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Syntheses, molecular structure and reactivity of $(\eta^6\text{-toluene})Mn(CO)_xL_{3-x}$, PF_6

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Abstract

Addition of 2-lithio-2-methylpropionitrile to three new complexes of cationic (η^6-toluene–Mn) complexes where one or two CO ligands have been substituted by phosphine or phosphite, leads to the corresponding (η^5-cyclohexadienyl) complexes with a very high regioselectivity in the case of the complex where two CO have been replaced by two phosphite ligands.

Keywords: Manganese; Cationic complexes; X-ray structure; η^5-Cyclohexadienyl; Nucleophilic addition; Ligand substitutions

1. Introduction

As part of our current studies on the arene functionalization by means of transition metal complexes, we were interested in the reactivity of cationic arene Mn complexes [1] which are known to be much more reactive than those of chromium [2]. The factors influencing the observed regiochemistry of nucleophilic attack are very important and still need clarification; it has been shown that the selectivity of the addition is strongly dependent on the nature of the nucleophile, on the substituent of the arene, and on the reaction medium [3]. In order to gain insight into the influence of the nature of the ligands around the Mn atom on this selectivity, we have studied the addition of the same anion on Mn complexes where one or two CO ligands have been substituted by phosphorus ligands. In this communication, we report the syntheses of ((toluene)-Mn(CO)$_x$L$_{3-x}$)PF$_6$ complexes ($x = 2$, L = PPh$_3$ **1b**; x

= 2, L = P(OEt)$_3$ **1c**; $x = 1$, L = P(OEt)$_3$ **1d**), the molecular structure of **1d**, and the addition of 2-lithio 2-methylpropionitrile to **1b** and **1d**. The present work demonstrates the effect of two phosphite ligands on the regiochemistry of the arene functionalization.

2. Results and discussion

Compounds **1b** ((toluene)Mn(CO)$_2$L)PF$_6$ (L = PPh$_3$) and **1c** (L = P(OEt)$_3$) have been synthesized from ((toluene)Mn(CO)$_3$)PF$_6$ by following an improved synthetic procedure relative to that described in the literature [4] for benzene derivatives (38% and 69% yield respectively) [5]. Treatment of compound **1c** with P(OEt)$_3$ followed by addition of Me$_3$NO in CH$_2$Cl$_2$ at room temperature led to the isolation of complex **1d** after column chromatography (48% yield) [6]. An alternative, more straightforward method consists of starting from complex **1a**. Under the same conditions, using two equivalents of phosphite, the disubstituted complex **1d** was directly obtained in 27% yield. No substitution (or
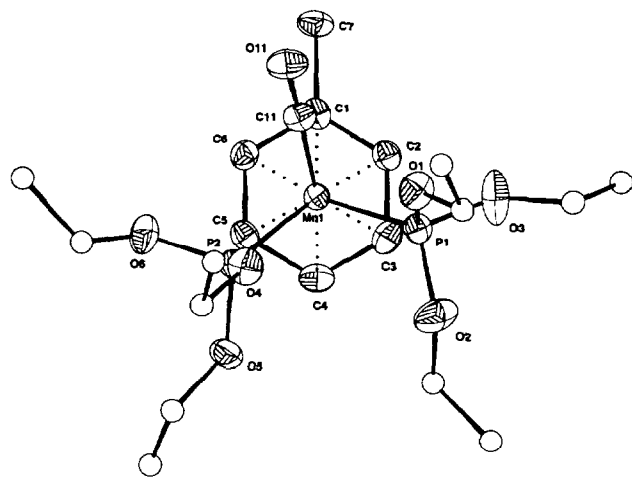
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Fig. 1. ORTEP drawing of complex 1d. Selected bond distances (Å): C$_1$–Mn 2.199(7), C$_3$–Mn 2.162(7), C$_5$–Mn 2.160(7); selected bond angles (deg): C$_{11}$–Mn–P$_1$ 87.2(2), C$_{11}$–Mn–P$_2$ 87.7(2), P$_2$–Mn–P$_1$ 92.86(8).

in very low yield) of two of the carbonyl groups by PPh$_3$ occurred whatever the experimental conditions used. X-ray crystallographic studies of compounds 1b [7] and 1d [8] (Fig. 1) have enabled us to determine the conformation of the organometallic entity in both cases. In the first case, the cation displays a staggered orientation relative to the C atoms of the aromatic ring; one of the carbonyl groups is rotated 29° away from the methyl substituent. In the second case, the structure shows a nearly *syn* eclipsed conformation: the two phosphite ligands are rotated by 13° and 12° from the C atoms *meta* to the methyl group. To the best of our knowledge, this is the first example of the structure of a mono-alkylated η^6-arene monocarbonyldiphosphite-manganese cation. Brown et al. [9] have described the X-ray structure of $((C_6H_6)Mn(CO)(\eta^2\text{-dppm}))PF_6$, the tripod of which showed an almost *syn* eclipsed conformation.

