

Influence on Transition-metal–Arene Complex Formation of Hydrogenation and Rearrangement of Polyaromatic Substrates induced by Aluminium Trichloride. Octahydrophenanthrene Complexes from Tetralin: X-Ray Crystal Structure of η^5 -1,2,3,4,5,6,7,8,9,-endo-Nonahydro-9-exo-methylphenanthrenyl(tricarbonyl)-manganese†

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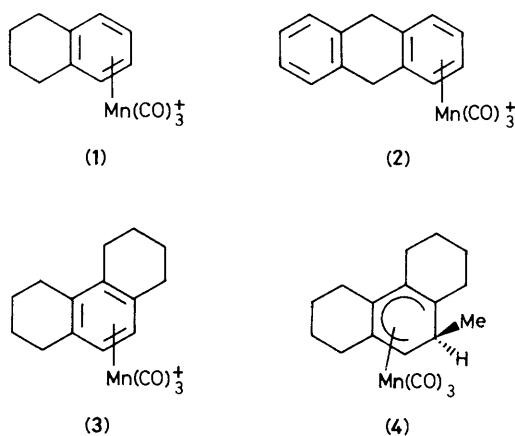
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Formation of cationic tricarbonylmanganese complexes of tetralin or 9,10-dihydroanthracene from reactions of $\text{Mn}(\text{CO})_5\text{Br}$ with naphthalene or anthracene in the presence of AlCl_3 is attributed to action of the latter since it alone reduces the polyaromatic substrates under comparable conditions; reaction of tetralin with $\text{Mn}(\text{CO})_5\text{Br}-\text{AlCl}_3$ affords in addition to the expected η^6 -tetralin–manganese cation an η^6 -octahydrophenanthrene analogue, the title neutral methyl derivative of which has been characterized by an X-ray crystal structure determination.

We have identified an AlCl_3 -induced modification of polycyclic hydrocarbon structures which accounts *inter alia* for the formation of complexes of hydroaromatic ligands from polyaromatic substrates^{1,2} in reactions which follow a general synthetic route³ to transition metal–arene derivatives. On stirring naphthalene or anthracene with AlCl_3 (1:2 mol ratio, 20 °C, N_2 atmosphere, hexane), an immediate darkening of

the suspension was evident, to black or reddish–black respectively. Filtration after 3 h at 70 °C followed by g.c.–mass spectrometry (Finnigan 3300) of the hexane-soluble material showed the presence of components giving rise to parent ions at *m/z* (relative g.c. peak area) 128(1.0) and 132(1.0) (naphthalene); 178(0.9), 180(1.0), and 182(0.6) (anthracene), in addition to a multiple of minor less volatile fractions. Significant conversion of naphthalene into tetralin, and of anthracene into 9,10-dihydroanthracene (DHA) and 1,2,3,4-tetrahydroanthracene (THA) occurs under conditions which have been used in the synthesis of cationic arene

† *Endo* and *exo* refer to orientations on the aromatic ring with respect to the $\text{Mn}(\text{CO})_3$ group.



complexes.¹⁻³ This behaviour may explain the unusual outcome of our attempts to isolate several tricarbonylmanganese cations.

Treatment of $\text{Mn}(\text{CO})_5\text{Br}$ with naphthalene (2 mol equiv.) and AlCl_3 (2 mol equiv., methylcyclohexane, 18 h, 70 °C) afforded as the only isolable arene complex (*ca.* 10%) after aqueous work-up and precipitation with NH_4PF_6 the tetralin-tricarbonylmanganese derivative ‡ [$\text{Mn}(\eta^6\text{-C}_{10}\text{H}_{12})(\text{CO})_3$] PF_6 , (1). Reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with anthracene under similar conditions yielded only the 9,10-dihydroanthracene (DHA) complex § [$\text{Mn}(\eta^6\text{-C}_{14}\text{H}_{12})(\text{CO})_3$] PF_6 , (2). Formation of compounds (1), (2), or their iron analogues³ contrasts with corresponding tricarbonylchromium chemistry⁵ where naphthalene and anthracene derivatives are straightforwardly accessible *via* reactions which do not require addition of AlCl_3 .

