Tricarbonyl Derivatives of Manganese(I) with Diphosphinite Chelating Ligands

Jorge Bravo, Jesús A. Castro, Eduardo Freijanes*, Soledad García-Fontán, Elvira M. Lamas, and Pilar Rodríguez-Seoane*

Vigo/Spain, Departamento de Química Inorgánica, Facultade de Química, Universidade de Vigo

Received November 26th, 2004; accepted March 10th, 2005.

Abstract. Reaction of $[MnBr(CO)_3L] [L = Ph_2POCH_2CH_2OPPh_2, L^1, {(CH_3)_2CH}_2POCH_2CH_2OP{CH(CH_3)_2}_2, L^2] with AgO_3SCF_3 and AgO_2CCF_3 in dichloromethane afforded the new complexes <math>[Mn(O_3SCF_3)(CO)_3L]$ and $[Mn(O_2CCF_3)(CO)_3L]$, respectively. Substitution of O_3SCF_3 resulted in the new species $[Mn(SCN)(CO)_3L]$, $[Mn(NCCH_3)(CO)_3L](O_3SCF_3)$ and, in the case of L², $[Mn(CN)(CO)_3L^2]$. By contrast, any attempt to displace the O_2CCF_3 ligand in the same way was unsuccessful. After maintaining for some days the complex $[Mn(CH_3CN)(CO)_3L^1](O_3SCF_3)$ in dichloromethane at room temperature, the new complex $[MnCl(CO)_3L^1]$ was formed. All the new complexes were characterized by elemental analysis, mass spectrometry and IR and NMR

1 Introduction

The synthesis of transition metal complexes containing a weakly bound ligand has been widely treated, since such compounds are useful as a source of other species resulting from the substitution of the labile ligand for another more coordinating base [1]. Furthermore, this kind of complexes is of great interest for catalytic purposes: in fact, a requirement for catalysis is the availability of free coordination sites on the metal atom. In this sense, the triflate (O_3SCF_3) anion is usually considered a special case, since its lability is strongly dependent on the electronic nature of the metal atom [2–4]. So that, in an electron-donating ligand environment, such as [Ti(Cp)₂(O_3SCF_3)₂], both triflate ligands are much more easy to substitute than in, for example, [Re(O_3SCF_3)(CO)₅], where they can only be replaced by strong donors [5, 6].

In a previous work [7], we reported the synthesis of a series of complexes resulting from the substitution of two CO ligands from $[MnBr(CO)_5]$ for a variety of phosphite, phosphonite and phosphinite bidentate ligands. By using two of those complexes as starting material, we carried out the abstraction of Br and its substitution for triflate and trifluoroacetate ligands. Subsequently, the new complexes provided the possibility of substituting the loosely held O_3SCF_3 ligand by other more basic ligands.

spectroscopies. In the case of $[Mn(O_3SCF_3)(CO)_3L^1]$, $[Mn(O_2CCF_3)(CO)_3L^1]$, $[MnCl(CO)_3L^1]$, $[Mn(CH_3CN)(CO)_3L^2]$ -(O_3SCF_3), $[Mn(CN)(CO)_3L^2]$ and $[Mn(O_2CCF_3)(CO)_3L^2]$, together with the previously synthesized complex $[MnBr(CO)_3L^2]$, suitable crystals for X-ray structural analysis were isolated. In all of them the Mn atom adopts six-coordination by bonding to the three CO ligands, the two P atoms of L and either one C atom (CN), one oxygen atom (O_2CCF_3 , O_3SCF_3), one N atom (CH₃CN, SCN) or the halogen atom (Cl, Br).

Keywords: Manganese; Diphosphinite complexes; Chelating ligands

This paper describes the isolation and characterization of the new complexes arisen from this substitution, as well as the unexpected chloro-complex [MnCl(CO)₃L¹], formed after maintaining for some days one of the aforesaid compounds, [Mn(CH₃CN)(CO)₃L¹](O₃SCF₃), in dichloromethane.

2 Experimental Section

2.1 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 [8]. Deuterated solvent (CDCl₃ Merck) for NMR measurements was dried over molecular sieves. 1,2-Bis(diphenylphosphinoxy)ethane and 1,2 bis(diisopropylphosphinoxy)ethane were prepared as described previously [9], [MnBr(CO)₅] was obtained from [Mn₂(CO)₁₀] by the method described in literature [10] and the starting product [MnBr(CO)₃L¹] has been previously reported [7]. AgSO₃CF₃, AgCO₂CF₃ (Aldrich), CH₃CN, KCN and KSCN (Merck) were used as supplied.

The IR spectra of samples in KBr pellets were recorded on a Bruker Vector 22 FT spectrophotometer, and NMR spectra on a Bruker AMX 400 spectrometer. ¹H and ¹³C{¹H} signals are referred to internal TMS, ³¹P{¹H} chemical shifts to 85 % H₃PO₄, and ¹⁹F{¹H} signals to CFCl₃ 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 Gallenkamp MFB–595 apparatus and are uncorrected.

