

Table 2. Crystallographic data of complex **6** (CCDC 813148).

	Complex 6
Empirical formula	C ₃₂ H ₂₃ MnO ₄ PS
Fw(g.mol ⁻¹)	589.47
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	<i>P</i> na2 ₁
a (Å)	23.588(4)
b (Å)	9.1363(9)
c (Å)	13.1639(10)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å ³)	2836.9(6)
Z	4
Density ρ (g cm ⁻³)	1.380
Absorption coef (mm ⁻¹)	0.631
F (000)	1212
θ limits(deg)	3.22 to 30.00
hkl limits	-33,20;-12,12;-18,18
Reflections collected	12347
Independent reflections	7238 [R(int) = 0.0359]
Refinement method	Full-matrix least-squares
Completeness to θ =30.00°	96.2%
Max.and min. transmission	0.812 and 0.552
Data/restraints/parameters	7238 / 1 / 353
GOF	1.014
Final indices [I>2σ(I)]	R1=0.0416,wR2=0.0947
R indices (all data)	R1=0.0594,wR2= 0.1015
Absolute structure parameter	0.037(15)
Largest dif peak and hole (Å ⁻³)	0.505 and -0.565

Preparation of complexes **1** and **2**

(η⁶-1-Chloro-4-methoxybenzene)tricarbonylmanganese **1**^{i,3a} In a 50 mL two-neck flask under Ar atmosphere, AgBF₄ (1.22 g, 6.3 mmol, 1 equiv) and Mn(CO)₅Br (1.73 g, 6.3 mmol, 1 equiv) were dissolved in CH₂Cl₂ (15 mL) giving an orange solution. After 3h under reflux, grey solid of AgBr appeared in the flask. *para*-Chloroanisole (3 mL, 25.2 mmol, 4 equiv) were added at rt, then the reaction mixture was heated for 18h under reflux and cooled at rt. The mixture was filtered on celite and rinsed with CH₂Cl₂ and then with acetone. The solution was evaporated under N₂ flow. Slow addition of this solution into 200 mL of Et₂O induced the precipitation of a yellow product (1.94 g, 5.2 mmol, 84%) which was recovered by filtration. M = 368,36 g.mol⁻¹ ¹H NMR (200 MHz, (CD₃)₂CO) δ (ppm) 4.23 (s, 3H, OMe), 6.67 (d, ³J = 7.6 Hz, 2H, H³ et H⁵), 7.53 (d, ³J = 7.6 Hz, 2H, H² et H⁶). ¹³C NMR (100 MHz, (CD₃)₂CO) δ ppm 60.1 (OMe), 84.8 (C³, C⁵), 105.4 (C², C⁶), 108.2 (C¹), 149.2 (C⁴), 216.2 (Mn(CO)₃⁺). IR (ATR mant) ν 2020 (Mn(CO)₃⁺), 2077 (Mn(CO)₃⁺) cm⁻¹.

(η⁵-1-Chloro-4-methoxy-6-phenylcyclohexadienyl)tricarbonyl manganese **2**^{4a} In a 50 mL two-neck flask [(η⁶-*para*-chloroanisole)Mn(CO)₃][BF₄] **1** (0.478 g, 1.29 mmol, 1 equiv) was added in 15 mL of dry THF. The reaction medium was cooled at 0°C. Then a solution of PhMgCl (1.3 mL, 2.72 mmol, 2.1 equiv) in THF (c = 1 mol.L⁻¹) was added. The color of the reaction became yellow. After 20 mn stirring at 0°C, the reaction was warmed at rt and 40 mL of HCl (2M) were added. The organic phase was separated and the aqueous phase was extracted twice with 30 mL of Et₂O. All the organic phases were extracted with 50 mL of H₂O and 50 mL of a saturated solution of NaCl and dried over celite. The evaporation of the solvents under reduced pressure gave a yellow solid which was purified by silica gel chromatography column using petroleum ether. Complex **2**, 0.236 g (0.450 g, 1.25 mmol, 96 %) was recovered. C₁₆H₁₂ClMnO₄ M = 358, 66 g.mol⁻¹. ¹H NMR (200 MHz, CDCl₃) δ (ppm) 3.49 (m, 4H, H⁵ and OMe), 4.31 (d, ³J = 6.5 Hz, 1H, H⁶), 5.22 (dd, ³J = 6.0 Hz, ⁴J = 1.9 Hz, 1H, H²), 5.56 (dd, ³J = 6.0 Hz, ⁴J = 2.7 Hz, 1H, H³), 7.03

(m, 5H, H^{Ar}). ¹³C NMR (100 MHz, CDCl₃) : δ (ppm) 45.0 (C⁵), 52.2 (C⁶), 54.9 (OMe), 64.5 (C³), 80.0 (C¹), 92.4 (C²), 126.1 (CH^{Ar}), 127.7 (CH^{Ar}), 128.6 (CH^{Ar}), 141.6 (C⁴ ou C^{Ar}), 143.7 (C⁴ ou C^{Ar}), 221.6 (Mn(CO)₃). IR (ATR Diamant) ν 1921 (Mn(CO)₃), 2009 (Mn(CO)₃) cm⁻¹.

ⁱ A. J. Pearson and I. C. Richards, *J. Organomet. Chem.* 1981, **204**, C25.