Journal of Organometallic Chemistry 696 (2011) 559–567

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Nitrosyl derivatives of the unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ ($L_2 = Ph_2PCH_2PPh_2$, $(EtO)_2POP(OEt)_2$)

M. Esther García [a], Sonia Melón [a], Miguel A. Ruiz [a,*], Luciano Marchiò [b], Antonio Tiripicchio [b]

[a] Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, Julian Clavería, E-33071 Oviedo, Spain
[b] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Viale G. P. Usberti 17/A, I-43100 Parma, Italy

ARTICLE INFO

Article history:
Received 2 August 2010
Received in revised form
9 September 2010
Accepted 9 September 2010
Available online 21 October 2010

Keywords:
Manganese
Metal–metal interactions
Hydride ligands
Nitrosyl ligands
Carbonyl ligands
Diphosphine ligands

ABSTRACT

The title dimanganese complexes react with NO (5% in N_2) at room temperature to give as major products the corresponding hexanitrosyl derivatives $[Mn_2(NO)_6(\mu\text{-}L_2)]$ in moderate yields, and they react rapidly with NO_2 to give the corresponding hydride derivatives $[Mn_2(\mu\text{-}H)(\mu\text{-}NO_2)(CO)_6(\mu\text{-}L_2)]$, these having a nitrite ligand bridging the dimetal centre through the N and O atoms. The dppm-bridged dihydride also reacts selectively at 273 K with $(PPN)NO_2$ to give first the nitro derivative $(PPN)[Mn_2(\mu\text{-}H)(H)(NO_2)(CO)_6(\mu\text{-}dppm)]$, which then transforms into the nitrosyl complex $(PPN)[Mn_2(\mu\text{-}CO)(CO)_5(NO)(\mu\text{-}dppm)]$ at room temperature or above (dppm = $Ph_2PCH_2PPh_2$; $PPN^+ = [N(PPh_3)_2]^+$). The latter anion reacts with $(NH_4)PF_6$ to give the hydride-bridged nitrosyl complex $[Mn_2(\mu\text{-}H)(\mu\text{-}NO)(CO)_6(\mu\text{-}dppm)]$ and with $[AuCl(PPh_3)]$ to give the trinuclear cluster $[AuMn_2(\mu\text{-}NO)(CO)_6(\mu\text{-}dppm)(PPh_3)]$ (Mn–Au = ca. 2.68 Å; Mn–Mn = 2.879(2) Å). Both products are derived from the addition of the added electrophile at the intermetallic bond and rearrangement of the nitrosyl ligand into a bridging position. In contrast, methylation of the anion with CF_3SO_3Me takes place at the nitrosyl ligand to yield the unstable methoxylimide derivative $[Mn_2(\mu\text{-}NOMe)(CO)_6(\mu\text{-}dppm)]$. Analogous reactions at the nitrosyl ligand take place upon the addition of $HBF_4\cdot OEt_2$ to the nitrosyl-bridged hydrides $[Mn_2(\mu\text{-}H)(\mu\text{-}NO)(CO)_n(\mu\text{-}dppm)_m]$ ($n = 6$, $m = 1$; $n = 4$, $m = 2$) to give the corresponding hydroxylimide derivatives $[Mn_2(\mu\text{-}H)(\mu\text{-}NOH)(CO)_n(\mu\text{-}dppm)_m]BF_4$, which were also thermally unstable and could not be isolated nor fully characterized.

1. Introduction

Nitrogen monoxide is a remarkable molecule able to strongly bind to transition metal atoms both in high and low oxidation states, thus giving rise to a wide variety of coordination and organometallic complexes exhibiting a rich chemistry [1,2]. Further interest in this molecule stems from its biological activity [1,3], and also because nitrogen monoxide is one of the important air pollutants requiring catalytic abatement [1,4,5]. Therefore the activation and cleavage of the strong N–O bond of nitrogen monoxide when bound to a metal atom is a process not only of academic interest, but of particular relevance too for the understanding of the biological role of this molecule and also to developing better catalysts for its abatement in diverse gas effluents. In this context we have carried out a prospective study on this important reaction using different binuclear carbonyl complexes as potential activators of the N–O bond of the nitrosyl ligand.

Recently we have shown that full cleavage of the N–O bond in a coordinated nitrosyl ligand can take place at quite low temperatures on *heterometallic* complexes combining group 6 and group 7 metal atoms. Thus, the anionic complexes $[MCp(CO)_2L]^-$ (M = Mo, W; Cp = $\eta^5\text{-}C_5H_5$; L = CO, $P(OMe)_3$, PPh_3) reacted with the nitrosyl cations $[M'Cp'(CO)_2(NO)]^+$ (M′ = Mn, Re; Cp′ = $\eta^5\text{-}C_5H_4Me$) to give the nitride-bridged derivatives $[MM'CpCp'(\mu\text{-}N)(CO)_3L]$ [6] and, in a different type of reaction, the dimolybdenum anion $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2]^-$ reacted with the mentioned nitrosyl cations to give the corresponding oxonitride derivatives $[Mo_2MCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PPh_2)(CO)_3]$ [7]. It was thus of interest to explore in this context the potential of *homometallic* complexes having either group 6 or group 7 metal atoms. In this paper we report the synthesis and some reactions of several new dimanganese nitrosyl complexes derived from the unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ ($L_2 = Ph_2PCH_2PPh_2$ or dppm (**1a**), $(EtO)_2POP(OEt)_2$ or tedip (**1b**)). At this point we should note that only a handful of dimanganese nitrosyl complexes have been reported so far, perhaps due to synthetic difficulties, these being limited to the neutral dinitrosyls $[Mn_2(CO)_7(NO)_2]$ [8],

---

* Corresponding author. Fax: +34 985103446.
E-mail address: mara@uniovi.es (M.A. Ruiz).

0022-328X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.09.079

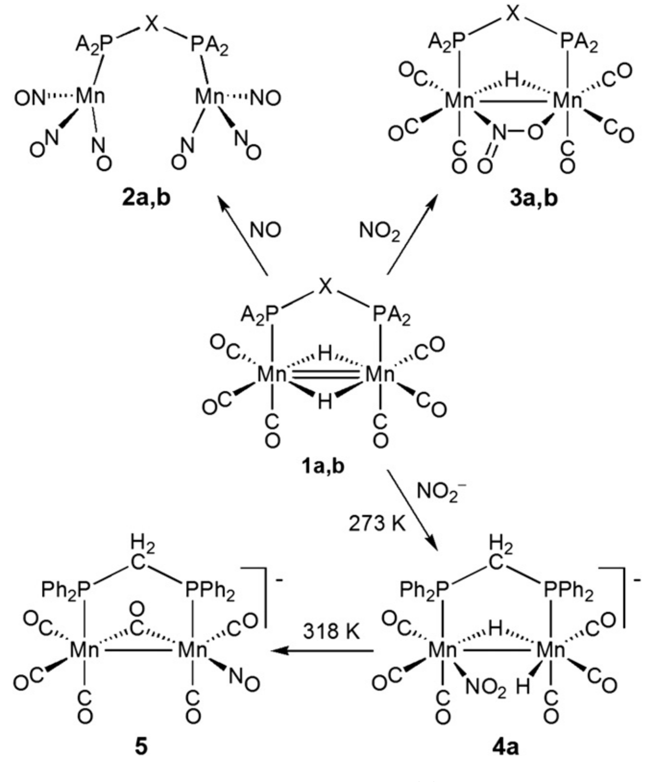
$[Mn_2L^*_2(CO)_2(NO)_2]$ [L^* = Cp [9a], Cp′ [9b]], $[Mn_2Cp_2(\mu\text{-}SR)_2(NO)_2]$ [10], $[Mn_2Cp_2(CS)_2(NO)_2]$ [11] and $[Mn_2Cp_2(\mu\text{-}S_2)_2(NO)_2]$ [12], the trinitrosyls $[Mn_2L^*_2X(NO)_3]$ (X = halogen, NO_2, alkyl, aryl) [13], the cation $[Mn_2L^*_2(\mu\text{-}NH_2)(\mu\text{-}CO)(NO)_2]^+$ [14] and the anion $[Mn_2(CO)_6(NO)_2]^{2-}$ [15]. Moreover, except for the dicarbonyl complexes $[Mn_2L^*_2(CO)_2(NO)_2]$, the chemical behaviour of this reduced group of compounds has not been examined.

Because of the unsaturated nature of their central $Mn_2(\mu\text{-}H)_2$ core, the dihydride complexes **1a,b** are highly reactive towards a great variety of molecules under mild conditions [16–18], and thus were ideal candidates as starting substrates for the synthesis of novel dimanganese nitrosyl complexes via their reactions with different sources of NO under mild conditions. As it will be seen below, the direct reaction of compounds **1a**,**b** with NO caused full substitution of CO ligands, but a more controlled nitrosylation could be achieved through their reaction with the nitrite ion, this giving with good yield the anionic nitrosyl complex $[Mn_2(CO)_6(NO)(\mu\text{-}dppm)]^-$, which in turn proved to have a multisite reactivity, then being an useful synthetic precursor to several derivatives having nitrosyl as well as hydroxyl- and methoxylimide bridges.