^{*} Eduardo Freijanes

Pilar Rodríguez-Seoane

Facultade de Química Universidade de Vigo

E-36200 Vigo/Spain

Fax: +34-986-813798

E-mail (E.F.): erivas@uvigo.es

2.2 Synthesis of the complexes

$[Mn(O_3SCF_3)(CO)_3L^1]$ (1)

[MnBr(CO)₃L¹] (0.10 g, 0.15 mmol) and AgSO₃CF₃ (0.04 g, 0.15 mmol) were dissolved in CH₂Cl₂ (15 cm³). The reaction mixture was refluxed for 2 h and filtered through *celite*. The solvent was removed under vacuum from the obtained solution, and the residue was triturated with ethanol, affording a yellow product that was filtered out, washed with ethanol and vacuum dried. Yield: 0.08 g (74 %); mp: 175 °C. $C_{30}H_{24}F_3MnO_8P_2S$ (718.46): C, 49.9 (calc. 50.1); H, 3. 7 (3.4); S, 4.3 (4.5) %.

Suitable crystals for X-ray structural analysis were obtained from a solution of EtOH by slow evaporation.

$[Mn(SCN)(CO)_{3}L^{1}]$ (2)

From [Mn(O₃SCF₃)(CO)₃L¹] (0.08 g, 0.13 mmol) and an excess of KSCN (0.05 g, 0.60 mmol), a solution in a dichloromethane/methanol mixture (10/5 cm³) was formed and stirred for 24 h at room temperature. The solvent was then removed under vacuum and dichloromethane was added to the residue in order to eliminate the excess of KSCN, which was filtered off. The solvent of the resulting solution was removed under vacuum and the obtained product was triturated with diethyl ether affording a yellowish product, which was washed with diethyl ether and vacuum dried. Yield: 0.02 g (38 %); mp: 157 °C. $C_{30}H_{24}NMnO_5P_2S$ (627.47): C, 57.8 (calc. 58.1); H, 4.0 (4.0); N, 2.3 (2.3); S, 5.3 (5.3) %.

MS (8 eV, 150 °C) m/z = 627 (M, 14 %), 569 (M–SCN, <5 %), 543 (M–3CO, 56 %), 485 (M–3CO–SCN, 34 %). **IR** (KBr): v(CO) 2035, 1970, 1933; v(CN) 2099; v(CS) 818 cm⁻¹; ³¹P{¹H} **NMR** (CDCl₃) $\delta = 156.2$ (s); ¹H NMR (CDCl₃) $\delta = 4.29$ (m, 2H, CH₂), 3.97 (m, 2H, CH₂), 7.92-7.26 (m, 20 H, Ph); ¹³C{¹H} **NMR** (CDCl₃, δ): 213.3 (m, CO), 144.9-127.4 (m, Ph), 65.5 (s, $-OCH_2-CH_2O-$), 124.0 (s, SCN).

$[Mn(CH_3CN)(CO)_3L^1](O_3SCF_3)$ (3)

[Mn(O₃SCF₃)(CO)₃L¹] (0.08 g, 0.13 mmol) was disolved in CH₂Cl₂ (15 cm³) and an excess of CH₃CN (0.65 mmol) was added. After stirring for 1 h at room temperature, the solvent was removed under vacuum and the residue was triturated with *n*-hexane, affording a brown product that was filtered out, washed with *n*-hexane and dried under vacuum. Yield: 0.08 g (89 %); mp: 148 °C. $C_{32}H_{27}F_{3}NMnO_{8}P_{2}S$ (759.46): C, 49.9 (calc. 50.6); H, 3.8 (3.6); N, 1.6 (1.8); S, 4.0 (4.2) %.

$[MnCl(CO)_{3}L^{1}]$ (4)

After maintaining the compound $[Mn(CH_3CN)(CO)_3L^1](SO_3CF_3)$ for 2 days at room temperature in dichloromethane solution, yel-

MS (8 eV, 150 °C) m/z = 604 (M, <5 %), 520 (M–3CO, 100 %), 569 (M–Cl, < 5 %), 485 (M–CO–Cl, 28 %). IR (KBr): v(CO) 2034, 1978, 1908 cm⁻¹; ³¹P{¹H} NMR (CDCl₃) δ = 153.4 (s); ¹H NMR (CDCl₃) δ = 4.54 (m, 2H, CH₂), 3.98 (m, 2H, CH₂), 7.89-7.24 (m, 20 H, *Ph*).

$[Mn(O_2CCF_3)(CO)_3L^1]$ (5)

 $[MnBr(CO)_3L^1] \quad (0.10 \text{ g}, 0.15 \text{ mmol}) \text{ and } AgCO_2CF_3 \quad (0.03 \text{ g}, 0.15 \text{ mmol}) \text{ were dissolved in } 20 \text{ cm}^3 \text{ of } CH_2Cl_2. The reaction mixture was refluxed for 3 h and filtered through$ *celite* $. From the obtained solution solvent was removed under vacuum, and the residue was triturated with ethanol, affording a yellow product that was filtered off, washed with ethanol and vacuum dried. Yield: 0.07 g (71 %); mp: 165 °C. C_{31}H_{24}F_3MnO_7P_2 (682.41): C, 54.0 (calc. 54.5); H, 3.8 (3.6) %.$

