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Bis(pyrazol-1-yl)acetates as tripodal "scorpionate" ligands in transition metal carbonyl chemistry: syntheses, structures and reactivity of manganese and rhenium carbonyl complexes of the type $[LM(CO)_3]$ (L = bpza, bdmpza)

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Abstract

The coordination of the ligands bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) and bis(pyrazol-1-yl)acetate (bpza) to Group VII metal carbonyls has been investigated. The compounds $[LM(CO)_3]$, where M = Mn, Re and L = bpza, bdmpza (**2a**–**3b**), have been synthesised. The new complexes $[(bdmpza)Mn(CO)_3]$ (**2b**), $[(bpza)Re(CO)_3]$ (**3a**) and $[(bdmpza)Re(CO)_3]$ (**3b**), and bis(pyrazol-1-yl)acetic acid (**1a**) have been characterised by single-crystal X-ray analyses. Based on IR-spectroscopic and structural data the electronic properties of these ligands are compared with those of Tp, Tp^{Me_2}, Cp and Cp*. The reaction of $[(bdmpza)Re(CO)_3]$ (**3b**) with $NOBF_4$ afforded $[(bdmpza)Re(CO)_2(NO)]BF_4$ (**4**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Rhenium; Carbonyl; Bis(pyrazol-1-yl)acetate; Scorpionate ligands

1. Introduction

Tris(pyrazol-1-yl)borate, $[(HB(pz)_3)]^-$ (Tp), first introduced by S. Trofimenko more than 30 years ago, now represents a ligand that is widely used in transition metal carbonyl chemistry [1–4]. So Tp and its variations are often taken as an equivalent to C_5H_5 (Cp) or C_5Me_5 (Cp*). One of the most widely used Tp variations is the easily accessible tris(3,5-dimethylpyrazol-1-yl)borate (Tp^{Me_2}).

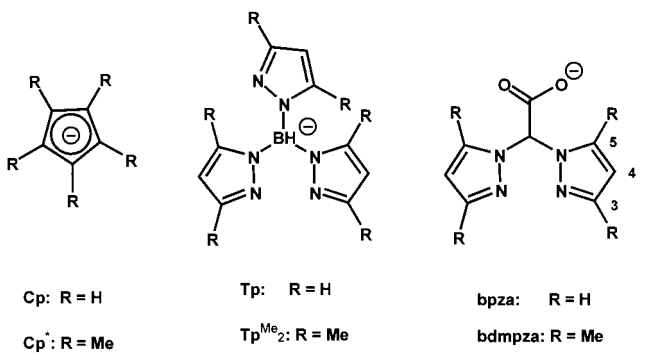

Fig. 1. The ligands Cp, Cp*, Tp, Tp^{Me_2}, bpza and bdmpza.

Recent investigations with Tp and Tp^{Me_2} focused on the electron donating properties of these two ligands. It was found that their electron donating ability varies with the coordinating metal and its oxidation state [5]. For all Group VII metal carbonyl complexes of the type $[LM(CO)_3]$ (L = Cp*,Cp,Tp,Tp^{Me_2}) structural and infrared data are available from the literature [5–21]. Based on this data Bergman and co-workers recently surmised the following trend in the donor capabilities of these ligands towards manganese: Cp* ~ Tp^{Me_2} > Cp ~ Tp. For rhenium they suggested Cp* > Tp^{Me_2} > Tp > Cp [5].

Because of the enormous steric hindrance of Tp ligands — for Tp complexes a Tolman angle close to 180° was observed [22] — it is rather difficult in transition metal carbonyl complexes with tripodal bound Tp to exchange more than one carbonyl ligand by bulky substituents [6]. The steric hindrance can be

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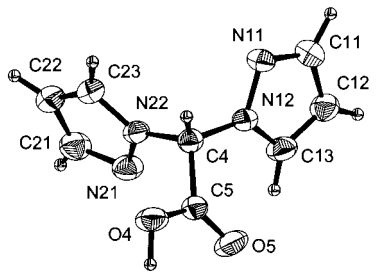


Fig. 2. Molecular structure of the bis(pyrazol-1-yl)acetic acid (**1a**).

Table 1
Selected bond distances and bond angles of bis(pyrazol-1-yl)acetic acid (**1a**)

Bond distance (Å)	**1a**	Bond angle (°)	**1a**
C(4)–C(5)	1.554(3)	O(4)–C(5)–O(5)	125.4(2)
C(5)–O(4)	1.318(3)	C(5)–C(4)–N(12)	112.8(2)
C(5)–O(5)	1.215(3)	C(5)–C(4)–N(22)	109.2(2)
C(4)–N(12)	1.468(3)	N(12)–C(4)–N(22)	111.8(2)
C(4)–N(22)	1.467(3)		

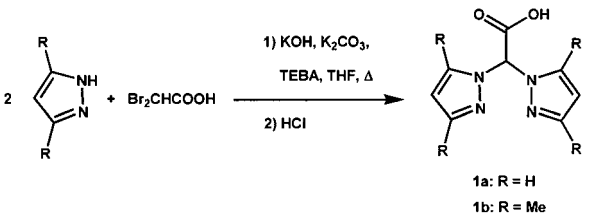
reduced by replacing one pyrazole by a less bulky donor group. Furthermore, a pyrazolyl group is a good and relatively hard σ donor while a moderate acceptor. These properties cause some Tp carbonyl complexes to be more stable than their Cp or Cp* analogues [23]. So one weaker donor group in the tripod ligand might also modify the reactivity of these complexes.

