

Synthesis of new carbonyl complexes of manganese(I) containing monodentate $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm)

Gabino A. Carriedo, M. Carmen Crespo, Carlos Diaz and Victor Riera

Departamento de Química Organometálica, Universidad de Oviedo, 33071-Oviedo (Spain)

(Received May 14th, 1990)

Abstract

The complex *fac*- $[\text{Mn}(\text{CO})_3(\text{bipy})(\text{P}-\text{P}')]\text{A}$ [$\text{P}-\text{P}'$ = monodentate $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), $\text{A} = \text{ClO}_4^-$ or PF_6^-] reacts with ONMe_3 in CH_2Cl_2 to give *cis*- $[\text{Mn}(\text{CO})_2(\text{bipy})(\text{P}-\text{P})]\text{A}$, and with dppm in refluxing acetone, to give *cis,trans*- $[\text{Mn}(\text{CO})_2(\text{bipy})(\text{P}-\text{P}')_2]\text{A}$. Irradiation with UV light of the latter gives the monocarbonyl *mer*- $[\text{Mn}(\text{CO})(\text{bipy})(\text{P}-\text{P})(\text{P}-\text{P}')]\text{A}$, containing one chelated and one monodentate dppm. Although the *fac*- $[\text{Mn}(\text{CO})_3(\text{bipy})(\text{P}-\text{P}')]\text{PF}_6$, reacted with *fac*- $[\text{MnBr}(\text{CO})_3(\text{bipy})]$ and TIPF_6 , to give the binuclear bridged species $\{[\text{Mn}(\text{CO})_3(\text{bipy})]_2(\mu-\text{P}-\text{P}')\}(\text{PF}_6)_2$, attempts to use the complexes with monodentate dppm as ligands to form compounds of higher nuclearity resulted in splitting of the dppm bridges.

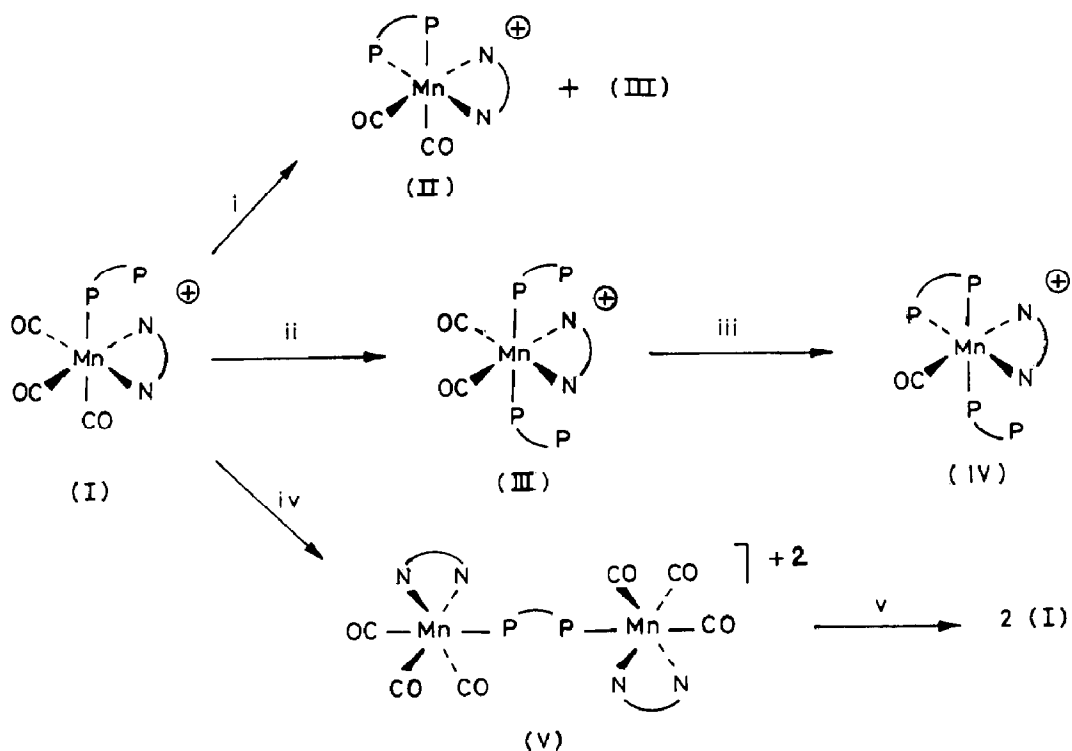
Introduction

We have previously described various ways for preparing octahedral carbonyl complexes of Mn^{I} of various types [1]. We report here the syntheses of new derivatives containing monodentate dppm($\text{Ph}_2\text{PCH}_2\text{PPh}_2$), and the results obtained when these complexes were used as ligands for preparing dppm-bridged polynuclear species.