MS (8 eV, 150 °C) m/z = 682 (M, <5%), 598 (M-3CO, 100%), 485 (M-3CO-OOCCF₃, 100%), 569 (M-OOCCF₃, 39%), 541 (M-OOCCF₃-CO, <5%). IR (KBr): v(CO) 2033, 1969, 1933, 1913 cm⁻¹; 3¹P{¹H} NMR (CDCl₃) δ = 158.6 (s); ¹⁹F{¹H} NMR (CDCl₃) δ = -74.7 (s); ¹H NMR (CDCl₃) δ = 4.32 (m, 2H, CH₂), 4.14 (m, 2H, CH₂), 7.58-7.45 (m, 20 H, Ph); ¹³C{¹H} NMR (CDCl₃), 137.5-127.4 (m, Ph), 66.3 (s, -OCH₂-CH₂O-), 114.4 (q, J_{C-F} = 291 Hz, O₂CCF₃).

Suitable crystals for X-ray structural analysis were obtained from an ethanol solution by slow evaporation.

$[MnBr(CO)_{3}L^{2}]$ (6)

[MnBr(CO)₅] (0.20 g, 0.73 mmol) was dissolved in 15 cm³ of toluene and 9 ml (2 mmol) of $\{(CH_3)_2CH\}_2POCH_2CH_2OP\{CH-(CH_3)_2\}_2$ (L²) were added under argon. The reaction mixture was heated at 90 °C for 3 h, the solvent was removed under vacuum, and the resulting oil was triturated with ethanol, yielding a yellow product that was filtered out, washed with ethanol and dried under vacuum. Yield: 0.37 g (70 %); mp: 149 °C. $C_{17}H_{32}BrMnO_5P_2$ (513.23): C, 39.9 (calc. 39.8); H, 6.4 (6.3) %.

MS (8 eV, 150 °C) m/z = 512 (M, <5 %), 428 (M–3CO, 100 %), 433 (M–Br, 74 %), 377 (M–Br–2CO, 19 %), 349 (M–Br–3CO, 32 %). **IR** (KBr): v(CO) 2016, 1949, 1903 cm⁻¹; ³¹P{H} **NMR** (CDCl₃) $\delta = 180.0$ (s); ¹H **NMR** (CDCl₃) $\delta = 4.39$ (m, 2H, CH₂), 3.84 (m, 2H, CH₂), 2.95 (m, 2H, CH), 2.57 (m, 2H, CH), 1.28 (m, 24 H, CH₃); ¹³C{H} **NMR** (CDCl₃, δ): 215.4 (m, CO), 64.9 (s, $-OCH_2 - CH_2 O -$), 30.9 (vt, ¹J_{C-P} + ³J_{C-P} = 13, CHCH₃), 30.5 (m, CHCH₃), 17.5 (s, CHCH₃), 16.8 (s, CHCH₃), 16.5 (s, CHCH₃), 16.2 (s, CHCH₃).

Suitable crystals for X-ray structural analysis were obtained by slow evaporation from an ethanol solution.

$[Mn(O_3SCF_3)(CO)_3L^2]$ (7)

[MnBr(CO)₃L²] (0.10 g, 0.20 mmol) and AgSO₃CF₃ (0.05 g, 0.20 mmol) were dissolved in 20 cm³ of CH₂Cl₂. The reaction mixture was refluxed for 3 h and filtered through *celite*. Solvent was then removed from the solution under vacuum and ethanol was added to the residue, affording a yellowish product that was filtered out, washed with *n*-hexane and dried under vacuum. Yield: 0.12 g (65 %); mp: 125 °C. $C_{18}H_{32}F_3MnO_8P_2S$ (582.39): C, 37.0 (calc. 37.1); H, 5.8 (5.5); S, 5.3 (5.5) %.

 NMR (CDCl₃) δ = 183.0 (s); ¹⁹F{¹H} NMR (CDCl₃) δ = -77.5 (s); ¹H NMR (CDCl₃) δ = 4.04 (m, 4H, CH₂), 2.61 (m, 4H, CH), 1.32 (m, 24 H, CH₃); ¹³C{¹H} NMR (CDCl₃, δ): 222.9 (m, CO), 214.6 (m, CO), 119.6 (q, J_{C-F} = 318, O₃SCF₃), 66.9 (s, $-OCH_2 - CH_2O -$), 33.2 (vt, ¹J_{C-P} + ³J_{C-P} = 13 Hz, CH-CH₃), 31.0 (vt, ¹J_{C-P} + ³J_{C-P} = 6 Hz, CH), 18.3 (m, CH₃).

$[Mn(SCN)(CO)_{3}L^{2}]$ (8)

[Mn(O₃SCF₃)(CO)₃L²] (0.08 g, 0.12 mmol) and an excess of KSCN (0.06 g, 0.60 mmol) were dissolved in a dicloromethane/methanol mixture (10/5 cm³). This solution was stirred for 24 h at room temperature. The solvent was then removed under vacuum and dichloromethane was added to the residue in order to eliminate the excess of KSCN, which was filtered off. The solvent of the resulting solution was also removed under vacuum and the obtained product was triturated with *n*-hexane affording a yellowish product, which was washed with the same solvent and vacuum dried. Yield: 0.03 g (46 %); mp: 110 °C. $C_{18}H_{32}MnNO_5P_2S$ (491.40): C, 43.7 (calc. 43.9); H, 6.9 (6.5); N, 2.9 (2.8); S, 6.3 (6.5) %.

