5**) showed no occupancy of the polymer sites and subsequently no A_1 and E signals but a typical IR spectrum of Merrifield polymer (Figure 6b). Therefore, the results of our experiments prove a solid phase fixation of the ligand and the resulting tricarbonyl complex as well as a facial coordination of rhenium(I) by the monoanionic *N,N,O* tripod ligand.

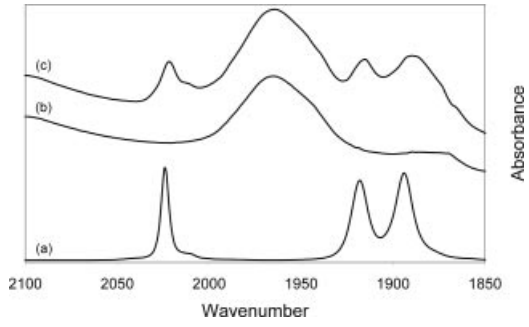
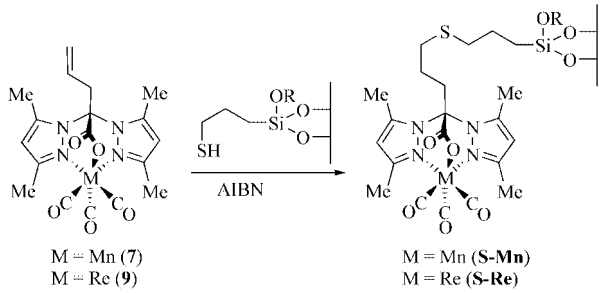


Figure 6. IR spectra of (a) [Re(bdmpzap)(CO)$_3$] (**10**) (THF), (b) Merrifield polymer (THF) and (c) **P**-Re – the rhenium tricarbonyl complex anchored on Merrifield polymer (THF).

Unfortunately, the solvents compatible to reactions with Merrifield polymer are quite limited. Especially, reactions in water are almost impossible. To overcome this limitation for future applications, the fixation on silica solid phase can be achieved by mercaptopropyl functionalised silica. Immobilisation of chelating *N,N* ligands bearing allyl linker groups on such functionalised silica has been reported recently by Mayoral et al.[5b] Following a similar procedure, 2,2-bis(3,5-dimethylpyrazol-1-yl)pent-4-enoic acid (**2**) was immobilised by a radical induced reaction with mercaptopropyl silica in the presence of azobisisobutyronitrile (AIBN). An analysis of the nitrogen content of resulting silica **S-2** showed an occupancy of more than 17% of the mercaptopropyl sites (Table 1). Unfortunately, the mercaptopropyl functionalised silica itself as well as the modified silica **S-2** can undergo complexation with [MnBr(CO)$_5$] and [ReBr(CO)$_5$]. After reaction with [ReBr(CO)$_5$], both silica exhibit various rather broad IR signals, which could be assigned to signals of various carbonyl species.

In an attempt to overcome this problem we tried to immobilise the [Mn(bdmpzpen)(CO)$_3$] (**7**) and [Re(bdmpzpen)(CO)$_3$] (**9**) complexes themselves. On following this approach, complexes **7** and **9** were grafted onto mercaptopropyl silica in the presence of AIBN (Scheme 5).



Scheme 5.

Elemental analyses of resulting silica samples **S**-Mn and **S**-Re were accomplished to determine the nitrogen content. The deduced occupancy of mercaptopropyl sites by the tricarbonyl complexes add up to 3.6% (**S**-Mn) and 4.2% (**S**-Re) (Table 1). IR spectra of silica phases **S**-Mn and **S**-Re show signals that can be assigned to the A_1 and E signals of the grafted manganese and rhenium tricarbonyl complexes [**S**-Mn: $\tilde{\nu}$(CO) = 2039, 1948 and 1923 cm^{-1} (Figure 7d); **S**-Re: $\tilde{\nu}$(CO) = 2027, 1920 and 1905 cm^{-1} (Figure 7f)]. A longer reaction time (48 h) results in higher occupancies

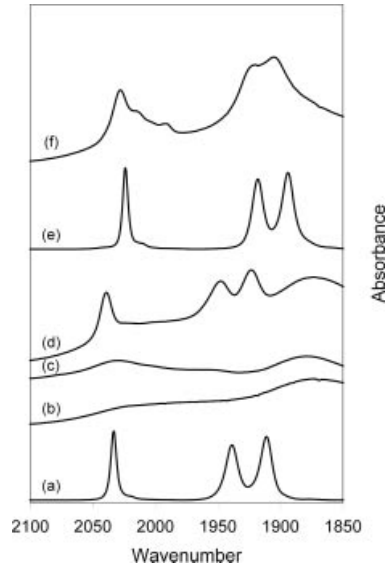


Figure 7. IR spectra of (a) [Mn(bdmpzpen)(CO)$_3$] (**7**) (THF), (b) mercaptopropyl silica (Nujol), (c) control experiment with [Mn(bdmpza)(CO)$_3$], (d) manganese tricarbonyl complex **7** immobilised on silica (**S**-Mn) (Nujol), (e) [Re(bdmpzpen)(CO)$_3$] (**9**) (THF) and (f) rhenium tricarbonyl complex **9** immobilised on silica (**S**-Re) (Nujol).