Treatment of compounds 1a, 1b or 1c with 2-lithio

Table 1
Fractional parameters for [Mn(CO)(ΦMe)(P(OEt)$_3$)$_2$](PF$_6$)

Atom	x	y	z	U_{eq}	
Mn(1)	0.9151(1)	0.78642(8)	0.30517(7)	0.0542	
P(1)	0.7992(2)	0.8232(2)	0.1660(1)	0.0658	
P(2)	0.7746(2)	0.6301(1)	0.2779(1)	0.0652	
O(1)	0.8406(7)	0.7500(5)	0.0737(4)	0.0895	
O(2)	0.6114(8)	0.8128(7)	0.1311(4)	0.1095	
O(3)	0.856(1)	0.9409(5)	0.1616(5)	0.1155	
O(4)	0.7304(7)	0.5626(4)	0.1716(4)	0.0877	
O(5)	0.6086(6)	0.6373(4)	0.3116(4)	0.0834	
O(6)	0.8587(8)	0.5483(5)	0.3391(4)	0.0959	
O(11)	1.1456(7)	0.6744(5)	0.2031(4)	0.0929	
C(1)	1.1202(9)	0.8802(5)	0.4077(5)	0.0643	
C(2)	1.0186(9)	0.9505(5)	0.3687(5)	0.0639	
C(3)	0.856(1)	0.9444(6)	0.3719(5)	0.0690	
C(4)	0.7931(9)	0.8675(7)	0.4153(5)	0.0713	
C(5)	0.893(1)	0.7955(6)	0.4543(5)	0.0681	
C(6)	1.0543(9)	0.8018(6)	0.4511(5)	0.0651	
C(7)	1.2997(9)	0.8875(7)	0.4056(6)	0.0806	
C(11)	1.0539(9)	0.7187(6)	0.2422(5)	0.0685	
C(12)	0.765(1)	0.738(1)	−0.0236(7)	0.1259	
C(13)	0.833(2)	0.660(1)	−0.0864(8)	0.1422	
C(14)	0.497(1)	0.8418(9)	0.1808(7)	0.1140	
C(15)	0.355(1)	0.8733(8)	0.1199(7)	0.1082	
C(16)	0.822(2)	1.008(1)	0.100(1)	0.1572	
C(17)	0.876(2)	1.118(1)	0.142(1)	0.1689	
C(181)	0.643(2)	0.464(1)	0.138(2)	0.0912	0.5000
C(182)	0.807(3)	0.504(2)	0.114(2)	0.1247	0.5000
C(19)	0.694(2)	0.411(1)	0.045(1)	0.1595	
C(20)	0.499(2)	0.554(1)	0.318(2)	0.1617	
C(21)	0.412(2)	0.567(1)	0.383(1)	0.1389	
C(221)	0.985(2)	0.493(1)	0.332(1)	0.0775	0.5000
C(222)	0.844(3)	0.449(2)	0.335(2)	0.1299	0.5000
C(23)	0.985(1)	0.3913(8)	0.3653(8)	0.1111	
P(3)	0.5471(3)	0.8046(2)	0.6771(2)	0.0890	
F(1)	0.600(1)	0.8166(9)	0.5828(6)	0.1983	
F(2)	0.638(1)	0.7052(6)	0.6795(8)	0.2018	
F(3)	0.3995(9)	0.7364(7)	0.6143(6)	0.1855	
F(4)	0.690(1)	0.8716(7)	0.7394(7)	0.2010	
F(5)	0.459(1)	0.9042(6)	0.6716(7)	0.1783	
F(6)	0.493(1)	0.787(1)	0.7661(7)	0.2263	