$[Mn(CH_3CN)(CO)_3L^2](SO_3CF_3)$ (9)

To 0.07 g (0.01 mmol) of $[Mn(O_3SCF_3)(CO)_3L^2]$ dissolved in 15 cm³ of CH₂Cl₂ an excess of CH₃CN (0.05 mmol) was added. After stirring the mixture for 1 h at room temperature, the solvent was removed under vacuum and the residue was triturated with hexane, affording a brown product that was filtered out, washed with hexane and dried under vacuum. Yield: 0.04 g (52 %); mp: 137 °C. C₂₀H₃₅F₃MnNO₈P₂S (623.44): C, 38.0 (calc. 38.5); H, 5.9 (5.7); N, 2.0 (2.2); S, 4.9 (5.1) %.

Suitable crystals for X-ray structural analysis were obtained by slow evaporation from an ethanol solution.

$[Mn(CN)(CO)_3L^2]$ (10)

[Mn(O₃SCF₃)(CO)₃L²] (0.07 g, 0.12 mmol) and an excess of KCN (0.04 g, 0.60 mmol) were dissolved in a dichloromethane/methanol mixture (10/5 cm³). After stirring for 24 h at room temperature, the solvent was removed under vacuum and the residue was dissolved in dicloromethane, affording a brown solid (the excess of KCN) which was filtered off. From the solution the solvent was removed under vacuum and the resulting oil was triturated with *n*-hexane, affording a yellowish product which was washed with the same solvent and dried under vacuum. Yield: 0.02 g (45 %); mp: 115 °C. $C_{18}H_{32}MnNO_5P_2$ (459.34): C, 45.5 (calc. 47.1); H, 7.0 (7.0); N, 3.3 (3.1) %.

MS (8 eV, 150 °C) m/z = 460 (M⁺, 33 %), 375 (M-3CO, 100 %), 377 (M-2CO-CN, 8 %), 431 (M-CO, 7 %), 349 (M-CN-3CO, 26 %). **IR**

(KBr): v(CO) 2014, 1946, 1921; v(CN) 2112 cm⁻¹; ³¹P{¹H} NMR (CDCl₃) $\delta = 186.2$ (s); ¹H NMR (CDCl₃) $\delta = 4.45$ (m, 2H, *CH*₂), 3.89 (m, 2H, *CH*₂), 2.75 (m, 2H, *CH*), 2.52 (m, 2H, *CH*), 1.27 (m, 24 H, *CH*₃).

Suitable crystals for X-ray structural analysis were obtained by slow evaporation from an ethanol solution.

$[Mn(O_2CCF_3)(CO)_3L^2]$ (11)

 $[MnBr(CO)_3L^2]$ (0.08 g, 0.17 mmol) and AgCO₂CF₃ (0.04 g, 0.17 mmol) were dissolved in 20 cm³ of CH₂Cl₂. The reaction mixture was refluxed for 4 h and filtered through *celite*. From the obtained solution the solvent was removed under vacuum, and the residue was triturated with ethanol, affording a yellowish product that was filtered out, washed with hexane and dried under vacuum. Yield: 0.05 g (53 %); mp: 129 °C. C₁₉H₃₂F₃MnO₇P₂ (546.34): C, 41.2 (calc. 41.7); H, 6.1 (5.9) %.

2.3 X-ray data collection, structure analysis and refinement

Crystallographic measurements were obtained on a Bruker SMART CCD area-detector diffractometer. All of them were performed at room temperature (293 K) using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ Å}$). All data were corrected for absorption using the program SADABS [11]. The structures were solved by direct methods using the program SHELXS-97 [12]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F² using the program SHELXL-97 [12]. Hydrogen atoms were inserted at calculated positions and constrained with isotopic thermal parameters. Drawings were produced with ORTEP [13]. Crystallographic data and structure refinement parameters are listed in tables 1 and 2. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication No. CCDC 256209-256215 for compounds 1, 5, 4, 6, 9, 10 and 11, 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) 3 36-0 33; E-mail for inquiry: fileserv@ccdc.cam.ac.uk.

3 Results and Discussion

3.1 Synthesis of the complexes

Substitution of the bromo ligand, in the starting complexes, by triflate or trifluoroacetate ligands, was carried out in each case by direct reaction with the adequate silver salt and subsequent isolation of the new complex from the resulting solution. Nevertheless, the easiness of ulterior displacement of the new ligand by another more coordinating base showed not to be the same in all cases. Schemes 1 and 2 summarize this different behaviour: while any attempt to displace the trifluoroacetate ligand was unsuccessful, trifl-