In our aim to find suitable tripod *N,N,O* ligands as mimics for the active sites of iron and zinc enzymes we were interested in the new Tp-like ligand bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) (Fig. 1), recently introduced by Otero et al. [24,25] on niob complexes such as $[NbCl_2(bdmpza)(PhCCMe)]$ and their structures.

As an alternative to the multi-step synthesis published there, we recently developed a simple route to bis(3,5-dimethylpyrazol-1-yl)acetic acid starting from purchasable reagents [26]. Here we report on: (a) a one-step synthesis of bis(pyrazol-1-yl)acetic acid; (b) the application of its anion bpza as a new tripod ligand not accessible by the synthetic route of Otero et al.; and (c) the syntheses of new pseudotetrahedral tricarbonyl complexes of manganese and rhenium with bpza or bdmpza as tripod ligands.

2. Results and discussion

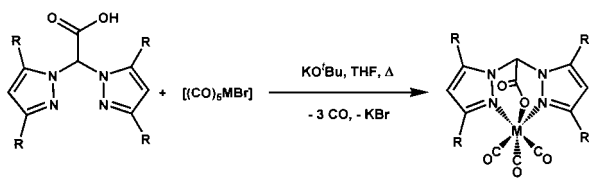
As reported earlier bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1b**) and its acetate bdmpza can be synthesised by a phase transfer catalysed reaction of 3,5-dimethylpyrazole with base and dibromoacetic acid in 45% yield. This synthetic route can also be used to obtain bis(pyrazol-1-yl)acetic acid (**1a**) in even higher yield (Eq. 1). Although a reaction of bis(pyrazol-1-yl)acetic acid with biotin hydrazide was reported for radiopharmaceutical studies recently [27], no synthetic route or analytical data for **1a** was available from the literature until now.



(1)

This new, sterically less hindered *N,N,O* tripod ligand **1a** is not accessible via deprotonation of bis(pyrazol-1-yl)methane and subsequent addition of carbon dioxide, similar to the literature method for bdmpza reported by Otero et al. [24,25], due to deprotonation of the pyrazolyl group in positions 3 and 5. Suitable crystals for X-ray structure determination were obtained from an acetonitrile solution (Fig. 2). Selected distances and angles are given in Table 1. The structure of **1a** deviates only slightly from that of bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid [26]. The differences are caused by the less bulky pyrazolyl groups.

Usually the pentacarbonyl complexes $[BrMn(CO)_5]$ and $[BrRe(CO)_5]$ are the starting materials to synthesise tris(pyrazol-1-yl)borate complexes of manganese and rhenium [9]. Using these substrates we were able to obtain bis(3,5-dimethylpyrazol-1-yl)acetate and bis(pyrazol-1-yl)acetate tricarbonyl complexes of these metals in a reaction with potassium carboxylates of bpza and bdmpza (Eq. 2). These carboxylates were produced in situ from the acids and potassium *tert*-butylate. The reactions were monitored by IR spectroscopy. During the reactions CO evolution was observed. KBr and *tert*-butanol were removed from the products by washing with degassed water.



(2)

	Mn	Re
R = H	2a	3a
R = Me	2b	3b

The tricarbonyl complexes **2a**–**3b** are rather stable and can be stored as solids for days in air. The complexes are soluble in THF, **2b** and **3b** in dichloromethane and acetone as well due to the 3,5-dimethylpyrazole groups. Crystals suitable for X-ray determination of $[(bdmpza)Mn(CO)_3]$ (**2b**),

[(bpza)Re(CO)$_3$] (**3a**) and [(bdmpza)Re(CO)$_3$] (**3b**) could be obtained (Figs. 3–5). Selected distances and angles are summarised in Tables 2 and 3.

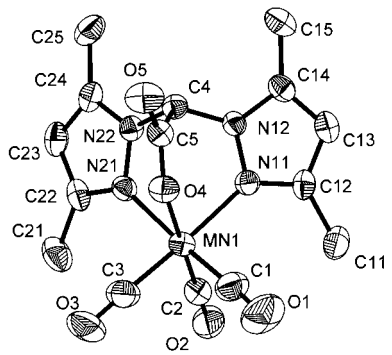


Fig. 3. Molecular structure of [(bdmpza)Mn(CO)$_3$] (**2b**).