Results and discussion

The compound *fac*- $[\text{MnBr}(\text{CO})_3(\text{bipy})]$ reacted with dppm and TIPF_6 in acetone to give mainly *fac*- $[\text{Mn}(\text{CO})_3(\text{bipy})(\text{P}-\text{P}')]\text{PF}_6$ (Ia), containing one monodentate dppm ligand (see scheme 1). This compound, which is analogous to the known dppe derivative [2], was characterized spectroscopically (see Experimental Section). Other compounds were also detected along with this product. Those compounds proved to be *cis,trans*- $[\text{Mn}(\text{CO})_2(\text{bipy})(\text{P}-\text{P}')_2]\text{PF}_6$ (IIIa) and the monocarbonyl *mer*- $[\text{Mn}(\text{CO})(\text{bipy})(\text{P}-\text{P})(\text{P}-\text{P}')]\text{PF}_6$ (IVa) (see later) *. However, the perchlorate salt Ib

* Attempts to purify Ia did not remove these by-products, and also led to the formation of another product, which was later characterized as *cis*- $[\text{Mn}(\text{CO})_2(\text{bipy})(\text{P}-\text{P})]\text{PF}_6$ (IIa).



Scheme 1. N-N = bipy, P-P = dppm. (i) ONMe₃/CH₂Cl₂; (ii) dppm excess, refluxing acetone; (iii) *hν* CH₂Cl₂; (iv) *fac*-[MnBr(CO)₃(bipy)] and TlPF₆ in CH₂Cl₂ at room temperature; (v) dppm excess, CH₂Cl₂, room temperature.

was prepared from *fac*-[Mn(OCIO₃)(CO)₃(bipy)] and dppm in CH₂Cl₂ without appreciable formation of the substituted carbonyls III and IV.

Complex Ib reacted with ONMe₃ in CH₂Cl₂ (reaction i in Scheme 1) to give mainly the *cis*-dicarbonyl *cis*-[Mn(CO)₂(bipy)(P-P)]ClO₄ (IIb) in which the dppm is chelating, and which is analogous to the previously known complexes *cis*-[Mn(CO)₂(N-N)(dppe)]ClO₄ (dppe = Ph₂PCH₂CH₂PPh₂, N-N = bipy or phen) [3].

In reaction i (Scheme 1) another dicarbonyl, characterized as *cis,trans*-[Mn(CO)₂(bipy)(P-P')₂]ClO₄ (IIIb), was also formed. This new compound, which contains two monodentate dppm ligands, was conveniently prepared by treating Ib with a large excess of dppm in refluxing acetone (reaction ii in Scheme 1). This reaction is akin to the well documented CO-substitution reactions of the cations *fac*-[Mn(CO)₃(N-N)L]⁺ with monodentate ligands L, which give the cationic *cis,trans*-dicarbonyls [Mn(CO)₂(N-N)L₂]⁺ [3,4]. The compounds *cis*-[Mn(CO)₂(N-N)(dppe)]ClO₄, analogous to IIb, were prepared from *fac*-[Mn(OCIO₃)(CO)₃(dppe)] and the ligand N-N in refluxing ethanol [3]. We found that the analogous reaction of [Mn(OCIO₃)(CO)₃(dppm)] with bipy gives a mixture of the perchlorate salts of the cations II and III (IIb and IIIb, respectively). This reflects the greater tendency of the dppm than of the dppe ligand to act as monodentate.

In reaction ii (Scheme 1), the dicarbonyl cation III is formed, together with a small amount of the monocarbonyl *mer*-[Mn(CO)(bipy)(P-P)(P-P')]⁺ (IV). The perchlorate salt of this latter monocarbonyl, which has one dppm monodentate and

