Synthesis and Crystal Structure of Bis[σ-tricarbonyl(η^5-cyclopentadienyl)manganese]di-η^5-cyclopentadienyltitanium †

By **Romeu J. Daroda** and **Geoffrey Wilkinson**, Chemistry Department, Imperial College of Science and Technology, London SW7 2AY
Michael B. Hursthouse, **K. M. Abdul Malik**, and **Mark Thornton-Pett**, Chemistry Department, Queen Mary College, Mile End Road, London E1 4NS

The reaction of $Ti(\eta\text{-}C_5H_5)_2Cl_2$ with $Li[Mn(\eta\text{-}C_5H_4)(CO)_3]$ in a mixture of tetrahydrofuran and diethyl ether (5 : 1) at −78 °C gives the compound $Ti(\eta\text{-}C_5H_5)_2[\sigma\text{-}(\eta\text{-}C_5H_4)Mn(CO)_3]_2$, the structure of which has been determined by single-crystal *X*-ray diffraction methods. Crystals are monoclinic, space group *C*2/*c*, a = 13.474, b = 8.085, c = 22.327 Å, β = 105.08°, and Z = 4. The structure, solved by the heavy-atom method and refined by least squares {R = 0.032 for 2 140 observed [$F_o > 3\sigma(F_o)$] data}, comprises molecules with C_2 symmetry in which the Ti atom is σ bonded to the cyclopentadienyl rings of two $Mn(\eta\text{-}C_5H_4)(CO)_3$ groups. Bond lengths and angles are as expected but with significant distortions in the manganese C_5H_4 rings.

THE interaction of the lithium and mercury derivatives of $Mn(\eta\text{-}C_5H_5)(CO)_3$ with gold and platinum phosphine complexes gives $Mn(\eta\text{-}C_5H_4)(CO)_3[Au(PPh_3)]$ [1] and $Mn(\eta\text{-}C_5H_4)(CO)_3[Pt(PPh_3)_2Cl]$.[2] Other similar derivatives, $Mn(\eta\text{-}C_5H_4)L(CO)_2[Fe(CO)_2(\eta\text{-}C_5H_5)]$[3] and $Mn(\eta\text{-}C_5H_4)L(CO)_2[W(CO)_3(\eta\text{-}C_5H_5)]$,[4] are made by reaction of $Mn(\eta\text{-}C_5H_4)L(CO)_2(COCl)$ (L = CO or PPh_3) with $Fe(\eta\text{-}C_5H_5)(CO)_2Na$ and $W(\eta\text{-}C_5H_5)(CO)_3Na$ with further decarbonylation of the intermediate complex.

We describe the synthesis, i.r. and n.m.r. spectra, and *X*-ray crystal structure of a new trimetallic species $Ti(\eta\text{-}C_5H_5)_2[\sigma\text{-}(\eta\text{-}C_5H_4)Mn(CO)_3]_2$ (1).