Compound (1) was also obtained by stirring $\text{Mn}(\text{CO})_5\text{Br}$ and AlCl_3 (2 mol equiv.) in redistilled tetralin alone (18 h, 20 °C). Aqueous quenching followed by addition of NH_4PF_6 afforded a yellow precipitate (*ca.* 70% yield) consisting (¹H and ¹³C n.m.r. spectroscopy) of complex (1) and a minor proportion (*ca.* 25%) of a second product (3). Sequential refrigeration of CH_2Cl_2 solutions at -20 °C allowed successive removal of microcrystalline (1), concentrating to >95% purity the more soluble component (3). The latter was subsequently characterized ¶ as an η^6 -octahydrophenanthrene analogue [$\text{Mn}(\eta^6\text{-C}_{14}\text{H}_{18})(\text{CO})_3$] PF_6 , a surprising result for which supporting evidence was provided by conversion into a crystalline methyl derivative amenable to an X-ray structure determination. After treatment with MeLi (1 mol equiv.,

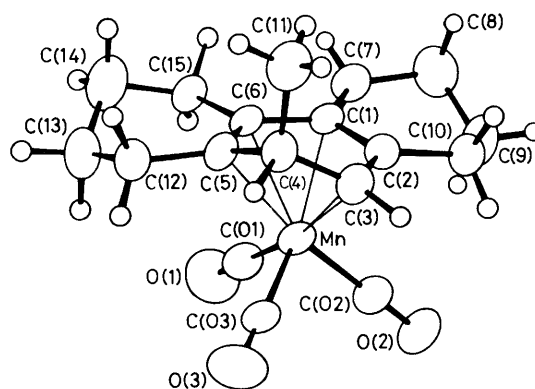


Figure 1. ORTEP view of η^5 -1,2,3,4,5,6,7,8,9-*endo*-nonahydro-9-*exo*-methylphenanthrenyl(tricarbonyl)manganese, (4).[†] Selected bond distances: Mn-C(1) 2.152(3), Mn-C(2) 2.140(3), Mn-C(3) 2.177(3), Mn-C(5) 2.273(3), Mn-C(6) 2.189(3), Mn-CO_{av} 1.800 ± 0.002 Å. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

tetrahydrofuran, -70 °C), recovery of the hexane-soluble material yielded a yellow product** (4), crystals of which were obtained by slow sublimation *in vacuo* (70 °C, 10⁻² mm Hg).

Crystal data for (4): $\text{MnC}_{18}\text{H}_{21}\text{O}_3$, $M = 340.3$, monoclinic, space group $P2_1/c$, $a = 6.586(3)$, $b = 14.101(5)$, $c = 15.366(6)$ Å, $\beta = 101.22(3)^\circ$, $U = 1612.3 \text{ \AA}^3$, $D_c = 1.40 \text{ g cm}^{-3}$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 8.7 \text{ cm}^{-1}$. The structure was solved using MULTAN and refined using SHELX, leading to final values of $R = 0.042$ and $R_w = 0.045$ based upon 2249 observed reflections $I > 3\sigma(I)$, to $\theta = 50^\circ$. All hydrogen atoms were located and fixed to the appropriate carbon atoms. The molecular arrangement (ORTEP view, Figure 1) confirms that nucleophilic addition of Me^- to the tricyclic ring system of compound (3) has occurred, substituting *exo* to the tricarbonylmanganese fragment to generate in an asymmetric configuration a cyclohexadienyl-metal interaction which is virtually identical with that⁶ in the prototypal analogue $\text{Mn}(\eta^5\text{-C}_6\text{H}_7)(\text{CO})_3$.

There is evidence⁷ for promotion of high-temperature hydrogenation of polyaromatics by AlCl_3 , complementing the long-established activity of the same reagent in inducing carbocyclic skeletal rearrangements.⁸ The observations described here cast doubt on the claim¹ that analogous chemistry encountered in substitution reactions of $\text{Fe}(\eta\text{-C}_5\text{R}_5)(\text{CO})_2\text{X}$ ($\text{R} = \text{H}$, $\text{X} = \text{Cl}$; $\text{R} = \text{Me}$, $\text{X} = \text{Br}$) is attributable to hydrogenation mediated by the iron centre: co-ordination of DHA or THA to the metal centre would be expected to predominate in circumstances which favour acid-catalysed⁹ arene-exchange phenomena.¹⁰ The origin of the phenanthrene skeleton in complexes (3) and (4) may be attributed to AlCl_3 -induced dismutation of tetralin, first reported as early as 1924, to afford products including tricyclic hydroaromatics,⁸ again coupled with preferential complexation of the latter *via* arene-exchange.