Table 2
Anisotropic thermal parameters for [Mn(CO)(ΦMe)(P(OEt)$_3$)$_2$](PF$_6$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn(1)	0.0559(6)	0.0528(6)	0.0534(6)	0.0094(4)	0.0107(5)	0.0023(4)
P(1)	0.073(1)	0.072(1)	0.054(1)	0.0137(9)	0.011(1)	0.005(1)
P(2)	0.064(1)	0.053(1)	0.082(1)	0.0134(9)	0.015(1)	0.0034(9)
O(1)	0.119(5)	0.117(4)	0.054(3)	0.016(3)	0.016(3)	0.025(4)
O(2)	0.089(5)	0.241(9)	0.074(4)	0.052(5)	0.008(3)	0.048(5)
O(3)	0.231(8)	0.080(4)	0.094(5)	0.038(4)	−0.006(5)	−0.001(5)
O(4)	0.108(5)	0.068(3)	0.087(4)	−0.006(3)	0.012(3)	−0.002(3)
O(5)	0.074(4)	0.068(3)	0.139(5)	0.026(3)	0.042(3)	0.001(3)
O(6)	0.126(5)	0.068(4)	0.122(5)	0.031(3)	0.023(4)	0.031(4)
O(11)	0.078(4)	0.112(5)	0.104(4)	0.002(4)	0.034(3)	0.020(3)
C(1)	0.082(5)	0.057(4)	0.054(4)	0.004(3)	0.008(4)	−0.007(4)
C(2)	0.071(5)	0.058(4)	0.061(4)	0.009(3)	0.009(4)	−0.004(4)
C(3)	0.085(6)	0.057(4)	0.067(5)	0.001(4)	0.002(4)	0.018(4)
C(4)	0.064(5)	0.088(5)	0.064(5)	−0.005(4)	0.017(4)	0.002(4)
C(5)	0.083(6)	0.073(5)	0.056(4)	0.018(4)	0.018(4)	−0.003(4)
C(6)	0.066(5)	0.072(4)	0.059(4)	0.018(3)	0.002(3)	0.006(4)
C(7)	0.051(5)	0.107(6)	0.095(6)	0.016(5)	0.008(4)	−0.011(4)
C(11)	0.066(5)	0.068(5)	0.067(5)	0.001(4)	0.005(4)	0.002(4)
C(12)	0.132(9)	0.22(1)	0.069(6)	−0.010(7)	0.023(6)	0.016(9)
C(13)	0.20(1)	0.19(1)	0.081(7)	−0.014(8)	0.040(8)	0.00(1)
C(14)	0.093(7)	0.16(1)	0.111(8)	0.042(7)	0.022(6)	0.034(7)
C(15)	0.083(7)	0.126(8)	0.123(8)	0.016(6)	−0.006(6)	0.027(6)
C(16)	0.26(2)	0.14(1)	0.16(1)	0.09(1)	0.01(1)	−0.00(1)
C(17)	0.25(2)	0.12(1)	0.25(2)	0.10(1)	−0.00(1)	−0.04(1)
C(181)	0.09(1)	0.07(1)	0.15(2)	−0.02(1)	0.01(1)	−0.028(9)
C(182)	0.19(3)	0.10(2)	0.10(1)	0.01(1)	0.02(2)	0.02(2)
C(19)	0.20(1)	0.110(9)	0.21(1)	−0.065(9)	−0.02(1)	−0.018(9)
C(20)	0.17(1)	0.090(9)	0.58(4)	0.06(1)	0.22(2)	0.012(8)
C(21)	0.15(1)	0.14(1)	0.24(1)	0.08(1)	0.11(1)	0.009(9)
C(221)	0.06(1)	0.08(1)	0.15(2)	0.06(1)	0.03(1)	0.012(9)
C(222)	0.16(3)	0.10(2)	0.14(2)	0.03(1)	0.00(2)	0.01(2)
C(23)	0.116(8)	0.095(7)	0.17(1)	0.061(7)	0.038(7)	0.039(6)
F(3)	0.083(2)	0.077(1)	0.114(2)	0.027(1)	0.017(1)	0.007(1)
F(1)	0.222(9)	0.31(1)	0.189(8)	0.084(8)	0.123(7)	0.030(8)
F(2)	0.24(1)	0.132(6)	0.32(1)	0.050(7)	0.025(9)	0.078(6)
F(3)	0.142(6)	0.234(9)	0.231(9)	0.053(7)	−0.019(6)	−0.081(6)
F(4)	0.168(8)	0.182(8)	0.29(1)	0.011(7)	−0.074(7)	−0.043(6)
F(5)	0.208(8)	0.158(7)	0.254(9)	0.033(6)	0.005(7)	0.107(6)
F(6)	0.24(1)	0.48(2)	0.190(9)	0.19(1)	0.100(8)	0.08(1)

Table 3
Interatomic distances (Å) for [Mn(CO)(ΦMe)(P(OEt)$_3$)$_2$](PF$_6$)

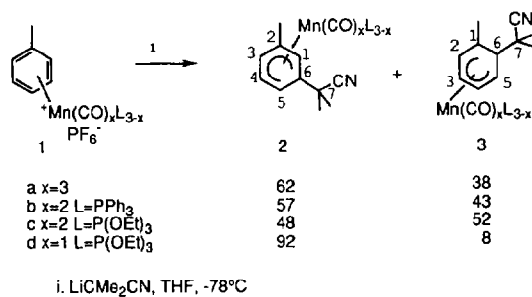|			
Mn(1)–P(1)	2.203(2)	Mn(1)–P(2)	2.193(2)
Mn(1)–C(1)	2.199(7)	Mn(1)–C(2)	2.171(6)
Mn(1)–C(3)	2.162(7)	Mn(1)–C(4)	2.168(7)
Mn(1)–C(5)	2.160(7)	Mn(1)–C(6)	2.177(7)
Mn(1)–C(11)	1.771(8)	O(11)–C(11)	1.149(8)
P(1)–O(1)	1.568(5)	P(1)–O(2)	1.582(6)
P(1)–O(3)	1.561(6)	P(2)–O(4)	1.565(6)
P(2)–O(5)	1.582(5)	P(2)–O(6)	1.593(6)
O(1)–C(12)	1.40(1)	O(2)–C(14)	1.34(1)
O(3)–C(16)	1.35(1)	O(4)–C(181)	1.37(2)
O(4)–C(182)	1.29(2)	O(5)–C(20)	1.40(1)
O(6)–C(221)	1.31(2)	−O(6)–C(222)	1.25(2)
C(1)–C(2)	1.392(9)	C(1)–C(6)	1.414(9)
C(1)–C(7)	1.54(1)	C(2)–C(3)	1.40(1)
C(3)–C(4)	1.39(1)	C(4)–C(5)	1.40(1)
C(5)–C(6)	1.38(1)	C(12)–C(13)	1.42(1)
C(14)–C(15)	1.48(1)	C(16)–C(17)	1.42(2)
C(181)–C(19)	1.52(2)	C(182)–C(19)	1.55(2)
C(20)–C(21)	1.28(2)	C(221)–C(23)	1.46(2)
C(222)–C(23)	1.48(3)		
P(3)–F(1)	1.533(7)	P(3)–F(2)	1.505(7)
P(3)–F(3)	1.527(7)	P(3)–F(4)	1.493(7)
P(3)–F(5)	1.503(6)	P(3)–F(6)	1.487(8)

