Pyrazolylamidino- and Bis(pyrazole)manganese(I) Complexes

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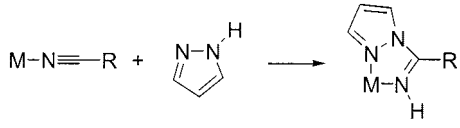
The pyrazolylamidino complexes *fac*-[MnBr(CO)$_3${NH=C(R)-pz-κ^2*N*,*N*}] or *fac*-[MnBr(CO)$_3${NH=C(R)dmpz-κ^2*N*,*N*}] (R = CH_3, C_6H_5) are obtained by reaction of *fac*-[MnBr(CO)$_3$-(NCR)$_2$] and equimolar amounts of pzH or dmpzH (dmpz = 3,5-Me_2pz), although these reactions also afford the bis(pyrazole) complexes as by-products. The bispyrazole complexes *fac*-[MnBr(CO)$_3$(pzH)$_2$] or *fac*-[MnBr(CO)$_3$(dmpzH)$_2$] are selectively obtained from [MnBr(CO)$_5$] and two equivalents of pzH or dmpzH. Their solid-state structures, determined by X-ray diffraction methods, show the N-bound hydrogens of the pyrazoles pointing towards the bromine atom. The pyrazolylamidino complexes can also be prepared by reactions of equimolar amounts of the bispyrazole and the bisnitrile complexes. The solid-state structures of the pyrazolylamidino complexes containing the dmpz fragment were determined by X-ray diffraction methods.

Introduction

An increasing interest is being dedicated to pyrazole-containing chelating ligands.[1] Among them, those containing pyridyl and pyrazolyl fragments are receiving the highest attention, probably because they are involved in different and interdisciplinary aspects, such as the synthesis of supramolecular assemblies or the design of molecules displaying physical properties of interest.[2,3] At the opposite side concerning the attention received are pyrazolylamidines, since only molybdenum, iridium, ruthenium, and platinum complexes containing these ligands have been described so far.[4] However, amidino has been found to be a promising ligand,[5] which may be attributed to several special features of pyrazolylamidino complexes: (a) the different properties of the two donor atoms and the electron delocalization within the ligand makes them potentially interesting for electron-transfer processes and related physical properties, as occurs for the related pyridyl- and pyrazolyl-containing polydentate ligands; (b) the pyrazolylamidino ligands are synthesized in situ (Scheme 1), thus using different nitriles and pyrazoles allows the opportunity of controlling both the electronic and steric properties of the metal complexes, in contrast with most of the ligands, which must be previously synthesized; (c) the NH group may be deprotonated, giving rise to further reactivity by attack of different electrophiles including metal fragments, which would afford heterometallic complexes.



Scheme 1. General method for the synthesis of pyrazolylamidino complexes.

As part of our studies on the chemistry of group 6 and 7 complexes with N-donor chelating ligands,[6] we decided to study the coordination of the pyrazolylamidino ligand to these metals, which has not been explored so far. The first pyrazolylamidinomanganese complexes are reported here.[7] During the course of this work we unexpectedly obtained bis(pyrazole) manganese complexes, which had not been previously reported, therefore their selective syntheses are also described.

The chemistry of bis(pyrazole) complexes is also attracting our attention,[8] since both their structures and reactivity are promising aspects. Concerning their structures, the N-bound hydrogen of pyrazole complexes is commonly involved in hydrogen bonds that give rise to supramolecular arrangements.[9,10] Concerning their reactivity, terminal pyrazole ligands are very useful precursors for bridging pyrazolate homo- or heterobimetallic complexes, which may be obtained by deprotonating the N-bound hydrogen of the coordinated pyrazole when a second metallic substrate is present. This strategy has been successively used by different groups, mainly with middle and late transition elements.[11]

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Results and Discussion

Synthesis and Characterization of Bis(pyrazole)manganese Complexes

The bis(pyrazole)manganese(I) complexes *fac*-[$MnBr(CO)_3(pzH)_2$] (**1a**) and *fac*-[$MnBr(CO)_3(dmpzH)_2$] (**1b**) were obtained when [$MnBr(CO)_5$] was treated with a twofold excess of pzH or dmpzH in warm CH_2Cl_2. A white insoluble solid was detected in the reactions with pzH, although the yield of **1a** is still high.[12]

The *fac* geometry of both complexes is evident from their IR spectra in the C–O stretching region, which show three absorptions. The C–O frequencies are slightly higher for **1a** than for **1b**, as is to be expected considering that Hdmpz is a better donor than Hpz. This geometry is supported by the NMR spectroscopic data, as both pyrazole ligands are equivalent. The broadness of the HN signal must be due to a protolysis process involving this proton, which is common in pyrazole complexes. Homodecoupling experiments at low temperature carried out on previously reported complexes have allowed the unequivocal assignment of the signals of the pyrazolic hydrogens.[8a] However, this assignment cannot be unequivocally extended to the complexes described herein, since the chemical shifts of the hydrogens or methyl groups in positions 3 and 5 seem to be affected by different factors that are difficult to evaluate: whether the hydrogen (or methyl) group at position 3 resonates at higher field than that at position 5, or vice versa, may vary in the same family of complexes,[11g] or even depending on the solvent used.[13] Therefore, the assignment proposed for the rest of complexes in the Experimental Section shoud be considered as tentative.

Structure reports of pyrazolemanganese(II) complexes are quite common, but we have only been able to find one report of a crystal structure of a pyrazolemanganese(I) complex,[14] therefore the geometries of complexes **1** were determined by X-ray diffractometric studies. The structures are shown in Figure 1 and relevant distances and angles are collected in Table 1.[15] The distances and angles are very similar in both complexes, and the latter are also similar to those found in previously reported structures of halotricarbonylmanganese(I) complexes containing two monodentate N-donor ligands, which show a slightly distorted octahedral geometry.[16] These distortions are evidenced by the slight deviation from linearity shown by the ligands coordinated *trans* [174.84(17)–176.7(2)°], as well as by the angles formed by the ligands coordinated *cis* [85.71(13)–96.3(2)°]. In both structures the smaller angles are those formed by the two pyrazoles, as occurs in the related manganese(I) complexes containing two monodentate N-donor ligands indicated above.[16]

The N-bound hydrogens of the pyrazoles point to the bromine atom, which may be attributed both to steric and electronic reasons. Steric factors are obviously more important in **1b**, where this orientation brings the methyl groups bound to the 5-carbon close to a carbonyl group, which is smaller than the bromine atom. Therefore, this orientation