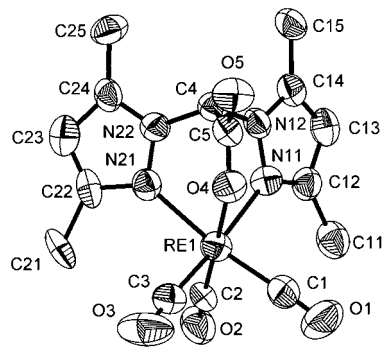


Fig. 4. Molecular structure of [(bdmpza)Re(CO)$_3$] (**3b**).

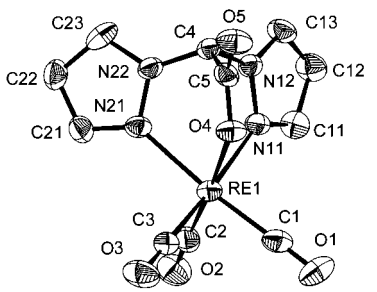


Fig. 5. Molecular structure of [(bpza)Re(CO)$_3$] (**3a**).

Table 2
Selected bond distances of the complexes **2b**, **3a** and **3b**

Bond distance (Å)	**2b**	**3a**	**3b**
M–N(11)	2.079(3)	2.216(6)	2.214(10)
M–N(21)	2.093(3)	2.211(6)	2.200(10)
M–O(4)	2.055(2)	2.184(5)	2.164(8)
M–C(1)	1.819(4)	1.952(9)	1.956(14)
M–C(2)	1.804(4)	1.930(10)	1.943(12)
M–C(3)	1.816(4)	1.947(8)	1.973(13)
O(5)–C(5)	1.242(4)	1.230(9)	1.251(14)
O(4)–C(5)	1.273(4)	1.295(8)	1.293(14)
C(4)–C(5)	1.558(4)	1.570(10)	1.579(15)

Table 3
Selected bond angles of the complexes **2b**, **3a** and **3b**

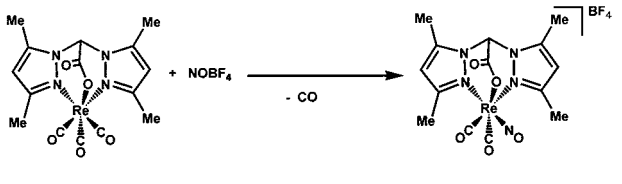
Bond angle (°)	**2b**	**3a**	**3b**
N(11)–M–N(21)	85.98(10)	81.8(2)	80.9(4)
O(4)–M–N(11)	85.44(9)	81.4(2)	82.1(3)
O(4)–M–N(21)	84.83(9)	80.4(2)	81.0(3)
O(4)–M–C(2)	179.52(14)	176.3(3)	177.2(4)
N(11)–M–C(3)	175.82(15)	174.1(3)	174.3(4)
N(21)–M–C(1)	174.19(15)	174.4(3)	171.7(5)
C(1)–M–C(2)	90.8(2)	88.7(3)	90.4(6)
C(1)–M–C(3)	87.7(2)	87.8(3)	87.8(5)
C(2)–M–C(3)	90.0(2)	88.4(3)	89.3(5)

The distances in the bpza and bdmpza ligands as well as those of the carbonyl groups are in all structures (**2b**,**3a**,**3b**) similar to those reported in literature for the Tp or Tp^{Me_2} homologous [TpM(CO)$_3$] and [Tp^{Me_2}M(CO)$_3$] [9]. Due to the clamp of the tripod ligand the angles N–M–N and N–M–O differ 4–5° from the 90° octahedral angle. The sterically demanding pyrazolyl groups force two of the carbonyl groups to close up 2°. The third carbonyl group forms a nearly perfect 180° angle to the carboxylate donor. This emphasises the much smaller steric hindrance of bdmpza compared to Tp^{Me_2}. Of the three metal–carbonyl distances M–C(2) is the shortest in all three structures. This is due to the *trans* influence of the two pyrazolyl π acceptor groups onto the other two metal–carbonyl bonds. Most striking is the fact that in **2b**, **3a** and **3b** all three metal–carbonyl distances are significantly longer than those of their Tp^{Me_2}, Cp* and even Cp analogues (see Table 4). This implies that bdmpza and bpza are less electron donating than even the Cp ligand.

The two pyrazolyl groups in **2a**–**3b** are spectroscopically equivalent, showing only one set of signals in the NMR spectra. The ^{1}H-NMR signals of the manganese complexes **2a** and **2b** are broad. The IR spectra of **2a**–**3b** are similar to those of "piano stool" type complexes. Two strong signals A$_1$ and E are observed, of which E in THF is split into two absorptions. In a KBr matrix these signals are in some cases split again. Due to a smaller reduced mass of the metal the manganese CO signals are found at slightly higher wavenumbers compared with those of the rhenium compounds.