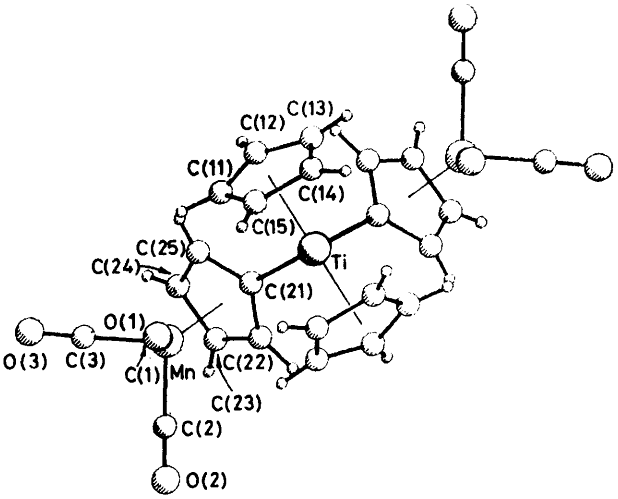
RESULTS AND DISCUSSION

The interaction of $Ti(\eta\text{-}C_5H_5)_2Cl_2$ with a solution of $Li[Mn(\eta\text{-}C_5H_4)(CO)_3]$ leads to red-orange crystals of (1). The compound slowly decomposes in the solid state in the presence of moisture giving $Mn(\eta\text{-}C_5H_5)(CO)_3$ and an unidentified black powder. In solution it is less stable to moisture giving the same mixture. Instability is also observed on heating a solution under N_2, giving a mixture of $Mn(\eta\text{-}C_5H_5)(CO)_3$, $(CO)_3(\eta\text{-}C_5H_4)Mn\text{-}Mn(\eta\text{-}C_5H_4)(CO)_3$,[1,‡] and other unidentified materials. It reacts rapidly with hydrogen chloride in solution, giving $Ti(\eta\text{-}C_5H_5)_2Cl_2$ and $Mn(\eta\text{-}C_5H_5)(CO)_3$. This reaction was also observed for bis(ferrocenyl)titanocene.[5]

Although the molecular ion is not observed in the mass spectrum the highest peak seen is at m/e = 528 showing the characteristic isotopic pattern for titanium. This corresponds to the loss of two carbonyl groups from the molecular ion. A fragmentation pattern is observed showing the successive losses of carbonyl groups, cyclopentadienyl groups, and manganese atoms.

In the i.r. spectrum three strong absorptions are observed in the carbonyl stretching region (2 000, 1 934, and 1 915 cm^{-1}) and at lower frequencies than those seen in $Mn(\eta\text{-}C_5H_5)(CO)_3$.

The ^1H n.m.r. shows a very simple spectrum with a singlet at δ = 5.9 p.p.m. (10 H) (relative to $SiMe_4$ δ = 0 p.p.m.) due to the equivalent η-cyclopentadienyl rings on titanium and two multiplets at δ = 4.16 p.p.m. (4 H) and δ = 3.90 p.p.m. (area ratio 1 : 1), assigned to the cyclopentadienyl rings σ-bonded to titanium and π-bonded to manganese. The ^1H n.m.r. spectrum of substituted cyclopentadienyl complexes has been well studied.[6]



Molecular structure of (1) showing the atom labelling in the asymmetric unit. The hydrogen atoms represented by the smallest circles are not numbered

The molecular structure is shown in the Figure which also gives the atom-numbering scheme. Important bond lengths and angles are given in Table 1. The

---

† Bis(1—5-η-cyclopentadienyl)bis[tricarbonyl(2—5-η-cyclopentadienylidene)manganese-C^1]titanium.

‡ Identified by ^1H n.m.r. and i.r.

molecule is structurally very similar to that of Ti(η-C_5H_5)$_2$(σ-C_5H_5)$_2$, differing only in that the Ti–C σ-bond attachment in the present molecule is to an sp^2 carbon.

The Ti–C bonds to the η^5 ring range from 2.374 to 2.406 Å and correspond to a very small tilt (*ca.* 2°) of the ring from perpendicular bonding. In Ti(C_5H_5)$_4$ [7] the distances are slightly smaller (2.339—2.400 Å) and this together with a difference in cp–Ti–cp angle [128.1° in (1), 129.9° in Ti(C_5H_5)$_4$] may be due, amongst other things, to the different relative orientations of the two cyclopentadienyl (cp) rings [eclipsed in (1), staggered in Ti(C_5H_5)$_4$].

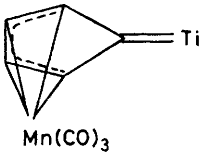
TABLE 1

Intramolecular interatomic distances (Å) and angles (°) [a]