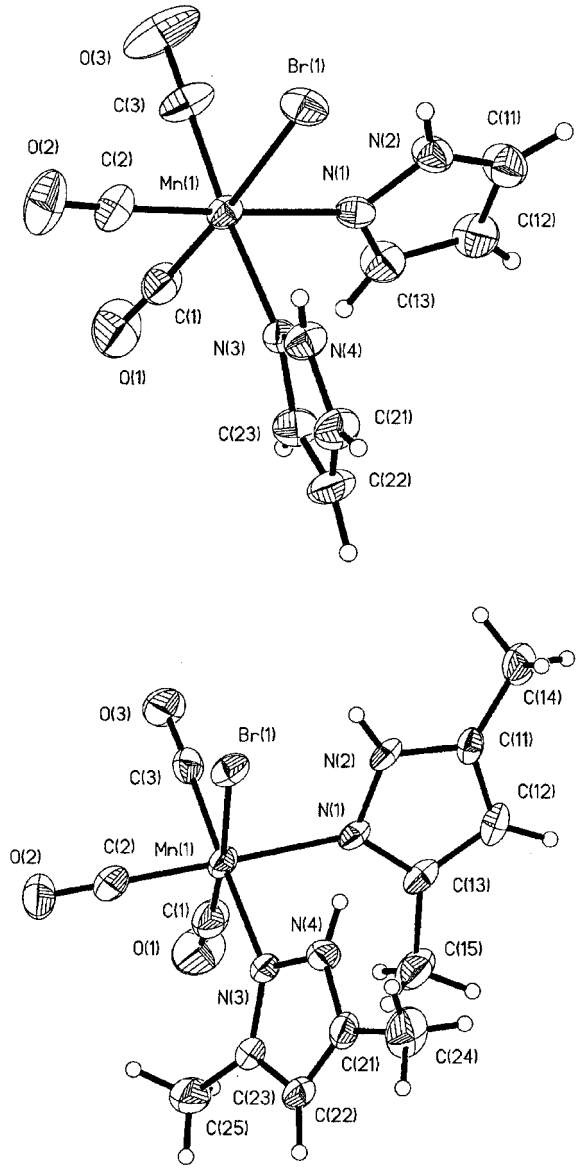


Figure 1. Perspective views of *fac*-[$MnBr(CO)_3(pzH)_2$] (**1a**, top), and *fac*-[$MnBr(CO)_3(dmpzH)_2$] (**1b**, bottom), showing the atom numbering.

reduces the steric hindrance, since the methyl groups bound to the 5-carbon and the bulky bromine atom are at opposite sides of the molecule. Steric hindrance is also responsible for the tilting of the Hdmpz ligands, which are bent in the same sense around the Mo–N bonds, as has been found in other bis(Hdmpz) complexes.[8b] The average dihedral angles are 37(1)° and 34(1)°, so they are close to the planes that bisect the angles between the *cis* substituents. This tilting is not observed in **1a**, where the deviation of the Hpz ligands from the plane perpendicular to that containing the metal and the nitrogen donor atoms is much lower [23(1)° and –10(1)°]. The second difference between the pyrazole ligands in **1a** and **1b** concerns their relative orientation: in **1b** they are tilted in the same direction in order to reduce their steric hindrance, whereas in **1a** the Hpz ligands are

Table 1. Selected distances [Å] and angles [°] for *fac*-[MnBr(CO)$_3$(pzH)$_2$] (**1a**) and *fac*-[MnBr(CO)$_3$(dmpzH)$_2$] (**1b**).

	1a	1b
Mn(1)–C(1)	1.776(5)	1.760(6)
Mn(1)–C(3)	1.790(5)	1.799(6)
Mn(1)–C(2)	1.817(6)	1.780(6)
Mn(1)–N(3)	2.070(3)	2.080(4)
Mn(1)–N(1)	2.078(3)	2.085(4)
Mn(1)–Br(1)	2.5448(9)	2.5420(10)
C(1)–O(1)	1.135(6)	1.159(6)
C(2)–O(2)	1.127(6)	1.152(6)
C(3)–O(3)	1.144(6)	1.147(5)
C(1)–Mn(1)–C(3)	90.2(3)	86.9(2)
C(1)–Mn(1)–C(2)	90.0(3)	90.7(3)
C(3)–Mn(1)–C(2)	89.9(2)	89.2(2)
C(1)–Mn(1)–N(3)	91.93(19)	96.3(2)
C(3)–Mn(1)–N(3)	175.6(2)	176.7(2)
C(2)–Mn(1)–N(3)	93.9(2)	91.5(2)
C(1)–Mn(1)–N(1)	93.6(2)	94.1(2)
C(3)–Mn(1)–N(1)	90.3(2)	92.7(2)
C(2)–Mn(1)–N(1)	176.4(2)	174.9(2)
N(3)–Mn(1)–N(1)	85.71(13)	86.39(16)
C(1)–Mn(1)–Br(1)	176.06(16)	174.84(17)
C(3)–Mn(1)–Br(1)	88.98(18)	88.31(16)
C(2)–Mn(1)–Br(1)	86.19(19)	87.37(19)
N(3)–Mn(1)–Br(1)	89.17(10)	88.48(12)
N(1)–Mn(1)–Br(1)	90.26(10)	88.01(11)

tilted slightly such that the C5-bound hydrogens are closer than the N-bound hydrogens.

Electronic factors also explain why these hydrogens point to the bromine atom, since they are involved in weak intermolecular hydrogen bonds. In **1a**, only intramolecular hydrogen bonds are detected: 2.66 Å for H(2)···Br and 2.57 Å for H(4)···Br. These and the corresponding N···Br distances [3.206(1) and 3.212(1) Å] confirm the presence of a hydrogen bond, which may be considered as "weak".[17] The bromine atom in **1b** is also involved in two weak intramolecular hydrogen bonds with the N-bound hydrogens [2.62 Å for H(2)···Br and 2.57 Å for H(4)···Br], the corresponding N···Br distances being 3.218(1) and 3.191(1) Å, and by a weak intermolecular hydrogen bond to one of the N-bound hydrogen atoms of an adjacent molecule [2.68 Å for H(2)···Br, with N···Br = 3.519(1)]. Similar hydrogen bond lengths have been found for other bromo complexes containing pyrazoles.[8a,18]

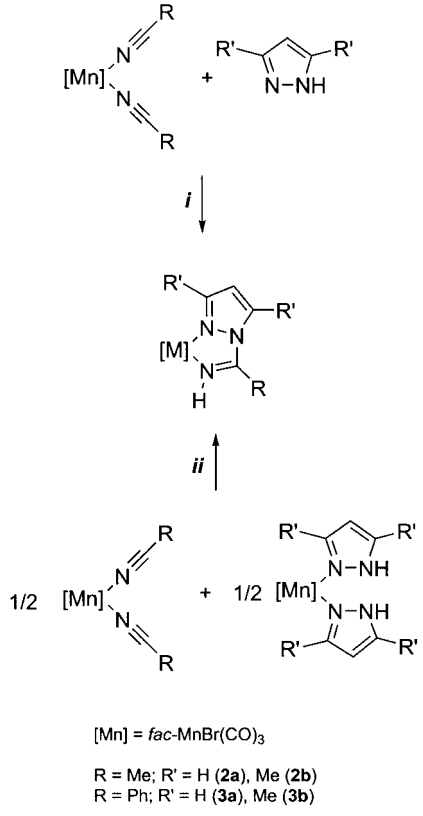
The structure of the related rhenium complex *fac*-[ReBr(CO)$_3$(pzH)$_2$][18a] shows some analogies and differences with those reported here: the relative orientation of the pzH ligands is similar to that of Hdmpz in **1b**, but only one of the N-bound hydrogens in the rhenium complex is involved in a intermolecular hydrogen bond.

