Synthesis, Structure and Reactivity of [1,2-Bis(diphenylphosphinite)ethane]bromotricarbonylmanganese(I) with Reactions of Phosphites, Phosphonites. and Phosphinites

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Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 60th Birthday.

Abstract. The manganese carbonyl complex $[MnBr(CO)_3L]$ (1), where $L = Ph_2POCH_2CH_2OPPh_2$, was prepared by reacting $[MnBr(CO)_5]$ with the bidentate ligand 1,2-Bis(diphenylphosphinite)ethane. From this compound and the appropriate phosphite, phosphinite or phosphonite ligands were synthesized the complexes $[MnBr(CO)_2LL']$, where $L' = P(OMe)_3$ (2) or $P(OEt)_3$ (3) and $[MnBr(CO)_3L'_2]$, where $L' = PPh(OEt)_2$ (4) or $PPh_2(OEt)$ (5). The obtained compounds have been characterized by elemental analysis, mass spectrometry, IR and NMR (1 H, 13 C and 31 P) spectroscopies and X-ray diffractometry for the complexes 1, 4 and 5.

Keywords: Manganese; 1,2-Bis(diphenylphosphinite)ethane complexes; Phosphite complexes; Phosphinite complexes; Phosphonite complexes

Synthese, Struktur und Reaktivität von [1,2-Bis(diphenylphosphinit)ethan]bromotricarbonylmangan(I) in Reaktionen mit Phosphiten, Phosphoniten und Phosphiniten

Inhaltsübersicht. Der Mangan-Carbonyl-Komplex $[MnBr(CO)_3L]$ (1) mit $L = Ph_2POCH_2CH_2OPPh_2$ wird durch Umsetzung von $[MnBr(CO)_5]$ mit dem zweizähnigen Liganden 1,2-Bis(diphenyl-phosphinit)ethan hergestellt. Aus dieser Verbindung werden mit verschiedenen Phosphit-, Phosphinit- und Phosphonit-Liganden

Introduction

The reactions of $[MnX(CO)_5]$ (X = Cl, Br, I) with a variety of phosphine ligands have been investigated by several groups of scientists [1–14]. Substitution of carbonyl groups and the stereochemistry of the resulting complex is demonstrated to be dependent, among other factors, on the size of the ligand.

Relatively little data are available on the bidentate ligand phosphite complexes. As ligands, phosphites are generally more electron withdrawing than phosphines and their use as ancillary ligands may have interesting effects on both the structure and reactivity of the resulting complexes. The used ligands have been selected due to their "carbonyl like" π -acceptor properties together with their low steric requirements.

We report here on the synthesis and spectroscopic and diffractometric characterization of [1,2-bis(diphenylphos-

die Komplexe [MnBr(CO)₂LL'] mit L' = P(OMe)₃ (2) und P(OEt)₃ (3) sowie [MnBr(CO)₃L'₂] mit L' = PPh(OEt)₂ (4) und PPh₂(OEt) (5) erhalten. Die Komplexe werden durch Elementaranalysen, Massenspektren, IR- und NMR-Spektren (¹H, ¹³C, ³¹P) sowie 1, 4 und 5 durch Kristallstrukturanalysen charakterisiert.

phinite)ethane]bromotricarbonyl-manganese(I) and its reactivity with different monodentate phosphite, phosphonite and phosphinite ligands.

Experimental Section

Materials and instrumentation

All synthetic operations were performed under argon. A standard vacuum system and Schlenk type glassware were used in handling metal complexes. Solvents were pre-dried over sodium wire or calcium chloride before reflux and subsequent distillation, under argon, from a suitable drying agent [15]. Deuterated solvents for NMR measurements (Aldrich and Merck) were dried over molecular sieves. 1,2-Bis(diphenylphosphinite)ethane was prepared by the method of *Bolaño* et al. [16] and [MnBr(CO)₅] was obtained from [Mn₂(CO)₁₀] by the method described in the literature [17]. Monodentate phosphites, phosphinites and phosphonites (Aldrich, Steinheim, Germany) were used as supplied.