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[6.4% (**S**-Mn-II) and 8.0% (**S**-Re-II)], but caused also obscure IR spectra probably due to degradation of the carbonyl complexes or a further reaction with surrounding non innocent free SH-groups.

Neither the IR spectra of the mercaptopropyl functionalised silica (Figure 7b) nor that of a control experiment with the unfunctionalised complex [Mn(bdmpza)$(CO)_3$] (Figure 7c) show any signals in this region. Thus, these results prove an immobilisation of manganese and rhenium tricarbonyl complexes on silica through a *N*,*N*,*O* tripod ligand with an allyl linker.

Conclusions

In conclusion, modifications to the in coordination chemistry well-established ligand Hbdmpza (**1**) led to the new functionalised ligands 2,2-bis(3,5-dimethylpyrazol-1-yl)pent-4-enoic acid (**2**) and 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic acid (**3**) bearing an allyl or an hydroxymethyl linker for solid phase fixation. These ligands, or their protected analogues, provide similar coordination properties as **1**, proven by the synthesis of various transition metal carbonyl complexes. By way of well-known solid phase coupling reactions, **2** and **3** have been grafted on silica and on Merrifield polymer. The degree of functionalisation of the solid phase can be determined by elemental analysis. Furthermore, we were able to prove the typical tripodal monoanionic *N*,*N*,*O* binding behaviour by the characteristic IR spectra of immobilised tricarbonyl complexes.

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 were recorded with a Biorad FTS 60 spectrometer or a Varian Excalibur FTS-3500 FTIR spectrometer in CaF_2 cuvettes (0.2 mm) or in Nujol. ^1H and ^{13}C NMR spectra were measured with Bruker AC 250 MHz, Varian Inova 400 MHz or Bruker DPX300 instruments. δ values are measured relative to TMS or the deuterated solvent. Mass spectra were recorded with a modified Finnigan MAT 312 instrument by using either EI or FAB technique with 3-nitrobenzyl alcohol as matrix for complexes **7** and **9** and glycerine/NaI as matrix for ligands **2** and **3** or were recorded on a Jeol JMS-700 instrument using FD technique. Elemental analyses were measured with a Heraeus CHN-O-Rapid, Euro EA 3000 (Euro Vector) and EA 1108 (Carlo Erba) ($\sigma \pm 1$% of the measured content). A modified Siemens P4 diffractometer and a STOE IPDS II diffractometer were used for X-ray structure determination. Chemicals were used as purchased without further purification. Chloromethylated resin, "Merrifield polymer" [polystyrene-divinylbenzene, 1% cross linking, 1.1 mmol Cl g^{-1}, 200–400 mesh (Fluka)] and 3-mercaptopropyl functionalised silica [0.98 mmol S g^{-1} (Aldrich)] were used as purchased. Both solid phases were evacuated for 2 h (10^{-2} mbar) and flushed with dry nitrogen prior to use. Bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1**) was synthesised as described earlier but starting from dichloroacetic acid instead of dibromoacetic acid and with a reaction time of 72 h.[2b] [$ReBr(CO)_5$], [$MnBr(CO)_5$] and [Mn(bdmpza)$(CO)_3$] were synthesised according to the literature.[2a,9a,9b] Solid phase fixation on mercaptopropyl silica was achieved according to the literature.[5b]