2-methylpropionitrile [10] (Eq. (1)) led to the isolation of the corresponding *ortho* and *meta* addition adducts **2** and **3** [11] (in 90, 59, and 54% yield respectively), in the *o/m* ratios 52/48, 43/57, and 38/62 respectively. When complex **1d** was treated with LiCMe₂CN, a mixture of *o* and *m* regioisomers was obtained in the

Table 4
Bond angles (deg) for [Mn(CO)(ΦMe)(P(OEt)₃)₂](PF₆)

P(1)–Mn(1)–P(2)	92.86(8)	P(1)–Mn(1)–C(1)	126.4(2)
P(2)–Mn(1)–C(1)	140.1(2)	P(1)–Mn(1)–C(2)	95.5(2)
P(2)–Mn(1)–C(2)	162.9(2)	C(1)–Mn(1)–C(2)	37.1(2)
P(1)–Mn(1)–C(3)	86.6(2)	P(2)–Mn(1)–C(3)	128.5(2)
C(1)–Mn(1)–C(3)	67.8(3)	C(2)–Mn(1)–C(3)	37.6(3)
P(1)–Mn(1)–C(4)	107.2(2)	P(2)–Mn(1)–C(4)	95.7(2)
C(1)–Mn(1)–C(4)	80.3(3)	C(2)–Mn(1)–C(4)	67.5(3)
C(3)–Mn(1)–C(4)	37.4(3)	P(1)–Mn(1)–C(5)	143.9(2)
P(2)–Mn(1)–C(5)	84.8(2)	C(1)–Mn(1)–C(5)	67.8(3)
C(2)–Mn(1)–C(5)	79.7(3)	C(3)–Mn(1)–C(5)	67.7(3)
C(4)–Mn(1)–C(5)	37.8(3)	P(1)–Mn(1)–C(6)	162.6(2)
P(2)–Mn(1)–C(6)	104.0(2)	C(1)–Mn(1)–C(6)	37.7(2)
C(2)–Mn(1)–C(6)	67.2(3)	C(3)–Mn(1)–C(6)	79.8(3)
C(4)–Mn(1)–C(6)	67.6(3)	P(1)–Mn(1)–C(11)	87.2(2)
P(2)–Mn(1)–C(11)	87.7(2)	C(1)–Mn(1)–C(11)	87.6(3)
C(2)–Mn(1)–C(11)	107.6(3)	C(3)–Mn(1)–C(11)	143.5(3)
C(4)–Mn(1)–C(11)	164.9(3)	C(5)–Mn(1)–C(6)	37.2(3)
C(5)–Mn(1)–C(11)	128.5(3)	C(6)–Mn(1)–C(11)	97.3(3)
Mn(1)–P(1)–O(1)	115.1(2)	Mn(1)–P(1)–O(2)	122.5(2)
O(1)–P(1)–O(2)	97.6(3)	Mn(1)–P(1)–O(3)	109.2(3)
O(1)–P(1)–O(3)	104.9(4)	O(2)–P(1)–O(3)	105.8(4)
Mn(1)–P(2)–O(4)	118.7(2)	Mn(1)–P(2)–O(5)	114.0(2)
O(4)–P(2)–O(5)	103.7(3)	Mn(1)–P(2)–O(6)	112.6(3)
O(4)–P(2)–O(6)	104.4(3)	O(5)–P(2)–O(6)	101.7(3)
P(1)–O(1)–C(12)	128.7(6)	P(1)–O(2)–C(14)	130.0(7)
P(1)–O(3)–C(16)	136.2(8)	P(2)–O(4)–C(181)	128.8(11)
P(2)–O(4)–C(182)	135.0(12)	P(2)–O(5)–C(20)	129.8(7)
P(2)–O(6)–C(221)	132.4(9)	P(2)–O(6)–C(222)	135.4(13)
Mn(1)–C(1)–C(2)	70.4(4)	Mn(1)–C(1)–C(6)	70.3(4)
C(2)–C(1)–C(6)	118.0(7)	Mn(1)–C(1)–C(7)	131.5(5)
C(2)–C(1)–C(7)	121.6(7)	C(6)–C(1)–C(7)	120.4(7)
Mn(1)–C(2)–C(1)	72.5(4)	Mn(1)–C(2)–C(3)	70.8(4)
C(1)–C(2)–C(3)	121.4(7)	Mn(1)–C(3)–C(2)	71.5(4)
Mn(1)–C(3)–C(4)	71.5(4)	C(2)–C(3)–C(4)	120.0(7)
Mn(1)–C(4)–C(3)	71.1(4)	Mn(1)–C(4)–C(5)	70.8(4)
C(3)–C(4)–C(5)	119.4(7)	Mn(1)–C(5)–C(4)	71.4(4)
Mn(1)–C(5)–C(6)	72.0(4)	C(4)–C(5)–C(6)	120.5(7)
Mn(1)–C(6)–C(1)	72.0(4)	Mn(1)–C(6)–C(5)	70.8(4)
C(1)–C(6)–C(5)	120.7(6)	Mn(1)–C(11)–O(11)	178.6(7)
O(1)–C(12)–C(13)	112.1(10)	O(2)–C(14)–C(15)	112.5(9)
O(3)–C(16)–C(17)	113.3(12)	O(4)–C(181)–C(182)	51.1(9)
O(4)–C(181)–C(19)	107.9(15)	O(4)–C(182)–C(19)	110.7(20)
O(5)–C(20)–C(21)	121.5(15)	O(6)–C(221)–C(23)	116.6(12)
O(6)–C(222)–C(23)	119.8(21)		
F(1)–P(3)–F(2)	90.2(6)	F(1)–P(3)–F(3)	87.4(5)
F(2)–P(3)–F(3)	91.1(5)	F(1)–P(3)–F(4)	93.3(6)
F(2)–P(3)–F(4)	89.2(5)	F(3)–P(3)–F(4)	179.3(6)
F(1)–P(3)–F(5)	87.9(5)	F(2)–P(3)–F(5)	178.1(6)
F(3)–P(3)–F(5)	88.9(5)	F(4)–P(3)–F(5)	90.8(5)
F(1)–P(3)–F(6)	177.1(7)	F(2)–P(3)–F(6)	88.1(6)
F(3)–P(3)–F(6)	90.2(6)	F(4)–P(3)–F(6)	89.1(6)
F(5)–P(3)–F(6)	93.8(6)		