The IR spectra of samples in KBr pellets were recorded on a Bruker Vector IFS28 FT spectrophotometer, and the NMR spectra on a Bruker AMX 400 spectrometer. ¹H and ¹³C{¹H} are referred to internal TMS, and ³¹P{¹H} chemical shifts to 85 % H₃PO₄, with downfield shifts considered positive. Mass spectra were recorded in the LSIMS, Cs⁺ mode on a Micromass Autospec M instrument. Elemental analyses were carried out on a Fisons EA-1108 apparatus. Melting points were determined on a Gallen Kamp MFB-595 apparatus and are uncorrected.

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Synthesis of fac- $[MnBr(CO)_3L]$ (1)

[MnBr(CO)₅] (0.2 g, 0.7 mmol) was dissolved in 20 ml of toluene and 7.3 ml (1.75 mmol) of Ph₂POCH₂CH₂OPPh₂ (L) were added under argon. The reaction mixture was heated at 90 °C for 4 h, the solvent was removed under vacuum, and the residue was treated with ethanol, affording a yellow product that was filtered out, washed with ethanol and dried under vacuum. Yield: 0.42 g (93 %); mp: 188 °C. $C_{29}H_{24}BrMnO_5P_2$ (649.3); C, 53.81 (calc. 53.65); H, 3.79 (3.73) %.

MS (8 eV, 150 °C) m/z = 648 (M, <5%), 564 (M-3CO, 98%), 571 (M-Ph, 11%), 569 (M-Br, 35%). IR (KBr): v(CO) 2027 s, 1954 m, 1913 s cm⁻¹; ³¹P{¹H} NMR (CDCl₃) δ = 153.2 (s); ¹H NMR (CDCl₃) δ = 4.5 (m, 2H, CH₂), 3.9 (m, 2H, CH₂), 7.2–7.8 (m, 20 H, Ph); ¹³C{¹H} NMR (CDCl₃) δ = 215.8 (m, CO), 219.9 (m, CO), 139.2 (t, J = 22.2 Hz, *ipso*-C of Ph), 137.6 (t, J = 8.5 Hz, *ipso*-C of Ph), 132.3 (t, J = 5.7 Hz, *ortho*-C), 130.8 (t, J = 6.0 Hz, *ortho*-C), 128.3 (t, J = 5.1 Hz, *meta*-C of Ph), 128.2 (t, J = 4.9 Hz, *meta*-C of Ph), 131.0 (s, *para*-C of Ph), 130.7 (s, *para*-C of Ph), 66.8 (s, $-OCH_2$ -CH₂O-).

Suitable crystals for X-ray structural analyses were obtained from a solution in 1:20 (v/v) $CH_2Cl_2/EtOH$ mixture by slow evaporation.

Synthesis of cis, mer- $[MnBr(CO)_2L\{P(OMe)_3\}]$ (2)

[MnBr(CO)₃L] (100 mg, 0.15 mmol) was dissolved in 20 ml of benzene and 0.078 ml (0.6 mmol) of P(OMe)₃ were added under argon. The reaction mixture was refluxed for 2 h, the solvent removed under vacuum, and the residue treated with a mixture 1:1 (v/v) ethanol-methanol, affording a yellowish product that was filtered out, washed with ethanol and dried under vacuum. Yield: 51.4 mg, (46 %); mp: 156 °C. $C_{31}H_{33}BrMnO_7P_3$ (745.36); C, 50.24 (calc. 49.95); H, 4.75 (4.46) %.

MS (8eV, 150 °C): 744 (M, < 5%), 564 (M–2CO–P(OMe)₃, 99%), 665 (M–Br, 24%), 485 (M–Br–2CO–P(OMe)₃, 24%). IR (KBr): v(CO) 1957 s, 1889 s cm⁻¹; ³¹P{¹H} NMR (CDCl₃) δ = 169.6 (m, P(OMe)₃), 153.5 (m, Ph₂POCH₂CH₂OPPh₂, P_A), 157.5 (m, Ph₂POCH₂CH₂OPPh₂, P_B); ¹H NMR (CDCl₃) δ = 5.0, 4.3, 4.1, 4.0 (4H, 1:1:1:1, each a m, $-OCH_2CH_2O-$), 3.6 (d, 9H, CH₃), 7.2–8.1 (m, 20 H, Ph); ¹³C{¹H} NMR (CDCl₃) δ = 222.3 (m, CO), 215.8 (m, CO), from 142.5 to 127.2 (C of *Ph*), 66.4 (d, J = 8.8 Hz, $-OCH_2$ -CH₂O–), 53.4 (d, J = 8.8 Hz, $-OCH_3$).