The bpza and bdmpza carboxylate groups are weaker σ donors compared with the pyrazolyl groups. Therefore, the IR spectra show CO vibrations that are at higher wavenumbers by 4–15 cm^{-1} than those of the corresponding complexes [TpM(CO)$_3$] and [Tp^{Me_2}M(CO)$_3$] (Table 5). Also, the comparison with the CO absorptions of the Cp and Cp* analogues indicates that bpza and bdmpza are slightly less electron donating ligands, although the differences are only minor and some of the data vary through different publications.

To verify these conclusions the reactivity of [(bdmpza)Re(CO)$_3$] (**3b**), which should be quite close to that of [CpRe(CO)$_3$], was checked in the first reaction. The chemical behaviour of [(bdmpza)Re(CO)$_3$] (**3b**) towards nitrosyltetrafluoroborate is similar to that of [CpRe(CO)$_3$] [29]: **3b** reacts with $NOBF_4$ to form the complex [(bdmpza)Re(CO)$_2$(NO)]BF_4 (**4**) (Eq. 3).



3b 4 (3)

In addition to the IR spectra and the structural data this reactivity clearly shows the very similar electronic properties of **3b** compared with [CpRe(CO)$_3$].

The IR spectra of **4** show a broad NO vibration at 1712 cm^{-1}. Two sets of signals are detected for the pyrazolyl groups in the ^{1}H- and ^{13}C-NMR spectra. This clearly indicates a transposition of the NO group to one of the good pyrazolyl σ donors. **4** is a racemic mixture of two enantiomers.

3. Conclusions

Bis(pyrazol-1-yl)acetic acid (**1a**) and bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1b**) can be obtained in a simple one-step synthesis from dibromoacetic acid. The reaction of the Group VII metal carbonyls [BrMn(CO)$_5$] and [BrMn(CO)$_5$] with bis(pyrazol-1-yl)acetate (bpza) and bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) has been shown to yield the products [(bpza)Mn(CO)$_3$] (**2a**), [(bdmpza)Mn(CO)$_3$] (**2b**), [(bpza)Re(CO)$_3$] (**3a**) and [(bdmpza)Re(CO)$_3$] (**3b**). From the IR-spectroscopic data of these complexes and the single-crystal X-ray analyses of **2b**–**3b** it follows that for Group VII metal carbonyls bpza and bdmpza are less electron donating than Tp, Tp^{Me_2}, Cp* and even Cp. In the case of [(bdmpza)Re(CO)$_3$] (**3b**) a CO–NO$^+$ exchange yielded [(bdmpza)Re(CO)$_2$(NO)]BF_4 (**4**), showing a reactivity similar to [CpRe(CO)$_3$]. In future bpza and bdmpza might be as useful in coordination and organometallic chemistry as Tp and its analogues.

4. Experimental

4.1. General

All experiments involving metal carbonyls were carried out in Schlenk tubes under an atmosphere of argon and using suitable purified solvents, although these precautions might not be necessary. Micro-crystalline precipitates were separated by centrifugation with a Hettich Rotina 46 R Schlenk tube centrifuge. IR: Biorad FTS 60 and Perkin–Elmer FT 2000, CaF_2 cuvets

Table 4
Metal–carbonyl distances of the complexes [LM(CO)$_3$] (M = Mn, Re; L = Cp*, Tp^{Me_2}, Cp, B(Pz)$_4^-$, bpza, bdmpza)

Ligand	Cp* [17,18]	Tp^{Me_2} [9]	Cp [15,16]	B(Pz)$_4^-$ [a] [21]	bpza	bdmpza
d(Mn–CO)	1.738(9)	1.798(6)	1.7947(25)	1.802(5)	–	1.819(4)
	1.712(13)	1.782(7)	1.7876(25)	1.806(4)	–	1.804(4) [b]
		1.794(6)	1.797(3)	1.820(5)	–	1.816(4)
d(Re–CO)	1.875(10)	1.904(9)	1.899(7)	–	1.952(9)	1.956(14)
	1.908(10)	1.899(10)	1.888(7)	–	1.930(10) [b]	1.943(12) [b]
	1.891(10)	1.904(10)	1.894(8)	–	1.947(8)	1.973(12)

[a] Due to isotropic refinement of the carbon atoms, the structural data of [TpMn(CO)$_3$] and [TpRe(CO)$_3$] are less accurate [9] and were left out.
[b] Distance *d*(M–CO) *trans* to the carboxylate donor.