| | 1 | 4 | 5 |
|---|---|--|--|
| Empirical formula Formula weight Temperature /K Wavelength /Å Crystal system Space group Unit cell dimensions | $C_{30}H_{24}F_{3}MnO_{8}P_{2}S$ 718.43 293(2) 0.71073 monoclinic P2 ₁ /c a = 9.9401(15) Å b = 19.018(3) Å c = 16.783(2) Å $\beta = 90.888(3)^{\circ}$ | $\begin{array}{c} C_{29}H_{24}ClMnO_5P_2\\ 604.81\\ 293(2)\\ 0.71073\\ orthorhombic\\ P2_12_12_1\\ a=9.7046(8)~\mathring{A}\\ b=14.3651(12)~\mathring{A}\\ c=19.8881(16)~\mathring{A} \end{array}$ | $\begin{array}{c} C_{31}H_{24}F_{3}MnO_{7}P_{2}\\ 682.38\\ 293(2)\\ 0.71073\\ triclinic\\ P\bar{1}\\ a=10.0425(11) \text{ Å}\\ b=17.9299(18) \text{ Å}\\ c=18.2498(19) \text{ Å}\\ \alpha=68.821(2)^{\circ}\\ \beta=88.733(2)^{\circ} \end{array}$ |
| Valuma /Å ³ | 2172 4(9) | 2772 6(4) | $\gamma = 89.510(2)^{\circ}$ |
| volume /A | 5172.4(8) | 2//2.0(4) | 5065.4(6) |
| Density (calculated) (Mg/m^3) | 1.504 | 1.449 | 1.480 |
| Absorption coefficient/mm ⁻¹ | 0.649 | 0.726 | 0.600 |
| F(000) | 1464 | 1240 | 1392 |
| Crystal size /mm | 0.25 x 0.24 x 0.08 | 0.25 x 0.13 x 0.09 | 0.67 x 0.47 x 0.14 |
| Theta range for data collection /° | 1.62 to 28.04 | 1.75 to 28.03 | 1.99 to 28.03 |
| Index ranges | -13<=h<=12; -25<=k<=25; -11<=1<=22 | -11 <=h <= 12; -16 <=k <= 18; -26 <= 1 <= 25 | $-13 \le h \le 12;$ $-23 \le k \le 19;$ $-23 \le 1 \le 23$ |
| Reflections collected | 20917 | 16383 | 17962 |
| Independent reflections | 7625 | 6318 | 12494 |
| F | [R(int) = 0.1017] | [R(int) = 0.0752] | [R(int) = 0.0282] |
| Reflections observed (>2sigma) | 2564 | 2890 | 6284 |
| Data Completeness | 0.992 | 0.978 | 0.841 |
| Refinement method | Full-matrix least-squares on F ² | Full-matrix least-squares on F ² | Semi-empirical from equivalents |
| Data / restraints / parameters | 7625 / 0 / 406 | 6318 / 0 / 3430 | 12494 / 0 / 793 |
| Goodness-of-fit on F ² | 0.675 | 0.696 | 0.810 |
| Final R indices | $R_1 = 0.0455$ | $R_1 = 0.0444$ | $R_1 = 0.0462$ |
| [I>2sigma(I)] | $wR_2 = 0.0460$ | $wR_2 = 0.0470$ | $wR_2 = 0.0756$ |
| R indices (all data) | $R_1 = 0.1830$ w $R_2 = 0.0613$ | $R_1 = 0.1302$ $wR_2 = 0.0575$ | $R_1 = 0.1111$ w $R_2 = 0.0883$ |
| Largest diff. peak and hole | 0.368 and -0.273 e.Å ⁻³ | $0.754 \text{ and } -0.358 \text{ e.Å}^{-3}$ | 0.432 and -0.449 e.Å ⁻³ |

Table 1 Crystal data and structure refinement details for complexes 1, 4 and 5.

ate was quickly substituted by acetonitrile, and, in more drastic conditions, by SCN. Formation of the CN complex was only possible from the corresponding L^2 compound.

After maintaining complex 3 for 2 days in CH_2Cl_2 , yellowish crystals were formed. Solid-state structure of the new compound has been obtained from single-crystal X-ray structural analysis, revealing the substitution of the CH_3CN ligand by Cl. This displacement was not achieved in the analogous L^2 compound (complex 9).

3.2 Crystal structures

Figures 1–7 show ORTEP diagrams of the complexes with the numbering scheme. The crystallographic data are listed in Tables 1 and 2, and Table 3 lists some selected bond lengths and angles. In all the complexes the coordination sphere around the metal atom is a distorted octahedron, with the three CO ligands in a *facial* disposition. The Mn-P bond lengths range from 2.3172(10) to 2.3922(10) Å, as found in other similar phosphane manganese(I) complexes [14], and are smaller than the sum of their covalent radii (2.49 Å) [15], as a consequence of the π interaction. Besides, the CO ligands *trans* to Br or Cl are closer to the Mn atom,

as expected from the π -donor character of the halogen [e.g. 1.775(4) vs. 1.807(4) and 1.803(4) Å in the chloro-, 1.805(7) vs. 1.835(6) and 1.841(7) Å in the bromo-complex]. Similarly, the Mn-C bond lengths for the CO ligands *trans* to oxygen are 1.769(4) [vr. 1.823(4), 1.845(4)], 1.770(3) [vr. 1.826(4), 1.851(4)] and 1.743(6) Å [vr. 1.814(6), 1.806(6)] for complexes **1**, **5** and **11**, respectively. Finally, the Mn-O bond leads to a lengthening of the corresponding C-O or S-O distance in the carboxylato or the thiolato group, respectively. For instance, in complex **11**: C(4)-O(4) = 1.274(6), C(4)-O(5) = 1.200(6) Å; in complex **1**: S-O(11) = 1.467(2), S-O(13) = 1.427(2) Å. In the same way, the C-N bond in CH₃CN is slightly weakened upon coordination to the metal [1.136(4) Å vs. 1.158 Å in the free acetonitrile] [16].