Synthesis and Characterization of Pyrazolylamidinomanganese Complexes

The synthesis of pyrazolylamidinomanganese(I) complexes was carried out by reacting equimolar amounts of the corresponding bis(nitrile) complexes and pyrazole (Scheme 1). Nucleophilic addition to metal-activated nitriles is a well-known reaction that has been extensively used to obtain a wide variety of ligands.[19]

The acetonitrile complex *fac*-[MnBr(CO)$_3$(NCMe)$_2$], which was first described more than thirty years ago,[20] was synthesized by heating [MnBr(CO)$_5$] in acetonitrile under controlled conditions in order to avoid bromide displacement to yield the cationic product. It is well known that the carbonyls are ejected before the substitution of the bromide when a thermal process is carried out.[21] A similar method was used to obtain *fac*-[MnBr(CO)$_3$(NCPh)$_2$] (see Exp. Sect.), for which we have not been able to find any previous report.[22]

The reactions of the bis(nitrile) complexes and pyrazole (Scheme 2, route *i*) afford the desired pyrazolylamidino complexes *fac*-[MnBr(CO)$_3${*N*H=C(R)pz-κ^2*N*,*N*}] (R = CH$_3$, **2a**; Ph, **3a**) or *fac*-[MnBr(CO)$_3${*N*H=C(R)dmpz-κ^2*N*,*N*}] (R = CH$_3$, **2b**; Ph, **3b**). However, variable amounts of the bis(pyrazole) complexes **1** are also obtained as by-products. The presence of the bispyrazole complexes could be due to the instability of the bisnitrile complexes under these reaction conditions, which would decrease the amount of available manganese and therefore would increase the manganese/pyrazole ratio. Thus, we decided to attempt the syntheses of the pyrazolylamidino complexes by reacting equimolar amounts of the bis(nitrile) and bis(pyrazole) complexes (Scheme 2, route *ii*) as we believed this would increase the amount of manganese present in the mixture and would not increase the manganese/pyrazole ratio. However, this method did not improve the selectivity of the



Scheme 2. Synthesis of pyrazolylamidino complexes.

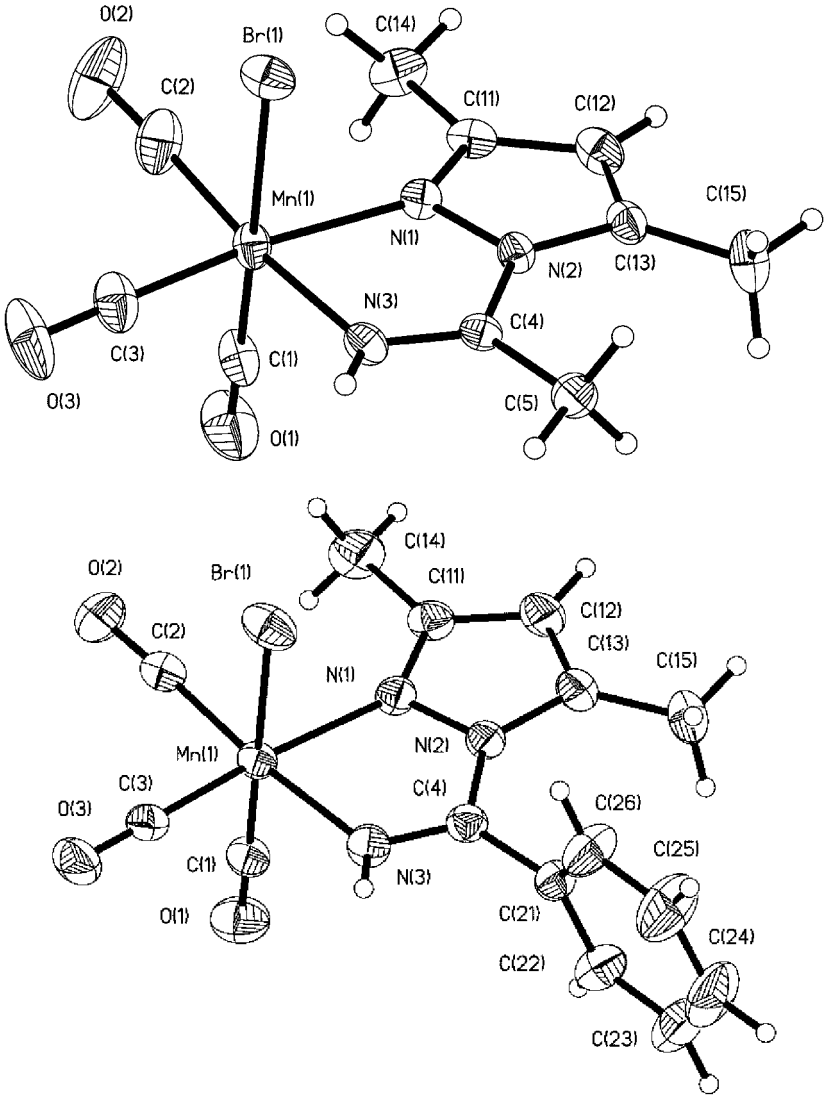


Figure 2. Perspective views of *fac*-[MnBr(CO)$_3${*N*H=C(Me)dmpz-κ^2*N*,*N*}] (**2b**, top) and *fac*-[MnBr(CO)$_3${*N*H=C(Ph)dmpz-κ^2*N*,*N*}] (**3b**, bottom) showing the atom numbering.

process since it afforded similar mixtures of **1** and **2** (see Exp. Sect.).

The C–O stretching region of **2** in the IR spectra also shows three absorptions, as expected for a *fac* geometry. The C–O frequencies follow the expected trends considering the better donor properties of (a) Hdmpz compared to Hpz, and (b) amidino ligands derived from acetonitrile compared to those derived from benzonitrile. The C–N stretching absorption of the amidine ligand is also evident in the IR spectra. The C–N frequencies are slightly higher for complexes **2** than for complexes **3**, which could point to a higher delocalization in the latter due to the presence of a phenyl group instead of a methyl.

The NMR spectroscopic data do not provide structural information, therefore one of each type of complex was subjected to a crystallographic study. The structures are shown in Figure 2 and relevant distances and angles are collected in Table 2. The structural data are essentially the same in both complexes, and very similar to those found in previously reported structures of halotricarbonylmanganese(I) complexes containing a bidentate N-donor ligand.[23] The distances and angles found in the pyrazolylamidino ligands are also similar to those found in other pyrazolylamidino complexes.[4]

The N-bound hydrogen atoms of both structures are involved in intermolecular hydrogen bonds, with the bromine atom in **2b** [H(3)···Br = 2.66 Å; N(3)···Br = 3.483(1) Å], which may be considered as "weak",[17] whereas in **3b** they are linked to a molecule of tetrahydrofuran present in the lattice [H(3)···O(90) = 1.90 Å; N(3)···O(90) = 2.873(7) Å] by a hydrogen bond which may be considered as "moderate".[17]

Experimental Section

General Remarks: All manipulations were performed under N_2 by conventional Schlenk techniques. Filtrations were carried out with dry Celite under N_2. Solvents were purified according to standard

Table 2. Selected distances [Å] and angles [°] for *fac*-[MnBr(CO)$_3$-{*N*H=C(Me)dmpz-κ^2*N*,*N*}] (**2b**) and *fac*-[MnBr(CO)$_3${*N*H=C(Ph)-dmpz-κ^2*N*,*N*}] (**3b**).

