Pyrazolato Metal Complexes: Synthesis, Characterization and X-ray Crystal Structures of Polynuclear Organometallic Re–Mn Derivatives

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By reacting $[Re(CO)_3(Hpz)_2(pz)]$ (Hpz = pyrazole) with $[Mn(CO)_5Br]$ in toluene in the presence of Et_3N, the dinuclear complex $[(CO)_3Re(pz)_3Mn(CO)_3](Et_3NH)$ (**1**) was obtained. The reaction of **1** with molecular oxygen affords the tetranuclear compound $[(CO)_3Re(pz)_3Mn(O)_3Mn(pz)_3Re(CO)_3](Et_3NH)_2$ (**3**) or the trinuclear compound $[(CO)_3Re(pz)_3Mn(pz)_3Re(CO)_3](Et_3NH)_2$ (**5**) depending on the experimental conditions. Complexes **1**, **3** and **5** were characterized in the solid state by single crystal X-ray diffraction analysis and were showed to contain Re···Mn interactions linked by and tris-μ_2-pyrazolato bridges. In **5**, a short [2.397(4) Å] tris(μ_2-oxo)bridged Mn^{IV}–Mn^{IV} contact is found, leading to strong antiferromagnetic coupling of the d^3 ions. The homometallic species $[(CO)_3Mn(pz)_3Mn(CO)_3](Et_3NH)$ (**2**) was also prepared and found to be isostructural with **1**.

Introduction

The formation of polynuclear complexes whose atoms are kept at nearly fixed distances by ancillary ligands is a strict requirement for multicentred catalysis; in particular, when specific synthetic routes to heteropolymetallic species can be devised, complexes where the synergic effects of metals of different nature, geometry or oxidation state are present can be prepared.[1]

In a recent paper we have demonstrated that the organometallic complex $[(CO)_3Re(Hpz)_2(pz)]$,[2] once deprotonated, can act as a multidentate ligand toward the metals of group 11 in the +I oxidation state.[3] The proposed analogy of this ligand with the trispyrazolylborate anion was, however, partially obscured by the observation that "tripod-like" coordination of group 11 metal atoms did not occur, probably because of their peculiar electronic and steric requirements which favour low-coordination numbers. Therefore, in order to substantiate our hypothesis, we decided to react $[(CO)_3Re(Hpz)_2(pz)]$ with molecular fragments prone to hexacoordination. For this we have chosen $[Mn(CO)_5Br]$ which, upon removal (and substitution) of three ligands, can easily afford stable 18-electron Mn^I species. Accordingly, in this paper we report the synthesis and chemical reactivity of polynuclear Re−Mn species which contain metal-metal interactions linked by rare tris(μ_2-pyrazolato) bridges, along with their spectroscopic, magnetic and structural characterization.

Results and Discussion

The pyrazole/pyrazolate derivative compound $[(CO)_3Re(Hpz)_2(pz)]$ reacts with $[Mn(CO)_5Br]$ in the presence of Et_3N leading to the dinuclear ionic derivative $[(CO)_3Re(pz)_3Mn(CO)_3](Et_3NH)$ **(1)** according to Equation 1.

$$[(CO)_3Re(Hpz)_2(pz)] + [Mn(CO)_5Br] \longrightarrow [(CO)_3Re(pz)_3Mn(CO)_3](Et_3NH) \qquad (1)$$

The IR spectrum of **1** in toluene shows four strong carbonyl stretching absorptions at 2023, 2008, 1915 and 1901 cm^{-1}, respectively. The latter two (broad) bands are due to the superimposition of the E vibration modes expected for a facial coordination of the carbonyl ligands bonded to the metal centres,[4] later confirmed by the X-ray diffraction study reported below, while the first two absorptions are assigned to the A_1 mode of carbonyls coordinated to the manganese(I) and rhenium(I) centres, respectively.

In order to draw useful structural and spectroscopic comparisons, we tried to synthesize the homometallic dirhenium derivative $[(CO)_3Re(pz)_3Re(CO)_3](Et_3NH)$, by reacting $[(CO)_3Re(Hpz)_2(pz)]$ with a stoichiometric amount of $[Re(CO)_5Br]$ in the presence of Et_3N. Unfortunately, all attempts to reach this goal failed, unreacted $[(CO)_3Re(Hpz)_2(pz)]$ being always recovered. In contrast to this, when $[Mn(CO)_5Br]$ was reacted with pyrazole in the presence of triethylamine, the homobimetallic manganese(I) derivative $[(CO)_3Mn(pz)_3Mn(CO)_3](Et_3NH)$ **(2)** could be easily prepared in high yields. The proposed structure of complex **2**, originally prepared and spectroscopically characterized by Trofimenko[5] as its tetraethylammonium salt, is here confirmed by means of a X-ray powder diffraction study (see Experimental Section).