Synthesis of 2,2-Bis(3,5-dimethylpyrazol-1-yl)pent-4-enoic Acid (2): A solution of Hbdmpza (**1**) (3.30 g, 13.3 mmol) in dry THF (200 mL) was treated with LDA (≈ 1.8 M in heptane/THF/ethylbenzene, 23.0 mL, 41.4 mmol) at –80 °C. The solution was warmed up to –40 °C over a period of 2 h and was stirred for 1 h at –40 °C. Allyl bromide (9.00 mL, 12.6 g, 104 mmol) was added, and the mixture was warmed up to ambient temperature. The solution was heated under reflux for 30 min and then stirred overnight. The solvent was removed in vacuo, and the residue was dissolved in water. The aqueous solution was acidified with dilute HCl to pH 7–8 and extracted with pentane (1×100 mL) to remove impurities. The aqueous solution was further acidified to pH 4 and **2** precipitated immediately. The crude mixture was extracted with pentane (4×200 mL) and the combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. Product **2** was recrystallised from pentane in colourless blocks suitable for X-ray structure determination. Yield: 1.68 g (5.82 mmol, 44%). M.p. 84–86 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.71 [d, $J_{H,H}$ = 0.4 Hz (through space), 6 H, C^5-CH_3], 2.27 (s, 6 H, C^3-CH_3), 3.57 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.0 Hz, 2 H, CH_2), 5.09 (ddt, $^3J_{H,H}$ = 16.9 Hz, $^2J_{H,H}$ = 1.6 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, =$CH_{2,allyl}$), 5.10 (ddt, $^3J_{H,H}$ = 10.2 Hz, $^2J_{H,H}$ = 1.6 Hz, $^4J_{H,H}$ = 0.8 Hz, 1 H, =$CH_{2,allyl}$), 5.59 [dddt, $^3J_{H,H}$ = 16.3 Hz, $^3J_{H,H}$ = 10.8 Hz, $^3J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.1 Hz (through space), 1 H, =CH_{allyl}], 5.87 (s, 2 H, H_{pz}) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 10.7 (C^5-CH_3), 13.2 (C^3-CH_3), 44.0 (CH_2), 80.9 (C_{bridge}), 108.7 (C_{pz}-H), 121.2 (=$CH_{2,allyl}$), 129.3 (CH_{allyl}), 141.5 (C^5_{pz}), 146.3 (C^3_{pz}), 168.7 (CO_2H) ppm. IR (THF): $\tilde{\nu}$ = 1729 (CO_2H), 1563 (C=N) cm^{-1}. FAB-MS: *m*/*z* (%) = 311 (18) $[M + Na]^+$, 289 (28) $[M + H]^+$, 193 (28) $[M - pz]^+$, 149 (100) $[M - pz - CO_2H]^+$, 95 (62) $[pz]^+$. $C_{15}H_{20}N_4O_2$ (288.35): calcd. C 62.48, H 6.99, N 19.43; found C 62.46, H 6.81, N 18.91.

Synthesis of 2,2-Bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionic Acid (3): A solution of Hbdmpza (**1**) (3.30 g, 13.3 mmol) in dry THF (200 mL) was treated with LDA (≈ 1.8 M in heptane/THF/ethylbenzene, 23.0 mL, 41.4 mmol) at –80 °C and warmed up to –40 °C over a period of 2 h. After 1 h at –40 °C, paraformaldehyde (4.00 g, 132 mmol) was added. The mixture was warmed up to ambient temperature and finally heated under reflux for 60 min and stirred overnight. The solvent was removed in vacuo, the residue was dissolved in water and washed with pentane (200 mL). The aqueous phase was acidified with dilute HCl (pH 2) and extracted with diethyl ether (4×200 mL). The combined diethyl ether layers were dried (Na_2SO_4) and concentrated under reduced pressure. Product **3** was recrystallised from diethyl ether. Yield: 2.12 g (7.62 mmol, 57%). M.p. 119–121 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.72 (s, 6 H, C^5-CH_3), 2.29 (s, 6 H, C^3-CH_3), 4.43 (s, 2 H, $HOCH_2$) 5.96 (s, 2 H, H_{pz}) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 10.6 (C^5-CH_3), 13.2 (C^3-CH_3), 68.8 (CH_2-OH), 81.5 (C_{bridge}), 108.5 (C_{pz}-H), 143.1 (C^5_{pz}), 148.0 (C^3_{pz}), 168.9 (CO_2H) ppm. IR (KBr): $\tilde{\nu}$ = 1752 (CO_2H), 1561 (C=N) cm^{-1}. FAB-MS: *m*/*z* (%) = 300 (18) $[M + Na]^+$, 217 (100) $[M - CO_2H - OH]^+$, 203 (100) $[M - CO_2H - CH_2OH]^+$. $C_{13}H_{18}N_4O_3$ (278.31): calcd. C 56.10, H 6.52, N 20.13; found C 56.62, H 6.75, N 19.91.

Synthesis of 2,2-Bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionic Acid (4): To a solution of Hbdmpzhp (**3**) (1.00 g, 3.60 mmol) in dichloromethane (100 mL), excess NEt_3 (4.00 mL, 2.92 g,