ratio 8/92 (combined yield 85%). Several interesting observations can be deduced from these results.

i. LiCMe$_2$CN, THF, -78°C

	2	3
a x=3	62	38
b x=2 L=PPh$_3$	57	43
c x=2 L=P(OEt)$_3$	48	52
d x=1 L=P(OEt)$_3$	92	8

(1)

Firstly, the replacement of CO by a phosphite or a phosphine increases the electron density on the Mn atom such that the electrophilicity of complexes **1b**, **1c** and **1d** is less than that of **1a**. Because of this, the addition of the nucleophile could be achieved at −78°C for **1a** but required 0°C for **1b**, **1c** and **1d**. This observa-

Table 5
Crystal data for [C$_{20}$H$_{38}$O$_7$P$_2$Mn](PF$_6$)

FW	652.35
a (Å)	8.546(2)
b (Å)	12.623(2)
c (Å)	14.334(2)
α (°)	101.13(1)
β (°)	100.54(2)
γ (°)	92.55(2)
V (Å^3)	1483(7)
Z	2
Crystal system	triclinic
Space group	P1̄
Linear absorption coefficient μ (cm^{-1})	6.55
Density ρ (g cm^{-3})	1.46
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo K α (λ = 0.71069 Å)
Scan type	ω/2θ
Scan range (°)	0.8 + 0.345 tg θ
θ limits (°)	1–25
Temperature of measurement	room temperature
Octants collected	− 10, 9; − 14, 14; 0, 17
No. of data collected	5432
No. of unique data collected	5206
No. of unique data used for refinement	3051 (F_o)^2 > 3σ(F_o)^2
R(int)	1.21
$R = \Sigma \| F_o \| - \| F_c \| / \Sigma \| F_o \|$	0.0594
$Rw = \Sigma w(\| F_o \| - \| F_c \|)^2 / \Sigma w F_o^2$	0.0600 w = 1.0
Absorption correction	DIFABS (min 0.83, max 1.13)
Extinction parameter (× 10^{-6})	272
Goodness of fit	3.9
No. of variables	352
Δρ$_{min}$ (e Å^{-3})	−0.37
Δρ$_{max}$ (e Å^{-3})	0.54

tion has already been outlined in the literature [4b,12,13]: for example, Chung and coworkers [12] have studied the reactivity of ((phenylsilatrane)Mn(CO)$_2$-P(OMe)$_3$)ClO$_4$ **4**; the replacement of CO by a phosphite increases the electron density on the metal, and the electrophilicity of this compound would be much lower than that of the unsubstituted compound so that strong carbanions are needed for the addition to occur. It is also well known that alteration of the electronic character of the metal in cycloheptadienyl–Fe(CO)$_2$L complexes [13a] has a profound effect on the reactivity of these molecules towards a range of synthetically useful nucleophiles.

The second point concerns the regioselectivity of the reaction. Substitution of one CO ligand slightly affected the *o/m* ratio in favor of the *meta* addition product. This is in good agreement with what has been described in the case of LiCMe$_2$CN addition to the silatrane derivative **4** [12]: no regioselectivity is observed versus the corresponding tricarbonyl complex. However, a very high regioselectivity is observed in the reaction of complex **1d**, where two CO ligands have been substituted. This is the first time that such an increase of regioselectivity has been observed by simply changing the number of phosphite ligands around Mn. Further studies of nucleophilic additions to **1d** are in progress in order to rationalize these observations.