The ^1H NMR spectrum of **1**, measured in $[D_6]$acetone at −80°C, shows only one set of signals for each pyrazolate proton, revealing the equivalence of the three pyrazolate

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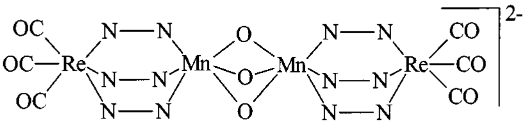
groups; on the other hand, bridging of two different metal centres causes the splitting of the H(3)/H(5) proton signals [two doublets at $\delta = 7.81$ ($J = 2.19$ Hz) and $\delta = 7.79$($J = 1.75$ Hz) and a *pseudo*-triplet centred at $\delta = 6.15$]. Moreover, the signals attributable to the triethylammonium cation are also clearly detected [$\delta = 1.41$ (t, $J = 6.29$ Hz, CH_3), $\delta = 3.40$ (q, $J = 6.29$ Hz, CH_2), $\delta = 4.00$ (br, NH)]. For the sake of comparison, in the related homometallic species $[(CO)_3Mn(pz)_3Mn(CO)_3](Et_3NH)$ **(2)** due to the equivalence of the H(3) and H(5) protons, only one doublet ($\delta = 7.79$, $J = 2.19$ Hz), a triplet at $\delta = 6.15$ and the signals attributable to the Et_3NH^+ cation are found. On the basis of the observed values of the $J_{4,(3,5)}$ coupling constants, we tentatively attribute the downfield doublet in the ^1H NMR spectrum of **1** to the H protons leaning out over the manganese(I) centre.

Reactivity of 1 With O_2

Complex **1** reacts with molecular oxygen leading, depending on the experimental conditions, to different species. When CH_2Cl_2 solutions of **1** are exposed to an O_2 atmosphere, a pronounced colour change of the solution from pale yellow to dark red occurs, and the formation of a brick-red precipitate takes place. An X-ray structure analysis (see later) revealed this species to be the tetranuclear rhenium(I)/manganese(IV) $[Re_2Mn_2(CO)_6(O)_3(pz)_6](Et_3NH)_2$ complex, **(3)**, where two $[(CO)_3Re(\mu\text{-}pz)_3Mn]$ sub-units are connected together through three μ_2-oxo bridges.



Therefore, the complete reaction leading to **3** can be written as:

$$2\,[(CO)_3Re(pz)_3Mn(CO)_3](Et_3NH) + 3/2\,O_2 \rightarrow [Re_2Mn_2(CO)_6(O)_3(pz)_6](Et_3NH)_2 + 6\,CO \quad (2)$$

The IR spectrum of solid **3** shows the typical pattern of carbonyl absorptions for a *fac* geometry around the rhenium(I) centre [2053(s) and 1903(br) cm^{-1}]; moreover, two strong, broad bands in the 1800−1600 cm^{-1} region are present and can be attributed to H-bonds between the triethylammonium protons and the oxo bridges, as found by the crystallographic study.

Depicting the organometallic residue $\{(CO)_3Re(pz)_3\}^{2-}$ as {L} and, hence, **3** as $[\{L\}Mn(O)_3Mn\{L\}]^{2-}$, it is easy to show that **3** belongs to the relatively large class of dinuclear face-sharing octahedral complexes of the $[L_nM(X)_3ML_n]^{m-}$ type, containing d^3-d^3 metals.[6] For this class of derivatives, it has been shown[6a] that the spin-exchange interaction is independent of the type of bridging ligand ($X = O^{2-}, OH^-, RO^-, Cl^-, Br^-, I^-$) and also of the nature of the metal centre [$M = Mn^{IV}, Cr^{III}, V^{II}$], the only relevant parameter being the metal−metal distance. A plot of ln(J) versus the M−M distance D_{M-M} (J being the spin-exchange coupling constant) is linear, leading to a phenomenological equation of the type $J = B\cdot\exp(-\varepsilon D_{M-M})$.[6a] The species which allowed the determination of this law contain d^3 ions with intermetallic distances in the 2.3−4.0 Å range depending on the type of the bridging ligands; consequently, many different values of spin interactions could be found, with $2J$ estimates ranging from 0 to -780 cm^{-1}, equivalent to μ_{RT} values in the 3.9−0.5 BM (per metal centre) range.[6a] For complex **3** we measured a μ_{RT} value of 0.99 BM, revealing a strong antiferromagnetic interaction between the two manganese(IV) centres, in agreement with the short Mn−Mn separation [2.394(3) Å, vide infra] and with that predicted on adopting the aforementioned equation.[7]

According to the strong antiferromagnetic coupling between the Mn^{IV} centres, the ^1H NMR spectrum of complex **3** shows well resolved signals, without substantial band broadening or paramagnetic shifts. Its spectral features are quite similar to those of the parent compound $[(CO)_3Re(pz)_3Mn(CO)_3](Et_3NH)$ **(1)**. In the pyrazolate proton region two doublets, centred at $\delta = 7.81$ and 7.76 ($J = 2.01$ and 1.83 Hz) and assigned to the H(3) and H(5) protons leaning out over the rhenium and manganese centres are present. The pyrazolate protons in the 4-position give rise to a pseudo-triplet centred at $\delta = 6.10$. The spectral features do not change significantly upon changing the temperature, revealing the high rigidity of the $M(\mu\text{-}pz)_3M'$ core.