Synthesis of cis, mer- $[MnBr(CO)_2L\{P(OEt)_3\}]$ (3)

Compound **3** was prepared in the same way as compound **2** using $P(OEt)_3$ (0.105 ml, 0.6 mmol) as monodentate phosphite ligand. Yield: 70 mg, (58 %); mp: 159 °C. $C_{34}H_{39}BrMn O_7P_3$ (787.44); C, 51.00 (calc. 51.86); H, 5.08 (4.99) %.

MS (8eV, 150 °C): 786 (M, <5%), 730 (M-2CO, 9%), 564 (M-2CO-P(OMe)₃, 99%), 707 (M-Br, 11%), 485 (M-Br-2CO-P-(OMe)₃, 19%). **IR** (KBr): v(CO) 1959 s, 1895 s cm⁻¹; ³¹P{¹H} **NMR** (CDCl₃) δ = 166.9 (m, P(OEt)₃), 153.6 (m, Ph₂POCH₂CH₂OPPh₂, P_A), 158.2 (m, Ph₂POCH₂CH₂OPPh₂, P_B); ¹H **NMR** (CDCl₃) δ = 7.3-8.0 (m, 20 H, *Ph*), 4.9, 4.3, 4.1 [each a m, 4H, 1:1:2 (the last partially masked by the ethoxy groups), $-OCH_2CH_2O-]$, 3.9 (m, 6H, OCH_2CH_3), 1.1 (m, 9H, $-OCH_2CH_3$); ¹³C{¹H} **NMR** (CDCl₃) δ = 222.3 (m, CO), 215.7 (m, CO), from 142.3 to 126.9 (C of *Ph*), 66.7 (br s, CH₂), 61.6 (d, CH₂, J = 8.0 Hz), 15.9 (m, CH₃).

Synthesis of mer, trans- $[MnBr(CO)_3{PPh(OEt)_2}_2]$ (4)

 $[MnBr(CO)_3L]$ (100 mg, 0.15 mmol) was dissolved in 20 ml of benzene and 0.12 ml (0.6 mmol) of PPh(OEt)₂ were added under argon. The reaction mixture was refluxed for 4 h, the solvent was removed under vacuum, and the residue was treated with ethanol (2 ml), affording a yellowish product that was filtered out. The filtrate was kept overnight at -4 °C affording crystals suitable for X-ray structural analysis. Yield: 49 mgl (52 %); mp: 136 °C; C₂₃H₃₀BrMnO₇P₂ (615.28); C 45.17 (calc. 44.90); H, 5.13 (4.91) %. **IR** (KBr): v(CO) 2048 w, 1977 s, 1905 m cm⁻¹; ³¹P{¹H} **NMR** (CDCl₃) δ = 184.9 (s); ¹H NMR (CDCl₃) δ = 7.5–7.2 (m, 10H, *Ph*), 4.1–3.4 (m, 8H, OCH₂CH₃), 1.2 (m, 12 H, OCH₂CH₃).

Synthesis of mer, trans- $[MnBr(CO)_3{PPh_2(OEt)}_2]$ (5)

Compound 5 was prepared in the same way as compound 4 using PPh₂(OEt) (0.130 ml, 0.6 mmol) as monodentate phosphinite ligand. The filtrate was kept overnight at -4 °C affording yellow crystals, suitable for X-ray structural analysis. Yield: 45 mgl (43 %) mp:141 °C; C₃₁H₃₀BrMnO₅P₂ (679.37); C 55.02 (calc. 54.81); H, 4.63 (4.45) %.

IR (KBr): ν(CO) 2046 w, 1955 s, 1921 m cm⁻¹; ³¹P{¹H} NMR (CDCl₃) δ = 154.1 (s); ¹H NMR (CDCl₃) δ = 8.0–7.2 (m, 20H, Ph), 3.7 (m, 4H, –OCH₂CH₃), 1.2 (t, 6H, J_H–H = 6.9, –OCH₂CH₃). ¹³C{¹H} NMR (CDCl₃) δ = 220.2 (m, CO), 215.7 (m, CO), from 137.6 to 128.0 (C of *Ph*), 62.9 (m, OCH₂CH₃), 16.1 (t, J_C–P = 3.6 Hz, OCH₂CH₃).