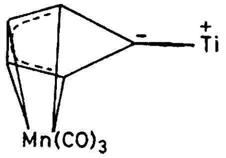
(*a*) Bond lengths			
Ti–C(11)	2.406(2)	Mn–C(21)	2.912(2)
Ti–C(12)	2.401(2)	Mn–C(22)	2.141(2)
Ti–C(13)	2.401(2)	Mn–C(23)	2.139(2)
Ti–C(14)	2.374(2)	Mn–C(24)	2.138(2)
Ti–C(15)	2.396(2)	Mn–C(25)	2.137(2)
Ti–C(21)	2.207(2)		
C(11)–C(12)	1.402(2)	C(21)–C(22)	1.442(3)
C(11)–C(15)	1.391(3)	C(21)–C(25)	1.441(3)
C(12)–C(13)	1.404(3)	C(22)–C(23)	1.427(3)
C(13)–C(14)	1.401(3)	C(23)–C(24)	1.394(3)
C(14)–C(15)	1.403(3)	C(24)–C(25)	1.419(3)
C(1)–O(1)	1.147(3)	Mn–C(1)	1.788(3)
C(2)–O(2)	1.147(3)	Mn–C(2)	1.790(3)
C(3)–O(3)	1.146(3)	Mn–C(3)	1.786(2)
C–H	0.86—0.98(2)		
(*b*) Bond angles			
Ti–C(21)–C(25)	129.6(1)	C(12)–C(11)–C(15)	108.0(2)
Ti–C(21)–C(22)	126.0(1)	C(11)–C(12)–C(13)	108.3(2)
Ti–C(21)–Mn	134.1(2)	C(12)–C(13)–C(14)	107.2(2)
C(21)–Ti–C(21′) [b]	88.6(2)	C(13)–C(14)–C(15)	108.4(2)
cent.–Ti–cent. [c]	128.1(1)	C(11)–C(15)–C(14)	108.1(2)
C(1)–Mn–C(2)	91.9(2)	C(22)–C(21)–C(25)	103.6(2)
C(2)–Mn–C(3)	92.8(2)	C(21)–C(22)–C(23)	110.6(2)
C(1)–Mn–C(3)	89.9(1)	C(22)–C(23)–C(24)	107.2(2)
Mn–C(1)–O(1)	179.5(2)	C(23)–C(24)–C(25)	108.4(2)
Mn–C(2)–O(2)	178.2(2)	C(21)–C(25)–C(24)	110.2(2)
Mn–C(3)–O(3)	178.5(2)		

[a] The estimated standard deviations are given in parentheses in all tables. [b] The primed atom is generated by the two-fold axis of symmetry at (0, *y*, $\frac{1}{4}$). [c] Cent. denotes the centre of gravity of the η-C_5H_5 group.

As expected, the Ti–C σ bond to the σ-C_5H_5 group in (1) is shorter than that in Ti(C_5H_5)$_4$. However, the difference is slightly larger than that expected (0.77 *vs.* 0.70 Å, for sp^3 *vs.* sp^2 carbon) and may indicate a stronger σ bond in the present case. The difference in C–Ti–C angles [88.6° in (1), 86.3° in Ti(C_5H_5)$_4$] may reflect the different packing of the four rings in the two compounds. All four cyclopentadienyl rings in (1) are accurately planar. Carbon–carbon distances in the η^5 rings are normal [1.391—1.404(3) Å] but are significantly disturbed in the σ ring. Bonds involving the carbon atom C(21) linked to the Ti atom are longest, at 1.441, 1.442(2) Å, the C–C bond directly opposite is shortest, at 1.394(3) Å, and the other two are intermediate at 1.419, 1427(4) Å. This conforms to representation of the electron distribution in the σ ring as either of the two formalisms (I) or (II) with a strengthened (*i.e.* by π-bonding or electrostatic attraction) Ti–C σ bond (see above). The small tilt of the Mn(CO)$_3$ group as evidenced by the spread of Mn–C(C_5H_5)$_4$ distances may have an electronic origin but may also have been influenced by steric factors.



(I)



(II)

Whilst the metal atom does not have any contacts <3.80 Å, the carbonyl carbon atom C(1) makes a contact of 3.39 Å with C(11) and this is probably also responsible for the slight bend of the C(21)–Ti bond out of the plane of the ring (see Table 2).