Complex **3** can be easily protonated to the neutral oxo/dihydroxo species $[(CO)_3Re(pz)_3Mn(OH)_2(O)Mn(pz)_3Re(CO)_3]$ **(4)** by employing stoichiometric amounts of aqueous HBF_4. In complex **4**, the ν(CO) absorptions are found at 2037 and 1926 cm^{-1}, slightly shifted with respect to the parent compound **3**; moreover, a broad band attributable to ν(OH) is found at about 3500 cm^{-1}. Such a reaction can be quantitatively reversed by treating **4** with Et_3N. Interestingly, excess HBF_4 does not lead to the formation of the cationic $[(CO)_3Re(pz)_3Mn(OH)_3Mn(pz)_3Re(CO)_3]^+$ species.

When $[(CO)_3Re(pz)_3Mn(CO)_3](Et_3NH)$ **(1)** was reacted with O_2 in the presence of free pyrazole [or when the mother liquors of reaction (1) were exposed to air], the trinuclear species $[(CO)_3Re(pz)_3Mn(pz)_3Re(CO)_3](Et_3NH)_2\cdot H_2O$ **(5)** was isolated in low yields (see Experimental Section) and crystallographically characterized. The IR spectrum of **5** shows two bands attributable to ν(CO) at 2018 (sharp) and 1901 (broad) cm^{-1}, in agreement with the facial geometry about the rhenium(I) centres. This latter reaction is accompanied by the formation of noncarbonylic manganese species. IR evidence suggests that, most probably, hydroxo/pyrazole derivatives of Mn^{II} are formed, but their real nature still remains unclear. Work is in progress in order to identify these species, which could not be easily isolated by standard chemical or chromatographic techniques.

Crystal Structures of 1, 3 and 5

All these compounds are ionic species, containing $[Et_3NH]^+$ cations and organometallic polynuclear anions; in addition, crystals of **5** contain clathrated water molecules. ORTEP drawings of the complex anions are shown in Figures 1, 2 and 3, respectively; a summary of chemically relevant bond lengths is presented in Table 1.

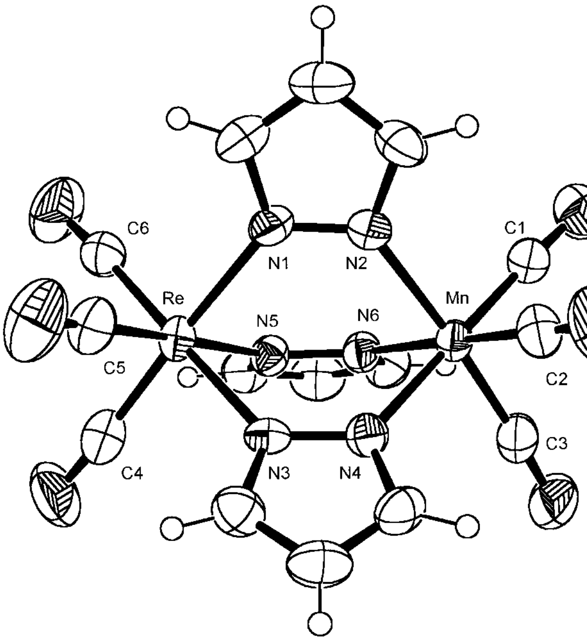


Figure 1. ORTEP drawing of the $[(CO)_3Re(pz)_3Mn(CO)_3]^-$ anion in **1**, with partial labelling scheme; thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are given arbitrary radii

Table 1. Synoptic collection of relevant bond lengths (e.s.d.'s in parentheses)

Compound	**1**[a]	**3**[b]	**5**[b]
Metals	Re^I-Mn^I	Re^I-Mn^{IV}	Re^I-Mn^{II}
Re−Mn	3.905(1)	3.897(2)	3.854(2)
Mn−Mn	–	2.394(3)	–
Re−C	1.874(9)	1.906(4)	1.89(1)
	1.889(9)	1.907(3) (2 ×)	1.90(2)
	1.906(8)	–	1.91(2)
<Re−C>	1.89	1.91	1.90
Mn−C	1.811(9)	–	–
Mn−C	1.811(9)	–	–
Mn−C	1.818(8)	–	–
<Mn−C>	1.81	–	–
Re−N	2.157(6)	2.156(8)	2.150(8)
Re−N	2.143(5)	2.162(3) (2 ×)	2.169(9)
Re−N	2.134(5)	–	2.174(9)
<Re−N>	2.14	2.16	2.16
Mn−N	2.086(6)	2.047(8)	2.030(9) (2 ×)
Mn−N	2.090(6)	2.029(5) (2 ×)	2.021(9) (2 ×)
Mn−N	2.110(6)	–	2.012(9) (2 ×)
<Mn−N>	2.09	2.03	2.02
Mn−O	–	1.835(7)	–
Mn−O	–	1.849(4) (2 ×)	–
<Mn−O>	–	1.84	–

[a] These values may be slighly affected by the Re/Mn disorder discussed in the text. – [b] The anion in **3** possesses crystallographically imposed *mm2* symmetry, while that of **5** lies on an inversion centre.

All three species contain "terminal" *fac*-$M(CO)_3$ (M = Re or Mn) fragments, connected by a tris-pyrazolato bridge (tpb) or longer (linear) spacers, i.e. $[(tpb)Mn(\mu-O)_3Mn(tpb)]$ in **3** and $[(tpb)Mn(tpb)]$ in **5**. Therefore, the nature of the metal atoms in **1**, **3** and **5** can be easily depicted by the Re^I-Mn^I, $Re^I-Mn^{IV}-Mn^{IV}-Re^I$ and $Re^I-Mn^{II}-Re^I$ sequences, respectively.