3. Conclusions

In conclusion, it has been demonstrated that the electronic environment of the metallic atom can influence tremendously the regioselectivity of a carbanion addition to the aromatic ring of an alkyl substituted arene Mn complex. Furthermore, the crystal structure of the new toluene Mn complex in which two CO have been substituted by two phosphites clearly shows that the *meta*-carbons to the methyl group are almost eclipsed by the phosphite ligands; further, the major product results from nucleophilic addition occurring at the *meta*-carbons.

Acknowledgements

References and notes

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[4] (a) D.A. Brown, W.K. Glass and K.M. Kreddan, *J. Organomet. Chem.*, *413* (1991) 233; (b) D.B. Snyder, S.J. Schauer, D.P. Eyman, J.L. Moler and J.J. Weers, *J. Am. Chem. Soc.*, *115* (1993) 6718; (c) T.M. Chung, Y.A. Lee, Y.K. Chung and I.N. Jung, *Organometallics*, *9* (1990) 1976; (d) Y. Huang, G.B. Carpenter, D.A. Sweigart, Y.K. Chung and B.Y. Lee, *Organometallics*, *14* (1995) 1423; (e) R.J. Bernhardt, M.A. Wilmoth, J.J. Weers, D.M. LaBrush, D.P. Eyman and J.C. Huffman, *Organometallics*, *5* (1986) 883.

[5] The compound **1a** (0.52 g, 1.38 mmol) was stirred in acetone (50 ml) under N_2 at room temperature while $P(OC_2H_5)_3$ (470 μl, 2.74 mmol) then Me_3NO (1 pinch) were added. After 2 h stirring, the solution was evaporated to dryness, yielding a yellow oil which was chromatographed with an acetone–CH_2Cl_2 (6%) solution as eluant. A yellow powder was obtained which was crystallised in an acetone–ether mixture: 0.489 g (69% yield) of **1c**. The same procedure was used for **1b**: 38% yield. Complex **1c**: m.p. 54°C. ^{1}H NMR (C_2D_6CO): δ 6.48 (td, $J = 6.5$ and 1.0 Hz, 2H, H^3 and H^5), 6.28 (d, $J = 6.5$ Hz, 2H, H^2 and H^6), 6.22 (td, $J = 6.5$ and 1.7 Hz, 1H, H^4), 4.19 (m, 6H, $P(OC_2H_5)_3$), 2.48 (s, 3H, CH$_3$), 1.35 (t, $J = 7.0$ Hz, 9H, $P(OC_2H_5)_3$). ^{13}C NMR (C_2D_6CO): δ 221.5 (d, $J = 42.4$ Hz, $Mn(CO)_2$), 116.5 (C^1), 100.5 (C^3 and C^5), 98.1 (C^2 and C^6), 96.4 (C^4), 64.2 (d, $J = 7.5$ Hz, $P(OC_2H_5)_3$), 20.1 (CH$_3$), 16.0 (d, $J = 6.6$ Hz, $P(OC_2H_5)_3$). ^{31}P NMR (C_2D_6CO) 176.1. IR (CHCl$_3$) ν(CO) 2000, 1965 cm^{-1}. Anal. Found: C, 34,52; H, 4.42. $C_{15}H_{23}MnO_5P_2F_6$ Calc.: C, 35.04, H, 4.51%. Complex **1b**: m.p. 188–192°C. ^{1}H NMR (C_2D_6CO): δ 7.56–7.61 (m, 15H, $P(C_6H_5)_3$), 6.32 (td, $J = 6.5$ and 1.5 Hz, 2H, H^3 and H^5), 6.07 (d, $J = 6.5$ Hz, 2H, H^2 and H^6), 6.02 (td, $J = 6.5$ and 1.5 Hz, 1H, H^4), 2.50 (s, 3H, CH$_3$). ^{13}C NMR (C_2D_6CO): δ 224.1 (d, $J = 30.3$ Hz, $Mn(CO)_2$), 134.5, 133.5, 132.1, 129.8 $(P(C_6H_5)_3)$, 116.1 (C^1), 101.9 (C^3 and C^5), 97.7 (C^2, C^4 and C^6), 20.1 (CH$_3$). ^{31}P NMR (C_2D_6CO) 73.3. IR (CHCl$_3$) ν(CO) 1995, 1955 cm^{-1}. Anal. Found: C, 52.97; H, 3.70. $C_{27}H_{23}MnO_2P_2F_6$ Calc.: C, 53.13; H, 3.80%.