Table 5
Selected IR signals (cm^{-1}) of [LMn(CO)$_3$] and [LRe(CO)$_3$]

Ligand L	bpza	bdmpza	Tp	Tp^{Me_2}	η^5-C$_5$H$_5$	η^5-C$_5$Me$_5$
v(CO) (THF) [LMn(CO)$_3$]	2041, 1946, 1925	2036, 1942, 1915	2033, 1930 [28]	2026, 1919 [28]	2026, 1938	2017, 1928 (hexane) [7]
v(CO) (KBr) [LMn(CO)$_3$]	2039, 1952, 1943, 1927, 1916	2036, 1924	2026, 1932, 1915 [9]	2023, 1912 [9]	–	–
v(CO) (THF) [LRe(CO)$_3$]	2029, 1924, 1904	2025, 1918, 1896	2024, 1914 [8]	–	2021, 1926 [5]	2008, 1912 [5]
v(CO) (KBr) [LRe(CO)$_3$]	2028, 1922, 1906, 1895	2023, 1915, 1903, 1883	2020, 1896 [9]	2017, 1893 [9]	2019, 1897 [5]	2000, 1908 [19]

(0.5 ml) or KBr matrix. ^{1}H-NMR and ^{13}C-NMR: Bruker WM 250, Bruker AC 250, JEOL GX 400, δ values relative to TMS; in some cases the ^{13}C-NMR signals of quaternary carbon atoms were too weak to be detected. EIMS and FABMS: modified Finnigan MAT 312. Elemental analyses: Analytical Laboratory of the Fachbereich Chemie. A modified Siemens P4 diffractometer was used for X-ray structure determinations.

Bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1b**) was synthesised from 3,5-dimethylpyrazole as reported recently [26]. 3,5-Dimethylpyrazole, pyrazole, dibromoacetic acid, nitrosotetrafluoroborate and metal decacarbonyls were used as purchased. [$BrMn(CO)_5$] and [$BrRe(CO)_5$] were obtained according to the standard literature method, from the decacarbonyls [30,31].

4.2. Ligand synthesis: synthesis of bis(pyrazol-1-yl)acetic acid (*1a*)

Dibromoacetic acid (8.71 g, 40.00 mmol), pyrazole (5.45 g, 80.00 mmol), KOH (8.70 g, 155.5 mmol), K_2CO_3 (20.90 g, 151.22 mmol) and benzyltriethylammonium chloride (1.00 g) serving as phase transfer catalyst were dissolved in tetrahydrofurane (200 ml) and heated under reflux for 5–6 h. The solvent was removed in vacuo and the residue dissolved in water (150 ml) and acidified to a pH value of 7 with half-concentrated HCl. To remove excess pyrazole, the solution was extracted with diethyl ether (2 × 150 ml). The water phase was acidified further to a pH value of 1–2 and extracted again with diethyl ether (6 × 150 ml). To improve the extraction of the water-soluble bis(pyrazol-1-yl)acetic acid (**1a**) tetrahydrofurane can be added. The organic layer was dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was re-crystallised from acetone, yielding **1a** as a colourless micro-crystalline powder and dried in vacuo over Sicapent®. For further purification bis(pyrazol-1-yl)acetic acid (**1a**) was re-crystallised from acetonitrile to obtain **1a** as colourless prisms.

Yield 4.64 g (24.14 mmol, 60%); m.p. 166°C (dec.). ^{1}H-NMR (CH_3CN-d_3, 250 MHz): $\delta = 6.35$ (dd, 2H, $^3J_{H-H} = 1.9$ Hz, $^3J_{H-H} = 1.6$ Hz, H_{pz}), 7.27 (s, 1H, CH), 7.57 (d, 2H, $^3J_{H-H} = 1.3$ Hz, H_{pz}), 7.84 (d, 2H, $^3J_{H-H} = 2.0$ Hz, H_{pz}) — ^{13}C-NMR (CH_3CN-d_3, 62.5 MHz): $\delta = 74.7$ (CH), 107.8 (C_{pz}), 131.5 (C_{pz}), 141.4 (C_{pz}), 165.9 (CO_2H) — EIMS (70 eV, 150°C): m/z (%) = 192 (5) [M^+], 147 (44) [$M^+ - CO_2H$], 125 (9) [$M^+ - C_3H_3N_2$], 81 (100) [$M^+ - CO_2 - C_3H_3N_2$] — IR (THF): νmax (cm^{-1}) = 1761 s, 1517 w — Anal. Found: C, 49.85; H, 4.19; N, 29.28. Calc. for $C_8H_8N_4O_2$ (192.18): Calc. C, 50.00; H, 4.20; N, 29.15%.

4.3. General procedure for the syntheses of the tricarbonyl complexes [$LM(CO)_3$] (*2a-3b*)

Equivalent amounts of the bis(pyrazol-1-yl)acetic acid (**1a**) or bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1b**) and potassium *tert*-butylate were dissolved in tetrahydrofurane and stirred at ambient temperature for 30 min. One equivalent of bromopentacarbonyl manganese or rhenium complex was added to the white suspension and the reaction mixture was heated under reflux. CO evolution was observed. The reaction was followed by IR spectroscopy. Finally the solvent was removed in vacuo, the residue was washed with degassed water to remove salts and *tert*-butanol, and dried in vacuo.

4.3.1. Synthesis of [(bpza)$Mn(CO)_3$] (*2a*)

The reaction of 192 mg (1.00 mmol) bis(pyrazol-1-yl)acetic acid (**1a**) with 112 mg (1.00 mmol) *tert*-butylate and 275 mg (1.00 mmol) [$BrMn(CO)_5$] in THF (50 ml) yielded [(bpza)$Mn(CO)_3$] (**2a**) as a yellow powder.