Only a few polynuclear complexes bearing tris-pyrazolato bridges are known, the only structurally characterized species being $[(ON)Ni(tpb)Ni(NO)]^-$ (containing a tris-3,5-dimethylpyrazolato bridge),[8] $[Cu_3(fpz)_5]$ [Hfpz = 3,5-bis(trifluoromethyl)pyrazole],[9] $[(C_5Me_5)Ir(tpb)Rh(OOH)(dppe)]^+$,[10] $[(C_5Me_5)Ir(tpb)Ni(R_3BH)]$ and [(*p*-cymene)-$Ru(tpb)Ni(R_3BH)$] (HR = 4-bromo-3-isopropylpyrazole).[11] In such species, as well as in compounds **1**, **3**, and **5**, the rare M(tpb)M fragment mimics structural features which are usual for tris(pyrazolyl)borato metal complexes. Indeed, the trispyrazolylborato derivatives of **1** and **3**, as well as a bis(μ_2-oxo) analogue of **5**, obtained by formally replacing the organometallic $(CO)_3Re(pz)_3$ fragment with the $HB(pz)_3$ tripod, have been known for a long time.[12] Differently, heterobridged metals possessing a $(\mu\text{-pz})_a(\mu\text{-X})_b$ (a + b = 2, 3) core are quite common.[13] In addition, several triazolato and tetrazolato complexes of this kind are present in the Cambridge Crystallographic Database but, since the vast majority are not organometallic species, they will not be discussed any further; however, these observations show that the M(tpb)M fragments should not be rare at all and, as confirmed by the present study, that they can easily be prepared if the proper synthons are used.[14]

As expected, in complexes **1**, **3** and **5**, the M−C distances of the *fac*-$M(CO)_3$ [average values (Å): Re−C 1.89 (in **1**), 1.90 (**3** and **5**); Mn−C 1.81 (**1**)] reflect the larger atomic radius of Re vs. Mn; analogously, Re^I-N bond lengths are about 0.1 Å larger than the Mn^I-N ones.[15] However, if compared to those found in the mononuclear precursors (for which, typically, Re^I-N ca. 2.19 Å),[2] a relevant shortening of the M−N bonds is evident; this effect can possibly be related to the Mn−N−N angles of the $(tpb)Mn(CO)_3$, $(tpb)Mn(\mu-O)_3Mn(tpb)$ and (tpb)Mn(tpb) fragments which are wider (>126°) than those found in the known species $[Re(CO)_3(Hpz)_2(pz)]$, $[Re(CO)_3(Hpz)(pz)(py)]$ and $[(CO)_3Re\{(pz)_2Br\}Re(CO)_3]^-$ (ca. 124°)[2]; indeed, overlap between the metal d orbital(s) and the nitrogen lone-pairs is most effective for Re−N vectors bisecting the $N_{ipso}-N-C_{ipso}$ angles (ca. 108°), i.e. for Re−N−N angles close to (360 − 108)/2 = 126°. The slightly divergent nature of the pyrazolato ligands in **1**, **3** and **5** is also confirmed by comparing the theoretical Re−Mn distances [$(Re-N_{avg.} + Mn-N_{avg})\cdot\sin(36°) + N-N_{avg.}$ = 3.85, 3.83 and 3.83 Å] to the observed values [3.905(1), 3.897(2) and 3.854(2) Å, respectively]. For the sake of comparison, a dimanganese(I) species, structurally similar to **1** but bearing 5-fluoromethyltetrazolates (Hftz), $[(CO)_3Mn(ftz)_3Mn(CO)_3]^-$, shows an Mn−Mn interaction of 3.79 Å.[16]

Since each tpb fragment binds through six donor nitrogen atoms, all metals in **1**, **3** and **5** are octahedrally coordinated: the manganese atoms of **3** are bound to three pyrazolates and three oxo-bridges, while Mn^{II} in **5** is bound to six different pyrazolates. Rather surprisingly, and in disagreement with Shannon's radii for octahedrally coordi-