2. Results and discussion

2.1. Reactions of the hydride complexes *1a,b* with NO

The dppm-bridged complex **1a** reacts with NO (5% in N_2) slowly at room temperature, but does it more rapidly at ca. 318 K to give as major product the hexanitrosyl derivative $[Mn_2(NO)_6(\mu\text{-}dppm)]$ (**2a**) in moderate yield (ca. 40%), along with variable amounts (0–25%) of the nitrite–hydride complex $[Mn_2(\mu\text{-}H)(\mu\text{-}NO_2)(CO)_6(\mu\text{-}dppm)]$ (**3a**), the reaction being completed in ca. 90 min at this temperature (Scheme 1). In spite of this, no intermediates could be spectroscopically detected in significant amounts in this obviously multistep reaction implying the elimination of hydrogen and the substitution of six CO molecules for an equal number of nitrosyl ligands. In addition, the variable yields in which the hydride **3a** was formed suggested that trace amounts of oxygen might be behind its formation, a matter to be dealt with in the next section. As expected, compound **2a** can be alternatively prepared through the thermal reaction of $[Mn(CO)_3(NO)]$ with substoichiometric amounts of the dppm ligand (see the experimental section).



Scheme 1. Reactions of the dihydride compounds **1a,b**[a]. [a] A = Ph, OEt; X = CH_2, O; .the PPN^+ cation of compounds **4** and **5** is omitted for clarity.

The tedip-bridged complex **1b** reacts somewhat faster with NO, and the reaction can be completed in ca. 3 h at room temperature to give $[Mn_2(NO)_6(\mu\text{-}tedip)]$ (**2b**) in moderate yield (ca. 40%). In this case, no nitrite–hydride side product analogous to compound **3a** was detected, although such a species can be prepared selectively in an independent way (Scheme 1). On the other hand, an IR monitoring of this reaction allowed the detection of small amounts of intermediate species having possibly partial degrees of CO substitution (ie. of the type $[Mn_2(NO)_x(CO)_y(\mu\text{-}tedip)]$) but unfortunately we could not find conditions to obtain them in significant amounts.

The structural characterization of compounds **2** is straightforward after considering that each of them exhibit a single resonance in the corresponding ^{31}P NMR spectrum and two N–O stretching bands in the IR spectrum with frequencies and relative intensities comparable to those reported previously for the isoelectronic complexes $[Mn(NO)_3(PPh_3)]$ and $[Mn_2(NO)_6(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]$ [19], consistent with a tetrahedral environment around the manganese centres (Table 1). As expected from the better donor properties of the dppm ligand (compared to those of the diphosphite tedip), the N–O stretching frequencies of **1a** are lower (by some 15 cm^{-1}) than those of **1b**.

2.2. Reactions of the hydride complexes *1a,b* with NO_2

As noted above, it was suspected that the formation of **3a** might require the concurrence of oxygen, but a separated experiment revealed that **1a** would not react with oxygen alone to give **3a**. By considering, however, that oxygen reacts readily with NO at room temperature to give NO_2, it was therefore likely that the latter species might be the actual reagent leading to the nitrite side product. Indeed an independent experiment revealed that compound **3a** was rapidly formed as the major product when a mixture of NO and NO_2 (generated in situ from nitric oxide an oxygen, see the experimental section) was allowed to react with a toluene solution of **1a** at room temperature. Moreover, the hydride **1b** reacted analogously to give the tedip-bridged complex $[Mn_2(\mu\text{-}H)(\mu\text{-}NO_2)(CO)_6(\mu\text{-}tedip)]$ (**3b**) as major product (Scheme 1).

The spectroscopic data for compounds **3a,b** (Table 1) are strongly reminiscent of those of the hydride–alkenyl complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^2\text{-}CRCH_2)(CO)_6(\mu\text{-}dppm)]$ previously reported by us [17b] and they are clearly indicative of the presence of a bridging hydride and an asymmetrically-bound NO_2 ligand in these molecules. The coordination of the hydride is revealed by the presence of strongly shielded ^1H NMR resonances at ca. −17 ppm, exhibiting essentially identical coupling to both phosphorus atom. The latter atoms are inequivalent, as indicated by the presence of two doublets in the low temperature ^{31}P NMR spectra of both complexes, but there is a slow dynamic process rendering the phosphorus atoms equivalent, since the room temperature spectra display two broad (**3a**) or just one averaged and broad (**3b**) resonances. All of this suggests that coordination of the NO_2 ligand to the dimetal centre must occur through both the N and one of the O atoms, and these would exchange their positions easily. Interestingly, the vinyl complex mentioned above also exhibited dynamic behaviour in solution [17b]. The asymmetric coordination of the NO_2 ligand in compounds **3** is further supported by the observation in both cases of two quite separated N–O stretching bands at ca. 1430 and 1160 cm^{-1}, as usually found for N,O-bound NO_2 ligands [20].

Table 1
Selected IR[a] and $^{31}P\{^1H\}$ NMR[b] data for new compounds.

Compound	ν(CO)	ν(NO)	δ(P)	J_{PP}
$[Mn_2(NO)_6(\mu\text{-dppm})]$ (**2a**)		1783 (w), 1685 (vs)	37.2	
$[Mn_2(NO)_6(\mu\text{-tedip})]$ (**2b**)		1795 (w), 1703 (vs)[c]	161.0[d]	
$[Mn_2(\mu\text{-H})(\mu\text{-NO}_2)(CO)_6(\mu\text{-dppm})]$ (**3a**)	2046 (vs), 2019 (s), 1969 (m), 1947 (s), 1924 (m)	1421, 1161[e]	49.6, 43.8[f]	66
$[Mn_2(\mu\text{-H})(\mu\text{-NO}_2)(CO)_6(\mu\text{-tedip})]$ (**3b**)	2059 (vs), 2029 (s), 1985 (m), 1958 (s), 1939 (m)	1437, 1164[e]	160.0, 159.0[g]	57
$(PPN)[Mn_2(\mu\text{-H})(H)(NO_2)(CO)_6(\mu\text{-dppm})]$ (**4a**)	2018 (vs), 1977 (m), 1937(m), 1912 (s), 1901 (m, sh), 1877(m)[h]	1326, 1302[e]	76.7, 64.8[i]	72
$(PPN)[Mn_2(\mu\text{-CO})(CO)_5(NO)(\mu\text{-dppm})]$ (**5**)	1982 (s), 1898 (vs), 1872 (m, sh), 1817 (m)[h]	1609 (m)[h]	69.4, 67.3[j]	
$[Mn_2(\mu\text{-H})(\mu\text{-NO})(CO)_6(\mu\text{-dppm})]$ (**6**)	2038 (s), 1999 (vs), 1969 (m), 1925 (s), 1917 (m, sh)	1471[e]	52.2	
$[AuMn_2(\mu\text{-NO})(CO)_6(\mu\text{-dppm})(PPh_3)]$ (**7**)	2007 (s), 1965 (vs), 1937 (w), 1918 (m, sh), 1902 (s)	1446[e]	64.5 (t), 53.1 (d)	13
$[Mn_2(\mu\text{-NOMe})(CO)_6(\mu\text{-dppm})]$ (**8**)	2035 (s), 2004 (vs), 1965 (s), 1947 (m), 1922 (s)		37.7, 33.6	35
$[Mn_2(\mu\text{-H})(\mu\text{-NO})(CO)_4(\mu\text{-dppm})_2]$ (**9a**)	1956 (w), 1925 (vs), 1862 (s)	1408[e]	61.7	
$[Mn_2(\mu\text{-H})(\mu\text{-NO})(CO)_4(\mu\text{-dmpm})(\mu\text{-dppm})]$ (**9c**)	1949(w), 1916 (vs), 1857 (s)		61.7, 48.6[k]	
$[Mn_2(\mu\text{-H})(\mu\text{-NOH})(CO)_6(\mu\text{-dppm})]BF_4$ (**10**)			55.6, 55.2[l]	129
$[Mn_2(\mu\text{-H})(\mu\text{-NOH})(CO)_4(\mu\text{-dppm})_2]BF_4$ (**11**)			63.0[m]	

[a] Recorded in dichloromethane solution, unless otherwise stated, ν in cm^{-1}.

[b] Recorded in CD_2Cl_2 solutions at 290 K and 121.50 MHz, unless otherwise stated, δ in ppm relative to external 85% aqueous H_3PO_4, J_{PP} in Hertz; all low temperature spectra recorded at 161.99 MHz.

[c] Petroleum ether solution.

[d] C_6D_6 solution.

[e] Recorded in a KBr disk.

[f] 228 K.

[g] 200 K.

[h] Tetrahydrofuran solution.

[i] Recorded at 213 K in tetrahydrofuran–C_6D_6 solution.

[j] Broad resonances recorded at166 K.

[k] AA′XX′multiplets, $J_{PP} + J_{PP'} = 91$.

[l] 185 K.

[m] Broad resonance recorded at 248 K.