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28.9 mmol) was added. Acetyl chloride (0.64 mL, 0.71 g, 9.00 mmol) was then added dropwise under continuous stirring. The mixture was stirred for 1 d. Water (20 mL) was added slowly and the two-phased mixture was vigourously stirred for 3 h. The solvents were removed in vacuo. The slurry residue was dissolved in water, acidified with dilute HCl (pH 2) and extracted with diethyl ether (4 × 200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to the oily residue of **4**. Product **4** was recrystallised from acetone in colourless blocks suitable for X-ray structure determination. Yield: 612 mg (2.65 mmol, 53%). M.p. 107–109 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.74 (s, 6 H, C^5-CH_3), 1.97 (s, 3 H, CH_3CO), 2.27 (s, 6 H, C^3-CH_3), 5.32 (s, 2 H, OCO-CH_2-), 5.93 (s, 2 H, H_{pz}) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz, 25 °C): δ = 10.6 (C^5-CH_3), 13.2 (C^3-CH_3), 20.4 (CH_3-CO), 66.6 (CH_2-O), 78.3 (C_{bridge}), 108.8 (C_{pz}-H), 142.0 ($C^5{}_{pz}$), 147.2 ($C^3{}_{pz}$), 167.9 (COOH), 169.4 (CH_3CO) ppm. IR (THF): $\tilde{\nu}$ = 1759 (CO_2H), 1718 (CH_3CO), 1565 (C=N) cm^{-1}. FD-MS: *m*/*z* (%) = 322 (100) [M + H]$^+$, 276 (60) [M + H – CO_2H]$^+$, 234 (28) [M + H – CO_2H – CH_3CO]$^+$. $C_{15}H_{20}N_4O_4$ (320.35): calcd. C 56.24, H 6.29, N 17.49; found C 56.59, H 6.47, N 17.89.

Synthesis of Methyl 2,2-Bis(3,5-dimethylpyrazol-1-yl)acetate (5): To a solution of Hbdmpza (**1**) (1.00 g, 4.03 mmol) in excess methanol (100 mL), conc. H_2SO_4 (0.15 mL, 0.28 g, 2.86 mmol) was added and stirred at ambient temperature for 3 d. The solvent was removed in vacuo and diethyl ether (200 mL) was added to the residue. The organic phase was extracted with a saturated aqueous solution of $NaHCO_3$ and dried with Na_2SO_4. The organic layer was concentrated in vacuo to a yellow crystalline powder of **5**. Recrystallisation from petroleum ether/ethyl acetate (3:1) yielded colourless blocks suitable for X-ray structure determination. Yield: 887 mg (3.38 mmol, 84%). M.p. 117–119 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 2.11 (s, 6 H, C^5-CH_3), 2.19 (s, 6 H, C^3-CH_3), 3.89 (s, 3 H, OCH_3), 5.85 (s, 2 H, H_{pz}), 6.95 (s, 1 H, H_{bridge}) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz, 25 °C): δ = 11.0 (C^5-CH_3), 13.5 (C^3-CH_3), 53.4 (OCH_3), 73.0 (C_{bridge}), 107.6 (C_{pz}-H), 141.3 ($C^5{}_{pz}$), 148.5 ($C^3{}_{pz}$), 165.3 (COOH) ppm. IR (THF): $\tilde{\nu}$ = 1771 (CO_2H), 1561 (C=N) cm^{-1}. FD-MS: *m*/*z* (%) = 263 (100) [M + H]$^+$. $C_{13}H_{18}N_4O_2$ (262.31): calcd. C 59.51, H 6.92, N 21.37; found C 59.88, H 7.20, N 21.11.

Synthesis of Methyl 2,2-Bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionate (6): A solution of Mebdmpza (**5**) (0.75 g, 2.86 mmol) in dry THF (100 mL) was treated with LDA (≈ 1.8 M in heptane/THF/ethylbenzene, 1.8 mL, 3.24 mmol) at –80 °C and warmed up to –40 °C over a period of 2 h. After 1 h at –40 °C, paraformaldehyde (0.90 g, 27.0 mmol) was added. The mixture was warmed up to ambient temperature and finally heated under reflux for 60 min and stirred overnight. The solvent was removed in vacuo, the residue was dissolved in water and extracted with diethyl ether (3 × 150 mL). The combined diethyl ether layers were dried (Na_2SO_4) and concentrated under reduced pressure. Recrystallisation from hexane/acetone (1:1) yielded **6** as colourless blocks. Yield: 0.63 g (2.16 mmol, 76%). M.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.69 (s, 6 H, C^5-CH_3), 2.20 (s, 6 H, C^3-CH_3), 3.98 (s, 3 H, OCH_3), 4.65 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, OCH_2), 5.34 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, OH), 5.86 (s, 2 H, H_{pz}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 11.2 (C^5-CH_3), 13.9 (C^3-CH_3), 53.9 (OCH_3), 66.7 (CH_2-OH), 84.3 (C_{bridge}), 108.8 (C_{pz}-H), 142.5 ($C^5{}_{pz}$), 148.3 ($C^3{}_{pz}$), 166.3 (CO_2R) ppm. IR (THF): $\tilde{\nu}$ = 1762 (CO_2Me), 1562 (C=N) cm^{-1}. FD-MS: *m*/*z* (%) = 292 (100) [M]$^+$, 234 (12) [M + H –CO_2Me]$^+$. $C_{14}H_{20}N_4O_3$ (292.34): calcd. C 57.52, H 6.90, N 19.17; found C 57.85, H 7.05, N 19.59.