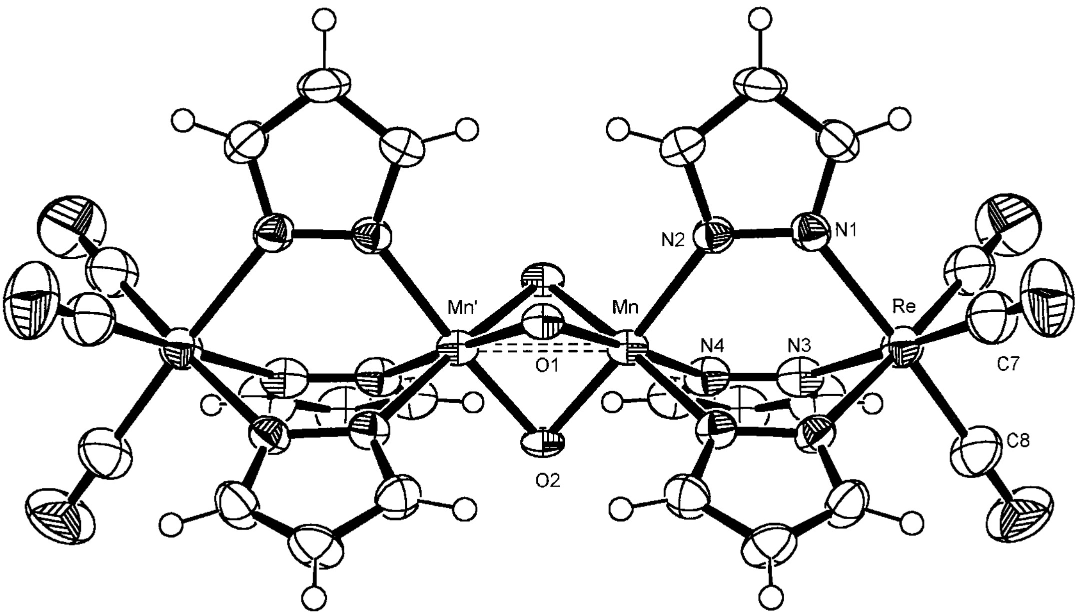


Figure 2. ORTEP drawing of the $[(CO)_3Re(pz)_3Mn(O)_3Mn(pz)_3Re(CO)_3]^{2-}$ anion in **3**, with partial labelling scheme; the dashed bond links Mn^{IV} ions which are 2.394(3) Å apart; thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are given arbitrary radii

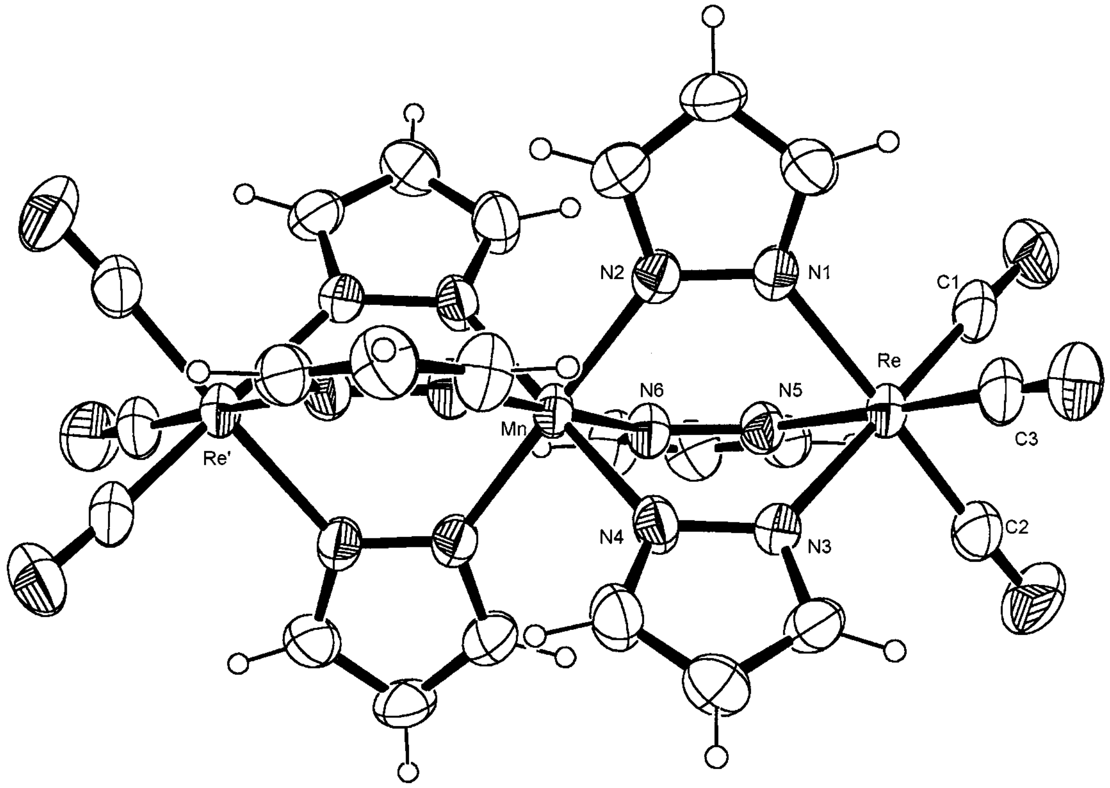


Figure 3. ORTEP drawing of the $[(CO)_3Re(pz)_3Mn(pz)_3Re(CO)_3]^{2-}$ anion in **5**, with partial labelling scheme; thermal ellipsoids are drawn at the 50% probability level; primed atoms are symmetry-equivalents; hydrogen atoms are given arbitrary radii

nated atoms,[17] Mn^{II} (probably a high-spin d^5 ion) in **5** shows bond lengths comparable with those found in tetravalent (d^3) Mn in **3** (see Table 1). This effect needs further comments: owing to the very short Mn···Mn interaction [2.394(3) Å],[18] and in agreement with the observed magnetic response of powders of **3**, a rather profound interaction occurs between the two d^3 ions, making each Mn atom formally seven- rather than six-coordinate; in addition, the very narrow Mn−O−Mn angles (ca. 81°) are also a consequence of this "incipient" bond.