The bond angles around the Mn range from $82.29(13)^{\circ}$ for C(2)-Mn-Cl in complex 4 to $97.07(3)^{\circ}$ for P(1)-Mn-P(2) in complex 10. In the case of the P-Mn-P angles, the values are in the range $88.17(3)-97.07(3)^{\circ}$ (i.e. very close to 90°), showing that the number of members of the chelating ring involved in this bond is great enough to induce no significant steric hindrance in the bidentate phosphane ligand.

The possibility of a weak interaction between the donor atom (Br, O, N) and one H atom of a CH_2 group on the

| | 6 | 9 | 10 | 11 |
|---|---|---|--|---|
| Empirical formula | C17H28BrMnO5P2 | C20H25F2MnNO8P2S | C18H22MnNO5P2 | C10H22F2MnO7P2 |
| Formula weight | 509.18 | 623.43 | 459.33 | 546.33 |
| Temperature /K | 293(2) | 293(2) | 293(2) | 293(2) |
| Wavelength /Å | 0.71073 | 0 71073 | 0 71073 | 0.71073 |
| Crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| Space group | P2 /n | PĪ | P2 / n | P2./c |
| Unit cell dimensions | a = 14.3682(13) Å | a = 0.0043(0) Å | a = 14.5201(15) Å | a = 0.3206(10) Å |
| Olift cell dimensions | a = 14.3082(13) A b = 0.7777(0) Å | a = 9.9943(9) A b = 11.0124(10) Å | a = 14.3291(13) A b = 0.7884(10) Å | a = 9.3290(10) A b = 16.2474(19) Å |
| | 0 = 9.777(9) A | 0 = 11.0134(10) A | 0 = 9.7884(10) A | 0 = 10.3474(10) A |
| | c = 10.0233(13) A | $\alpha = 71.415(2)^{\circ}$ | c = 10.3802(17) A | c = 17.1995(18) A |
| | $\beta = 103.987(2)^{\circ}$ | $\beta = 89.605(2)^{\circ}$ $\gamma = 84.980(2)^{\circ}$ | $\beta = 104.369(2)^{\circ}$ | $\beta = 93.409(2)^{\circ}$ |
| Volume /Å ³ | 2266 4(4) | 1453 4(2) | 2256 7(4) | 2618 5(5) |
| Z | 4 | 2 | 4 | 4 |
| Density (calculated) /(Mg/m ³) | 1.492 | 1.425 | 1.352 | 1.386 |
| Absorption coefficient | 2.509 | 0.696 | 0.753 | 0.681 |
| F(000) | 1040 | 648 | 968 | 1136 |
| Crystal size /mm | $0.24 \ge 0.21 \ge 0.14$ | $1.00 \times 0.41 \times 0.10$ | $0.48 \ge 0.36 \ge 0.19$ | $0.52 \times 0.28 \times 0.07$ |
| Thete range for | $1.68 \pm 0.28 0.7$ | 1.00 x 0.41 x 0.10 | 1 68 to 27 00 | $1.72 \pm 0.28 \times 0.07$ |
| data collection /° | 1.08 to 28.07 | 1.90 to 28.02 | 1.08 to 27.99 | 1.72 to 28.11 |
| Index ranges | -18c - bc - 18 | -12c-bc-13c | -18 < -h < -18 | -12c-bc-12c |
| Index Tanges | 10 < -11 < -10, 9 < -12 < -12 | 12 < -11 < -13, 14 < -1 < -12 | 12 < -12 < -12 | 12 < -12 < -12, 10 < -1 < -21 |
| | -3 < -K < -12, | -14 < -K < -12, | -12 - K - 12, 14 - 1 - 21 | -19 < -k < -21, |
| | -22<=1<=21 | -13<=1<=18 | -14<=1<=21 | -22<=1<=16 |
| Reflections collected | 12455 | 8641 | 13061 | 14079 |
| Independent reflections | 5082 | 6036 | 5152 | 5805 |
| 1 | [R(int) = 0.0647] | [R(int) = 0.0221] | [R(int) = 0.0526] | [R(int) = 0.0568] |
| Reflections observed | | 3729 | 3343 | 2049 |
| (>2sigma) | | | | |
| Data Completeness | 0.925 | 0.858 | 0.948 | 0.906 |
| Refinement method | Full-matrix least-squares | Full-matrix least-squares | Full-matrix least-squares | Full-matrix least-squares |
| remement method | on F^2 | on F^2 | on F^2 | on F^2 |
| Data/restraints/ parameters | 5082 / 0 / 243 | 6036 / 0 / 334 | 5152 / 0 / 252 | 5805 / 0 / 297 |
| Goodness-of-fit on F^2 | 0.831 | 0.910 | 0 894 | 0.813 |
| Final <i>R</i> indices | $R_1 = 0.0555$ | $R_1 = 0.0524$ | $R_1 = 0.0423$ | $R_1 = 0.0583$ |
| []>2sigma(])] | wR2 = 0.0555, | wR2 = 0.1254 | wP2 = 0.0838 | wR2 = 0.1223 |
| <i>R</i> indices (all data) | $R_1 = 0.1445$ | $R_1 = 0.0844$ | $R_1 = 0.0771$ | $R_1 = 0.1223$ |
| A mules (all data) | mD2 = 0.1442 | wP2 = 0.1365 | $mP_2 = 0.0014$ | mP2 = 0.2020 |
| Largest diff neak and hala | WIX = 0.1442 0.643 and $-0.720 \text{ s}^{\text{Å}=3}$ | $0.483 \text{ and } -0.368 \text{ a}^{\text{\AA}-3}$ | $0.468 \text{ and } -0.368 \text{ a}^{\text{\AA}-3}$ | WIX = 0.1357 0.305 and $-0.203 \circ h^{-3}$ |
| Largest dill. peak and hole | 0.045 and -0.729 e.A | 0.405 and -0.508 e.A | 0.408 and -0.308 e.A | 0.595 and -0.295 e.A |