	2b	**3b**
Mn(1)–C(1)	1.793(4)	1.790(5)
Mn(1)–C(2)	1.807(4)	1.802(5)
Mn(1)–C(3)	1.807(4)	1.786(5)
Mn(1)–N(1)	2.041(2)	2.039(3)
Mn(1)–N(3)	2.007(3)	1.995(4)
Mn(1)–Br(1)	2.5840(13)	2.5337(9)
N(1)–N(2)	1.391(3)	1.379(4)
N(2)–C(4)	1.391(3)	1.391(5)
N(3)–C(4)	1.275(3)	1.267(5)
C(1)–O(1)	1.148(4)	1.131(5)
C(2)–O(2)	1.147(4)	1.145(5)
C(3)–O(3)	1.140(3)	1.144(5)
C(1)–Mn(1)–C(3)	91.31(13)	90.37(19)
C(1)–Mn(1)–C(2)	89.78(15)	92.6(2)
C(3)–Mn(1)–C(2)	89.58(16)	88.81(19)
C(1)–Mn(1)–N(3)	95.65(13)	91.52(18)
C(3)–Mn(1)–N(3)	94.07(13)	94.88(18)
C(2)–Mn(1)–N(3)	173.38(13)	174.42(17)
C(1)–Mn(1)–N(1)	89.78(11)	93.97(17)
C(3)–Mn(1)–N(1)	170.62(12)	170.69(17)
C(2)–Mn(1)–N(1)	99.74(13)	93.97(17)
N(3)–Mn(1)–N(1)	76.56(10)	76.79(15)
C(1)–Mn(1)–Br(1)	177.55(10)	178.73(15)
C(3)–Mn(1)–Br(1)	89.26(9)	88.76(13)
C(2)–Mn(1)–Br(1)	87.84(12)	88.26(14)
N(3)–Mn(1)–Br(1)	86.68(8)	87.63(12)
N(1)–Mn(1)–Br(1)	90.04(7)	86.75(9)
N(2)–N(1)–Mn(1)	113.81(15)	113.1(2)
N(1)–N(2)–C(4)	115.0(2)	115.7(3)
C(4)–N(3)–Mn(1)	120.1(2)	120.3(3)
N(3)–C(4)–N(2)	114.4(2)	114.0(4)

procedures.[24] *fac*-[MnBr(CO)$_3$(NCMe)$_2$] was obtained as described below and its CO stretching bands were compared with those described previously.[20] *fac*-[MnBr(CO)$_3$(NCPh)$_2$] was obtained as described below and its CO stretching bands were compared with those displayed by a sample of *fac*-[MnBr(CO)$_3$-(NCPh)$_2$] obtained by the method previously described for the MeCN complex.[20] All other reagents were obtained from the usual commercial suppliers and used as received. IR spectra were recorded with a Perkin–Elmer RX I FT-IR apparatus as KBr pellets from 4000 to 400 cm^{-1}. NMR spectra were recorded with Bruker AC-300 or ARX-300 instruments in $(CD_3)_2CO$, at room temperature unless otherwise stated. NMR spectra are referenced to the internal residual solvent peak for ^{1}H and ^{13}C{^{1}H} NMR. Assignment of the ^{13}C{^{1}H} NMR spectroscopic data was supported by DEPT experiments and relative intensities of the resonance signals. Elemental analyses were performed on a Perkin–Elmer 2400B microanalyzer.

***fac*-[MnBr(CO)$_3$(Hpz)$_2$] (1a):** Hpz (0.041 g, 0.6 mmol) was added to a solution of [MnBr(CO)$_5$] (0.082 g, 0.3 mmol) in CH_2Cl_2 (20 mL). The solution was stirred at 40 °C for 2 h, during which time a white solid precipitated. The solvent was removed in vacuo and the yellow residue was extracted with THF (ca. 20 mL) and filtered. Hexane was added (ca. 20 mL) and the solution was concentrated and cooled to –20 °C to give a yellow-orange microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo to yield 0.094 g (88%) of **1a**. IR (THF): $\tilde{\nu}$ = 2030 cm^{-1} vs, 1940 vs, 1910 vs. IR (KBr): $\tilde{\nu}$ = 3341 cm^{-1} m, 3302 m, 3144 w, 2921 w, 2035 vs, 1940 vs, 1918 vs, 1468 w, 1352 w, 1139 w, 1127 m, 1056 m, 763 m, 676 w, 634 w, 602 w, 583 w, 512 w. ^{1}H NMR (300 MHz): δ = 6.47 (s, 2 H, *H*^{4} Hpz), 7.81 (s, 2 H, *H*^{3} Hpz), 7.89 (s, 2 H, *H*^{5} Hpz), 12.16 (br., 2 H, *H*N) ppm. ^{13}C{^{1}H} NMR (75.78 MHz): δ = 107.9 (s, *C*^{4} Hpz), 132.6 (s, *C*^{3,5} Hpz), 144.2 (s, *C*^{5,3} Hpz), 222.8 (br., *C*O) ppm. $C_9H_8BrMnN_4O_3$ (355.03): calcd. C 30.45, H 2.27, N 15.78; found C 30.60, H 2.32, N 15.98.

***fac*-[MnBr(CO)$_3$(Hdmpz)$_2$] (1b):** Hdmpz (0.058 g, 0.6 mmol) was added to a solution of [MnBr(CO)$_5$] (0.082 g, 0.3 mmol) in CH_2Cl_2 (20 mL). The solution was stirred at 40 °C for 2 h. Hexane was added (ca. 20 mL) and the solution was concentrated and cooled to –20 °C to give a yellow-orange microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo to yield 0.113 g (92%) of **1b**. IR (THF): $\tilde{\nu}$ = 2026 cm^{-1} vs, 1935 vs, 1904 vs. IR (KBr): $\tilde{\nu}$ = 3299 cm^{-1} m, 2930 w, 2022 vs, 1940 vs, 1898 vs, 1574 s, 1470 m, 1422 w, 1377 m, 1284 m, 1178 w, 1156 w, 1040 w, 1026 w, 817 w, 789 m, 686 w, 658 w, 637 m, 560 w, 519 w, 469 w. ^{1}H NMR (300 MHz): δ = 2.15 (s, 6 H, C*H*$_3$ Hdmpz), 2.25 (s, 6 H, C*H*$_3$ Hdmpz), 6.01 (s, 2 H, *H*^{4} Hdmpz), 11.02 (br., 2 H, *H*N) ppm. ^{13}C{^{1}H} NMR (75.78 MHz): δ = 10.8 (s, *C*H$_3$ Hdmpz), 14.2 (s, *C*H$_3$ Hdmpz), 107.8 (s, *C*^{4} Hdmpz), 143.1 (s, *C*^{3,5} Hdmpz), 154.2 (s, *C*^{5,3} Hdmpz), 222.8 (br., *C*O) ppm. $C_{13}H_{16}BrMnN_4O_3$ (411.13): calcd. C 37.98, H 3.92, N 13.63; found C 38.02, H 3.59, N 13.44.