Interestingly, a similar trioxo bridge with a very short M···M distance [M = Tc, a Mn congener, Tc···Tc = 1.867(4) Å] was extensively discussed in experimental[19] and theoretical[20] reports, but was eventually found to be a pure artifact stemming from poor structural analysis of a misinterpreted rhenium species, i.e. solid $(C_5Me_5)ReO_3$, which affords rare two-dimensional polytypes.[21] With these aspects in mind, and suspecting a similar behaviour, we also formulated a crystal disorder of the hypothetical $Re^{I}-Mn^{VII}$ $[(CO)_3Re(tpb)MnO_3]^-$ species, which was easily discarded on the basis of packing considerations, chemical and spectroscopic analyses and much poorer agreement factors. However, since it has been shown here that species such as tris-pyrazolylborates and their organometallic analogue $[(CO)_3Re(tpb)]^{2-}$ have similar coordinating capabilities, and thanks to the well-recognized similarity of the cyclopentadienyl and $[HB(pz)_3]^-$ fragments,[22] it is likely that the still elusive $[(CO)_3Re(tpb)MnO_3]^-$ may exist.

Conclusions

The present work has demonstrated that organometallic analogues of the tris-pyrazolylborato ligands can be successfully employed in building heterometallic species. In addition, selective oxidation of one of the metals was easily attained, opening the way to the synthesis of polynuclear species containing metals in different, and tunable, oxidation states, which may be of interest in multimetal-centred homogeneous catalysis. Accordingly, tris-pyrazolato-bridged $Re^{I}-Mn^{I}$, $Re^{I}-Mn^{II}$ and $Re^{I}-Mn^{IV}$ species were prepared. Also, preliminary results on analogous oxidation reactions of **2** revealed the formation of $Mn^{I}-Mn^{IMnII}-Mn^{I}$ and $Mn^{I}-Mn^{III}-Mn^{I}$ links, but their complete characterization will be reported in a forthcoming paper.

In addition, in the light of our continuous interest in the chemistry of coordination polymers containing metal−diazolato links,[23] the formation of {M(tpb)M} and {M(tpb)M(μ-O)$_3$M} fragments opens the way, at least in principle, to the preparation of robust species containing linear chains of metals and displaying a variety of physical properties such as interesting electrical, magnetic and optical effects.[24]

Experimental Section

Solvents were dried and purified by standard methods. Pyrazole and $[Mn(CO)_5Br]$ (Aldrich Chemical Co.) were used as supplied, $[Re(CO)_5Br]$[25] and $[Re(CO)_3(Hpz)_2(pz)]$[2] were prepared according to literature procedures. Infrared spectra were measured on a BIO RAD FTIR 7 instrument, ^1H NMR spectra were acquired on a Bruker AC-300 FT spectrometer operating at 300.13 MHz. Magnetic data were achieved employing a Sherwood Scientific magnetic susceptibility balance. Elemental analyses were performed at the Microanalytical Laboratory of this University (C, H, N). All reactions were carried out using standard Schlenk techniques.

$[(CO)_3Re(pz)_3Mn(CO)_3](Et_3NH)$ (1): $[(CO)_3Re(Hpz)_2(pz)]$ (360 mg, 0.761 mmol) was dissolved in 8 mL of toluene and solid $[Mn(CO)_5Br]$ (216 mg, 0.785 mmol) was added with stirring. Deoxygenated Et_3N (0.5 mL) was then added and the solution kept at 45°C for 4 h. During this time, evolution of CO from the reaction medium was accompanied by the formation of a pale yellow precipitate. The solid was then filtered, washed with water and dried under vacuum (481 mg, 89% yield) $-C_{21}H_{25}MnN_7O_6Re$ (712): calcd. C 35.39, H 3.51, N 13.76; found C 35.25, H 3.55, N 13.87. Crystals suitable for X-ray structure analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of **1**.

$[(CO)_3Mn(pz)_3Mn(CO)_3](Et_3NH)$ (2): $[Mn(CO)_5Br]$ (300 mg, 1.09 mmol) was added to a solution of pyrazole (134 mg, 1.97 mmol) in toluene (10 mL) kept at 60°C. Et_3N (0.5 mL) was then added and the formation of a yellow precipitate observed. After 6 h, the suspension was cooled to room temperature, and 10 mL of *n*-hexane were added to the reaction medium in order to reduce the solubility of **2**. The solid was then filtered, washed with water and dried under vacuum (550 mg, 86% yield). − $C_{21}H_{25}Mn_2N_7O_6$ (581): calcd. C 43.37, H 4.30, N 16.87; found C 43.01, H 4.21, N 16.41.

$[(CO)_3Re(pz)_3Mn(O)_3Mn(pz)_3Re(CO)_3](Et_3NH)_2$ (3): A solution of **1** (160 mg, 0.225 mmol) in CH_2Cl_2 (5 mL) was stirred under a dioxygen atmosphere for 6 h. During this time a brick-red solid formed. The solid was then filtered off, washed with diethyl ether and dried under vacuum (232 mg, 79% yield). − $C_{36}H_{50}Mn_2N_{14}O_9Re_2$ (1304): calcd. C 33.13, H 3.83, N 15.03; found C 33.22, H 3.45, N 14.67. Crystals suitable for X-ray structure analysis were obtained by slow diffusion of *n*-hexane into an acetone solution of **3**.