Table 2 Crystal data and structure refinement details for complexes 6, 9-11.



Scheme 1

bidentate ligand could also be considered in some cases. For instance, in the case of complex **6**, the Br...H distance (2.80 Å) for one of the conformational isomers (see Fig. 8) is shorter than the sum of the van der Waals radii (3.0 Å), so that this conformer could result favoured (i.e., of lower energy) with respect to the other one. On the contrary, in

the case of complex 1, the interaction between the O atom of the triflate ligand and one of the CH_2 groups is less probable since the O...H distance (2.67 Å) takes almost the same value as the sum of the v.d.W. radii (2.7 Å). In consequence, the energy gap between both conformers would be smaller in this case.



Scheme 2

Table 3 Selected bond lengths/Å and angles/° for the complexes

| | 1 | 4 | 5 | 6 | 9 | 10 | 11 |
|--------------|------------|------------|--------------------------|------------|------------|-----------|------------|
| Mn-C(1) | 1.769(4) | 1.775(4) | 1.770(3) 1.776(3) | 1.803(7) | 1.799(4) | 1.803(3) | 1.743(6) |
| Mn-C(2) | 1.823(4) | 1.807(4) | 1.826(4) 1.828(3) | 1.835(6) | 1.829(4) | 1.825(3) | 1.814(6) |
| Mn-C(3) | 1.845(4) | 1.803(4) | 1.851(4) 1.844(4) | 1.841(7) | 1.818(4) | 1.812(3) | 1.806(6) |
| Mn-O | 2.082(2) | - | 2.045(2) 2.0481(19) | - | - | - | 2.046(3) |
| Mn-Cl | _ | 2.4284(11) | _ | - | - | - | _ |
| Mn-Br | _ | _ | - | 2.5286(11) | - | - | _ |
| Mn-N(1) | - | _ | - | _ | 2.017(3) | - | - |
| Mn-C(4) | - | - | - | - | - | 1.992(3) | - |
| N(1)-C(4) | - | - | - | - | 1.136(4) | 1.146(3) | - |
| Mn-P(1) | 2.3208(10) | 2.3275(11) | 2.3172(10) 2.3222(10) | 2.3720(16) | 2.3782(10) | 2.3626(8) | 2.3617(15) |
| Mn-P(2) | 2.3673(10) | 2.3234(11) | 2.3364(11) 2.3351(9) | 2.3531(17) | 2.3922(10) | 2.3365(8) | 2.3559(15) |
| C(1)-O(1) | 1.155(4) | 1.143(4) | 1.160(3) | 1.093(6) | 1.144(4) | 1.157(3) | 1.173(5) |
| C(2)-O(2) | 1.146(4) | 1.153(4) | 1.140(4) 1.139(3) | 1.123(6) | 1.143(4) | 1.136(3) | 1.144(5) |
| C(3)-O(3) | 1.147(3) | 1.155(4) | 1.143(4) 1.132(4) | 1.049(6) | 1.141(4) | 1.152(3) | 1.146(5) |
| S-O(11) | 1.467(2) | | 11102(1) | | | | |
| S-O(13) | 1.427(2) | _ | _ | _ | _ | _ | |
| C(4)-O(4) | _ | _ | - | _ | _ | - | 1.274(6) |
| C(4)-O(5) | - | - | - | - | - | - | 1.200(6) |
| C(2)-Mn-Cl | - | 82.29(13) | - | - | _ | - | _ |
| P(1)-Mn-P(2) | 89.75(4) | 88.29(4) | 91.11(4) 88.17(3) | 96.70(6) | 94.93(3) | 97.07(3) | 93.44(5) |

3.3 Spectroscopic results

All the synthesized complexes show, in the IR spectrum, 3 strong bands in the carbonyl-stretching region, in a pattern that is characteristic of a *fac*-octahedral disposition, and at values of wave number similar to that found in other Mn complexes with analogous P coligands [17].