[6] The preparation of **1d** is as follows: $P(OEt)_3$ (0.489 ml, 2.85 mmol) then Me_3NO (0.214 g, 2.85 mmol) were added to a solution of complex **1c** (1.125 g, 2.19 mmol) in CH_2Cl_2 at room temperature. The reaction mixture was stirred under N_2 for 4 h at room temperature. The product **1d** (0.688 g, 1.06 mmol) was isolated by evaporation of the solvent followed by chromatography on a silica gel column with CH_2Cl_2–acetone (98/2) as eluant. Evaporation to dryness gave the product **1d** as a yellow powder (48% yield); m.p. 122–124°C. ^{1}H NMR (C_2D_6CO): δ 5.93 (m, 2H, H^3 and H^5), 5.81 (t, $J = 6.3$ Hz, 1H, H^4), 5.69 (d, $J = 6.1$ Hz, 2H, H^2 and H^6), 4.01 (m, 12H, $P(OC_2H_5)_3$), 2.31 (s, 3H, CH$_3$), 1.31 (t, $J = 7.0$ Hz, 18H, $P(OC_2H_5)_3$). ^{13}C NMR (C_2D_6CO): δ 227.1 (Mn(CO)), 109.7 (C^1), 96.4 (C^3 and C^5), 93.7 (C^2 and C^6), 93.0 (C^4), 63.1 $(P(OC_2H_5)_3)$, 20.1 (CH$_3$), 16.2 $(P(OC_2H_5)_3)$. ^{31}P NMR (C_2D_6CO) 182.1. IR (CHCl$_3$) ν(CO) 1930 cm^{-1}. Anal. Found: C, 36.59; H, 5.88. $C_{20}H_{38}MnO_7P_3F_6$ Calc.: C, 36.82; H, 5.87%.

[7] F. Rose-Munch, C. Susanne, C. Renard, E. Rose and J. Vaisserman, unpublished results.

[8] Crystals of **1d** grown by evaporation of an acetone/ether mixture at 0°C; triclinic; $a = 8.546(2)$ Å, $b = 12.623(2)$ Å, $c = 14.334(2)$ Å; $\alpha = 101.13(1)°$, $\beta = 100.54(2)°$, $\gamma = 92.55(2)°$; $V = 1483(7)$ Å^3; space group $P = \bar{1}$; $Z = 2$; $D_{calcd} = 1.46$ g cm^{-3}; Mo Kα radiation, Enraf-Nonius CAD-4 diffractometer, $\lambda = 0.71069$ Å, θ limits 1–28°; 352 variables refined with 3051 independent reflections $(F_o)^2 3\sigma(F_o)^2$ to $R = 0.0594$; $Rw = 0.0600$. Solution of the structure was accomplished using standard Patterson–Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a difference-Fourier map and their coordinates refined with an overall refinable isotropic thermal parameter. Atomic parameters for non-hydrogen atoms are given in Tables 1 and 2. Main interatomic distances and selected bond angles are listed in Tables 3 and 4. Crystal data for $[C_{20}H_{38}O_7P_2Mn]$ (PF_6) are given in Table 5. Details of the X-ray structure determination of **1d**, including text giving data collection and refinement details, tables of atomic coordinates, anisotropic thermal parameters, bond distances and angles (17 pages), have been deposited at the Cambridge Crystallographic Data Centre.

[9] D.A. Brown, W.K. Glass, K. Kreddan, D. Cunningham, P.A. McArdle and T. Higgins, *J. Organomet. Chem.*, *418* (1991) 91.

[10] (a) A typical procedure is as follows: preparation of **2d** and **3d**. In a solution of **1d** (0.652 mg, 1.0 mmol) in 5 ml of THF at −78°C was added a solution, in THF, of 2-lithio, 2-methylpropionitrile (prepared from reaction of 1.1 mmol of lithiumdiisopropylamide and 95.5 μl (1.05 mmol) of 2-methylpropionitrile). After 5 min stirring at 0°C under N_2, the reaction mixture was extracted with Et_2O. The organic phase was washed with water and brine, dried over $MgSO_4$, filtered through a Celite column and solvents were removed under reduced pressure. The oily residue was chromatographed on a silica gel column (15 μm) with Et_2O–EP (16%) as eluant to give 0.489 g (85% yield) of a 92/8 mixture of **2d**/**3d**. Complex **2d**. ^{1}H NMR (200 MHz, CDCl$_3$): δ 4.94 (d, $J = 5.4$ Hz, 1H, H^3), 4.69 (dd, $J = 5.7$ and 7.1 Hz, 1H, H^4), 3.86 (m, 12H, $P(OC_2H_5)_3$), 2.63 (t, $J = 5.4$ Hz, 1H, H^6), 2.45 (m, 2H, H^1 and H^5), 1.92 (s, 3H, CH$_3$), 1.18 (t, $J = 7.2$ Hz, 18H, $P(OC_2H_5)_3$), 0.90 (s, 6H, CH$_3$ on C^7). ^{13}C NMR (CDCl$_3$): δ 227.3 (dd, $J = 31$ and 32 Hz, Mn(CO)), 125.4 (CN), 104.2 (C^2), 96.0 (C^4), 77.0 (C^3), 59.6 $(P(OC_2H_5)_3)$, 49.1 (d, $J = 7.7$ Hz, C^1 or C^5), 47.5 (d, $J = 8.0$ Hz, C^5 or C^1), 43.8 (d, $J = 5.4$ Hz, C^6), 40.5 (d, $J = 5.3$ Hz, C^7), 22.7 (CH$_3$), 22.4 (CH$_3$), 16.5 $(P(OC_2H_5)_3)$. ^{31}P NMR (CDCl$_3$): 205.3 204.8, 196.7, 196.2. Complex **3d**. ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.12 (m, 1H, H^3), 4.51 (m, 2H, H^2 and H^4), 4.04 (m, 6H, $P(OC_2H_5)_3$), 2.94 (d, $J = 5.9$ Hz, 1H, H^6), 2.36 (m, 1H, H^5), 1.69 (s, 3H, CH$_3$), 1.29 (t, $J = 7.1$ Hz, 9H, $P(OC_2H_5)_3$), 1.01 (s, 3H, CH$_3$), 0.96 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 228.8 (Mn(CO)), 126.3 (CN), 92.0 (C^2, C^4), 74.5 (C^3), 65.9 (C^1), 59.7 $(P(OC_2H_5)_3)_2$, 48.7 (C^5), 44.2 (C^6), 40.4 (d, $J = 5.3$ Hz, C^7), 24.0 (CH$_3$), 23.7 (CH$_3$), 23.6 (CH$_3$), 16.3 $(P(OC_2H_5)_3)$. ^{31}P NMR (CDCl$_3$): 198.6, 196.7. IR(CHCl$_3$) ν(CN) 2215, ν(CO) 1845 cm^{-1}. Anal. Found: C, 50.07; H, 7.66; N, 2.44. $C_{24}H_{44}MnNO_7P_2$ (**2d** + **3d**) Calc.: C, 50.09; H, 7.71; N, 2.43%. (b) Addition of RMgX has been studied on complex **1a**: Y.K. Chung, P.G. Williard and D.A. Sweigart, *Organometallics*, *1* (1982) 1053. The authors observed an o/m ratio of 1/2.