X-ray data collection, structure analysis and refinement

Crystallographic measurements were obtained on a Bruker SMART CCD area-detector diffractometer. All measurements were performed at room temperature (293 K) using graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å), and were corrected for Lorentz and polarization effects. The frames were integrated with the Bruker SMART (control) and Bruker SAINT (integration) [18] software packages; all data were corrected for absorption using the program SADABS. The structures were solved by direct methods using the program SHELXS-97 [19]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F² using the program SHELXL-97 [20]. Hydrogen atoms were inserted at calculated positions and constrained with isotopic thermal parameters. Drawings were produced with ORTEP [21]. Crystallographic data and structure refinement parameters are listed in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication No. CCDC 194893-194895 for compounds 1, 4 and 5 respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (FAX: (+44) 1223 336-033; E-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Results and Discussion

The reaction of $[MnBr(CO)_5]$ with an excess of Ph_2POCH_2 . CH₂OPPh₂ (L) during four hours resulted in the complex $[MnBr(CO)_3L]$, identified as *fac*- $[MnBr(CO)_3L]$ by spectroscopic and X-ray diffractometric studies (Scheme 1).

$$[MnBr(CO)_5] + L \xrightarrow{L= Ph_2POCH_2CH_2OPPh_2}{Tol, 80-90^{\circ}C, 4h} [MnBr(CO)_3L]$$

Scheme 1 Synthesis of compound 1.

Treatment of [1,2-bis(diphenylphosphinite)ethane]bromotricarbonylmanganese(I) [MnBr(CO)₃L] with the appropriate monodentate phosphite $L' = P(OMe)_3$ or $P(OEt)_3$, in refluxing benzene for 4 h, resulted in the replacement of one carbonyl group by L' (Scheme 2).



Scheme 2 Synthesis of compounds 2, 3, 4, and 5.

However, when PPh(OEt)₂ or PPh₂(OEt) are used as L', the bidentate ligand, L, is replaced by two monodentate ligands, L', and complexes [MnBr(CO)₃L'₂] are isolated. This unexpected effect is probably due to the fact that phosphonite and phosphinite ligands are bulkier than phosphite.

Complexes 4 and 5 were identified as *mer,trans*- $[MnBr(CO)_3L'_2]$ by spectroscopic and X-ray diffractometric studies.

X-Ray structure analysis of complexes 1, 4 and 5.

The structure of complexes 1, 4 and 5 were determined by X-ray diffractometry. Crystallographic and refinement data are listed in table 1. Figures 1-3 show ORTEP plots [21] with the numbering schemes used and Table 2 lists both selected bond lengths and angles.

Structure of fac- $[MnBr(CO)_3L]$ (1)

The complex 1 crystallizes in the $P\bar{1}$ space group and its structure consists of discrete units with the Mn atom coor-

dinated to three terminal carbonyl groups, a Br atom and a bidentate chelating Ph₂POCH₂CH₂OPPh₂ (L) ligand, in a fac-octahedral arrangement. The Mn-Br bond length, 2.5269(9) Å, lies within the range spanned by a Mn-Br single bond and is comparable to that previously observed in fac-[MnBr(CO)₃(dmpm)] (2.528(1) Å) [11] and fac-[MnBr- $(CO)_3(dppe)$] (2.517(2) Å) [14]. The P-Mn-P bite of 89.97(5)° is very close to the 90° expected for a regular octahedron and is larger than that found in [MnBr(CO)₃(dppe)] $(84.14(10)^{\circ})$ and in [MnBr(CO)₃(dmpm)] (71.52(5)^{\circ}). This could be due to the number of members in the chelating ring involved in the bond P-Mn-P. The Mn-P distances of 2.3149(14) Å and 2.3476(14) Å, are also very similar to those reported in the literature for similar complexes. The coordination polyhedron around the Mn atom can be accordingly described as a slightly distorted octahedron, the main distortions giving as result the following angles: C(2)-Mn-C(3) (85.74(16)°), C(2)-Mn-P(1) (175.44(5)°), C(3)-Mn-P(2) (173.73(16)°), C(2)-Mn-Br (85.93(3)°) and C(1)-Mn-Br (175.30(15)°).