the other bidentate, was obtained in good yield by UV irradiation of the salt IIIb (reaction iii in Scheme 1). We had observed previously that the compounds *cis*-[Mn(CO)₂(N-N)(dppe)]ClO₄ react with phosphites P(OR)₃ under UV irradiation to give the highly coloured cationic monocarbonyls *mer*-[Mn(CO)(N-N)(dppe)L]ClO₄ [3]. Reaction iii is similar, and is probably favoured by the chelate effect and by the high local concentration of the entering PPh₂ group of the monodentate dppm in the cation III. The spontaneous formation of IV during the synthesis of I and in reaction ii (performed without exclusion of light) shows that the CO-substitution process iii can occur very readily. The uncoordinated PPh₂ groups in I, III and IV suggested that those cations could be used as ligand to obtain polynuclear cationic species. Compound Ia was, in fact, found to react with *fac*-[MnBr(CO)₃(bipy)] and TlPF₆, to give mainly the binuclear complex {*fac*-[Mn(CO)₃(bipy)]₂(μ-P-P)}(PF₆)₂ (Va) * (reaction iv in Scheme 1), analogous to the previously known dppe derivative [2], mixed with a small amount of the *cis*-dicarbonyl IIa. However, compounds of higher nuclearity could not be obtained from I or III because of the relative weakness of the dppm bridges. Thus, we found that Va reacted readily with dppm to give two equivalents of Ia, instead of the desired product {[*fac*-Mn(CO)₃(bipy)][*cis*-Mn(CO)₂(bipy)(P-P')](μ-P-P)}(PF₆)₂ (VI). Furthermore, the reaction of IIIb with *fac*-[MnBr(CO)₃(bipy)] and TlPF₆, which was also expected to give VI, gave a mixture of Ib and IIb, showing that the cation VI is unstable towards splitting involving loss of the dppm bridge.

Experimental

All reactions were carried out under dried N₂. The IR spectra were recorded on a Perkin-Elmer FT 1720-X spectrometer. ³¹P NMR are given in δ to high frequency of external H₃PO₄ (*J* in Hz), and were recorded on a Bruker AC-300 instrument. The compounds *fac*-[Mn(X)(CO)₃(bipy)] (X = Br, OClO₃) were prepared by a published method [4].

Preparation of *fac*-Mn(CO)₃(bipy)(P-P')PF₆ (Ia)

A mixture of *fac*-[MnBr(CO)₃(bipy)] (0.16 g, 0.42 mmol), the diphosphine (0.17 g, 0.44 mmol) and TlPF₆ (0.16 g, 0.45 mmol) in acetone (20 ml) was stirred at room temperature for 24 h. The mixture was filtered and the solvent removed in vacuo. The residual solid was washed with diethyl ether, to give Ia as a yellow brown solid (0.26 g, 74%), contaminated with IIIa and IVa. Data: Anal. Found: C, 56.8; H, 3.7; N, 3.2. C₃₈H₃₀F₆MnN₂O₃P₃ calcd.: C, 55.4; H, 3.6; N, 3.4%. IR (CH₂Cl₂): ν(CO) (cm⁻¹) 2040 vs, 1965s, 1934s. ³¹P NMR (CH₂Cl₂) (δ in ppm): -29.9, 45.5 [AX, *J*(PP) 90].

Preparation of *fac*-[Mn(CO)₃(bipy)(P-P')]ClO₄ (Ib)

To a solution of *fac*-[Mn(OClO₃)(CO)₃(bipy)] (0.2 g, 0.44 mmol) in CH₂Cl₂ (15 ml) was added the diphosphine dppm (0.68 g, 1.76 mmol). The mixture was stirred for 3 days at room temperature then filtered, and the filtrate concentrated to ca 2 ml. Addition of diethyl ether gave a dark-yellow precipitate, which was washed with diethyl ether and recrystallized from CH₂Cl₂/diethyl ether (0.27 g, 77.6%). Data: Anal. Found: C, 58.2; H, 4.0; N, 3.6. C₃₈H₃₀ClMnN₂O₇P₂ calcd.: C, 58.6; H, 3.9; N,

* IR ν(CO): CH₂Cl₂: 2043s, 1968s, 1934s, ³¹P NMR: 48 br.

3.6%. IR (CH₂Cl₂): $\nu(\text{CO})$ (cm⁻¹) 2039s, 1964s, 1933s. ³¹P NMR (CH₂Cl₂) (δ in ppm): -29.5, 46.4 [AX, *J*(PP) 93].