Synthesis of [Mn(bdmpzpen)(CO)$_3$] (7): To Hbdmpzpen (**2**) (176 mg, 0.610 mmol) in dry THF (30 mL), KO*t*Bu (68.0 mg, 0.610 mmol) was added, and the reaction mixture stirred at ambient temperature for 30 min. [$MnBr(CO)_5$] (167 mg, 0.610 mmol) was added, and the reaction mixture was heated under reflux and controlled by IR on a regular basis. After 12 h, the reaction was complete, and the solution was filtered. The filtrate was concentrated in vacuo, washed with water (2 × 1 mL) and dried in vacuo. Recrystallisation from $CHCl_3$ yielded yellow crystals suitable for X-ray structure determination. Yield: 119 mg (0.28 mmol, 46%). M.p. 194–198 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 2.53 (br., 12 H, CH_3), 3.83 (br., 2 H, CH_2), 5.04 (br., 1 H, =$CH_{2,allyl}$), 5.25 (br., 1 H, =$CH_{2,allyl}$), ≈ 5.75 (br., partly covered, 1 H, =CH_{allyl}), 5.98 (br., 2 H, H_{pz}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 15.3 (CH_3), 16.2 (CH_3), 35.6 (CH_2), 111.8 (C_{pz}-H), 117.7 (=$CH_{2,allyl}$), 128.0 (CH_{allyl}), 143.3 (C_{pz}), 153.8 (C_{pz}), 220.6 (CO), 222.4 (CO) ppm. IR (THF): $\tilde{\nu}$ = 2033 (s, C=O), 1939 (s, C=O), 1911 (s, C=O), 1687 (m, CO_2^-) cm^{-1}. FAB-MS: *m*/*z* (%) = 427 (70) [M + H]$^+$, 343 (36) [M – 3 CO]$^+$, 299 (100) [M – 3 CO – $CH_2CH=CH_2$]$^+$. $C_{18}H_{19}N_4O_5Mn$ (426.31): calcd. C 50.71, H 4.49, N 13.14; found C 50.77, H 4.60, N 13.08.

Synthesis of [Re(bdmpzpen)(CO)$_3$] (9): To Hbdmpzpen (**2**) (176 mg, 0.610 mmol) in dry THF (30 mL), KO*t*Bu (68.0 mg, 0.610 mmol) was added, and the reaction mixture was stirred at ambient temperature for 30 min. [$ReBr(CO)_5$] (250 mg, 0.610 mmol) was added, and the reaction mixture was heated under reflux and controlled by IR on a regular basis. After 24 h, the reaction was complete, and the solution was filtered. The filtrate was concentrated in vacuo, washed with water (2 × 1 mL) and dried in vacuo. Recrystallisation from acetone yielded colourless crystals suitable for X-ray structure determination. Yield: 139 mg (0.25 mmol, 41%). M.p. 228–230 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 2.53 (s, 6 H, CH_3), 2.57 (s, 6 H, CH_3), 3.97 (br., 2 H, CH_2), 5.27 (dtd, $^3J_{H,H}$ = 16.5 Hz, $^4J_{H,H}$ = 1.8 Hz, $^2J_{H,H}$ = 0.6 Hz, 1 H, =$CH_{2,allyl}$), 5.28 (dtd, $^3J_{H,H}$ = 12.0 Hz, $^4J_{H,H}$ = 1.8 Hz, $^2J_{H,H}$ = 0.6 Hz, 1 H, =$CH_{2,allyl}$), 5.71 (ddt, $^3J_{H,H}$ = 17.7 Hz, $^3J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 4.6 Hz, 1 H, =CH_{allyl}), 6.03 (s, 2 H, H_{pz}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 16.3 (CH_3), 16.4 (CH_3), 36.2 (CH_2), 84.8 (C_{bridge}), 111.7 (C_{pz}-H), 118.3 (=$CH_{2,allyl}$), 132.5 (CH_{allyl}), 143.7 (C_{pz}), 154.4 (C_{pz}), 164.5 (CO_2^-), 195.7 (CO), 196.0 (CO) ppm. IR (THF): $\tilde{\nu}$ = 2023 (s, C=O), 1915 (s, C=O), 1892 (s, C=O), 1697 (m, CO_2^-) cm^{-1}. FAB-MS: *m*/*z* (%) = 559 (100) [M + H]$^+$, 531 (47) [M – CO]$^+$, 473 (97) [M – 3 CO]$^+$, 435 (38) [M – 3 CO – $CH_2CH=CH_2$]$^+$. $C_{18}H_{19}N_4O_5Re$ (557.57): calcd. C 38.77, H 3.43, N 10.05; found C 38.41, H 3.19, N 9.81.