Yield 190 mg (0.58 mmol, 58%); m.p. 216–220°C (dec.). ^{1}H-NMR (DMSO-d_6, 250 MHz): $\delta = 6.58$ (s, 2H, H_{pz}), 7.29 (s, 1H, CH), 8.38 (s, 4H, H_{pz}) — ^{13}C-NMR (DMSO-d_6, 62.5 MHz): $\delta = 70.4$ (CH), 107.1 (C_{pz}), 133.1 (C_{pz}), 144.7 (C_{pz}), 219.1 (CO), 220.9 (CO) — EIMS (70 eV, 270°C): m/z (%) = 330 (1) [M^+], 274 (10) [$M^+ - 2$ CO], 246 (15) [$M^+ - 3$ CO], 202 (60) [$M^+ - CO_2 - 3$ CO] — IR (THF): νmax (cm^{-1}) = 2041 s, 1946 s, 1925 s, 1679 m, 1636 m, 1516 w — IR (KBr): νmax (cm^{-1}) = 2039 s, 1952 s, 1943 s, 1927 s, 1916 s, 1672 m, 1646 w — Anal. Found: C, 39.69; H, 2.28; N, 16.60. Calc. for $C_{11}H_7MnN_4O_5$ (330.14): C, 40.02; H, 2.14; N, 16.97%.

4.3.2. Synthesis of [(bdmpza)$Mn(CO)_3$] (*2b*)

The reaction of 248 mg (1.00 mmol) bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1b**) with 112 mg (1.00 mmol) *tert*-butylate and 275 mg (1.00 mmol) [$BrMn(CO)_5$] in THF (50 ml) yielded [(bdmpza)$Mn(CO)_3$] (**2b**) as a yellow powder. Crystals suitable for X-ray structure determination were obtained from a solution in THF.

Yield 309 mg (0.80 mmol, 80%); m.p. 245–250°C (dec.). ^{1}H-NMR ($CHCl_3$-d, 250 MHz): $\delta = 2.42$ (s, 6H, CH_3), 2.57 (s, 6H, CH_3), 6.26 (s, 2H, H_{pz}) — ^{13}C-NMR ($CHCl_3$-d, 62.5 MHz): $\delta = 11.4$ (CH_3), 14.5 (CH_3), 67.2 (CH), 108.3 (C_{pz}), 141.5 (C_{pz}), 154.2 (C_{pz}), 219.9 (CO), 223.4 (CO) — EIMS (70 eV, 265°C): m/z (%) = 386 (1) [M^+], 330 (10) [$M^+ - 2$ CO], 302 (35) [$M^+ - 3$ CO], 258 (88) [$M^+ - CO_2 - 3$ CO], 109 (43) [$C_5H_7N_2 + CH_2$] — IR (THF): νmax (cm^{-1}) = 2036 s, 1942 s, 1915 s, 1683 m, 1560 w — IR (KBr): νmax (cm^{-1}) = 3393 br, 2036 s, 1924 vs, 1664 m, 1560 w — Anal. Found: C, 46.86; H, 4.29; N, 14.14. Calc. for $C_{15}H_{15}MnN_4O_5$ (386.25): C, 46.65; H, 3.91; N,

14.51% — Crystals: Anal. Found: C, 45.14; H, 3.87; N, 13.89. Calc. for $C_{15}H_{15}MnN_4O_5 \times \frac{1}{2}$ H_2O (395.25): C, 45.58; H, 4.08; N, 14.17%.

4.3.3. Synthesis of [(bpza)Re(CO)$_3$] (**3a**)

The reaction of 473 mg (2.46 mmol) bis(pyrazol-1-yl)acetic acid (**1a**) with 276 mg (2.46 mmol) *tert*-butylate and 1.00 g (2.46 mmol) [(BrReCO)$_5$] in THF (50 ml) yielded [(bpza)Re(CO)$_3$] (**3a**) as a white powder. Crystals suitable for X-ray structure determination were obtained from a solution in acetone.

Yield 930 mg (2.02 mmol, 82%); m.p. 279°C (dec.). ^{1}H-NMR (DMSO-d_6, 250 MHz): $\delta = 6.69$ (t, 2H, $^3J_{H-H} = 2.0$ Hz, H_{pz}), 7.64 (s, 1H, CH), 8.45 (d, 4H, $^3J_{H-H} = 2.0$ Hz, H_{pz}) — ^{13}C-NMR (DMSO-d_6, 62.5 MHz): $\delta = 73.5$ (CH), 109.8 (C_{pz}), 135.6 (C_{pz}), 147.5 (C_{pz}), 164.2 (COO), 196.6 (CO), 197.0 (CO) — EIMS (70 eV, 290°C): m/z (%) = 462 (25) [M^+], 418 (20) [$M^+ - CO_2$], 390 (60) [$M^+ - CO_2 - CO$], 362 (25) [$M^+ - CO_2 - 2$ CO], 334 (100) [$M^+ - CO_2 - 3$ CO] — IR (THF): νmax (cm^{-1}) = 2029 s, 1924 s, 1904 s, 1695 w — IR (KBr): νmax (cm^{-1}) = 2028 s, 1922 vs, 1906 s, 1895 s, 1677 s, 1655 w — Anal. Found: C, 28.75; H, 1.64; N, 12.11. Calc. for $C_{11}H_7N_4O_5Re$ (461.41): C, 28.63; H, 1.53; N, 12.14%.