[11] Spectroscopic and analytical data for **2c** + **3c**. Complex **2c**. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.39 (td, $J = 5.5$ and 1.4 Hz, 1H, H^3), 4.84 (m, 1H, H^4), 3.86 (m, 6H, $P(OC_2H_5)_3$), 3.03 (d, $J = 5.5$ Hz, 1H, H^1), 2.84 (t, $J = 5.5$ Hz, H^6), 2.69 (m, 1H, H^5), 1.86 (s, 3H, CH$_3$), 1.21 (m, 9H, $P(OC_2H_5)_3$), 0.92 (s, 6H, CH$_3$). ^{13}C NMR (50 MHz CDCl$_3$): δ 230.9 (d, $J_{CP} = 28.0$ Hz) or 225.5 (d, $J_{CP} = 34.0$ Hz) (Mn(CO)$_2$), 124.6 (CN), 109.0 (C^2), 96.6 (C^4), 80.1 (C^3), 60.2 $(P(OC_2H_5)_3)$, 51.8 (C^1), 50.3 (C^6), 44.6 (C^5), 40.8 (C^7), 22.6 (CH$_3$), 22.4 (CH$_3$), 22.3

(CH_3), 16.2 $(P(OC_2H_5)_3)$. ^{31}P NMR (162 MHz, C_2D_6O) 196.1. Complex **3c**. ^1H NMR (400 MHz, $CDCl_3$): δ 5.39 (td, $J = 5.3$ and 1.4 Hz, 1H, H^3), 4.72 (m, 1H, H^4), 4.66 (d, $J = 5.3$ Hz, 1H, H^2), 3.86 (m, 6H, $P(OC_2H_5)_3$), 2.90 (d, $J = 5.3$ Hz, 1H, H^6), 2.69 (m, 1H, H^5), 1.77 (s, 3H, CH_3), 1.21 (m, 9H, $P(OC_2H_5)_3$), 1.02 (s, 3H, CH_3), 0.97 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 225.5 (d, $J_{CP} = 34.0$ Hz) or 230.9 (d, $J_{CP} = 28.0$ Hz, $Mn(CO)_2$), 125.4 (CN), 95.1 (C^4), 95.0 (C^2), 77.3 (C^3), 68.7 (C^1), 60.2 ($P(OC_2H_5)_3$), 49.2 (C^6), 44.9 (C^5), 39.9 (C^7), 25.0 (CH_3), 24.0 (CH_3), 23.5 (CH_3), 16.2 $(P(OC_2H_5)_3)$. ^{31}P NMR (162 MHz, C_2D_6O): 195.9. IR ($CHCl_3$)

of (**2c** + **3d**): ν(CN) 2220, ν(CO) 1875, 1945 cm^{-1}. Anal. Found: C, 52.29; H, 6.49; N, 3.08. $C_{19}H_{29}MnNO_5P$ (**2c** + **3c**) Calc.: C, 52.18. H, 6.68; N; 3.20%.

[12] A.S. Oh, Y.K. Chung and S. Kim, *Organometallics*, *11* (1992) 1394.

[13] See for example: (a) A.J. Pearson, S.L. Kole and T. Ray, *J. Am. Chem. Soc.*, *106* (1984) 6060; (b) K.F. McDaniel, L.R. Kracker II and P.K. Thamburaj, *Tetrahedron Lett.*, *17* (1990) 2373; (c) W.A. Donaldson and L. Shang, *Tetrahedron Lett.*, *10* (1995) 1575.