TABLE 2

Least-squares planes in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates. Deviations (10^3 Å) of relevant atoms are given in square brackets

Plane (1) through C(11)—C(15)

$$11.8752x + 3.4118y - 9.7007z = 0.2511$$

[Ti −2 078, C(11) −1, C(12) −3, C(13) 6, C(14) −7, C(15) 5]

Plane (2) through C(21)—C(25)

$$4.4673x - 4.6822y + 14.1302z = 2.3891$$

[Ti 323, C(21) 4, C(22) −1, C(23) −2, C(24) 5, C(25) −5, Mn −1 775]

Angle between normals to planes (1) and (2) = 96.3°

The geometry of the Mn(CO)$_3$ group seems to be normal with parameters very similar to those in Mn(η-C_5H_5)(CO)$_3$.[8] The linearity of all Mn–C–O units again suggests that the steric crowding is not very great.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College. Hydrogen-1 n.m.r. spectra were obtained using a Perkin-Elmer R-32, i.r. spectra using Perkin-Elmer PE-597. Molecular weights were determined osmometrically using a Perkin-Elmer–Hitachi osmometer.

All solvents were dried over sodium-benzophenone and distilled under N_2 before use. All manipulations were carried out in an N_2 atmosphere using transfer-tubing techniques.

Bis[*σ-tricarbonyl*(*η*^{5}*-cyclopentadienyl*)*manganese*]*-di-η*^{5}*-cyclopentadienyltitanium*(IV).— Tricarbonylcyclopentadienylmanganese (1.0 g, 4.9 mmol) was dissolved in tetrahydrofuran (thf) (27.5 cm^3) and diethyl ether (5.4 cm^3) and cooled to −78 °C. To this solution was added with vigorous stirring a solution of n-butyl-lithium (3.0 cm^3, 4.9 mmol; 1.6 mol dm^{-3}) in hexane and the mixture stirred for 30 to 60 min at −78 °C. Dichlorodicyclopentadienyltitanium (0.6 g, 2.4 mmol) dissolved in thf (30 cm^3) was then added slowly with stirring to the reaction mixture. After 30 min, the solution was allowed to warm slowly to room temperature and stirred for a further 60 min. The volatile materials were removed *in vacuo* and the residues dried. The solid was extracted several times with toluene (5 × 5 cm^3), and the red solution was concentrated and held at

-20 °C for 2 d, giving red-orange crystals. These were washed with light petroleum (b.p. 30—40 °C), dried *in vacuo*, and recrystallised from toluene. Yield: 1.4 g (40%) based on $Ti(\eta\text{-}C_5H_5)_2Cl_2$ (Found: C, 52.7; H, 3.0; *M*, 540. $C_{26}H_{18}Mn_2O_6Ti$ requires C, 53.4; H, 3.1%; *M*, 584). Infrared (cm^{-1}, Nujol) bands at: 2 000vs, 1 934vs, 1 915vs [ν(CO)]; 3 120w, 3 100w, 1 260w, 1 150—1 050m, br, 1 025m, 940w, 915w, 861m, 853m, 839w, 815s, 720w, 662s, 640m, 632s, 543m, 500w, and 490w.

Crystallography.—Crystals suitable for *X*-ray work were mounted under nitrogen in Lindemann capillaries. Preliminary cell data were obtained from photographs. Accurate cell dimensions and intensity data were obtained using a Nonius CAD4 diffractometer in a manner described previously.[9] (The systematic absences *hkl* for $h + k$ odd and *h0l* for *l* odd are consistent with space groups *C*2/*c* or *Cc*, the former being confirmed by structure analysis.)

TABLE 3

Fractional co-ordinates (Ti and Mn × 10^5; others × 10^4) of the non-hydrogen atoms