***fac*-[MnBr(CO)$_3${*N*H=C(CH$_3$)pz-κ^2*N*,*N*}] (2a). Method A:** A solution of [MnBr(CO)$_5$] (0.137 g, 0.5 mmol) in CH_3CN (20 mL) was maintained at 60 °C for 30 min. Then, Hpz (0.034 g, 0.5 mmol) was added and the solution was heated for 30 min. The solvent was removed in vacuo and the yellow residue was extracted with THF (ca. 20 mL) and filtered. Hexane was added (ca. 10 mL) and the solution was concentrated and cooled to –20 °C to give a yellow-orange microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo to yield 0.098 g (60%) of **2a**. Concentration of the mother liquor and further cooling to –20 °C, yielded 0.015 g (8% referred to manganese) of **1a** after decanting, washing with hexane (3 × 3 mL approximately), and drying in vacuo.

Method B: A solution of [MnBr(CO)$_5$] (0.082 g, 0.3 mmol) in CH_3CN (20 mL) was maintained at 60 °C for 30 min. Then, **1a** (0.106 g, 0.3 mmol) was added and the solution was heated for 30 min. The solvent was removed in vacuo and the yellow residue was extracted with THF (ca. 20 mL) and filtered. Hexane was added (ca. 10 mL) and the solution was concentrated and cooled to –20 °C to give a yellow-orange microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo to yield 0.123 g (62%) of **2a**. Concentration of the mother liquor and further cooling to –20 °C gave 0.018 g (8%) of **1a**, after decanting, washing with hexane (3 × 3 mL approximately), and drying in vacuo. IR (THF): $\tilde{\nu}$ = 2027 cm^{-1} vs, 1939 vs, 1912 vs. IR (KBr): $\tilde{\nu}$ = 3191 cm^{-1} m, 3143 w, 2034 vs, 1938 vs, 1918 vs, 1655 m, 1520 w, 1458 w, 1434 w, 1408 m, 1397 w, 1373 w, 1330 w, 1241 m, 1221 w, 1128 w, 1070 w, 1050 w, 1042 w, 1000 w, 962 w, 766 m, 686 w, 688 m, 632 m, 600 w, 517 m. ^{1}H NMR (300 MHz): δ = 2.87 [s, 3 H, N=C(C*H*$_3$)], 6.83 (s, 1 H, *H*^{4} pz), 8.38 (d, *J* = 1.5 Hz, 1 H, *H*^{3} pz), 8.61 (d, *J* = 3.0 Hz, 1 H, *H*^{5} pz), 11.06 (br., 1 H, *H*N) ppm. ^{13}C{^{1}H} NMR (75.78 MHz): δ = 19.0 [s, HN=C(*C*H$_3$)], 112.4 (s, *C*^{4} pz), 133.4 (s, *C*^{3,5} pz), 147.7 (s, *C*^{5,3} pz), 161.8 [s, HN=*C*(CH$_3$)] ppm; *C*O not observed. $C_8H_7BrMnN_3O_3$ (328.00): calcd. C 29.29, H 2.15, N 12.81; found C 28.97, H 2.31, N 13.07.

***fac*-[MnBr(CO)$_3${*N*H=C(CH$_3$)dmpz-κ^2*N*,*N*}] (2b). Method A:** A solution of [MnBr(CO)$_5$] (0.137 g, 0.5 mmol) in CH_3CN (20 mL) was maintained at 60 °C for 30 min. Then, Hdmpz (0.048 g, 0.5 mmol) was added and the solution was heated for 30 min.

Work-up as for **2a** yielded 0.090 g (50%) of **2b** and 0.005 g (2% referred to manganese) of **1b**.

Method B: A solution of $[MnBr(CO)_5]$ (0.082 g, 0.3 mmol) in CH_3CN (20 mL) was maintained at 60 °C for 30 min. Then, **1b** (0.106 g, 0.3 mmol) was added and the solution was heated for 30 min. Work-up as for **2a** yielded 0.135 g (57%) of **2b** and 0.007 g (2%) of **1b**. IR (THF): $\tilde{\nu}$ = 2023 cm^{-1} vs, 1934 vs, 1909 vs. IR (KBr): $\tilde{\nu}$ = 3444 cm^{-1} w, 3194 m, 2032 s, 1942 s, 1921 vs, 1909 vs, 1651 m, 1574 w, 1453 w, 1410 m, 1357 w, 1246 w, 1097 w, 1044 w, 843 w, 802 w, 684 w, 634 w, 520 w. ^1H NMR (300 MHz): δ = 2.58 (s, 3 H, CH_3 dmpz), 2.69 (s, 3 H, CH_3 dmpz), 2.89 [s, 3 H, N=C(CH_3)], 6.39 (s, 1 H, H^4 dmpz), 10.67 (br., 1 H, *H*N) ppm. $^{13}C\{^1H\}$ NMR (75.78 MHz): δ = 14.0 (s, *C*H_3 dmpz), 15.3 (s, *C*H_3 dmpz), 21.4 [s, HN=C(*C*H_3)], 114.3 (s, C^4 dmpz), 145.5 (s, $C^{5,3}$ dmpz), 157.0 (s, $C^{3,5}$ dmpz), 163.6 [s, HN=*C*(CH_3)] ppm; *C*O not observed. $C_{10}H_{11}BrMnN_3O_3$ (356.05): calcd. C 33.73, H 3.11, N 11.80; found C 33.63, H 3.00, N 11.51.

***fac*-[MnBr(CO)$_3${*N*H=C(C_6H_5)pz-κ^2*N*,*N*}] (3a). Method A:** C_6H_5CN (500 μL) was added to a solution of $[MnBr(CO)_5]$ (0.137 g, 0.5 mmol) in THF (20 mL) and the mixture was stirred at 70 °C for 1 h. Then, Hpz (0.034 g, 0.5 mmol) was added and the solution was heated at 70 °C for an additional hour. The solvent was removed in vacuo and the yellow residue was washed with hexane (5×3 mL approximately), extracted with THF (ca. 20 mL), and filtered. Hexane was added (ca. 10 mL) and the solution was concentrated and cooled to –20 °C to give a yellow-orange microcrystalline solid, which was decanted, washed with hexane (3×3 mL approximately), and dried in vacuo to yield 0.027 g (14%) of **3a**. Concentration of the mother liquor and further cooling to –20 °C, yielded 0.014 g (8% referred to manganese) of **1a**, after decanting, washing with hexane (3×3 mL approximately), and drying in vacuo.