Synthesis of [Mn(bdmpzap)(CO)$_3$] (8): To Hbdmpzap (**4**) (320 mg, 1.00 mmol) in dry THF (50 mL), KO*t*Bu (112 mg, 1.00 mmol) was added, and the reaction mixture was stirred at ambient temperature for 30 min. [$MnBr(CO)_5$] (275 mg, 1.00 mmol) was added, and the reaction mixture was heated under reflux and controlled by IR on a regular basis. After 12 h the reaction was complete, and the solution was filtered. The filtrate was concentrated in vacuo, washed with water (2 × 2 mL) and dried in vacuo. Recrystallisation from CH_2Cl_2 yielded yellow crystals suitable for X-ray structure determination. Yield: 340 mg (0.74 mmol, 74%). M.p. 174–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.05 (s, 3 H, CH_3CO), 2.42 (s, 6 H, CH_3), 2.51 (br., 6 H, CH_3), 5.04, 5.67 (AB system, br. coupling not resolved, 2 H, CH_2O), 5.95 (br., 2 H, H_{pz}) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 15.0 (CH_3), 15.3 (CH_3), 20.7 (CH_3), 61.0 (CH_2O), 81.4 (C_{bridge}), 111.9 (C_{pz}-H), 143.2 (C_{pz}), 154.0 (C_{pz}), 165.2 (CO_2), 169.6 (O_2CCH_3), 220.0 (2 × CO), 222.3 (CO) ppm. IR (THF): $\tilde{\nu}$ = 2034 (s, C=O), 1940 (s, C=O), 1913 (s, C=O), 1761 (m, CH_3CO), 1692 (m, CO_2^-) cm^{-1}. FD-MS: *m*/*z* (%) = 458 (100) [M]$^+$, 416 (18) [M + H – CH_3CO]$^+$. $C_{18}H_{19}N_4O_7Mn$

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(458.31): calcd. C 47.16, H 4.18, N 12.23; no suitable elemental analysis was obtained.

Synthesis of [Re(bdmpzap)(CO)$_3$] (10): To Hbdmpzap (**4**) (247 mg, 0.77 mmol) in dry THF (50 mL), KO*t*Bu (86 mg, 0.77 mmol) was added, and the reaction mixture was stirred at ambient temperature for 30 min. [ReBr(CO)$_5$] (313 mg, 0.77 mmol) was added, and the reaction mixture was heated under reflux and controlled by IR on a regular basis. After 20 h, the reaction was complete, and the solution was filtered. The filtrate was concentrated in vacuo, washed with water (2 × 2 mL) and diethyl ether (2 × 2 mL) and dried in vacuo. Yield: 305 mg (0.52 mmol, 52%). M.p. 233–236 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.05 (s, 3 H, CH_3CO), 2.46 (s, 12 H, CH_3), 5.11, 5.73 (AB system, J_{AB} = 9.6 Hz, 2 H, CH_2O), 5.98 (br., 1 H, H_{pz}), 6.03 (br., 1 H, H_{pz}) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 15.3 (CH_3), 16.4 (CH_3), 20.8 (CH_3), 61.6 (CH_2O), 82.9 (C_{bridge}), 111.8 (C_{pz}-H), 143.2 (C_{pz}), 154.5 (C_{pz}), 163.5 (CO_2), 169.5 (O_2CCH_3), 195.5 (2 × CO), 195.5 (CO) ppm. IR (THF): $\tilde{\nu}$ = 2024 (s, C=O), 1918 (s, C=O), 1894 (s, C=O), 1762 (m, O_2CCH_3), 1702 (m, CO_2^-) cm^{-1}. FD-MS: *m*/*z* (%) = 591 (100) $[M + H]^+$. $C_{18}H_{19}N_4O_7Re$ (589.58): calcd. C 36.67, H 3.25, N 9.50; found C 37.12, H 3.34, N 9.14.

Solid Phase Fixation of Methyl 2,2-Bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionate (P-6): A suspension of a chloromethylated resin [0.45 g, loading 1.1 mmol g^{-1}, 0.50 equiv.], Mebdmpzhp (**6**) (439 mg, 1.5 mmol), KO*t*Bu (112 mg, 1.0 mmol), 18-crown-6 (264 mg, 1.0 mmol) and CsBr (212 mg, 1.0 mmol) in dry THF was heated under reflux for 48 h under a nitrogen atmosphere. The suspension was filtered through a sintered glass filter with suction and washed thoroughly with THF, methanol and water and the remaining polymer was dried in vacuo. The content of ligand on the polymer is determined by elemental analysis to 0.23 mmol g^{-1}.

Ester Hydrolysis of Methyl 2,2-Bis(3,5-dimethylpyrazol-1-yl)-3-hydroxypropionate on Solid Phase – Polymer P-3: To a suspension of **P-6** (0.45 g) and NaOH (40 mg, 1.0 mmol) in THF (50 mL), excess water (1 mL, 1 g, 55.5 mmol) was added, and the suspension was heated under reflux for 12 h. The suspension was filtered through a sintered glass filter with suction and washed thoroughly with THF, water and again THF and the remaining polymer **P-3** with the deprotonated and solid phase bound ligand **3** was dried in vacuo.