Structure of mer, trans- $[MnBr(CO)_3{PPh(OEt)_2}_2]$ (4)

Complex 4 crystallizes in the P2₁/n space group and consists of discrete units where the manganese atom is located on a twofold axis perpendicular to the Br-Mn-C(1)-O(1) axis. A 180° rotation generates two equivalent *trans*-phosphonite ligands and two carbonyl groups, and results in an orientational disorder where there is a change between Br and C(1)-O(1) groups. This disorder has also been found in analogous rhenium complexes [22]. The Mn-Br bond length of 2.487(2) Å is within the range of a Mn-Br single bond and slightly smaller than the values found in the compound *mer, trans*-[MnBr(CO)₃{PPh(OMe)₂}₂] 2.524(7) Å [4], and in compound 1, perhaps due to the rotational dis-

 Table 1
 Crystal data and structure refinement for the obtained structures.

Empirical formula	$C_{29}H_{24}BrMnO_5P_2$ (1)	$C_{23}H_{30}BrMnO_7P_2$ (4)	$C_{31}H_{30}BrMnO_5P_2$ (5)
Formula weight	649.27	307.63	679.34
Temperature	173(2)K	293(2)K	293(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	triclinic	monoclinic	monoclinic
Space group	PĪ	$P2_1/n$	$P2_l/c$
Unit cell dimensions	$a = 10.2789(7)$ Å $\alpha = 97.3770(10)^{\circ}$.	a = 10.1726(18) Å.	a = 11.6638(7)Å.
	$b = 11.2225(8)$ Å $\beta = 103.6190(10)^{\circ}$.	$b = 12.477(2) \text{ \AA} \beta = 95.665(4)^{\circ}.$	$b = 14.2608(9) \text{\AA} \beta = 104.127(2)^{\circ}.$
	$c = 12.6751(9)$ Å $\gamma = 90.9490(10)^{\circ}$.	c = 10.866(2) Å.	c = 18.9589(12)Å.
Volume	1407.60(17) Å ³	1372.4(4) Å ³	3058.2(3) Å ³
Z	2	2	4
Calculated density	1.532 Mg/m ³	1.489 Mg/m ³	1.475 Mg/m ³
Absorption coefficient	2.039 mm^{-1}	2.091 mm^{-1}	1.881 mm^{-1}
Crystal size	0.42 x 0.34 x 0.15 mm	0.04 x 0.14 x 0.15 mm	0.2 x 0.13 x 0.09 mm
Theta range for data collection	1.67 to 27.87°	2.49 to 28.04°.	1.80 to 28.02°.
Limiting indices	$-13 \le h \le 13, -10 \le k \le 14, -16 \le l \le 15$	$-10 \le h \le 13, -16 \le k \le 16, -14 \le l \le 9$	$-15 \le h \le 11, -18 \le k \le 18, -16 \le l \le 24$
Reflections collected	8683	7427	16267
Independent reflections	6071[R(int) = 0.0432]	3049 [R(int) = 0.0631]	6730[R(int) = 0.0748]
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	1.00000 and 0.755451	1.000000 and 0.723467	1.0 and 0.797251
Goodness-of-fit on F ²	1.075	0.793	0.912
Final R indices[I>2 sigma (I)]	R1 = 0.0652, $wR2 = 0.1894$	R1 = 0.0442, wR2 = 0.0721	R1 = 0.0751, $wR2 = 0.1862$
R indices (all data)	R1 = 0.0784, $wR2 = 0.1972$	R1 = 0.1417, wR2 = 0.0895	R1 = 0.2044, $wR2 = 0.2195$