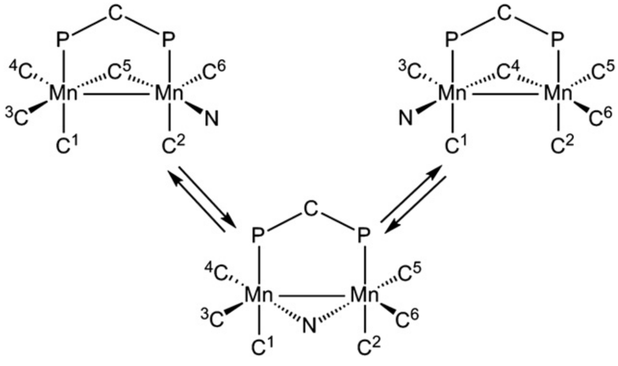
2.3. *Reactions of the hydride complexes* ***1a,b*** *with (PPN)NO_2*

Compound **1a** reacts readily with (PPN)NO_2 at 273 K ($PPN^+ = [N(PPh_3)_2]^+$) to give the anionic nitro complex $(PPN)[Mn_2(\mu\text{-H})(H)(NO_2)(CO)_6(\mu\text{-dppm})]$ (**4a**) as the single product. This compound, however, could not be isolated as a pure solid, because it progressively transforms (even at low temperature) into the nitrosyl derivative $(PPN)[Mn_2(\mu\text{-CO})(CO)_5(NO)(\mu\text{-dppm})]$ (**5**), the reaction being completed in a few hours at room temperature or just in about 1 h at 318 K (Scheme 1). The tedip-bridged compound **1b** reacts initially with (PPN)NO_2 at 273 K in a similar way to give a related compound **4b**, as deduced from the IR spectrum of the reaction mixture after a few minutes, but this species rapidly decomposes at that temperature to give a complex mixture of compounds, and thus no further attempts were made to characterize it.

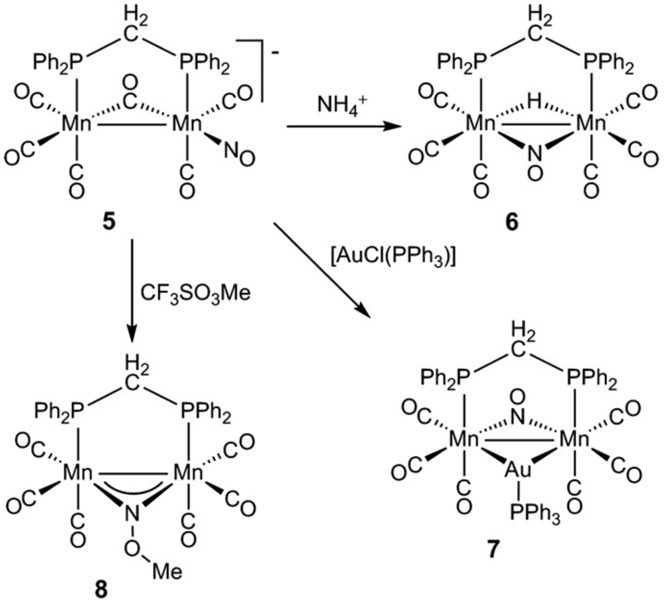
Compound **4a** displays six C–O stretching bands of strong to medium intensity in the IR spectrum (Table 1), which is indicative of a low symmetry for the anion (C_s or below), while the intensity of the two more energetic bands is suggestive of the retention of a local facial arrangement in both $Mn(CO)_3$ oscillators [21], as also found for the halide-bridged anions $[M_2(\mu\text{-X})(CO)_6(\mu\text{-L}_2)]^-$ (M = Mn, Re; L_2 = dppm, tedip; X = Br, Cl) [22]. The average C–O stretching frequency for **4a**, however, is substantially higher than those of the mentioned halide complexes and only some 20 cm^{-1} lower than the average value for the neutral hydride **1a**, thus indicating that the negative charge in the anion of **4a** is largely located at the NO_2 ligand. The latter is proposed to be coordinated exclusively through the N atom (*nitro* coordination), with this being supported by the observation of two N–O stretches of similar frequency at ca. 1300 cm^{-1}, corresponding to the respective asymmetric and symmetric stretches [20].

The presence of two inequivalent hydride ligands in **4a** is clearly indicated by the appearance, in the ^1H NMR spectrum recorded at 223 K, of two very differently shielded resonances at ca. −7 (terminal H) and −19 ppm (bridging H). In agreement with this, the ^{31}P NMR spectrum displays two doublet resonances at that temperature. However, upon warming of the solution, the hydride resonances further broaden and eventually disappear into the baseline of the spectrum at room temperature, this suggesting the operation of some exchange process between the terminal and bridging hydrides in solution, as previously observed for the related trihydride anions $[Mn_2(\mu\text{-H})(H)_2(\mu\text{-L}_2)]^-$ (L_2 = tedip [16b], dppm [23]) and also for the neutral dihydride $[Re_2(\mu\text{-H})(H)(CO)_6\{P(OMe)_3\}]$ [24].

The IR spectrum of **5** displays four strong to medium bands in the 2000–1800 cm^{-1} region that can be assigned to C–O bond stretches of terminal carbonyls, and a fifth band whose low frequency (1609 cm^{-1}) might be indicative of the presence of either a terminal nitrosyl (cf. 1646 and 1609 cm^{-1} for the mononuclear anion $[Mn(CO)_2(NO)_2]^-$ [25]) or a bridging carbonyl (cf. 1660–1550 cm^{-1} for the binuclear anions $[Mo_2Cp_2(\mu\text{-PR}_2)(\mu\text{-CO})_2]^-$ [26]), or to both of them. The pattern of the terminal stretches, however, is substantially different from that shown by the mentioned halide-bridged anions $[M_2(\mu\text{-X})(CO)_6(\mu\text{-L}_2)]^-$; in particular, the anion in **5** exhibits just one (instead of two) strong band above 1900 cm^{-1}, this indicating the presence of just a single facial $Mn(CO)_3$ oscillator in the anion. We thus can safely exclude for **5** a structure with a bridging nitrosyl and six terminal carbonyls. Instead, the IR spectrum of **5** is consistent with the presence of a bridging carbonyl and facial $Mn(CO)_3$ and $Mn(NO)(CO)_2$ oscillators (Scheme 1). In apparent disagreement with this, however, the room temperature NMR spectra of **5** display single resonances for both phosphorus atoms and for all six carbonyl ligands of the anion, obviously revealing the presence of dynamic effects. Indeed, on lowering the temperature, the ^{31}P resonance broadens and eventually splits below ca. 173 K into two separated resonances, as expected. In the same way, the single ^{13}C carbonyl resonance observed at room temperature (at 235 ppm) eventually splits into three ones of roughly the same intensity at 241.9, 234.7 and 230.6 ppm at 213 K. Although the latter are still averaged resonances, the expected limiting spectrum with six different carbonyl resonances was not reached on further cooling of the solution. To explain the partial averaging of carbonyl resonances observed at 213 K we propose the dynamic process depicted in the Scheme 2, inspired in that observed for the carbonyl-bridged complexes $[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_4(\mu\text{-dppm})_2]$ [27] and $[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CO})(CO)_5(PPh_3)(\mu\text{-dppm})]$



Scheme 2. Fluxional process proposed for the anion of compound **5** in solution[a]. [a] P–C–P = dppm; O atoms of nitrosyl and carbonyl ligands omitted for clarity.



Scheme 3. Reactions of compound **5**[a]. [a] The PPN$^+$ cation of compound **5** is omitted for clarity.

[28], and involving a limited rearrangement of the ligands placed in the plane perpendicular to the average place defined by the diphosphine and the metal atoms. As a result, the carbonyl ligands are averaged pairwise (1/2, 3/6 and 4/5 in Scheme 2), as they are the phosphorus atoms of the molecule. The full averaging of all CO resonances observed at room temperature obviously requires the concurrence of additional rearrangements, possibly a local rotation of the pyramidal moieties $Mn(CO)_3$ and $Mn(CO)_2(NO)$ through their false local C_3 axis, this being a common dynamic process found in transition metal carbonyl clusters [29].

The formation of **5** from **4a** formally implies the conversion of NO_2 into NO via the hydride ligands present in the anion of **4a**, presumably with formation of water. This is an unusual evolution of a nitro–carbonyl complex, more likely to evolve to the corresponding nitrosyl derivative via elimination of CO_2 [2c,d, 30]. However, from a mechanistic point of view, this might not be considered as an unusual evolution in the chemistry of the hydrides **1**, because these compounds have been shown to be able to transfer their hydride ligands to the incoming reagent in a number of reactions. In particular, the hydride **1a** has been shown to react with several 1-alkynes HC≡CR to give a molecule of the corresponding alkenylidene complex $[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CCHR})(CO)_6(\mu\text{-dppm})]$ and a molecule of the free alkene $CH_2{=}CHR$, this implying the full transfer of two hydride atoms to a molecule of alkyne [17b].

2.4. Reactions of **5** with H^+ and $Au(PPh_3)^+$ cations

Compound **5** reacts readily with weak protic acids such as the ammonium ion to give the corresponding hydride derivative $[Mn_2(\mu\text{-H})(\mu\text{-NO})(CO)_6(\mu\text{-dppm})]$ (**6**), this being derived from the expected addition of the proton to the intermetallic bond and a less anticipated rearrangement of the nitrosyl ligand, from a terminal into a bridging coordination position. A similar reaction takes place between **5** and $[AuCl(PPh_3)]$ to give the trinuclear cluster $[AuMn_2(\mu\text{-NO})(CO)_6(\mu\text{-dppm})(PPh_3)]$ (**7**), this resulting from the addition at the intermetallic bond of a $Au(PPh_3)^+$ cation, isolobal with a proton [30], and a comparable rearrangement of the nitrosyl ligand (Scheme 3).

