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Preliminary Communication

X-ray structure of $[Mn(\eta\text{-}C_6H_5Me)_2]^+I^-$

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Abstract

The cocondensation of Mn atoms, I_2 and toluene at 77 K yields small quantities of $[Mn(\eta\text{-}C_6H_5Me)_2]^+I^-$. A single crystal X-ray structure determination shows that the manganese sits on a crystallographic inversion centre with a $Mn_{\text{ring centroid}}$ distance of 1.56(1) Å.

Recently Billups et al. [1] briefly reported a low yield synthesis of $[Mn(\eta\text{-}C_6H_5Me)_2]^+PF_6^-$ by evaporation of manganese using resistive heating with a mixture of toluene and iodine at 77 K. It is believed that the role of the iodine is to oxidise *in situ* the thermally unstable 19-electron species $[Mn(\eta\text{-}C_6H_5\text{-}Me)_2]$. Here we report the synthesis and crystal structure of $[Mn(\eta\text{-}C_6H_5Me)_2]^+I^-$, the first structurally characterised bis(arene)manganese derivative.

The metal vapour technique which incorporates an electron beam furnace and a dual ligand inlet system was used as described previously [2]. Typically 3–4 g of manganese metal vapour was cocondensed with a mixture of toluene (100 cm^3) and elemental iodine (2–3 g) onto the wall of the glass bell jar at 77 K. After the cocondensation was finished the product was extracted with THF, and the extract passed through a bed of Celite and then concentrated to give a deep orange solution. Cooling to −20°C gave a small quantity of X-ray quality orange crystals (yield *ca.* 1%).

The most successful experiment conducted involved the use of a dual liquid and solid ligand inlet system. This enabled independent control over the rate of flow of iodine and toluene into the reactor. Manganese and toluene were cocondensed for 30 min before any iodine was introduced into the system. A steady flow of iodine vapour was then allowed into the system for a further 3 h. It appears that a subtle control over the flow rates and ratios of the starting materials is required in order to synthesise these compounds. We believe that the manganese atoms react much faster with iodine vapour than with toluene both in the vapour phase and/or in the frozen matrix giving MnI_2.

A single crystal X-ray diffraction structure determination of $[Mn(\eta\text{-}C_6H_5Me)_2]^+I^-$ is shown in Fig. 1 together with the atomic labelling scheme. The compound crystallises in the monoclinic space group $C2/m$ with the manganese atom located on the crystallographic inversion centre (0, 0, 0). The C_6 fragments of the toluene rings are therefore constrained to adopt an eclipsed geometry and the methyl substituents diagonally opposed. This is in contrast to the structures reported for $Mo(\eta\text{-}C_6H_5Me)_2$, in which the methyl groups adopt a disordered arrangement around the rings [3], and for $W(\eta\text{-}C_6H_5Me)_2$ in which the toluene rings are fully eclipsed [4]. The dimensions of the toluene rings do not vary significantly from the expected values; the C–C distances range from 1.36–1.50 Å. The Mn–C bond lengths lie in the range 2.061–2.141 Å, significantly shorter than those reported for $Mo(\eta\text{-}C_6H_5Me)_2$ (2.255–2.282 Å) and $W(\eta\text{-}C_6H_5Me)_2$