Method B: C_6H_5CN (300 μL) was added to a solution of $[MnBr(CO)_5]$ (0.082 g, 0.3 mmol) in THF (20 mL) and the mixture was stirred at 70 °C for 1 h. Then, **1a** (0.106 g, 0.3 mmol) was added and the solution was heated at 70 °C for 45 min. Work-up as for **3a** yielded 0.039 g (17%) of **3a** and 0.013 g (5%) of **1a**. IR (THF): $\tilde{\nu}$ = 2027 cm^{-1} vs, 1941 s, 1914 s. IR (KBr): $\tilde{\nu}$ = 3401 cm^{-1} s, 2030 vs, 1936 vs, 1916 vs, 1628 m, 1560 w, 1452 w, 1429 w, 1406 w, 1383 w, 1262 w, 1218 w, 1088 w, 1054 w, 867 w, 776 m, 699 w, 684 w, 639 w, 625 w, 521 w. ^1H NMR (300 MHz): δ = 6.85 (s, 1 H, H^4 pz), 7.68 (d, *J* = 7.1 Hz, 2 H, C_6H_5), 7.72 (d, *J* = 7.1 Hz, 1 H, C_6H_5), 7.80 (d, *J* = 7.1 Hz, 2 H, C_6H_5), 8.34 (s, 1 H, H^3 pz), 8.51 (s, 1 H, H^5 pz), 11.53 (br., 1 H, *H*N) ppm. $^{13}C\{^1H\}$ NMR (75.78 MHz): δ = 112.4 (s, C^4 pz), 128.5 (s, C_6H_5), 128.7 (s, C_6H_5), 129.6 (s, C_6H_5), 132.9 (s, C_6H_5), 134.2 (s, $C^{3,5}$ pz), 143.3 (s, C_{ipso} C_6H_5), 147.9 (s, $C^{5,3}$ pz), 161.8 [s, HN=*C*(C_6H_5)] ppm; *C*O not observed. $C_{13}H_9BrMnN_3O_3$ (390.07): calcd. C 40.03, H 2.32, N 10.77; found C 40.31, H, 2.30, N 10.43.

***fac*-[MnBr(CO)$_3${*N*H=C(C_6H_5)dmpz-κ^2*N*,*N*}] (3b): Method A:** C_6H_5CN (300 μL) was added to a solution of $[MnBr(CO)_5]$ (0.082 g, 0.3 mmol) in THF (20 mL) and the mixture was stirred at 70 °C for 1 h. Then, Hdmpz (0.029 g, 0.3 mmol) was added and the solution was heated at 70 °C for 30 min. Work-up as for **3a** yielded 0.031 g (24%) of **3b** and 0.038 g (32%) of **1b**.

Method B: C_6H_5CN (300 μL) was added to a solution of $[MnBr(CO)_5]$ (0.082 g, 0.3 mmol) in THF (20 mL) and the mixture was stirred at 70 °C for 1 h. Then, **1b** (0.123 g, 0.3 mmol) was added and the solution was heated at 70 °C for 45 min. Work-up as for **3a** yielded 0.064 g (25%) of **3b** and 0.013 g (22%) of **1b**. IR (THF): $\tilde{\nu}$ = 2024 cm^{-1} vs, 1936 vs, 1912 vs. IR (KBr): $\tilde{\nu}$ = 3164 cm^{-1} w, 2026 s, 1918 vs, 1637 w, 1508 w, 1420 m, 1356 m, 1259 w, 1122 w, 1055 w, 887 w, 822 w, 706 w, 683 w, 669 w, 646 w, 634 w, 520 w. ^1H NMR (300 MHz): δ = 1.80 (s, 3 H, CH_3 dmpz), 2.65 (s, 3 H,

Table 3. Crystal data and refinement details for **1a**, **1b**, **2b**, and **3b**.

	1a	**1b**	**2b**	**3b**·THF
Formula	$C_9H_8BrMnN_4O_3$	$C_{13}H_{16}BrMnN_4O_3$	$C_{10}H_{11}BrMnN_3O_3$	$C_{19}H_{21}BrMnN_3O_4$
Mol. mass	355.04	411.15	356.07	490.24
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a [Å]	8.194(2)	13.562(3)	8.721(6)	8.150(2)
b [Å]	8.447(2)	18.551(4)	11.356(7)	13.754(4)
c [Å]	10.857(3)	13.973(3)	14.363(9)	19.635(6)
α [°]	84.365(5)	90	90	90
β [°]	83.156(5)	96.008(4)	101.665(12)	98.714(6)
γ [°]	65.663(4)	90	90	90
V [Å^3]	678.8(3)	3496.2(12)	1393.1(15)	2175.5(11)
Z	2	8	4	4
T [K]	296	296	296	296
$D_{calcd.}$ [g cm^{-3}]	1.737	1.562	1.698	1.497
F(000)	348	1648	704	992
λ (Mo-$K_α$) [Å]	0.71073	0.71073	0.71073	0.71073
Crystal size [mm]	0.18×0.19×0.30	0.07×0.14×0.29	0.12×0.15×0.22	0.10×0.11×0.35
Color	orange	orange	orange	orange
μ [mm^{-1}]	3.920	3.056	3.818	2.471
Scan range [°]	1.89 ≤ *θ* ≤ 23.30	1.51 ≤ *θ* ≤ 23.29	2.30 ≤ *θ* ≤ 23.30	1.81 ≤ *θ* ≤ 23.30
Absorption correction	SADABS	SADABS	SADABS	SADABS
Corr. factors (max., min.)	1.000000, 0.249439	1.000, 0.658220	1.00000, 0.694409	1.00000, 0.605570
No. of refl. measured	2979	15633	6110	9576
No. of refl. independent [*R*(int.)]	1924 [0.0184]	5029 [0.0616]	2002 [0.0223]	3118 [0.0391]
No. of refl. observed [$I \geq 2\sigma(I)$]	1677	3141	1606	2155
GOF on F^2	1.051	1.006	1.014	1.005
No. of parameters	172	421	170	259
Residuals *R*, wR_2	0.0429, 0.1274	0.0412, 0.0721	0.0240, 0.0564	0.0383, 0.0922

CH_3 dmpz), 6.40 (s, 1 H, H^4 dmpz), 7.45 (m, 1 H, C_6H_5), 7.64 (m, 3 H, C_6H_5), 7.77 (m, 1 H, C_6H_5), 11.11 (br.,, 1 H *H*N) ppm. $^{13}C\{^1H\}$ NMR (75.78 MHz): δ = 14.0 (s, *C*H_3 dmpz), 15.3 (s, *C*H_3 dmpz), 114.6 (s, C^4 dmpz), 128.9 (s, C_6H_5), 129.9 (s, C_6H_5), 131.3 (s, C_{ipso} C_6H_5), 132.6 (s, C_6H_5), 146.0 (s, $C^{3,5}$ dmpz), 157.9 (s, $C^{3,5}$ dmpz), 164.3 [s, HN=*C*(C_6H_5)], 221.1 (s, *C*O), 223.9 (s, *C*O), 224.0 (s, *C*O) ppm. $C_{15}H_{13}BrMnN_3O_3$ (418.12): calcd. C 43.09, H 3.13, N 10.05; found C 42.84, H, 3.03, N 9.99.