The structure of **7** in the crystal is shown in the Fig. 1, while the Table 2 collects some relevant bond lengths and angles. This molecule can be described as two facial $Mn(CO)_3$ fragments bridged by nitrosyl and $Au(PPh_3)$ fragments, with the diphosphine ligand acting as a third bridge and positioned perpendicularly to the average Mn_2AuN plane. This bioctahedral structure is thus very similar to that previously determined by us for the isoelectronic cluster $[AuMn_2(\mu\text{-Br})(CO)_6(\mu\text{-tedip})(PPh_3)]$ [22]. The Mn–Au lengths is these two compounds are comparable to each other (ca. 2.68 Å) but the Mn–Mn length in **7** (2.879(2) Å) is some 0.2 Å shorter than the one measured in the electron-precise bromide-bridged cluster (3.090(3) Å), and it actually approaches the Mn–Mn separation measured in the electron-deficient (with a 32-electron dimanganese centre) cluster $[Au_2Mn_2(CO)_6(\mu\text{-dppm})(PPh_3)_2]$ (2.865(4) Å [23]). We attribute this shortening effect not to an electronic deficiency of the dimanganese centre in **7**, but to the small covalent radius of the N atom (compared to Br). For instance, a comparable shortening effect has been measured previously for the azavinylidene complex $[Mn_2(\mu\text{-H})(\mu\text{-N{=}CHPh})(CO)_6(\mu\text{-dppm})]$ (2.818(4) Å, [18f]), which also is an electron-precise complex.

Spectroscopic data in solution for **7** (Table 1) are fully consistent with the structure found in the crystal. In particular, its IR spectrum exhibits a five C–O stretching band pattern common to many binuclear manganese complexes of the type $[Mn_2(\mu\text{-X})(\mu\text{-Y})(CO)_6(\mu\text{-L}_2)]$ (X, Y = 1 or 3-electron donor ligand, [18]) having two facial $Mn(CO)_3$ oscillators. We only note the large separation

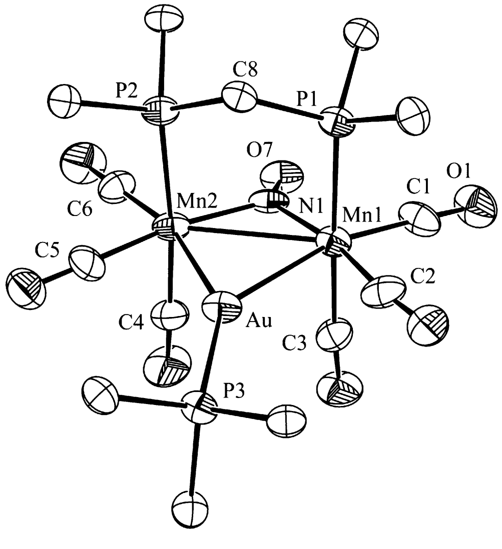


Fig. 1. ORTEP diagram (25% probability) of compound **7**, with H atoms and phenyl groups (except their ipso carbons) omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (deg) for compound **7**.

Mn(1)–Mn(2)	2.879(2)	Au–P(3)	2.321(2)
Mn(1)–Au	2.694(2)	Mn(2)–Au	2.668(2)
Mn(1)–P(1)	2.329(3)	Mn(2)–P(2)	2.336(3)
Mn(1)–N(1)	1.876(8)	Mn(2)–N(1)	1.940(8)
Mn(1)–C(1)	1.76(1)	Mn(2)–C(6)	1.77(1)
Mn(1)–C(2)	1.78(1)	Mn(2)–C(4)	1.83(1)
Mn(1)–C(3)	1.84(1)	Mn(2)–C(5)	1.81(1)
P(1)–C(8)	1.81(1)	P(2)–C(8)	1.80(1)
P(1)–Mn(1)–Mn(2)	91.4(1)	P(2)–Mn(2)–Mn(1)	91.6(1)
P(1)–Mn(1)–N(1)	92.7(2)	P(2)–Mn(2)–N(1)	94.6(2)
P(1)–Mn(1)–Au	92.4(1)	P(2)–Mn(2)–Au	90.1(1)
N(1)–Mn(1)–C(2)	169.4(5)	N(1)–Mn(2)–C(5)	168.7(5)
N(1)–Mn(1)–Au	98.9(3)	N(1)–Mn(2)–Au	98.1(2)

between the two more energetic bands (42 cm^{-1}), to be compared with the values of ca. 30 cm^{-1} usually found for this short of metal–metal bonded compounds, an observation that must be taken as indicative of a strong Mn–Mn interaction for **7** also in solution, in agreement with the short intermetallic length found in the crystal. On the other hand, the NMR data (Table 1 and Experimental Section) reveal the chemical equivalence in solution of the P atoms of the diphosphine and the inequivalence of the methylenic protons, and deserve no further comments. As for the nitrosyl ligand, it gives rise to a medium intensity band at 1450 cm^{-1}, a position only slightly lower than those reported for the μ$_2$-NO ligands in the manganese complexes [$Mn_2Cp_2(CO)_2(NO)_2$] and [Mn_3Cp_3(μ$_3$-NO)(μ$_2$-NO)$_3$] (1480–1520 cm^{-1} [9a]).

Spectroscopic data for the hydride **6** are similar to those of **7** (IR pattern, ^{31}P chemical shifts) and therefore support a structure comparable to that of the gold cluster just discussed. The C–O and N–O stretching frequencies in **6** are higher than those in **7**, as expected from the higher electronegativity of the H atom compared to that of the gold fragment, but the chemical shift for the bridging hydride (−8.31 ppm) is significantly higher than usually found for our dimanganese complexes (−12 to −17 ppm). We can attribute this relative deshielding effect to the presence of the bridging nitrosyl in the molecule, placed almost in the Mn_2H plane, an effect previously described for mononuclear complexes having hydride and nitrosyl ligands arranged *trans* to each other [31]. Binuclear species having H and NO bridging ligands are exceedingly rare. Actually, the only other binuclear species we can use for comparative purposes is the dirhodium complex [Rh_2(μ-H)(μ-NO)($P^iPr_3)_4$] a molecule displaying also a poorly shielded resonance at −7.14 ppm [32].

2.5. Methylation reactions of compound 5

Compound **5** failed to react below 273 K with MeI or (Me_3O)BF_4, while a generalized decomposition was observed when carrying out these reactions at room temperature. In contrast, a fast and selective reaction took place at 243 K when using CF_3SO_3Me as the methylating agent, to give the methoxylimide derivative [Mn_2(μ-NOMe)$(CO)_6$(μ-dppm)] (**8**). Unfortunately, compound **8** decomposes in solution at room temperature and could be not isolated as a pure solid in the usual way.

The IR spectrum of **8** in solution exhibits five medium to strong C–O stretching bands with a pattern not very different from that of the hydride **6**, but its ^{31}P NMR spectrum denotes the chemical inequivalence of the P atoms, indicative of the presence of an asymmetric bridging group. The latter is identified as a bridging methoxylimide group on the basis of the appearance of the corresponding proton resonance at 3.41 ppm, although the alternative possibility of the methyl group being attached at the nitrogen atom of the former nitrosyl ligand cannot be ruled out completely.

The formation of **8** implies the binding of the Me group at the oxygen atom of the nitrosyl anion, as opposed to the formation of compounds **6** and **7**, these implying the binding of the electrophile at the intermetallic bond in the anion of **5**. This is an unusual result for a terminal nitrosyl ligand, that at most would have been expected to react with a small and hard electrophile such as H$^+$ or Me$^+$ at its nitrogen atom [33]. In contrast, trinuclear complexes having μ$_2$- or μ$_3$-bridging nitrosyl ligands actually have been shown to react with H$^+$ or Me$^+$ at their O(nitrosyl) atoms to give the corresponding hydroxylimide (μ$_3$-NOH) [34–36] and methoxylimide (μ$_3$-NOMe) derivatives [34,36]. In this context we should note that the dimanganese complexes [$Mn_2L^*_2(CO)_2(NO)_2$], displaying in solution different isomers with both bridging and terminal nitrosyls, were reported to react with $HBF_4\cdot OEt_2$ to give no NOH derivatives, but a mixture of compounds, one of the being the already mentioned amide complex [$Mn_2L^*_2$(μ-NH_2)(μ-CO)$(NO)_2$]$^+$ [14]. Since compound **8** therefore represents a rare example of a binuclear species having a μ$_2$-NOX ligand, we decided to pursue these transformations of the nitrosyl ligands by examining the protonation reactions of the neutral hydride **6** as well as some electron-richer diphosphine-substituted derivatives (see below). Related reactions with the methylating agents [Me_3O]BF_4 or CF_3SO_3Me led to mixtures of unstable products that could not be characterized.