Polymer Bound Rhenium Tricarbonyl Complexes: A suspension of polymer **P-3** (90 mg) in THF and [Re(CO)$_5$Br] (0.25 mmol, 102 mg) was heated under reflux for 48 h, filtered through a sintered glass filter with suction and washed thoroughly with THF, water, methanol and dichloromethane. IR (THF): $\tilde{\nu}$ = 2022 (CO), 1915 (CO), 1890 (CO) cm^{-1}.

Solid Phase Fixation of 2,2-Bis(3,5-dimethylpyrazol-1-yl)pent-4-enoic Acid (S-2): A suspension of mercaptopropyl silica [0.5 g, loading 0.98 mmol g^{-1}, 0.49 equiv.], Hbdmpzpen (**2**) (141 mg, 0.49 mmol) and azobisisobutyronitrile (10 mg, 0.06 mmol) in dry chloroform was heated at reflux for 48 h under a nitrogen atmosphere. The suspension was filtered through a sintered glass filter with suction and washed thoroughly with dichloromethane, toluene and methanol and the remaining silica was dried in vacuo. The procedure was repeated once. The content of ligand on the silica is determined by elemental analysis to 0.17 mmol g^{-1}.

Silica Bound Manganese Tricarbonyl Complexes: A suspension of mercaptopropyl silica [0.20 g, loading 0.98 mmol g^{-1}, 0.20 equiv.],

Table 2. Details of the structure determination for **2**, **3**, **4**, **7** and **8**.

	2	**3**	**4**	**7**	**8**
Empirical formula	$C_{15}H_{20}N_4O_2$	$C_{13}H_{18}N_4O_3$	$C_{15}H_{20}N_4O_4$	$C_{18}H_{19}MnN_4O_5$	$C_{18}H_{19}MnN_4O_7$
Formula mass	288.35	278.31	320.35	426.31	458.31
Crystal colour/habit	colourless block	colourless block	colourless block	yellow block	yellow block
Crystal system	triclinic	monoclinic	orthorhombic	orthorhombic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	*Pbca*	$P\bar{1}$
a [Å]	8.369(5)	12.167(5)	8.6376(17)	12.924(7)	6.8735(12)
b [Å]	9.351(6)	8.099(3)	10.996(2)	14.337(5)	11.4738(18)
c [Å]	10.774(6)	15.854(7)	16.882(3)	20.167(8)	13.423(2)
α [°]	86.45(6)	90.00	90.00	90.00	104.165(12)
β [°]	88.14(4)	108.41(4)	90.00	90.00	103.862(13)
γ [°]	67.44(4)	90.00	90.00	90.00	100.881(13)
V [Å^3]	777.1(8)	1482.2(10)	1603.4(6)	3737(3)	961.5(3)
θ [°]	2.64–27.00	2.71–26.99	3.37–29.29	2.02–26.99	3.45–25.56
H	–3 to 10	–15 to 0	–11 to 11	–16 to 16	–8 to 8
K	–9 to 11	–10 to 0	–15 to 15	–18 to 0	–13 to 13
L	–13 to 13	–19 to 19	–23 to 23	–13 to 25	–16 to 16
F(000)	308	592	680	1760	472
Z	2	4	4	8	2
μ (Mo-K_α) [mm^{-1}]	0.085	0.091	0.098	0.745	0.737
Crystal size [mm]	0.5 × 0.5 × 0.5	0.5 × 0.4 × 0.3	0.2 × 0.15 × 0.1	0.5 × 0.4 × 0.3	0.4 × 0.23 × 0.1
$D_{calcd.}$ [g cm^{-3}], *T* [K]	1.232, 188(2)	1.247, 188(2)	1.327, 100(2)	1.516, 188(2)	1.583, 100(2)
Reflections collected	3539	3380	30272	4382	11953
Indep. reflections	3342	3219	2467	4077	3585
Obsd. refl. (>2σI)	2878	1930	2146	2488	2554
Parameter	194	187	211	253	271
Weight parameter *a*	0.0583	0.0768	0.0434	0.0417	0.0354
Weight parameter *b*	0.2387	0.3199	0.6164	2.1574	0.0096
R_1 (obsd.)	0.0425	0.0632	0.0486	0.0570	0.0590
R_1 (overall)	0.0494	0.1172	0.0612	0.1161	0.0990
wR_2 (obsd.)	0.1112	0.1404	0.0975	0.1045	0.0908
wR_2 (overall)	0.1174	0.1674	0.1016	0.1253	0.0996
Diff. peak/hole [e/Å^3]	0.309/–0.225	0.285/–0.328	0.235/–0.265	0.371/–0.454	0.377/–0.406

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[Mn(bdmpzpen)$(CO)_3$] (**2**) (85 mg, 0.20 mmol) and azobisisobutyronitrile (10 mg, 0.06 mmol) in dry chloroform was heated at reflux for 8 h under a nitrogen atmosphere. The suspension was filtered through a sintered glass filter with suction and washed thoroughly with dichloromethane, THF, toluene and methanol and the remaining yellow silica was dried in vacuo. The content of ligand on the silica is determined by elemental analysis to 0.036 mmol g^{-1}. A longer reaction time of 48 h leads to a content of 0.063 mmol g^{-1}. IR (nujol): $\tilde{\nu}$ = 2039 (CO), 1948 (CO), 1923 (CO) cm^{-1}.