$[(CO)_3Re(pz)_3Mn(OH)_2(O)Mn(pz)_3Re(CO)_3]$ (4): Complex **3** (200 mg, 0.153 mmol) was dissolved in acetone (5 mL) and aqueous HBF_4 (48% wt, solution in water, 60 μL) was added. The colour of the solution turned from red to violet. After 15 min. stirring, the solution was evaporated to dryness and the solid was extracted with CH_2Cl_2 (in order to remove the formed $Et_3NH{\cdot}BF_4$). The violet solution was then evaporated to dryness and the residue was triturated with diethyl ether, filtered off and dried under vacuum. (115 mg, 68% yield). − $C_{24}H_{20}Mn_2N_{12}O_9Re_2$ (1102): calcd. C 26.13, H 1.82, N 15.25; found C 26.22, H 2.15, N 15.37.

$[(CO)_3Re(pz)_3Mn(pz)_3Re(CO)_3](Et_3NH)_2{\cdot}H_2O$ (5): To a solution of pyrazole (160 mg, 1.17 mmol) in CH_2Cl_2 (10 mL) was added complex **1** (200 mg, 0.281 mmol) with stirring. The solution was maintained overnight under a dioxygen atmosphere. During this time, the colour of the solution turned from yellow to deep red. The solution was evaporated to dryness and the solid treated with water, filtered and dried under vacuum. The crude product was then dissolved in acetone (3 mL) and *n*-hexane (15 mL) was allowed to diffuse into the solution. Complex **5** was isolated as well-shaped red crystals. (92 mg, 27% yield). − $C_{36}H_{52}MnN_{14}O_7Re_2$ (1219): calcd. C 35.44, H 4.27, N 16.08; found C 35.28, H 4.31, N 15.97.

Crystallography. − Single Crystal Data Collection and Reduction: Crystals of **1**, **3**, **5** were mounted, in air and at room temperature, on the tip of a glass fiber and optically centred in the X-ray beam with the aid of goniometer heads. For **1** and **5**, a CAD4 Enraf−Nonius diffractometer, equipped with graphite monochromated Mo-*Kα* radiation ($\lambda = 0.71073$ Å) was used, and the HV generator set at 50 kV and 30 mA. Cell parameters were determined by least-squares on the basis of the setting angles of 25 reflections having $10 < \theta < 14°$. The data collections were performed by the ω-technique with constant scan speed but variable scan range. The crystal stabilities under diffraction conditions were checked by monitoring three standard reflections every 180 minutes: relative decay values of about 6.5 and 20.4% were observed. Analytical absorption corrections were applied, using ψ-scans of three suitable reflections having χ near 90°. The measured intensities were corrected for decay, Lorentz, polarization and background effects and reduced to F_o^2. The crystal of **3** was measured on a SMART Bruker diffractometer, equipped with a CCD area detector and graphite monochromatized Mo-*Kα* radiation (generator setting: 40 kV, 45 mA). Initial cell parameters were determined on the basis of the angular settings of 34 unique reflections. A full hemisphere of data (1350 frames, ω scan, $\Delta\omega = 0.3°$, $t = 50$s) was collected; integration by SAINT[26] and absorption correction by SADABS[27] lead to a total of 18908 F_o^2 values.

Single Crystal Structure Solution and Refinement: All three structures have been solved by direct methods (SIR97[28]) and difference Fourier methods, and subsequently refined by full-matrix least-squares against F_o^2 using all reflections and the program SHELX[29] on an IBM compatible PC. Scattering factors for neutral atoms (including dispersion corrections) were taken from the internal library of SHELX. Owing to the very similar packing environment of the $Mn(CO)_3$ and $Re(CO)_3$ fragments in **1**, a partial disorder [refined values 0.773(1):0.227(1)] is observed for Re/Mn substitution, which has been modeled using the EXYZ and EADP options of SHELX97; this disorder is also reflected by the presence of a few weak reflections which violate the systematic absences conditions. The very small size of the acicular crystal of **3** (10 × 10 × 200 μm) and the larger sphere of data collected are reflected by rather poor estimates of the integrated intensities of the weak reflections (see *R*1 and R_{int} in Table 2); a parallel refinement, performed only with intense data [$I > 10\sigma(I)$], resulted in much better agreement factors ($R1 = 0.027$ and $wR2 = 0.048$ for the same structural model). Apart from the cation and water oxygen atoms in **5** (which experience very large thermal motion or unrationalized static disorder, leading to poor(er) agreement factors), all remaining non-H atoms have been treated anisotropically. Hydrogen atoms were ultimately included in calculated positions and refined isotropically riding on the atoms to which they are attached. A list of crystal data, refinement parameters and final agreement factors can be found in Table 2.[30]

X-ray Powder Diffraction: The light yellow powders of **2** were gently ground in an agate mortar and then deposited on the clean surface of a Si(511) monocrystal with the aid of a thin layer of silicone grease. XRPD data were collected in the step-scan θ:2θ mode on a Rigaku D-III/Max horizontal-scan diffractometer equipped with parallel (Soller) slits and a graphite monochromator (Cu-*Kα* λ = 1.5418 Å) in the diffracted beam. Generator set at 40 kV and 40 mA; Slits used: DS = 1.0°; AS = 1.0°; RS = 0.3 mm. Δ2θ = 0.02°, t = 5 s; the sample was rotated at about 60 rpm about the scattering axis in order to minimize preferred orientation effects. A whole pattern profile fitting performed by the Le Bail method[31]