2.6. Tetracarbonyl derivatives of the hydride 6

Two carbonyls *trans* to the dppm ligand are easily replaced in the hydride **6** with a second molecule of dppm under photochemical conditions, or under moderate heating (333 K) if using the more basic $Me_2PCH_2PMe_2$ (dmpm) diphosphine, to give respectively the corresponding tetracarbonyl derivatives [Mn_2(μ-H)(μ-NO)$(CO)_4$(μ-dppm)$_2$] (**9a**) and [Mn_2(μ-H)(μ-NO)$(CO)_4$(μ-dppm)(μ-dmpm)] (**9c**), that can be isolated as dark blue solids with good yields (Chart 1).

The spectroscopic data for compounds **9** are comparable to those reported previously for the related diphosphine-bridged complexes [Mn_2(μ-H)(μ-X)$(CO)_4$(μ-dppm)$_2$] (X = OEt, Br, [37]) or the diphosphite-bridged [Mn_2(μ-H)(μ-Br)$(CO)_4$(μ-tedip)$_2$] [22], and

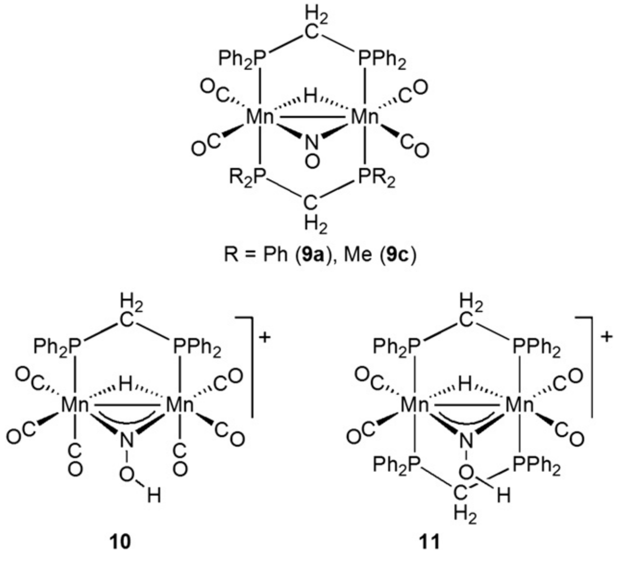


Chart 1. ^{a} The BF_4^- anion of compounds **10** and **11** is omitted for clarity.

therefore deserve no detailed comments. We just note the significant reduction by some 60 cm^{-1} in the N–O stretching frequency for **9a** compared to its hexacarbonyl precursor, this reflecting a considerable increase of electron density at the dimetal centre as a result of the substitution of two CO ligands with a diphosphine molecule. We also notice the appearance of poorly shielded hydride resonances in both cases (ca. −9 ppm), also observed for **6** and attributed to influence of the bridging nitrosyl in the flat Mn_2(μ-H)(μ-NO) central core of all these molecules.

*2.7. Protonation reactions of the hydrides **6** and **9a***

The title hydride complexes react with $HBF_4 \cdot OEt_2$ in dichloromethane solution at 243 K to give a single species in each case (as determined by low temperature NMR spectroscopy), which we propose to be the corresponding hydroxylimide derivatives [Mn_2(μ-H)(μ-NOH)$(CO)_6$(μ-dppm)]BF_4 (**10**) and [Mn_2(μ-H)(μ-NOH)$(CO)_4$(μ-dppm)$_2$]BF_4 (**11**) respectively (Chart 1). Unfortunately, these products were thermally unstable and decomposed rapidly above 273 K, and therefore could not be isolated as pure solids nor fully characterized in the desired way (even an IR spectrum in solution could not be obtained). We note, however, that these products were easily deprotonated by Et_2O or solid Na_2CO_3 to give the corresponding neutral precursors, this therefore excluding any irreversible transformation of the nitrosyl ligand upon protonation of these hydride complexes.

The spectroscopic data and dynamic behaviour of compounds **10** and **11** (Table 1 and Experimental Section) are comparable to each other, although the low solubility of the tetracarbonyl product at low temperature precluded a more detailed spectroscopic analysis in that case. In both complexes, the averaged ^{31}P NMR resonance is close to that of the corresponding starting substrate, thus suggesting little modification on the electron density at the dimetal centre upon protonation, and being therefore consistent with a protonation located at the nitrosyl ligand. Both compounds display a hydride resonance at ca. –14 ppm and a strongly deshielded resonance at 19.2 (**10**) or 16.6 ppm (**11**) which we attribute to the presence of a hydroxylimide ligand on the basis of their very high chemical shift, while the more “normal” shielding of the hydride resonances is also consistent with the transformation of the bridging nitrosyl.

In a static structure, the angular N–O–H ligand in compounds **10** and **11** is expected to be placed in the Mn_2N plane, due to the likely persistence of some residual multiplicity in the N–O bond, as found for the related hydroxy- and alkoxycarbyne ligands (μ_2-COH, μ_2-COR) in binuclear complexes [38]. This renders inequivalent environments for the metal fragments of these complexes. Indeed, the ^{31}P NMR spectrum of **10** at 185 K displays an AB multiplet consistent with the above proposal. Upon warming of the solution, these resonances broaden and eventually collapse into a single resonance, thus revealing the concurrence of a dynamic process averaging the chemical environments of both metal fragments. At the same time, the ^{1}H NMR resonance at ca. 19 ppm also broadens and eventually disappears in the baseline of the spectrum, so that above 203 K only a broad resonance due to the excess $HBF_4 \cdot OEt_2$ present in the solution is detected in the spectrum, while other resonances (hydride, diphosphine ligands) remained little perturbed. This strongly suggests a protonation/deprotonation sequence as the most probable mechanism for the averaging of the chemical environments of the metal atoms in the complexes **10** and **11**. At this point we should note that, due to the lower solubility of **11**, it was not possible to record a ^{31}P NMR spectrum of this complex below 248 K, and therefore the limiting spectrum with separate ^{31}P resonances could not be obtained in that case.

3. Experimental

All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use [39]. Compounds **1a** [17b], **1b** [16b], [Mn(CO)$(NO)_3$] [40], and [AuCl(PPh_3)] [41] were prepared as described previously, and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338–243 K. Photochemical experiments were performed using jacketed Schlenk tubes, cooled by tap water (ca. 288 K). A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was typically used in these the experiments. Filtrations were carried out using diatomaceous earth. Chromatographic separations were carried out using jacketed columns cooled by tap water at ca. 285 K or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. Commercial Florisil (100–200 mesh) and aluminium oxide (activity I, 150 mesh) were degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR stretching frequencies of CO and NO ligands were measured in solution using CaF_2 windows or in the solid state, in KBr discs. Nuclear Magnetic Resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 ($^{31}P\{^{1}H\}$) or 75.47 MHz ($^{13}C\{^{1}H\}$), at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in Hertz.

*3.1. Preparation of [$Mn_2(NO)_6$(μ-dppm)] (**2a**)*

3.1.1. Method A

A toluene solution (12 mL) of compound **1a** (0.030 g, 0.045 mmol) was stirred at 318 K for 1.5 h while gently bubbling nitric oxide (5% in N_2) through the mixture, to give a dark green solution. After removal of most of the solvent under vacuum, the concentrated solution was chromatographed through Florisil at 285 K. Elution with petroleum ether gave first a dark green fraction and then a red-purple one containing some residual starting material. Removal of the solvent from the first fraction gave compound **2a** (0.011 g, 36%) as a dark green powder. A yellow fraction was afterwards eluted with dichloromethane–petroleum ether (1:1), which gave analogously variable amounts of compound **3a** as a yellow solid (0–25%).

3.1.2. Method B

Solid dppm (0.050 g, 0.130 mmol) was added to a toluene solution (25 mL) of [Mn(CO)$(NO)_3$] (0.100 g, 0.580 mmol), and the mixture was stirred at room temperature for 90 min to give a dark green solution that was filtered through a Florisil pad at 285 K. Removal of the solvent from the filtrate and washing of the residue with petroleum ether at 273 K gave compound **2a** as a dark green powder (0.081 g, 42%). Anal. Calc. for $C_{25}H_{22}Mn_2N_6O_6P_2$: C, 44.53; H, 3.28; N, 12.46. Found: C, 44.39; H, 3.21; N, 12.31. ^{1}H NMR (200.13 MHz) δ 7.56–7.19 (m, Ph, 20H), 3.89 (t, $J_{HP} = 9$, CH_2, 2H).

*3.2. Preparation of [$Mn_2(NO)_6$(μ-tedip)] (**2b**)*

A toluene solution (15 mL) of compound **1b** (0.050 g, 0.093 mmol) was stirred at room temperature for 3 h while gently bubbling nitric oxide (5% in N_2) through the mixture, to give a dark green solution. After removal of the solvent under vacuum, the residue was extracted with petroleum ether and the extracts were chromatographed on an alumina column (activity III) at 285 K.

Elution with petroleum ether gave a dark green fraction which gave, upon removal of the solvent, compound **2b** as a spectroscopically pure, but oily residue (0.015 g, 35%). All attempts to further purify this product resulted in the progressive decomposition of the complex. ^{1}H NMR (C_6D_6) δ 3.78 (m, OCH_2, 8H), 0.93 (t, $J_{HH} = 7$, CH_3, 6H).