[MnBr(CO) ₃ (L)] (1)		$[MnBr(CO)_3(L')] (4)$ L'=PPh(OEt)_2		$[MnBr(CO)_3(L')_2] (5)$ L' = PPh ₂ (OEt)	
Mn-Br	2.5269(9)	Mn-Br	2.487(2)	Mn-Br	2.5343(15)
Mn-C(1)	1.8288(7)	Mn-C(1)	1.774(11)	Mn-C(1)	1.783(10)
Mn-C(3)	1.830(6)	Mn-C(3)	1.853(5)	Mn-C(3)	1.8924(11)
Mn-C(2)	1.847(6)	Mn-C(2)	1.853(5)	Mn-C(2)	1.858(10)
Mn-P(1)	2.3149(14)	Mn-P(1)	2.267(7)	Mn-P(1)	2.304(2)
Mn-P(2)	2.3476(14)	Mn-P(1)'	2.267(7)	Mn-P(2)	2.290(2)
P(1)-Mn-Br	89.59(4)	P(1)-Mn-Br	90.66(6)	P(1)-Mn-Br	93.36(7)
P(2)-Mn-Br	88.41(4)	P(1)'-Mn-Br	89.33(6)	P(2)-Mn-Br	88.16(7)
C(2)-Mn-Br	85.93(3)	C(2)-Mn-Br	89.34(13)	C(2)-Mn-Br	83.7(3)
C(1)-Mn-Br	175.30(15)	C(1)-Mn-Br	176.8(6)	C(1)-Mn-Br	173.1(3)
C(3)-Mn-Br	87.80(15)	C(2)'-Mn-Br	90.66(13)	C(3)-Mn-Br	94.85(5)
P(1) - Mn - P(2)	89.97(5)	P(1)-Mn-P(1)'	180.00(5)	P(1) - Mn - P(2)	178.13(10)
C(1) - Mn - C(2)	90.40(16)	C(1) - Mn - C(2)	88.2(5)	C(1) - Mn - C(2)	90.9(4)
C(2) - Mn - C(3)	85.74(16)	C(2) - Mn - C(2)'	179.999(2)	C(2) - Mn - C(3)	177.9(3)
C(1) - Mn - C(3)	89.0(2)	C(1) - Mn - C(2)'	91.8(5)	C(1) - Mn - C(3)	90.7(3)
C(1)-Mn-P(1)	94.12(16)	C(1) - Mn - P(1)	87.3(6)	C(1) - Mn - P(1)	90.8(3)
C(2) - Mn - P(1)	175.44(5)	C(2)' - Mn - P(1)	90.32(13)	C(2) - Mn - P(1)	89.0(3)
C(3)-Mn-P(1)	94.99(16)	C(2)' - Mn - P(2)	89.68(13)	C(3) - Mn - P(1)	89.61(7)
C(1) - Mn - P(2)	94.47(16)	C(1) - Mn - P(2)	92.7(6)	C(1) - Mn - P(2)	87.6(3)
C(2) - Mn - P(2)	89.01(4)	C(1)-Mn-Br'a)	3.2(6)	C(2) - Mn - P(2)	90.1(3)
C(3) - Mn - P(2)	173.73(16)	Br'-Mn-Br	180.00(13)	C(3) - Mn - P(2)	91.36(7)

Table 2 Selected bond lengths/Å and angles/° for the obtained molecular structures

^{a)} Referred to the rotational disorder of bromine and carbonyl atoms.

Symmetry transformations used to generate equivalent atoms: ': -x, 2-y, -2z.



Figure 1 Crystal structure of compound *fac*-[MnBr(CO)₃(Ph₂POCH₂CH₂OPPh₂)] (1).



Figure 2 Crystal structure of compound *mer,trans*-[MnBr(CO)₃-{PPh(OEt)₂}₂] (4). (Rotational disorder has been eliminated for a better representation)



Figure 3 Crystal structure of compound *mer,trans*-[MnBr(CO)₃-{PPh₂(OEt)}₂] (5).

order between the Br atom and the CO groups. This kind of packing disorder is possible in this crystal since a bromine atom with a covalent radius of 1.14 Å is similar in size with a carbonyl group at an interatomic distance of 1.15 Å and will, therefore, coincide with the centre of the carbonyl C-O bond.