‡ Characterization of this product establishes as incorrect the identification⁴ of the corresponding perchlorate salt as a η^6 -naphthalene-manganese derivative. We have synthesized [$\text{Mn}(\eta^6\text{-C}_{10}\text{H}_8)(\text{CO})_3$] PF_6 by a different route and find it to be very sensitive to arene displacement by donor solvents. I.r. (KBr disc), $\nu(\text{CO})$ 2060 and 1995 cm^{-1} ; ¹H n.m.r. (250 MHz, CD_2Cl_2) δ 6.37 m, 4H, 2.85 m, 4H(α), and 1.90 m, 4H(β); ¹³C n.m.r. (62.9 MHz, CD_2Cl_2) δ 118.9, 100.9, 98.9 (aromatic), 28.3 ($\alpha\text{-CH}_2$), and 21.4 ($\beta\text{-CH}_2$). An X-ray diffraction study of crystalline (1) provided further support for its formulation although the refinement did not converge below $R = 0.11$ owing to crystallographic disorder.

§ I.r. (KBr disc), $\nu(\text{CO})$ 2070, 2010, and 1995 cm^{-1} ; ¹H n.m.r. (60 MHz, [²H₆]acetone), δ 7.50 s, 4H, 6.95 m, 4H, and 4.35 s, 4H.

¶ I.r. (KBr disc), $\nu(\text{CO})$ 2060 and 1995 cm^{-1} ; ¹H n.m.r. (60 MHz, CDCl_3) δ 6.28 s, 2H, 2.85 m, 8H, and 2.00 m, 8H. ¹³C n.m.r. (62.9 MHz, CD_2Cl_2) δ 216.2, 116.8, 116.1, 98.9, 28.7, 25.7, 21.5, and 21.0. Resolution of four CH_2 signals eliminates the alternative isomeric η^6 -octahydroanthracene formulation.

** Satisfactory elemental analysis was obtained. I.r. (KBr disc), $\nu(\text{CO})$ 1985 and 1905 cm^{-1} ; ¹³C n.m.r. (62.9 MHz, CDCl_3) δ 224.4, 109.4, 105.7, 93.1, 82.8, 50.0, 38.5, 30.6, 29.9, 26.0, 25.3, 25.0, 23.6, 22.4, 21.7, and 20.8. The ¹H n.m.r. spectrum (250 MHz, CDCl_3) showed in addition to a complex multiplet at δ 2.90–1.35, a sharp doublet at δ 0.38 (*exo*-Me).

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References

- 1 V. Guerschais and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1983, 1115.
 - 2 R. G. Sutherland, S. C. Chen, J. Pannekoek, and C. C. Lee, *J. Organomet. Chem.*, 1975, **101**, 221; R. G. Sutherland, W. J. Pannekoek, and C. C. Lee, *Can. J. Chem.*, 1978, **56**, 1782.
 - 3 T. H. Coffield, V. Sandel, and R. D. Closson, *J. Am. Chem. Soc.*, 1957, **79**, 5826; A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Tetrahedron Lett.*, 1963, 1725; W. E. Silverthorn, *Adv. Organometal. Chem.*, 1975, **13**, 50; R. G. Sutherland, *J. Organomet. Chem. Lib.*, 1977, **3**, 311.
 - 4 G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 3807.
 - 5 O. Fischer, K. Oefele, H. Essler, W. Froehlich, J. P. Mortensen, and W. Semmlinger, *Chem. Ber.*, 1958, **91**, 2763; V. Kunz and W. Nowacki, *Helv. Chim. Acta*, 1967, **50**, 1052.
 - 6 M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, 1969, **8**, 1950. While numerous η^5 -cyclohexadienyl-metal complexes have been reported, very few X-ray structural data are currently available: M. R. Churchill and P. H. Bird, *J. Chem. Soc., Chem. Commun.*, 1967, 777; A. Mawby, P. J. C. Walker, and R. J. Mawby, *J. Organomet. Chem.*, 1973, **55**, C39; M. F. Semmelhack, H. T. Hall, R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535; M. J. Barrow and O. S. Mills, *Acta Crystallogr., Sect. B*, 1974, **30**, 1635.
 - 7 S. S. Salim and A. T. Bell, *Fuel*, 1982, **61**, 745.
 - 8 G. Schroeter, *Ber.*, 1924, **57B**, 1990, 2003, 2025; A. L. Glasebrook, N. E. Phillips, and W. G. Lovell, *J. Am. Chem. Soc.*, 1936, **58**, 1944; Y-H. Lai, L. S. Benner, and K. P. C. Vollhardt, *Fuel*, 1984, **63**, 231.
 - 9 F. Hein and K. Kartte, *Z. Anorg. Allg. Chem.*, 1960, **307**, 22.
 - 10 E. L. Muetterties, J. R. Bleeke, and A. C. Sievert, *J. Organomet. Chem.*, 1979, **178**, 197.
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