4.3.4. Synthesis of [(bdmpza)Re(CO)$_3$] (**3b**)

The reaction of 526 mg (2.12 mmol) bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1b**) with 242 mg (2.12 mmol) *tert*-butylate and 860 mg (2.12 mmol) [BrRe(CO)$_5$] in THF (50 ml) yielded [(bdmpza)Re(CO)$_3$] (**3b**) as a white powder. Crystals suitable for X-ray structure determination were obtained from a solution in THF.

Yield 849 mg (1.64 mmol, 77%); m.p. 270–280°C (dec.). ^{1}H-NMR ($CHCl_3$-*d*, 250 MHz): $\delta = 2.45$ (s, 6H, CH_3), 2.51 (s, 6H, CH_3), 6.11 (s, 2H, H_{pz}), 6.47 (s, 1H, CH) — ^{13}C-NMR ($CHCl_3$-*d*, 62.5 MHz): $\delta = 11.0$ (CH_3), 15.5 (CH_3), 68.1 (CH), 108.2 (C_{pz}), 141.5 (C_{pz}), 154.4 (C_{pz}), 163.8 (COO), 195.1 (CO), 196.2 (CO) — EIMS (70 eV, 240°C): m/z (%) = 518 (15) [M^+], 474 (20) [$M^+ - CO_2$], 446 (32) [$M^+ - CO_2 - CO$], 418 (15) [$M^+ - CO_2 - 2$ CO], 390 (100) [$M^+ - CO_2 - 3$ CO] — IR (THF): νmax (cm^{-1}) = 2025 s, 1918 s, 1896 s, 1694 m, 1559 w — IR (KBr): νmax (cm^{-1}) = 3399 s, 2023 s, 1915 vs, 1903 m, 1883 m, 1670 m, 1559 w — Crystals: Anal. Found: C, 34.31; H, 3.21; N, 10.63. Calc. for $C_{15}H_{15}N_4O_5Re \times \frac{1}{2}$ H_2O (526.52): C, 34.22; H, 3.06; N, 10.64%.

4.4. CO–NO$^+$ exchange: synthesis of [(bdmpza)Re(CO)$_2$(NO)]BF$_4$ (**4**)

To a solution of 460 mg (0.89 mmol) [(bdmpza)Re(CO)$_3$] (**3b**) in dichloromethane (20 ml) 270 mg (2.31 mmol) $NOBF_4$ was added and the solution stirred for 24 h at ambient temperature. CO evolution was observed. $NOBF_4$ addition was repeated until CO evolution stopped and a yellow precipitate formed. The solvent was removed in vacuo and the residue was dissolved in acetone (40 ml) to quench the excess $NOBF_4$. The acetone solvent was evaporated, the residue was washed with THF (5 ml) and the pale yellow residue was dried in vacuo. Additional portions of [(bdmpza)Re(CO)$_2$(NO)]BF_4 (**4**) were obtained from the THF solution upon standing for three days at ambient temperature.

Yield 260 mg (0.43 mmol, 48%); m.p. 165–170°C (dec.). ^{1}H-NMR (acetone-d_6, 250 MHz): $\delta = 2.63$ (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 2.75 (s, 3H, CH_3), 6.58 (s, 1H, H_{pz}), 6.61 (s, 1H, CH), 7.10 (s 1H, H_{pz}) — ^{13}C-NMR (acetone-d_6, 62.5 MHz): $\delta =$ 11.2 (CH_3), 11.5 (CH_3), 15.1 (CH_3), 16.0 (CH_3), 68.5 (CH), 110.5 (C_{pz}), 110.7 (C_{pz}), 147.1 (C_{pz}), 148.2 (C_{pz}), 157.1 (C_{pz}), 157.3 (C_{pz}), 161.7 (COO) — FABMS (NBOH-matrix): m/z (%) = 520 (35) [M^+], 492 (14) [$M^+ - CO$], 464 (4) [$M^+ - 2$ CO] — IR (CH_2Cl_2): νmax (cm^{-1}) = 2113 s, 2045 s, 1824 s, 1712 m, 1558 w — IR (KBr): νmax (cm^{-1}) = 2117 s, 2044 vs, 1823 s, 1706 m, 1556 w — Anal. Found: C, 27.59; H, 2.77; N 11.33. Calc. for $C_{14}H_{15}BF_4N_5O_5Re$ (606.31): C, 27.73; H, 2.49; N, 11.55%.