Table 2. Summary of X-ray single-crystal data and structure refinement parameters

Compound	**1**	**3**	**5**
Formula	$C_{21}H_{25}MnN_7O_6Re$	$C_{36}H_{50}Mn_2N_{14}O_9Re_2$	$C_{36}H_{52}MnN_{14}O_7Re_2$
Formula weight	712.62	1305.17	1220.26
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*P*21/*n*	*Pnmm*	*P*-1
a [Å]	9.807(1)	7.926(1)	11.003(2)
b [Å]	16.376(2)	17.524(1)	11.067(2)
c [Å]	16.095(3)	17.120(1)	12.619(5)
α [°]	−	−	65.64(2)
β [°]	92.33(1)	−	88.77(2)
γ [°]	−	−	60.12(2)
V [Å^3]	2582.7(6)	2377.9(2)	1171.0(6)
Z	4	2	1
F(000)	1392	1272	597
D(calcd.) [g cm^{-3}]	1.833	1.823	1.730
Temperature [K]	293(2)	293(2)	293(2)
Diffractometer	CAD4	SMART	CAD4
Radiation [Å]	0.71073	0.71073	0.71073
Absorption coeff [mm^{-1}]	5.22	5.65	5.48
Crystal size [mm]	0.30×0.15×0.10	0.01 × 0.01 × 0.20	0.05 × 0.05 × 0.08
Scan method	ω	ω	ω
Scan interval [°]	0.9+0.35tanθ	0.3[a]	0.8+0.35tanθ
Max time per refl [s]	60	50[a]	50
θ range [°]	3.0−25.0	1.7−30.7	3.0−25.0
Index ranges	$-11 \le h \le 11, 0 \le k \le 19$ $0 \le l \le 19$	$-11 \le h \le 11, -25 \le k \le 16$ $-24 \le l \le 24$	$-13 \le h \le 13, -11 \le k \le 13$ $0 \le l \le 14$
Reflections collected	4515	18371	4094
Independent reflections	4515 [$R_{int} = 0.00$]	3825 [$R_{int} = 0.121$]	4094 [$R_{int} = 0.000$]
Crystal decay	6.4%	none	20.5
Absorption correction	Ψ-scan	Sadabs	Ψ-scan
Min. transmission factor	0.62	0.89	0.93
Obsd. reflection criterion	−	all reflections	−
Refinement method	[full matrix	least-squares	on F_o^2]
Data/restraints/parameters	4515/0/329	3825/0/154	4094/0/229
Goodness−of−fit[b] on F_o^2	1.173	1.228	1.005
*R*1, *wR*2 indices[c] [$F_o > 4\sigma(F_o)$]	0.0419, 0.1013	0.1046, 0.0845	0.0543, 0.1067
*R*1, *wR*2 indices (all data)	0.0541, 0.1067	0.1801, 0.0962	0.1090, 0.1270
Largest diff. peak and hole [eÅ^{-3}]	1.02, −0.96	0.84, −1.11	1.28, −0.87
Weighting scheme,[d] *a*, *b*	0.0426, 9.54	0.0184, 2.57	0.0590, 0

[a] Frame width and exposure time per frame. − [b] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ where *n* is the number of reflections and *p* is the number of refined parameters. − [c] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. − [d] $w = 1/[\sigma(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

using GSAS[32] afforded the following lattice parameters (a = 9.774; b = 16.286, c = 16.002 Å, β = 92.09°), indicating the strict isomorphous character of the powders of **2** with compound **1**. Since these two unit cells are very similar, they probably share atoms with similar fractional coordinates: indeed a Rietveld refinement for fixed, isotropic atoms, whose coordinates are taken from **1** (with the obvious replacement of Re by Mn), rapidly converged to R_p = 0.083 and R_F = 0.085, demonstrating the validity of such a structural model (see Figure 4); however, since powder diffraction is known to afford only approximate bonding parameters, no further refinements were performed in the search for better powder data fitting by the customary (for single-crystal data) independent atom model.

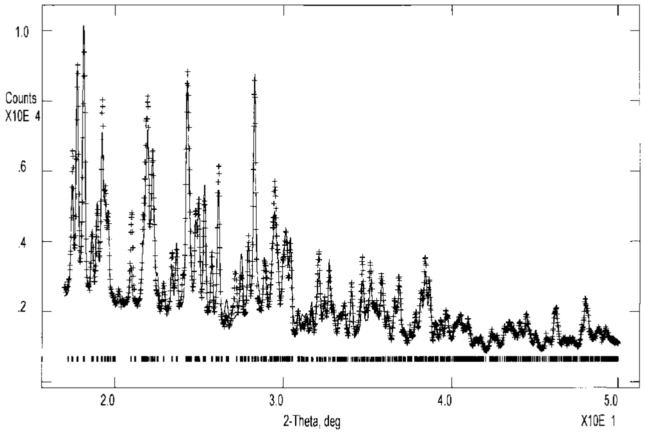


Figure 4. Rietveld refinement plot for $[(CO)_3Mn(pz)_3Mn(CO)_3](Et_3NH)$ (**2**) in the 17 < 2θ < 50° range, with peak markers at the bottom

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