*3.3. Preparation of [$Mn_2(\mu\text{-}H)(\mu\text{-}NO_2)(CO)_6(\mu\text{-dppm})$] (**3a**)*

Nitrogen dioxide was generated in situ by introducing a gentle stream of nitric oxide (5% in N_2) into a 100 mL Schlenk tube previously filled with dry oxygen, until the gaseous phase adopted an intense red-brown colour. Then a toluene solution (12 mL) of compound **1a** (0.030 g, 0.045 mmol) was transferred to this tube, and the mixture was stirred for 15 min to yield a lemon yellow solution. After removal of most of the solvent under vacuum, the concentrated solution was chromatographed through alumina (activity III) at 253 K. Elution with dichloromethane–petroleum ether (1:1) gave a yellow fraction yielding, after removal of solvents, compound **3a** as a yellow, quite air-sensitive powder (0.013 g, 41%). ^{1}H NMR (200.13 MHz) δ 7.33–7.27 (m, Ph, 20H), 3.40 (dt, $J_{HH} = 13$, $J_{HP} = 14$, CH_2, 1H), 2.91 (dt, $J_{HH} = 13$, $J_{HP} = 10$, CH_2, 1H), −16.57 (t, $J_{HP} = 25$, μ-H, 1H). ^{31}P{^{1}H} NMR (161.99 Hz, 293 K) δ 49.0, 45.0 (2s, vbr, μ-dppm). ^{31}P{^{1}H} NMR (161.99 Hz, 228 K) δ 49.6, 43.8 (2d, $J_{PP} = 66$, μ-dppm).

*3.4. Preparation of [$Mn_2(\mu\text{-}H)(\mu\text{-}NO_2)(CO)_6(\mu\text{-tedip})$] (**3b**)*

The procedure is analogous to that described for **3a**, but using compound **1b** (0.030 g, 0.056 mmol). The crude reaction product was extracted with dichloromethane–petroleum ether (1:2) and the extracts were chromatographed through alumina (activity IV) at 285 K. Elution with the same solvent mixture gave a fraction yielding, after removal of solvents, compound **3b** as a yellow solid (0.012 g, 37%). This solid was crystallized from a petroleum ether solution at 253 K. Anal. Calc. for $C_{14}H_{21}Mn_2NO_{13}P_2$: C, 28.83; H, 3.26; N, 2.40. Found: C, 28.65; H, 3.21; N, 2.55. ^{1}H NMR (C_6D_6) δ 3.81 (m, OCH_2, 8H), 0.94 (m, CH_3, 12H), −17.61 (t, $J_{HP} = 32$, μ-H, 1H). ^{1}H NMR (400.13 MHz, CD_2Cl_2, 253 K) δ 4.33–3.92 (m, OCH_2, 8H), 1.43 (t, $J_{HH} = 6$, CH_3, 6H), 1.32, 1.31 (2t, $J_{HH} = 6$, CH_3, 2 × 3H), −18.09 (t, $J_{HP} = 32$, μ-H, 1H). ^{31}P{^{1}H} NMR (121.49 Hz, C_6D_6, 293 K) δ 161.0 (br, μ-tedip). ^{31}P{^{1}H} NMR (161.99 Hz, CD_2Cl_2, 200 K) δ 160.0, 159.0 (AB mult, $J_{PP} = 57$, μ-tedip).

*3.5. Preparation of (PPN)[$Mn_2(\mu\text{-}H)(H)(NO_2)(CO)_6(\mu\text{-dppm})$] (**4a**)*

Solid (PPN)NO_2 (0.089 g, 0.152 mmol; $PPN^+ = [N(PPh_3)_2]^+$) was added to a tetrahydrofuran solution (25 mL) of compound **1a** (0.100 g, 0.151 mmol) cooled at 273 K, and the mixture was stirred at that temperature for 30 min to give a yellow solution which was filtered. Removal of the solvent from the filtrate gave an oily residue which was crystallized from dichloromethane–petroleum ether at 253 K to give compound **4a** (0.181 g, 96%) as a dark yellow solid. This crude product was found to be unstable at room temperature, and it quantitatively gave back the starting material **1a** upon addition of diethyl ether. ^{1}H NMR (400.13 MHz, thf-C_6D_6, 213 K) δ −7.0 (br, Mn–H, 1H), −19.0 (br, μ-H, 1H).

*3.6. Preparation of (PPN)[$Mn_2(\mu\text{-}CO)(CO)_5(NO)(\mu\text{-dppm})$] (**5**)*

A tetrahydrofuran solution of compound **4a**, prepared in situ as described above from compound **1a** (0.100 g, 0.151 mmol) was stirred at 318 K for 90 min to give a brown solution which was filtered at room temperature. Removal of the solvent from the filtrate gave an oily residue which was crystallized from dichloromethane–diethyl ether at room temperature to give compound **5** (0.167 g, 90%) as a pale brown solid. Anal. Calc. for $C_{67}H_{52}Mn_2N_2O_7P_4$: C, 65.37; H, 4.26; N, 2.27. Found: C, 65.45; H, 4.39; N, 2.34. ^{1}H NMR (200.13 MHz) δ 7.49–7.21 (m, Ph, 50H), 3.83 (t, $J_{HP} = 9$, CH_2, 2H). ^{31}P NMR (161.99 MHz, 293 K) δ 68.5 (s, μ-dppm), 21.5 (s, PPN). ^{31}P{^{1}H} NMR (161.99 MHz, 173 K) δ 68.7 (s, vbr, μ-dppm), 21.8 (s, PPN). ^{31}P{^{1}H} NMR (161.99 MHz, 166 K) δ 69.4, 67.3 (2s, vbr, μ-dppm), 21.7 (s, PPN). ^{13}C{^{1}H} NMR (50.33 MHz, 293 K) δ 235 (br, s, CO), 140.1–126.4 (m, Ph), 49 (t, $J_{PC} = 15$, CH_2). ^{13}C{^{1}H} NMR (100.63 MHz, 213 K) δ 241.9, 234.7, 230.6 (3s, br, CO), 139.0–125.6 (m, Ph), 47.2 (s, br, CH_2).

*3.7. Preparation of [$Mn_2(\mu\text{-}H)(\mu\text{-}NO)(CO)_6(\mu\text{-dppm})$] (**6**)*

Solid $(NH_4)PF_6$ (0.025 g, 0.153 mmol) was added to a dichloromethane solution (15 mL) of compound **5** (0.050 g, 0.040 mmol) and the mixture was vigorously stirred at room temperature for 45 min to give a cherry-red suspension. After removal of the solvent under vacuum, the residue was extracted with dichloromethane–petroleum ether (1:1) and the extracts were filtered through an alumina pad (activity III) at 285 K. Removal of the solvents from the filtrate and washing of the residue with petroleum ether (3 × 5 mL) gave compound **6** as a red-purple solid (0.018 g, 62%). Anal. Calc. for $C_{31}H_{23}Mn_2NO_7P_2$: C, 53.70; H, 3.34; N, 2.02. Found: C, 53.61; H, 3.91; N, 1.99. ^{1}H NMR δ 7.45–6.85 (m, Ph, 20H), 3.05 (dt, $J_{HH} \sim J_{HP} = 11$, CH_2, 1H), 2.83 (dtd, $J_{HH} = 11, 4$, $J_{HP} = 11$, CH_2, 1H), −8.31 (td, $J_{HP} = 12$, $J_{HH} = 4$, μ-H, 1H).

*3.8. Preparation of [$AuMn_2(\mu\text{-}NO)(CO)_6(\mu\text{-dppm})(PPh_3)$] (**7**)*

Solid [$AuCl(PPh_3)$] (0.017 g, 0.037 mmol) was added to a dichloromethane solution (15 mL) of compound **5** (0.050 g, 0.040 mmol) and the mixture was stirred at room temperature for 45 min to give an orange solution. After removal of the solvent under vacuum, the residue was extracted with toluene and the extracts were filtered through an alumina pad (activity III) at 285 K. Removal of the solvents from the filtrate and washing of the residue with petroleum ether (5 mL) gave compound **7** as an orange solid (0.037 g, 79%). The crystals used in the X-ray study were grown by the slow diffusion at room temperature of a layer of petroleum ether into a concentrated benzene solution of the complex. Anal. Calc. for $C_{49}H_{37}AuMn_2NO_7P_3$: C, 50.97; H, 4.02; N, 1.01. Found: C, 51.11; H, 3.24; N, 1.22. ^{1}H NMR (400.13 MHz) δ 7.60–6.86 (m, Ph, 35H), 2.78, 2.73 (ABM_2X mult, $J_{HH} = 11$, CH_2, 2H).

*3.9. Preparation of [$Mn_2(\mu\text{-}NOMe)(CO)_6(\mu\text{-dppm})$] (**8**)*

Neat CF_3SO_3Me (5 μL, 0.044 mmol) was added to a dichloromethane solution (15 mL) of compound **5** (0.050 g, 0.040 mmol) at 243 K, and the mixture was stirred at that temperature for 15 min to give an orange solution. After removal of the solvent under vacuum, the residue was extracted with toluene and the extracts were filtered through an alumina pad (activity III) at 243 K. Removal of the solvents from the filtrate and washing of the residue with petroleum ether (5 mL) at 273 K or below gave compound **8** as an orange solid (0.015 g, 52%). This product decomposed at room temperature either as a solid or (more rapidly) in solution. ^{1}H NMR (400.13 MHz, 243 K) δ 7.65–7.13 (m, Ph, 20H), 3.41 (s, OMe, 3H), 2.92 (dt, $J_{HH} \sim J_{HP} = 13$, CH_2, 1H), 2.27 (dt, $J_{HH} \sim J_{HP} = 13$, CH_2, 1H).