X-ray Crystallographic Study of 1a, 1b, 2b, and 3b: Crystals were grown by slow diffusion of hexane into concentrated solutions of the complexes in CH_2Cl_2 (for **1a** and **1b**) or THF (for **2b** and **3b**) at –20 °C. Relevant crystallographic details are given in Table 3. A crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromated Mo-K_α radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to 2θ = 48.6°. Raw frame data were integrated with the SAINT program.[25] The structure was solved by direct methods with SHELXTL.[26] A semi-empirical absorption correction was applied with the program SADABS.[27] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL.

CCDC-266383 (for **1a**), -266384 (for **1b**), -266385 (for **2b**), and -266386 (for **3b**) 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] R. Mukherjee, *Coord. Chem. Rev.* **2000**, *203*, 151–218.
[2] Review: E. C. Constable, P. J. Steel, *Coord. Chem. Rev.* **1989**, *93*, 205–223.
[3] For some recent references, see: a) S. A. Willison, H. Jude, R. M. Antonelli, J. M. Rennekamp, N. A. Eckert, J. A. K. Bauer, W. B. Connick, *Inorg. Chem.* **2004**, *43*, 2548–2555; b) B. A. Leita, B. Moubaraki, K. S. Murray, J. P. Smith, J. D. Cashion, *Chem. Commun.* **2004**, 156–157; c) V. A. Money, I. R. Evans, M. A. Halcrow, A. E. Goeta, J. A. K. Howard, *Chem. Commun.* **2003**, 158–159; d) P.-C. Wu, J.-K. Yu, Y.-H. Song, Y. Chi, P.-T. Chou, S.-M. Peng, G.-H. Lee, *Organometallics* **2003**, *22*, 4938–4946; e) D. B. Grothjahn, S. Van, D. Combs, D. A. Lev, C. Schneider, C. D. Incarvito, K.-C. Lam, G. Rossi, A. L. Rheingold, M. Rideout, C. Meyer, G. Hernandez, L. Mejorado, *Inorg. Chem.* **2003**, *42*, 3347–3355; f) K. Singh, J. R. Long, P. Stavropoulos, *Inorg. Chem.* **1998**, *37*, 1073; g) M. H. W. Lam, S. T. C. Cheung, K.-M. Fung, W.-T. Wong, *Inorg. Chem.* **1997**, *36*, 4618–4619; h) J. C. Jeffery, P. L. Jones, K. L. V. Mann, E. Psillakis, J. A. McCleverty, M. D. Ward, C. M. White, *Chem. Commun.* **1997**, 175–176.
[4] a) M. R. Kollipara, P. Sarkhel, S. Chakraborty, R. Lalrempuia, *J. Coord. Chem.* **2003**, *56*, 1085–1091; b) D. Carmona, J. Ferrer, F. J. Lahoz, L. A. Oro, M. P. Lamata, *Organometallics* **1996**, *15*, 5175–5178; c) J. López, A. Santos, A. Romero, A. M. Echavarren, *J. Organomet. Chem.* **1993**, *443*, 221–228; d) M. A. Cinellu, S. Stoccoro, G. Minghetti, A. L. Bandini, G. Banditelli, B. Bovio, *J. Organomet. Chem.* **1989**, *372*, 311–325; e) G. D. Gracey, S. T. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* **1987**, *65*, 2469–2477; f) A. Romero, A. Vegas, A. Santos, *J. Organomet. Chem.* **1986**, *310*, C8–C10; g) C. J. Jones, J. A. McCleverty, A. S. Rothin, *J. Chem. Soc., Dalton Trans.* **1986**, 109–111.
[5] J. Baker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219–300.
[6] For some recent references concerning group 6 complexes, see: a) J. Pérez, D. Morales, S. Nieto, L. Riera, V. Riera, D. Miguel, *Dalton Trans.* **2005**, 884–888; b) L. Coue, L. Cuesta, D. Morales, J. A. Halfen, J. Pérez, L. Riera, V. Riera, D. Miguel, N. G. Connelly, S. Boonyuen, *Chem. Eur. J.* **2004**, *10*, 1906–1912; c) D. Morales, M. E. Navarro Clemente, J. Pérez, L. Riera, V. Riera, D. Miguel, *Organometallics* **2003**, *22*, 4124–4128; d) D. Morales, J. Pérez, L. Riera, V. Riera, D. Miguel, M. E. G. Mosquera, S. García-Granda, *Chem. Eur. J.* **2003**, *9*, 4132–4143; e) J. Pérez, E. Hevia, L. Riera, V. Riera, S. García-Granda, E. García-Rodríguez, D. Miguel, *Eur. J. Inorg. Chem.* **2003**, 1113–1120; f) D. Morales, M. E. Navarro Clemente, J. Pérez, L. Riera, V. Riera, D. Miguel, *Organometallics* **2002**, *21*, 4934–4938; g) E. Hevia, J. Pérez, L. Riera, V. Riera, I. del Río, S. García-Granda, D. Miguel, *Chem. Eur. J.* **2002**, *8*, 4510–4521; h) D. Morales, J. Pérez, L. Riera, V. Riera, D. Miguel, *Inorg. Chem.* **2002**, *41*, 4111–4113; i) E. Hevia, J. Pérez, L. Riera, V. Riera, D. Miguel, *Organometallics* **2002**, *21*, 1750–1752; j) D. Morales, J. Pérez, L. Riera, V. Riera, R. Corzo-Suárez, S. García-Granda, D. Miguel, *Organometallics* **2002**, *21*, 1540–1545; k) J. Pérez, L. Riera, V. Riera, S. García-Granda, E. García-Rodríguez, D. Miguel, *Organometallics* **2002**, *21*, 1622–1626; l) J. Pérez, L. Riera, V. Riera, S. García-Granda, E. García-Rodríguez, D. Miguel, *Chem. Commun.* **2002**, 384–385. For some recent references concerning group 7 complexes, see: m) L. Cuesta, E. Hevia, D. Morales, J. Pérez, V. Riera, M. Seitz, D. Miguel, *Organometallics* **2005**, *24*, 1772–1775; n) S. Nieto, J. Pérez, V. Riera, D. Miguel, C. Alvarez, *Chem. Commun.* **2005**, 546–548; o) L. Cuesta, E. Hevia, D. Morales, J. Pérez, V. Riera, E. Rodríguez, D. Miguel, *Chem. Commun.* **2005**, 116–116; p) L. Cuesta, D. C. Gerbino, E. Hevia, D. Morales, M. E. N. Clemente, J. Pérez, L. Riera, V. Riera, D. Miguel, I. del Río, S. García-Granda, *Chem. Eur. J.* **2004**, *10*, 1765–1777; q) E. Hevia, J. Pérez, V. Riera, D. Miguel, P. Campomanes, M. I. Menéndez, T. L. Sordo, S. García-Granda, *J. Am. Chem. Soc.* **2003**, *125*, 3706–3707; r) D. C. Gerbino, E. Hevia, D. Morales, M. E. N. Clemente, J. Pérez, L. Riera, V. Riera, D. Miguel, *Chem. Commun.* **2003**, 328–329; s) E. Hevia, J. Pérez, V. Riera, D. Miguel, *Organometallics* **2003**, *22*, 257–263; t) E. Hevia, J. Pérez, V. Riera, D. Miguel, *Angew. Chem. Int. Ed.* **2002**, *41*, 3858–3860; u) E. Hevia, J. Pérez, V. Riera, D. Miguel, *Chem. Commun.* **2002**, 1814–1815.
[7] We have also obtained pyrazolylamidino Mo, W, and Re complexes, which will be published separately elsewhere.
[8] a) P. Paredes, D. Miguel, F. Villafañe, *Eur. J. Inorg. Chem.* **2003**, 995–1004; b) P. Paredes, M. Arroyo, D. Miguel, F. Villafañe, *J. Organomet. Chem.* **2003**, *667*, 120–125.
[9] For some examples of chains, see: a) R. Graziani, U. Castellato, R. Ettore, G. Plazzogna, *J. Chem. Soc., Dalton Trans.* **1982**, 805–808; b) J. D. Crane, O. D. Fox, E. Sinn, *J. Chem. Soc., Dalton Trans.* **1999**, 1461–1465; c) K. Sakai, Y. Tomita, T. Ue, K. Goshima, M. Ohminato, T. Tsubomura, K. Matsumoto, K. Ohmura, K. Kawakami, *Inorg. Chim. Acta* **2000**, *297*, 64–71; d) A. Chadghan, J. Pons, A. Caubet, J. Casabó, J. Ros, A. Alvarez-Larena, J. F. Piniella, *Polyhedron* **2000**, *19*, 855–862.
[10] For some examples of dimers, see: a) M. A. Cinellu, S. Stoccoro, G. Minghetti, A. L. Bandini, G. Banditelli, B. Bovio, *J. Organomet. Chem.* **1989**, *372*, 311–325; b) M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, S. Kawata, S. Kitagawa, *J. Chem. Soc., Dalton Trans.* **1995**, 4099–4106; c) G. A. Ardizzoia, G. La Monica, S. Cenini, M. Moret, N. Maschioni, *J. Chem. Soc., Dalton Trans.* **1996**, 1351–1357; d) I. A. Guzei, C. H. Winter, *Inorg. Chem.* **1997**, *36*, 4415–4420; e) S. M. Couchman, J. C. Jeffery, M. D. Ward, *Polyhedron* **1999**, *18*, 2633–2640.
[11] See, for example: a) L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, F. H. Cano, *J. Chem. Soc., Dalton Trans.* **1986**, 31–37;