The symmetry around the manganese atom is slightly distorted from an ideal octahedron, being the C(1)-Mn-Br angle the main expression of this deviation. The Mn-P bond length of 2.267(7) Å is similar to the distances found in the complex *mer*, *trans*-[MnBr(CO)₃{PPh(OMe)₂}₂] [4] (2.279(8) Å and 2.260(8) Å), and slightly shorter than the values observed in complex 1 or in compounds where a bidentate chelating ligand is involved in the Mn-P bond. This shortening arises probably from both the *trans* influence of the CO group and the size of the ligand, producing less steric hindrance than a bidentate ligand.

Structure of mer, trans- $[MnBr(CO)_3{PPh_2(OEt)}_2]$ (5)

Complex 5 crystallizes in the P2₁/c space group and consists of discrete units with the manganese atom coordinated to three (meridional) terminal carbonyl groups, a bromine atom and two monodentate phosphinite ligands, PPh₂(OEt). The bromine atom is *trans* to a carbonyl, whereas the two monodentate phosphinite ligands are *trans* to each other.

The Mn-Br bond length of 2.5343(15) Å is within the range for a Mn-Br single bond and similar to complex **1** and to the previously observed in $[MnBr(CO)_3{PPh(OMe)_2}_2]$ [4] (2.524(7) Å). There is some deviation from an ideal octahedral symmetry around the manganese atom, which is reflected in the value of the angles P-Mn-P (178.13(10)°), C(1)-Mn-Br (173.1(3)°), C(2)-Mn-Br (83.7(3)° and C(3)-Mn-Br (94.85(5)°). The Mn-P bond lengths of 2.290(2) Å and 2.304(2) Å are slightly longer than those found in complex 4 and slightly shorter than in complex 1. This could be due to the size of the monodentate phosphinite ligand, bigger than the ligand PPh(OEt)₂ in complex 4, but not so bulky as the bidentate ligand in complex 1.

Spectroscopic results

In the carbonyl-stretching region of the IR spectra, in the case of complex 1 two strong and one medium v(CO) bands at 2027s, 1954m and 1913s cm⁻¹ arise. This pattern is characteristic of a *fac*-tricarbonyl compound.

There are two bands for complexes 2 and 3 at 1957s, 1889s and 1958s, 1895s, respectively, in accordance with a

Table 3 Selected ${}^{31}P{}^{1}H$, ${}^{1}H$ and ${}^{13}C{}^{-}{H^{1}}$ - NMR data for compounds $1-5^{a),b)}$.

Compound	³¹ P{ ¹ H} NMR			¹ H NMR		
	$\delta (P_A, P_B)$	δP_C	δPh	δ CH ₂	δ CH ₃	
$[MnBr(CO)_{3}L] (1)$ L=Ph ₂ POEtOPPh ₂	153.2 (s)		7.8–7.2 (m, 20H)	4.5 (m, 2H, L) 3.9 (m, 2H, L)		
$[MnBr(CO)_2LL'] (2)$ L' = P(OMe)_3	153.5 (m), 157.5 (m)	169.6 (m)	8.1-7.2 (m, 20H)	5.0 (m, 1H, L) 4.3 (m, 1H, L) 4.1 (m, 1H, L) 4.0 (m, 1H, L)	3.6 (d, 9H, L') J(¹ H- ³¹ P)= 6.9 Hz	
$[MnBr(CO)_{2}LL'] (3)$ L' = P(OEt)_{3}	153.2 (m), 158.6 (m)	166.9 (m)	8.0-7.3 (m, 20H)	4.9 (m, 1H, L) 4.3 (m, 1H, L) 4.1 (m, 1H, L) 3.9 (m, 7H) (1H L y 6H L')	1.1 (br s, 9H, L')	
$[MnBr(CO)_{3}L'_{2}] (4)$ L' = PPh(OEt)_{2}	184.9(s)	7.5-7.2 (m, 10 H)	4.1–3.4 (m, 8H, L')	1.2 (m, 12 H, L')		
$[MnBr(CO)_{3}L'_{2}] (5)$ L'= PPh ₂ (OEt)	154.1(s)	8.0-7.2 (m, 20 H)	3.7 (m, 4H, L')	1.2 (t, 6H, L') $J(^{1}H^{-31}P)= 6.9 \text{ Hz}$		
Compound	$^{I3}C{^IH}-NMR$					
	δ СО		δ CH ₂	δ CH ₃		
$[MnBr(CO)_{3}(L)] (1)$ L=Ph ₂ POEtOPPh ₂	219.9 (m) 215.8 (m)	66.8 (s) (L)				
$[MnBr(CO)_2(L)L'] (2)$ L' = P(OMe)_3	222.3 (m) 215.8 (m)	$\begin{array}{ccc} 66.4 \ (\text{br s}) \ (\text{L}) & 53.4(\text{d}), \ \text{L}' \\ J(^{13}\text{C}-^{31}\text{P}) = 8.8 \ \text{Hz} & J(^{13}\text{C}-^{31}\text{P}) = \end{array}$		= 8.8 Hz		
$[MnBr(CO)_2(L)L'] (3)$ L'= P(OEt) ₃	222.3 (m) 215.7 (m)	66.7 (br s) (L) 15.9 (d), L' 61.6 (d), L' $J(^{13}C^{-31}P)= 3.0$ Hz		= 3 Hz		
$[MnBr(CO)_3(L')_2] (4)$ L' = PPh(OEt)_2	220.2 (m) 215.2 (m)		62.7 (br s), L'		16.1 (br s); L'	
$[MnBr(CO)_3(L')_2] (5)$ L' = PPh ₂ (OEt)	220.2 (m) 215.7 (m);		62.9 (m), L' $\begin{array}{c} 16.1 \text{ (t); L'} \\ J(^{13}\text{C}-^{31}\text{P})=3.6 \text{ Hz} \end{array}$			