*3.10. Preparation of [$Mn_2(\mu\text{-}H)(\mu\text{-}NO)(CO)_4(\mu\text{-dppm})_2$] (**9a**)*

Solid dppm (0.056 g, 0.146 mmol) was added to a tetrahydrofuran solution (25 mL) of compound **6** (0.100 g, 0.144 mmol) and the mixture was irradiated with visible–UV light for 90 min at

285 K with a gentle N_2 purge, to give a dark greenish solution. After removal of the solvent under vacuum, the residue was dissolved in a minimum dichloromethane and chromatographed on alumina (activity III) at 285 K. Elution with dichloromethane–petroleum ether (1:1) gave a pale yellow fraction containing some residual dppm and the mononuclear complex $[Mn(H)(CO)_3(dppm)]$. Elution with dichloromethane gave a dark blue fraction yielding, after removal of solvent, compound **9a** as a deep blue solid (0.109 g, 74%). Anal. Calc. for $C_{54}H_{45}Mn_2NO_5P_4$: C, 63.48; H, 4.43; N, 1.37. Found: C, 63.09; H, 4.60; N, 1.30. ^1H NMR (200.12 MHz) δ 7.4–6.9 (m, Ph, 40H), 2.96, 2.83 (2m, CH_2, 2 × 2H), −8.90 (qn, J_{HP} = 14, μ-H, 1H).

*3.11. Preparation of $[Mn_2(\mu\text{-}H)(\mu\text{-}NO)(CO)_4(\mu\text{-}dppm)(\mu\text{-}dmpm)]$ (**9c**)*

Neat dmpm (23 μL, 0.147 mmol; dmpm = $Me_2PCH_2PMe_2$) was added to a tetrahydrofuran solution (25 mL) of compound **6** (0.100 g, 0.144 mmol) and the mixture was stirred for 30 min at 333 K to give a dark blue solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane–petroleum ether (1:1) and the extracts were chromatographed on an alumina column (activity III) at 285 K. Elution with dichloromethane–petroleum ether (2:1) gave an orange fraction containing small amounts of several unidentified species. Elution with dichloromethane–petroleum ether (3:1) gave a dark blue fraction yielding, after removal of solvents, compound **9c** as a lead-gray solid (0.092 g, 83%). Anal. Calc. for $C_{34}H_{37}Mn_2NO_5P_4$: C, 52.79; H, 4.82; N, 1.81. Found: C, 52.55; H, 4.71; N, 1.97. ^1H NMR (200.12 MHz) δ 7.49–6.85 (m, Ph, 20H), 2.95 (m, CH_2-dppm, 2H), 1.42 ($AA'X_3X'_3$ mult, $J_{HP} + J_{HP'}$ = 7, CH_3, 6H), 1.35 (m, CH_2-dmpm, 1H), 1.29 ($AA'X_3X'_3$ mult, $J_{HP} + J_{HP'}$ = 7, CH_3, 6H), 1.03 (dt, J_{HH} = 13, J_{HP} = 10, CH_2-dmpm, 1H), −9.59 (qn, J_{HP} = 15, μ-H, 1H).

*3.12. Preparation of solutions of $[Mn_2(\mu\text{-}H)(\mu\text{-}NOH)(CO)_6(\mu\text{-}dppm)]BF_4$ (**10**)*

Neat $HBF_4 \cdot OEt_2$ (13 μL of a 54% solution in Et_2O, 0.050 mmol) was added to a dichloromethane solution (5 mL) of compound **6** (0.035 g, 0.050 mmol) cooled at 243 K, and the mixture was stirred for 1 min at that temperature to give a blue-green solution shown (by ^{31}P NMR) to contain compound **10** as the major species. All attempts to isolate this product as a solid led to its complete decomposition. ^1H NMR (200.12 MHz, 243 K) δ 7.58–7.92 (m, Ph, 20H), 3.27, 2.96 (2m, CH_2, 2 × 1H), −12.77 (br, μ-H, 1H). ^1H NMR (200.12 MHz, 185 K) δ 19.20 (br, NOH, 1H), 7.52–6.83 (m, Ph, 20H), 3.30, 2.90 (2m, CH_2, 2 × 1H), −13.54 (br, μ-H, 1H). $^{31}P\{^1H\}$ NMR (161.99 MHz, 243 K) δ 55.5 (br, μ-dppm). $^{31}P\{^1H\}$ NMR (161.99 MHz, 185 K) δ 55.6, 55.2 (AB mult, J_{PP} = 129, μ-dppm).

*3.13. Preparation of solutions of $[Mn_2(\mu\text{-}H)(\mu\text{-}NOH)(CO)_4(\mu\text{-}dppm)_2]BF_4$ (**11**)*

Neat $HBF_4 \cdot OEt_2$ (13 μL of a 54% solution in Et_2O, 0.050 mmol) was added to a dichloromethane solution (5 mL) of compound **9a** (0.051 g, 0.050 mmol) cooled at 243 K, and the mixture was stirred for 1 min at that temperature to give a greenish solution shown (by ^{31}P NMR) to contain compound **11** as the major species. All attempts to isolate this product as a solid led to its complete decomposition. ^1H NMR (400.13 MHz, 248 K) δ 16.62 (br, NOH, 1H), 7.5–6.7 (m, Ph, 40H), −14.62 (m, br, μ-H, 1H). The resonances for the methylenic protons of the complex were obscured by those of Et_2O arising from the added protonation reagent.

Table 3
Crystal data for compound **7**·3/2C_6H_6.

Mol formula	$C_{58}H_{46}AuMn_2NO_7P_3$
Mol wt	1268.71
Crystal syst	Monoclinic
Space group	$P2_1/a$
Radiation (λ, Å)	0.71073
a, Å	19.598(1)
b, Å	14.710(1)
c, Å	20.613(2)
α, deg	90.00
β, deg	98.98(2)
γ, deg	90.00
V, $Å^3$	5869.6(8)
Z	4
Calcd density, gcm^{-3}	1.436
Absorpt. coeff., mm^{-1}	3.047
Temperature, K	293(2)
θ range (°)	3.07–26.00
Index ranges (*h*, *k*, *l*)	−24, 23; 0, 18; 0, 25
Reflections collected	11769
Independent refln.	11454 [R_{int} = 0.0747]
Refln. with $I > 2\sigma(I)$	3656
R indexes ($I > 2\sigma(I)$)[a]	$R_1 = 0.0509$, $wR_2 = 0.0903$[b]
R indexes (all data)[a]	$R_1 = 0.2337$, $wR_2 = 0.1237$[b]
GOF	1.037
Restraints/parameters	12/593
$\Delta\rho$(max, min), e $Å^{-3}$	1.334, −1.499

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

[b] a = 0.0300, b = 0.0000.

*3.14. X-ray structure determination of compound **7***

Single crystal data were collected with a Philips PW 1100 diffractometer (Mo-K_α radiation, λ = 0.71073 Å). Cell constants were obtained by a least square refinement of the setting angles of 24 randomly distributed and carefully centered reflections. The absorption correction was applied using the program NEWABS92 (min. and max. transmission factors: 0.850–1.000) [42]. The structures were solved by direct methods (SIR97) [43] and refined on F^2 with full-matrix least squares (SHELXL-97) [44], using the WINGX software package [45]. The solvent of crystallization (benzene) was refined with isotropic thermal parameters. One of the benzene molecules was found disordered in two positions, which were refined with site occupancy factors of 0.6/0.4. Another benzene molecule was refined with a site occupancy factor of 0.5. The remaining non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at their calculated positions. Graphical material was prepared with the ORTEP3 program for Windows [46] (Table 3).

Acknowledgments

We thank the Consejería de Educación de Asturias for financial support (PA-MAS94-05).

Appendix A. Supplementary material

CCDC 787009 contains the supplementary crystallographic data for compound **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] G.B. Ritcher-Addo, P. Legzdins, Metal Nitrosyls. Oxford University Press, Oxford, U. K., 1992.