The ¹⁹F{¹H} NMR spectra of the fluor-containing compounds show all of them a singlet, which is located at about $\delta = -79$ in the case of complexes bearing the O₃SCF₃ anion out of the coordination sphere (-79.0 and -79.4 for complexes **3** and **9**, respectively). When this anion is coordinated to manganese, the signal is, as expected, slightly shifted downfield, namely at $\delta \approx -77$ (-77.3 and -77.5 for complexes 1 and 7, respectively). Finally, in the spectra of the trifluoroacetate complexes, the singlet occurs at $\delta \approx -75$ (-74.7 and -75.1 for 5 and 11, respectively).

The signal of ${}^{31}P{}^{1}H$ NMR spectrum is in all cases a singlet, showing the magnetic equivalence of both P atoms of each bidentate ligand at room temperature.

Regarding the ¹H NMR spectra, all of them show, at about 4 ppm, the signals attributable to the CH_2 groups of the bidentate ligand. Nevertheless, whereas the spectra of most of the complexes show two multiplets (at 4.13–4.54 and 3.84–4.14 ppm, respectively), in three of them both signals coalesce into one multiplet (at 4.07, 4.04 and 4.20 ppm for complexes **1**, **7** and **9**, respectively). The com-



Fig. 1 Displacement ellipsoid plot for complex 1 with the atom numbering scheme. Ellipsoids at 30% probability.



Fig. 2 Displacement ellipsoid plot for complex 4 with the atom numbering scheme. Ellipsoids at 30% probability.



Fig. 3 Displacement ellipsoid plot for one of the two molecules of the asymmetric unit for complex **5** with the atom numbering scheme. Ellipsoids at 30 % probability.



Fig. 4 Displacement ellipsoid plot for complex 6 with the atom numbering scheme. Ellipsoids at 30% probability.



Fig. 5 Displacement ellipsoid plot for the cation of complex 9 with the atom numbering scheme. Ellipsoids at 30 % probability.



Fig. 6 Displacement ellipsoid plot for complex 10 with the atom numbering scheme. Ellipsoids at 30 % probability.

plexes showing the more complicated spectra are the same that bear in the solid state the supposed C-H...X interaction commented above. Despite this coincidence, no relationship between both facts seems to be supported by the ${}^{13}C{}^{1}H{}$



Fig. 7 Displacement ellipsoid plot for complex 11 with the atom numbering scheme (isopropyl groups are omitted for clarity). Ellipsoids at 30% probability.

NMR spectra, which show for both C nuclides one single signal in all cases.

References

- See for instance: (a) R. V. Honeychuck, W. H. Hersh, *Inorg. Chem.* 1989, 28, 2869 and references therein.
- [2] G. A. Lawrence, Chem. Rev. 1986, 86, 17.
- [3] D. Veghini, H. Berke, Inorg. Chem. 1996, 35, 4770.
- [4] P. Bergamini, F. Fabrizi DeBiani, L. Marvelli, N. Mascellani, M. Peruzzini, R. Rossi, P. Zanello, *New J. Chem.* **1999**, 207.
- [5] T. K. Hollis, N. P. Robinson, B. Bosnich, *Organometallics* 1992, 11, 2745.



Fig. 8 Chelate ring showing the Br...HCH interaction.

- [6] T. K. Hollis, W. Odenkirk, N. P. Robinson, J. Whelan, B. Bosnich, *Tetrahedron* 1993, 49, 5415.
- [7] J. Bravo, J. Castro, S. García-Fontán, E. M. Lamas, P. Rodríguez-Seoane, Z. Anorg. Allg. Chem. 2003, 629, 297.
- [8] D. D. Perrin, W. L. F. Amarego, *Purification of Laboratory Chemicals*, 3rd. ed., Butterworth and Heinemann, Oxford, 1988.
- [9] S. Bolaño, J. Bravo, R. Carballo, S. García-Fontán, U. Abram, E. M. Vázquez-López, *Polyhedron* 1999, 18, 1431.
- [10] E. W. Abel, G. Wilkinson. J. Chem. Soc. 1959, 1501.
- [11] G. M. Sheldrick, SADABS, An Empirical Absorption Correction Program for Area Detector Data, University of Göttingen, Germany, 1996.
- [12] G. M. Sheldrick, SHELXL-97, A Program for the Refinement of Crystal Structures from X-ray Data, University of Göttingen, Germany, 1997.
- [13] L. J. Farrugia, J. Appl. Cryst. 1997, 30, 565.
- [14] T. M. Becker, J. A. Krause-Bauer, C. L. Homrighausen, M. Orchin, *Polyhedron* 1999, 18, 2563.
- [15] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry*. *Principles of Structure and Reactivity*, 4th. ed., Harper-Collins College Publishers, New York, 1993.
- [16] A. F. Wells, Structural Inorganic Chemistry, 5th. ed., Oxford University Press, 1993.
- [17] G. Albertin, S. Antoniutti, S. García-Fontán, R. Carballo, F. Padoan, J. Chem. Soc., Dalton Trans. 1998, 2071.