4.5. X-ray structure determinations

Single crystals of **1a, 2b, 3a** and **3b** were sealed in glass capillaries at room temperature. A modified Siemens P4-Diffractometer was used for data collection (Wyckhoff technique, graphite monochromator, Mo–K_α radiation, $\lambda = 0.71073$, scan rate ω 4–30° min^{-1}). The structures were solved by using direct methods (in case of **1a, 2b** and **3a**) and Patterson (in case of **3b**){Siemens SHELXS-93 (VMS) [32]} and refined with full-matrix least-squares against F^2 {Siemens SHELXL-96 (VMS) [33]}. A weighting scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \mathrm{Max}(F_0^2,0)]/3$. **2b** and **3b** were first solved in $P4_12_12$. Due to a Flack parameter close to 1, the structure coordinates had to be inverted and the symmetry operations were changed to those of the enantiomorphic space group $P4_32_12$, causing a significant decrease of the R factors. All the hydrogen atoms in the structure of compound **2b** were found and refined isotropically. The hydrogen atoms of **1a, 3a** and **3b** were included in their calculated positions and refined in a *riding model*.

2b and **3b** crystallised as the solvate with half a water molecule placed on a special position. These water molecules interact via a hydrogen bond with the carboxylate group of the ligands. In the structure determination of **3b** two restraints had to be applied to this hydrogen. IR signals of **2b** and **3b** at 3393 and 3399

Table 6
Structure determination details of compounds **1a**, **2b**, **3a** and **3b**

	1a	**2b**	**3a**	**3b**
Empirical formula	$C_8H_8N_4O_2$	$C_{15}H_{15}MnN_4O_5{\cdot}0.5H_2O$	$C_{11}H_7N_4O_5Re{\cdot}C_3H_6O$	$C_{15}H_{15}N_4O_5Re{\cdot}0.5H_2O$
Formula weight	192.18	395.26	519.48	526.52
Crystal colour/habit	White prism	Yellow prism	White plate	White cube
Crystal system	Monoclinic	Tetragonal	Orthorhombic	Tetragonal
Space group	$C2/c$	$P4_32_12$	$Pbca$	$P4_32_12$
a (Å)	10.106(10)	10.056(5)	9.130(12)	10.176(6)
b (Å)	11.001(11)	10.056(5)	13.967(16)	10.176(6)
c (Å)	16.493(17)	35.183(19)	27.776(30)	35.474(32)
α (°)	90.00	90.00	90.00	90.00
β (°)	105.12(2)	90.00	90.00	90.00
γ (°)	90.00	90.00	90.00	90.00
V (Å^3)	1770.1(31)	3557.9(30)	3541.9(71)	3673.1(46)
θ range (°)	2.56–25.00	2.11–27.00	2.67–27.01	2.08–27.00
H range	−12 to 6	−12 to 12	−11 to 10	−12 to 12
K range	−12 to 12	−12 to 12	−7 to 17	−12 to 12
L range	−18 to 19	−44 to 44	−12 to 35	−40 to 45
Z	8	8	8	8
μ (Mo–K$_\alpha$) (mm^{-1})	0.109	0.778	6.899	6.652
Crystal size (mm)	$0.3\times0.2\times0.2$	$0.4\times0.3\times0.3$	$0.3\times0.2\times0.2$	$0.6\times0.4\times0.4$
Temperature (K)	242(2)	243(2)	242(3)	243(2)
Reflections collected	2098	8852	6023	8400
Independent reflections	1552	3896	3861	3989
Obs. reflections ($>2\sigma I$)	1163	3153	2658	3632
Parameter	160	295	226	236
Restraints	0	0	0	2
WGHT parameter a	0.0493	0.0398	0.0479	0.0942
WGHT parameter b	2.0001	0.7485	6.5031	5.3358
R_1 (obs.)	0.0427	0.0410	0.0423	0.0591
R_2 (overall)	0.0654	0.0579	0.0760	0.0644
wR_1 (obs.)	0.1010	0.0880	0.0916	0.1558
wR_2 (overall)	0.1219	0.0957	0.1079	0.1806
Diff. peak/hole (eÅ^{-3})	0.174/−0.266	0.254/−0.290	1.150/−1.577	2.162/−1.989

cm^{-1} confirm such hydrogen bridged OH groups. Washing with water when working up the products (see Section 4.3) as well as crystallisation using not perfectly dry THF might be the sources of these water molecules. In the structure of **3a** one molecule of acetone co-crystallised per asymmetric unit.

5. Supplementary material

All the details and parameters of the measurements are summarised in Table 6. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 151037 (**1a**), 151038 (**2b**), 151039 (**3a**) and 151040 (**3b**). Copies of the data may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www/ccdc/cam/ac/uk). Structure pictures were prepared with the program DIAMOND 2.1c [34].

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