[2] (a) T.W. Hayton, P. Legzdins, W.B. Sharp, Chem. Rev. 102 (2002) 935;
(b) P.C. Ford, I.M. Lorkovic, Chem. Rev. 102 (2002) 993;
(c) D.M.P. Mingos, D.J. Sherman, Adv. Inorg. Chem. 34 (1989) 293;
(d) W.L. Gladfelter, Adv. Organomet. Chem. 24 (1985) 41.
[3] (a) A. Franke, F. Roncaroli, v.E. Rudi, Eur. J. Inorg. Chem. (2007) 773;
(b) A. Ghosh, Acc. Chem. Res. 38 (2005) 943;
(c) P.C. Ford, L. Laverman, I.M. Lorkovic, Adv. Inorg. Chem. 54 (2003) 203;
(d) P.G. Wang, M. Xian, X. Tang, X. Wu, Z. Wen, T. Cai, A.J. Janczuk, Chem. Rev. 102 (2002) 1091;
(e) A.R. Butler, I.L. Megson, Chem. Rev. 102 (2002) 1155;
(f) R.J.P. Williams, Chem. Soc. Rev. (1996) 77;
(g) M.J. Clarke, J.B. Gaul, Struct. Bond. 81 (1993) 147.
[4] (a) U.S. Ozkan, S.K. Agarwal, G. Marcelin (Eds.), Reduction of Nitrogen Oxide Emissions, American Chemical Society, Washington, DC, 1995;
(b) J.M. Armor (Ed.), Environmental Catalysis, American Chemical Society, Washington, DC, 1994;
(c) R.G. Silver, J.E. Sawyer, J.C. Summers (Eds.), Catalytic Control of Air Pollution, American Chemical Society, Washington, DC, 1992;
(d) J. Dunderdale (Ed.), Energy and the Environment, Royal Society of Chemistry, Cambridge, U.K., 1990;
(e) R.M. Harrison (Ed.), Pollution: Causes, Effects and Control, Royal Society of Chemistry, Cambridge, U.K., 1990.
[5] (a) S. Basu, Chem. Eng. Commun. 194 (2007) 1374;
(b) J.M. Tayyeb, I. Naseem, B.M. Gibbs, J. Environm. Manag. 83 (2007) 251;
(c) T.J. Wallington, E.W. Kaiser, J.T. Farrell, Chem. Soc. Rev. 35 (2006) 335;
(d) S.A. McMillan, L.J. Broadbelt, R.Q. Snurr, Environm. Catal. (2005) 287;
(e) T. Curtin, Environm. Catal. (2005) 197.
[6] M.E. García, S. Melón, M.A. Ruiz, R. López, T. Sordo, L. Marchiò, A. Tiripicchio, Inorg. Chem. 47 (2008) 10644.
[7] M.E. García, D. García-Vivó, S. Melón, M.A. Ruiz, C. Graiff, A. Tiripicchio, Inorg. Chem. 48 (2009) 9282.
[8] P.M. Treichel, E. Pitcher, R.B. King, F.G.A. Stone, J. Am. Chem. Soc. 83 (1961) 2593.
[9] (a) R.B. King, M.B. Bisnette, Inorg. Chem. 3 (1964) 791;
(b) T.A. James, J.A. McCleverty, J. Chem. Soc. (A) (1970) 850.
[10] H.P. Hydes, J.A. McCleverty, D.G. Orchard, J. Chem. Soc. (A) (1971) 3660.
[11] A. Efraty, R. Arneri, W.A. Ruda, Inorg. Chem. 16 (1977) 3124.
[12] A.A. Pasynskii, V.N. Grigoŕev, A.I. Blokhin, Y.V. Torubaev, K.A. Lysenko, V.V. Minin, Zh. Neorgan. Khim. 50 (2005) 1450.
[13] B.W. Hames, B.W.S. Kolthammer, P. Legzdins, Inorg. Chem. 20 (1981) 650 and references therein.
[14] P. Legzdins, D.T. Martin, C.R. Nurse, B. Wassink, Organometallics 2 (1983) 1238.
[15] (a) Y.S. Chen, J.E. Ellis, J. Am. Chem. Soc. 105 (1983) 1689;
(b) Y.S. Chen, J.E. Ellis, Inorg. Chim. Acta 300–302 (2000) 675.
[16] (a) V. Riera, M.A. Ruiz, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem. Soc. Chem. Commun. (1985) 1505;
(b) V. Riera, M.A. Ruiz, A. Tiripicchio, M. Tiripicchio-Camellini, Organometallics 12 (1993) 2962.
[17] (a) F.J. García-Alonso, M. García-Sanz, V. Riera, M.A. Ruiz, A. Tiripicchio, M. Tiripicchio-Camellini, Angew. Chem. Int. Ed. Engl. 27 (1988) 167;
(b) F.J. García-Alonso, V. Riera, M.A. Ruiz, A. Tiripicchio, M. Tiripicchio-Camellini, Organometallics 11 (1992) 370.
[18] (a) R. Carreño, V. Riera, M.A. Ruiz, Y. Jeannin, M. Philoche-Levisalles, J. Chem. Soc. Chem. Commun. (1990) 15;
(b) R. Carreño, V. Riera, M.A. Ruiz, J. Organomet. Chem. 419 (1991) 163;
(c) R. Carreño, V. Riera, M.A. Ruiz, C. Bois, Y. Jeannin, Organometallics 11 (1992) 2923;
(d) R. Carreño, V. Riera, M.A. Ruiz, C. Bois, Y. Jeannin, Organometallics 11 (1992) 4022;
(e) F.J. García-Alonso, M. García-Sanz, V. Riera, S. García-Granda, E. Perez-Carreño, J. Chem. Soc. Dalton Trans. (1992) 545;
(f) F.J. García-Alonso, M. García-Sanz, V. Riera, A. Anillo, A. Tiripicchio, F. Ugozzoli, Organometallics 11 (1992) 801;
(g) R. Carreño, V. Riera, M.A. Ruiz, C. Bois, Y. Jeannin, Organometallics 12 (1993) 1946;
(h) R. Carreño, V. Riera, M.A. Ruiz, A. Tiripicchio, M. Tiripichhio-Camellini, Organometallics 13 (1994) 993;
(i) F.J. García-Alonso, M. García-Sanz, X.Y. Liu, A. Oliveira, V. Riera, M.A. Ruiz, C. Bois, J. Organomet. Chem. 511 (1996) 93.
[19] M. Herberhold, A. Razavi, J. Organomet. Chem. 67 (1971) 81.
[20] M.A. Hitchman, G.L. Rowbottom, Coord. Chem. Rev. 42 (1982) 55.
[21] P.S. Braterman, Metal Carbonyl Spectra. Academic Press, London, U.K, 1975.
[22] V. Riera, M.A. Ruiz, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem. Soc. Dalton Trans. (1987) 1551.
[23] X.Y. Liu, V. Riera, M.A. Ruiz, M. Lanfranchi, A. Tiripicchio, Organometallics 22 (2003) 4500.
[24] D.W. Prest, M.J. Mays, P.R. Raithby, J. Chem. Soc. Dalton Trans. (1982) 2021.
[25] R.E. Stevens, W.L. Gladfelter, Inorg. Chem. 22 (1983) 2034.
[26] M.E. García, S. Melón, A. Ramos, M.A. Ruiz, Dalton Trans. (2009) 8171.
[27] J.A. Marsella, K.G. Caulton, Organometallics 1 (1982) 274.
[28] X.L. Liu, V. Riera, M.A. Ruiz, C. Bois, Organometallics 20 (2001) 3007.
[29] K.G. Orrel, V. Sik, Ann. Rep. NMR 19 (1987) 79.
[30] D.G. Evans, D.M.P. Mingos, J. Organomet. Chem. 233 (1982) 171.
[31] (a) H. Berke, P. Burguer, Comments Mod. Chem. 16 (1994) 279 and references therein;
(b) H.U. Hund, U. Ruppli, H. Berke, Helv. Chim. Acta 76 (1995) 963.
[32] J. Wolf, O. Nürnberg, H. Werner, Chem. Ber. 126 (1993) 1409.
[33] (a) R.D. Wilson, J.A. Ibers, Inorg. Chem. 18 (1979) 336;
(b) C.P. Casey, D.M. Roddick, Organometallics 5 (1986) 436;
(c) J.S. Southern, M.T. Green, G.L. Hillhouse, I.A. Guzel, A.L. Reingold, Inorg. Chem. 40 (2001) 6039.
[34] (a) R.E. Stevens, W.L. Gladfelter, J. Am. Chem. Soc. 104 (1982) 6454;
(b) R.E. Stevens, W.L. Gladfelter, R.D. Guettler, Inorg. Chem. 29 (1990) 451.
[35] P. Legzdins, C.R. Nurse, S.J. Rettig, J. Am. Chem. Soc. 105 (1983) 3727.
[36] E. Delgado, J.C. Jeffery, N.D. Simmons, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1986) 869.
[37] H.C. Aspinall, A.J. Deeming, J. Chem. Soc. Chem. Commun. (1983) 838.
[38] (a) M.A. Alvarez, M.E. García, V. Riera, M.A. Ruiz, Organometallics 18 (1999) 634;
(b) M.E. García, D. García-Vivó, M.A. Ruiz, S. Alvarez, G. Aullón, Organometallics 26 (2007) 4930;
(c) M.E. García, D. García-Vivó, M.A. Ruiz, S. Alvarez, G. Aullón, Organometallics 26 (2007) 5912.
[39] W.L.F. Armarego, C. Chai, Purification of Laboratory Chemicals, fifth ed. Butterworth-Heinemann, Oxford, UK, 2003.
[40] S.K. Satija, B.I. Swanson, Inorg. Synth. 16 (1976) 1.
[41] P. Braunstein, H. Lehner, D. Matt, Inorg. Synth. 27 (1990) 218.
[42] (a) N. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158;
(b) F. Ugozzoli, Comput. Chem. 11 (1987) 109.
[43] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[44] G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112.
[45] L.J. Farrugia, J. Appl, Crystallogr 32 (1999) 837.
[46] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 568.