Atom	*x*	*y*	*z*
Ti	0 *	17 525(5)	25 000 *
Mn	−15 380(2)	−2 122(4)	8 503(1)
C(11)	917(2)	2 517(3)	1 750(1)
C(12)	1 568(1)	1 487(3)	2 187(1)
C(13)	1 813(1)	2 300(3)	2 763(1)
C(14)	1 296(2)	2 819(3)	2 678(1)
C(15)	755(2)	3 957(3)	2 052(1)
C(21)	−557(1)	−201(1)	1 803(1)
C(22)	−1 458(2)	−1 210(2)	1 750(1)
C(23)	−1 485(2)	−2 528(2)	1 312(1)
C(24)	−612(2)	−2 377(3)	1 100(1)
C(25)	−50(2)	−971(3)	1 381(1)
C(1)	−1 473(2)	1 991(3)	802(1)
O(1)	−1 438(2)	3 405(2)	772(1)
C(2)	−2 914(2)	−185(3)	614(1)
O(2)	−3 795(2)	−181(3)	479(1)
C(3)	−1 439(2)	−380(3)	70(1)
O(3)	−1 353(2)	−487(3)	−426(1)

* Parameters held invariant due to space-group symmetry.

Crystal data. $C_{26}H_{18}MnO_6Ti$, $M = 584.2$, Monoclinic, $a = 13.474(2)$, $b = 8.085(1)$, $c = 22.327(3)$ Å, $\beta = 105.08(1)°$, $U = 2\,348.5$ Å^3, space group *C*2/*c*, $D_m = 1.64$ g cm^{-3}, $Z = 4$, $D_c = 1.65$ g cm^{-3}, $F(000) = 1\,176$, μ(Mo-K_α) = 13.5 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å. The crystal used was of dimensions 0.35 × 0.25 × 0.16 mm. A total of 2 856 intensities were measured ($\pm h, kl$; $1.5 < \theta < 27°$; ω—2θ scan) of which 2 140 were considered observed [$F_o > 3\sigma(F_o)$].

The structure was solved by Patterson and electron-density syntheses and refined by least squares to final *R* and *R'* values of 0.032 and 0.035 respectively, with all non-hydrogen atoms assigned anisotropic temperature factors, hydrogen atoms treated isotropically (refined $U_{iso.}$ values of 0.04—0.07 Å^2), and with the weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\,2\,(F_c)^2]$.

Final non-hydrogen atom co-ordinates are given in Table 3. Hydrogen-atom positions, all thermal parameters, and lists of $|F_o|$ and F_c have been deposited as Supplementary Publication No. SUP 22858 (12 pp.).*

Computers, programs, and scattering-factor data were as given in ref. 9.

We thank the S.R.C. for support of this work and the Brazilian Research Council (C.A.P.E.S.) for a studentship (to R. J. D.).

[0/334 *Received, 29th February*, 1980]

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

REFERENCES

[1] A. N. Nesmeyanov, K. I. Grandberg, T. V. Bankova, A. N. Kosina, and E. G. Perevalova, *Izvest. Akad. Nauk. S.S.S.R. Ser. khim.*, 1969, 2032.

[2] V. I. Sokolov, G. Z. Suleimanov, V. V. Bashilov, T. Kh. Kurbanov, I. A. Amiraslavov, and O. A. Reutov, *Izvest. Akad. Nauk. S.S.S.R. Ser. khim.*, 1977, 1895, 2147.

[3] A. N. Nesmeyanov, E. G. Perevalova, L. I. Leont'eva, and E. V. Shumilina, *Izvest. Akad. Nauk. S.S.S.R. Ser. khim.*, 1977, 1156.

[4] A. N. Nesmeyanov, E. G. Perevalova, E. V. Shumilina, and L. I. Leont'eva, *Izvest. Akad. Nauk. S.S.S.R. Ser. khim.*, 1977, 2328.

[5] G. A. Razuvaev, G. A. Domrachev, V. V. Sharutin, and O. N. Suvorova, *J. Organometallic Chem.*, 1977, **41**, 313.

[6] A. N. Nesmeyanov, E. I. Fedin, O. V. Nogina, N. S. Kochetkova, V. A. Dubovinsky, and P. V. Petrovsky, *Tetrahedron Suppl. Part II*, 1966, **8**, 389.

[7] J. L. Calderon, F. A. Cotton, B. G. De Boer, and J. Takats, *J. Amer. Chem. Soc.*, 1971, **93**, 3592.

[8] A. F. Berndt and R. E. Marsh, *Acta Cryst.*, 1963, **16**, 118.

[9] M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1979, **101**, 4128.