^{a)} In CDCl₃, δ = ppm, s= singlet, br s= broad singlet, m= multiplet, d= doublet, t= triplet ^{b)} See scheme 3.

cis,mer-[MnBr(CO)₃LL'] symmetry, as the cases of similar *cis,mer*-[ReBr(CO)₃LL'] [24].

The complexes $[MnBr(CO)_3L'_2]$ show the three $\nu(CO)$ bands analogous to the synthesized complex of Mn with similar monodentate ligands [25].

The ¹H NMR spectrum of compound **1** is very similar to that of the parent compound [ReBr(CO)₃L] showing the signal corresponding to the $-(CH_2)_2$ - group as a two sets of multiplets at 3.9 and 4.5 ppm [16].

The ¹³C{¹H} NMR spectrum shows two multiplets at 215.8 and 219.9 ppm, being the latter significantly wider. According to these data, the former could be assigned to the CO in *cis*-position with the P nuclei of the bidentate ligand, and the latter to the CO in *trans* to the bidentate ligand. (J(C-P_{trans}) are higher than the J(C-P_{cis}).

The signal of ${}^{31}P{}^{1}H$ NMR spectrum is a singlet that shows the magnetic equivalence of both P atoms of the bidentate ligand.

For compound 5, ${}^{13}C{}^{1}H$ NMR spectrum shows two broad signals at high field, and we assign the signal of 215.7 ppm to the carbonyl in *trans*-position to the Br similarly to compound 1. The signal at 220.2 ppm is assigned to the mutually *trans* carbonyls (see Table 3).

The ${}^{31}P{}^{1}H$ NMR spectra of compounds 4 and 5 show a singlet, suggesting the magnetic equivalence of the P nuclei, as expected from the proposed X-ray structures.

For compound **3**, the signals of the carbonyls in the ${}^{13}C{}^{1}H$ NMR spectrum are not properly resolved, but they are remarkably different. The signal at 215.7 ppm is much narrower (line width approximately of 15 Hz) than the one located at 222.3 ppm (line width approximately of 200 Hz). It seems to show that the signal at higher field ($\delta = 215.7$) corresponds to a carbonyl placed in *cis* to the three P atoms, and the other ($\delta = 222.3$) corresponds to a carbonyl group *trans* to the P_A nucleus and *cis* to P_B and P_C nuclei (see Scheme 3).



Scheme 3 Schematic representation of compounds 2 and 3.

For compound **2**, ${}^{13}C{}^{1}H$ NMR spectrum shows two very broad signals at low field, similarly to compound **3** (table 3), and analogous to Re complexes with similar ligands. The ${}^{31}P{}^{1}H$ NMR spectrum shows three multiplets indicating the different nature of P_A , P_B and P_C nuclei (see Scheme 3 and Table 3).

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