Preparation of cis-[Mn(CO)₂(bipy)(P-P)]ClO₄ (IIb)

To a solution of Ib (0.1 g, 0.13 mmol) in CH₂Cl₂ (10 ml) was added freshly sublimed ONMe₃ (0.012 g, 0.16 mmol). The solution changed from orange to red and after 5 min the solvent was evaporated in vacuo and the residue washed with diethyl ether. The solid was washed with deoxygenated water and dissolved in CH₂Cl₂. The solution was filtered, dried over anhydrous MgSO₄, and concentrated to ca. 5 ml. Addition of diethyl ether gave a precipitate of a red solid, which was washed with ether and dried in vacuo (0.057 g, 60%). The product was always contaminated with IIIb. Data: Anal. Found: C, 61.7; H, 4.2; N, 3.5. C₃₇H₄₀ClMnN₂O₆P₂ calcd.: C, 59.2; H, 4.0; N, 3.7%. IR (CH₂Cl₂): $\nu(\text{CO})$ (cm⁻¹) 1956s, 1890s. ³¹P NMR (CH₂Cl₂) (δ in ppm): 8.9, 42.2 [A, *J*(PP) 35].

Preparation of cis,trans-[Mn(CO)₂(bipy)(P-P')₂]PF₆ (IIIa)

A solution of Ia (0.24 g, 0.29 mmol) and dppm (0.76 g, 1.9 mmol) in acetone (20 ml) was refluxed for 2 h then filtered. The solvent was evaporated in vacuo to leave a solid residue, which was washed several times with diethyl ether to give a yellow solid (0.22 g, 64%). Data: Anal. Found: C, 63.5; H, 4.5; N, 2.5. C₆₂H₅₂F₆MnN₂O₂P₅ calcd.: C, 63.0; H, 4.4; N, 2.4%. IR (CH₂Cl₂): $\nu(\text{CO})$ (cm⁻¹) 1942 s, 1873s. ³¹P NMR (CH₂Cl₂) (δ in ppm): -28.9, 57.5 br [AA'XX', *N* = 72 Hz].

Preparation of cis,trans-[Mn(CO)₂(bipy)(P-P')₂]ClO₄ (IIIb)

A solution of Ib (0.25 g, 0.32 mmol) and dppm (0.24 g, 0.63 mmol) in acetone (20 ml) was refluxed for 5 h then filtered. The filtrate was concentrated to ca. 5 ml and diethyl ether was added to give an orange precipitate, which was washed with diethyl ether. Recrystallization was from CH₂Cl₂/Et₂O (0.23 g, 64.1%). Data: Anal. Found: C, 64.6; H, 4.5; N, 2.1. C₆₂H₅₂ClMnN₂O₆P₄ calcd.: C, 65.6; H, 4.6; N, 2.5%. IR (CH₂Cl₂): $\nu(\text{CO})$ (cm⁻¹) 1942s, 1873s. ³¹P NMR (CH₂Cl₂)(-50°C) (δ in ppm): -33.8, 57.7 br [AA'XX', *N* = 72 Hz].

Preparation of [Mn(CO)(bipy)(P-P)(P-P')]ClO₄ (IVb)

A solution of IIIb (0.1 g, 0.09 mmol) in CH₂Cl₂ (10 ml) was cooled to -10°C and irradiated with UV light for 20 min. The resulting deep green-brown solution was filtered and concentrated in vacuo to ca. 3 ml. Addition of diethyl ether gave a dark green precipitate, which was recrystallized from CH₂Cl₂/Et₂O (0.07 g, 68%). Data: Anal. Found: C, 64.8; H, 4.5; N, 2.2. C₆₁H₅₂ClMnN₂O₅P₄ calcd.: C, 66.2; H, 4.7; N, 2.5%. IR (CH₂Cl₂): $\nu(\text{CO})$ (cm⁻¹) 1843s. ³¹P NMR (CH₂Cl₂) (δ in ppm): -26.7 [d, *J*(PP) 33], 31.6 br, 36.2 br, 61.7 br.

Acknowledgments. We thank the D.G.I.C.Y.T. (Project PB88-0468) for financial support, the Spanish Ministerio de Educación y Ciencia for a Grant (M.C.C. and C.D.).

References

- 1 G.A. Carriedo and V. Riera, *J. Organomet. Chem.*, 394 (1990) 275.
- 2 M.P. Gamasa, M. Laguna, D. Miguel and V. Riera, *Transition Met. Chem.*, 6 (1981) 374.
- 3 G.A. Carriedo, J. Gimeno, M. Laguna and V. Riera, *J. Organomet. Chem.*, 269 (1981) 61.
- 4 R. Usón, V. Riera, J. Gimeno and M. Laguna, *Transition Met. Chem.*, 2 (1977) 123.