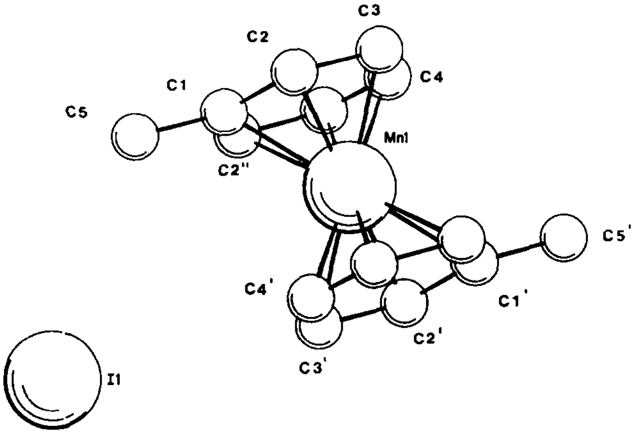

Fig. 1. Molecular structure of $[Mn(\eta\text{-}C_6H_5Me)_2]^+I^-$. Selected bond lengths (Å) and angles (°): C–C (C_6-ring mean), 1.46(1); Mn(1)–C(1), 2.141(5); Mn(1)–C(2), 2.120(5); Mn(1)–C(3), 2.086(7); Mn(1)–C(4), 2.061(7); Mn(1)–(C6-ring centroid), 1.56(1); C(1)–C(2), 1.41(1); C(2)–C(3), 1.45(1); C(3)–C(4), 1.36(1); C(1)–C(5), 1.50(1). C(1)–C(2)–C(3), 117.6(8); C(2)–C(3)–C(4), 121.1(9); (Hydrogen atoms have been omitted for clarity). Atoms denoted by (′) are generated by the crystallographic symmetry operator (− *x*, − *y*, − *z*), atoms denoted by (″) are generated by the crystallographic symmetry operator (− *x*,*y*, − *z*).

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(2.25–2.36 Å), but comparable with the value reported for $Cr(\eta\text{-}C_6H_6)_2$ ($Cr\text{–}C_6$ ring mean = 2.14 Å) [5]. The Mn atom lies 1.56 Å away from the C_6 ring centroid, a distance again significantly shorter than those reported for $Mo(\eta\text{-}C_6H_5Me)_2$ (1.78 Å) and $W(\eta\text{-}C_6H_5Me)_2$ (1.80 Å), but comparable with that reported for $Cr(\eta\text{-}C_6H_6)_2$ (1.62 Å). The methyl group deviates slightly (0.03 Å) from the plane of the C_6 ring in the direction of the metal centre.

Metal vapour synthesis using *in situ* oxidation has enabled us to determine the molecular structure of the first *bis*(arene)manganese compound. However the disappointing yield (*ca.* 1%) and our failure to significantly improve the yield of the reaction has prevented us from carrying out a full investigation of *bis*(arene)manganese chemistry.

Acknowledgements

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References and notes

1 W.E. Billups, A.W. Moorehead, P.J. Ko, J.L. Margrave, J.P. Bell and F.B. McCormick, *Organometallics*, *7* (1988) 2230.

2 M.L.H. Green, *J. Organomet. Chem.*, *200* (1980) 119.

3 F.M. Miao, *Cryst. Struct. Commun.*, *11* (1982) 153.

4 C.K. Prout, A. Gourdon, C. Couldwell, B. Meunier, F.M. Miao and J. Woolcock, *Acta Crystallogr., Sect. B*, *38* (1982) 456.

5 F.A. Cotton, W.A. Dollase and J.S. Wood, *J. Am. Chem. Soc.*, (1963) 1544.

6 E.P. Kündig, P.L. Timms, B.A. Kelly and P.J. Woodward, *J. Chem. Soc., Dalton Trans.*, (1983) 901.

7 M.L.H. Green, D. O'Hare and J.M. Wallis, *J. Chem. Soc., Chem. Commun.*, (1984) 233.

8 D.J. Watkin, R. Carruthers and P.W. Betteridge, *CRYSTALS manual*, Chemical Crystallography Laboratory, University of Oxford, 1985.

9 Physical data for $[Mn(\eta\text{-}C_6H_5Me)_2]I$. Anal. Found: C, 45.34; H, 4.28; Mn, 14.74. $C_{14}H_{16}IMn$ calc.: C, 45.93; H, 4.40; Mn, 15.01%.

10 Crystallographic details: $[Mn(\eta\text{-}C_6H_5Me)_2]I$; $C_{14}H_{16}IMn$, M = 366.12, monoclinic $C2/m$, $a = 13.019(5)$, $b = 6.853(8)$, $c = 7.955(9)$ Å, $\beta = 110.96(7)$, $F(000) = 366$, scan mode $\omega-2\theta$, $\theta_{max} = 25°$, $V = 663$ Å^3, $Z = 2$, $D_c = 1.83$ g cm^{-3}, μ(Mo Kα) = 32.34 cm^{-1}, crystal size *ca.* 0.6×0.4×0.3 mm, $R = 0.033$, $R_w = 0.037$, from 552 reflections $[I > 3\sigma(I)]$ and 49 independent parameters.

11 Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation. Empirical absorptions were applied and the structure solved using direct methods and subsequent difference Fourier syntheses. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions (C–H = 1.0 Å) with fixed isotropic thermal parameters and allowed to ride on their respective carbon atoms. Crystallographic calculations were carried out on a Microvax computer using the Oxford CRYSTALS system. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.