b) D. Carmona, J. Ferrer, F. J. Lahoz, L. A. Oro, J. Reyes, M. Esteban, *J. Chem. Soc., Dalton Trans.* **1991**, 2811–2820; c) G. López, J. Ruiz, C. Vicente, J. M. Martí, G. García, P. A. Chaloner, P. B. Hitchcock, R. M. Harrison, *Organometallics* **1992**, *11*, 4090–4096; d) D. Carmona, J. Ferrer, R. Atencio, F. J. Lahoz, L. A. Oro, M. P. Lamata, *Organometallics* **1995**, *14*, 2057–2065; e) G. A. Ardizzoia, G. La Monica, A. Maspero, N. Masciocchi, M. Moret, *Eur. J. Inorg. Chem.* **1999**, 1301–1307; f) G. A. Ardizzoia, G. La Monica, A. Maspero, M. Moret, N. Masciocchi, *Eur. J. Inorg. Chem.* **2000**, 181–187; g) R. Contreras, M. Valderrama, E. M. Orellana, D. Boys, D. Carmona, L. A. Oro, M. P. Lamata, J. Ferrer, *J. Organomet. Chem.* **2000**, *606*, 197–202.

[12] All attempts to determine the nature of this white solid were unsuccessful. Its IR spectra show bands which may be assigned to pzH but do not show CO stretching bands; no reliable ^{1}H NMR spectra could be obtained, which points to a paramagnetic material.

[13] T. Beringhelli, G. D'Alonso, M. Panigati, F. Porta, P. Mercandelli, M. Moret, A. Sironi, *Organometallics* **1998**, *17*, 3282–3292.

[14] S. E. Anslow, K. S. Chong, S. J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* **1981**, *59*, 3123–3135.

[15] For **1b**, two crystallographically independent but chemically equivalent molecules were found in the asymmetric unit, with their distances and angles being very similar. Figure 1 and Table 1 collect one of them.

[16] a) N. I. Pyshnograeva, V. N. Setkina, V. G. Andrianov, Y. T. Struchkov, D. N. Kursanov, *J. Organomet. Chem.* **1980**, *186*, 331–338; b) S. U. Son, K. H. Park, Y. K. Chung, *Organometallics* **2000**, *19*, 5241–5243; c) W.-Y. Wong, W.-K. Wong, C. Sun, W.-T. Wong, *J. Organomet. Chem.* **2000**, *612*, 160–171.

[17] a) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, **1997**. Chapter 2; b) T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76.

[18] a) G. A. Ardizzoia, G. La Monica, A. Maspero, M. Moret, N. Maschiocchi, *Eur. J. Inorg. Chem.* **1998**, 1503–1511; b) J. Cámpora, J. A. López, C. M. Maya, P. Palma, E. Carmona, C. Ruiz, *Organometallics* **2000**, *19*, 2707–2715.

[19] a) V. Y. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771–1802; b) R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299–338.

[20] M. F. Farona, K. F. Kraus, *Inorg. Chem.* **1970**, *9*, 1700–1704.

[21] R. H. Reimann, E. Singleton, *J. Chem. Soc., Dalton Trans.* **1974**, 808–813.

[22] In a separate experiment, *fac*-[$MnBr(CO)_3(NCPh)_2$] was synthesized as described previously for the MeCN complex (ref. [20]). Its molecular structure was determined by X-ray diffraction. Although the quality of the data are insufficient to be reported, they confirm the expected *fac*-tricarbonyl-*cis*-bis(benzonitrile)geometry.

[23] a) E. Horn, M. R. Snow, E. R. T. Tiekink, *Acta Crystallogr., Sect. C* **1987**, *43*, 792–794; b) G. Schmidt, H. Paulus, R. van Eldik, H. Elias, *Inorg. Chem.* **1988**, *27*, 3211–3214; c) G. J. Stor, D. J. Stufkens, P. Vernooijs, E. J. Baerends, J. Fraanje, K. Goubitz, *Inorg. Chem.* **1995**, *34*, 1588–1594.

[24] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, **1988**.

[25] *SAINT+*. SAX area detector integration program. Version 6.02. Bruker AXS, Inc. Madison, WI, **1999**.

[26] G. M. Sheldrick; *SHELXTL*, An integrated system for solving, refining, and displaying crystal structures from diffraction data. Version 5.1. Bruker AXS, Inc. Madison, WI, **1998**.

[27] G. M. Sheldrick; *SADABS*, Empirical Absorption Correction Program. University of Göttingen, Germany, **1997**.

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