Silica Bound Rhenium Tricarbonyl Complexes: A suspension of mercaptopropyl silica [0.20 g, loading 0.98 mmol g^{-1}, 0.20 equiv.], [Re(bdmpzpen)$(CO)_3$] (**9**) (112 mg, 0.20 mmol) and azobisisobutyronitrile (10 mg, 0.06 mmol) in dry chloroform was heated under reflux for 8 h under a nitrogen atmosphere. The suspension was filtered through a sintered glass filter with suction and washed thoroughly with dichloromethane, THF, toluene and methanol and the remaining silica was dried in vacuo. The content of ligand on the silica is determined by elemental analysis to 0.041 mmol g^{-1}. A longer reaction time of 48 h leads to a content of 0.078 mmol g^{-1}. IR (nujol): $\tilde{\nu}$ = 2027 (CO), 1920 (CO), 1905 (CO) cm^{-1}.

X-ray Structure Determinations: Single crystals of **2**, **3**, **4**, **7** and **8** were mounted with Paratone-N or glue on a glass fibre. A modified Siemens P4-Diffractometer and a STOE IPDS II diffractometer were used for data collection (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by using direct methods and refined with full-matrix least-squares against F^2 {Siemens SHELX-97}.[10] A weighting scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \max(F_o^2,0)]/3$. Most hydrogen atoms were included in their calculated positions and refined in a riding model. The protons of carboxylic acids (**2**–**4**) were found and their 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.[11] CCDC-232648 (for **2**), CCDC-289443 (for **3**), CCDC-619381 (for **4**), CCDC-289442 (for **7**) and CCDC-619380 (for **8**) 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.

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[1] a) 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; b) 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; c) 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; d) 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.

[2] a) N. Burzlaff, I. Hegelmann, B. Weibert, *J. Organomet. Chem.* **2001**, *626*, 16–23; b) A. Beck, B. Weibert, N. Burzlaff, *Eur. J. Inorg. Chem.* **2001**, 521–527; c) N. Burzlaff, I. Hegelmann, *Inorg. Chim. Acta* **2002**, *329*, 147–150; d) A. López-Hernández, R. Müller, H. Kopf, N. Burzlaff, *Eur. J. Inorg. Chem.* **2002**, 671–677; e) I. Hegelmann, A. Beck, C. Eichhorn, B. Weibert, N. Burzlaff, *Eur. J. Inorg. Chem.* **2003**, 339–347; f) A. Beck, A. Barth, E. Hübner, N. Burzlaff, *Inorg. Chem.* **2003**, *42*, 7182–7188; g) R. Müller, E. Hübner, N. Burzlaff, *Eur. J. Inorg. Chem.* **2004**, 2151–2159; h) I. Hegelmann, N. Burzlaff, *Eur. J. Inorg. Chem.* **2003**, 409–411; i) L. Peters, N. Burzlaff, *Polyhedron* **2004**, *23*, 245–251.

[3] For recent reviews, see: a) M. Tada, Y. Iwasawa, *Chem. Commun.* **2006**, 2833–2844; b) B. M. L. Dioos, I. F. J. Vankelecom, P. A. Jacobs, *Adv. Synth. Catal.* **2006**, *348*, 1413–1446.

[4] R. A. Findeis, L. H. Gade, *Dalton Trans.* **2003**, 249–254.

[5] a) J. M. Fraile, J. I. García, J. A. Mayoral, A. J. Royo, *Tetrahedron: Asymmetry* **1996**, *7*, 2263–2276; b) 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.

[6] D. L. Reger, T. C. Grattan, *Synthesis* **2003**, 350–356.

[7] D. Appleton, A. B. Duguid, S.-K. Lee, Y.-J. Ha, H.-J. Ha, F. J. Leeper, *J. Chem. Soc., Perkin Trans. 1* **1998**, *1*, 89–101.

[8] W. Kläui, M. Berghahn, W. Frank, G. J. Reiß, T. Schönherr, G. Rheinwald, H. Lang, *Eur. J. Inorg. Chem.* **2003**, 2059–2070.

[9] a) D. Vitali, F. Calderazzo, *Gazz. Chim. Ital.* **1972**, *102*, 586–596; b) E. W. Abel, G. Wilkinson, *J. Chem. Soc.* **1959**, 1501–1505.

[10] G. M. Sheldrick, SHELX-97, Program for Crystal Structure Analysis, University of Göttingen, Göttingen, Germany, **1997**.

[11] 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.

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