

**Synthesis and X-Ray Crystal Structure of the Ring-functionalised  
Bis- $\eta$ -cyclopentadienylmolybdenum Compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{I})_2\text{I}_2]$  and of  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$**

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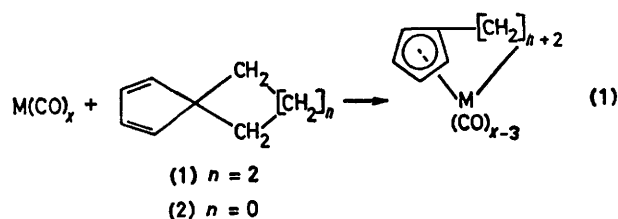
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*Summary* Cocondensation of molybdenum atoms with spiro[4.4]nona-1,3-diene or spiro[2.4]hepta-4,6-diene gives the compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4[\text{CH}_2]_3\text{CH}_2)_2]$  and  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$  respectively and the latter reacts with iodine giving  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{I})_2\text{I}_2]$ ; the structures of  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$  and  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{I})_2\text{I}_2]$  have been determined by X-ray crystallography.

THE study of the bent bis- $\eta$ -cyclopentadienyl derivatives of the transition metals of groups 4–7 has provided an extensive and interesting new chemistry. However, there have been relatively few studies of compounds in this class which have reactive groups attached to the  $\eta$ -cyclopenta-

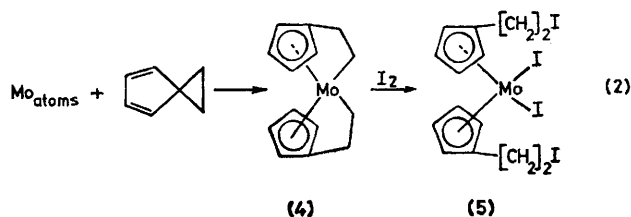
dienyl rings. The main reason for this lies in the problem of synthesising such compounds. Most synthetic routes to the parent bis- $\eta$ -cyclopentadienyl metal compounds occur under conditions where the presence of a functional group would be expected to disrupt the synthetic reaction. We have been seeking synthetic routes towards ring-functionalised, bent bis- $\eta$ -cyclopentadienyl transition metal compounds because they would enable the synthesis and study of many potentially interesting new compounds.

The migration of *endo*-alkyl groups of *endo*-alkylcyclopentadiene derivatives of transition metals has been demonstrated for the compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\eta\text{-endo-EtC}_5\text{H}_4)(\text{PMe}_2\text{Ph})\text{Cl}]$ ,<sup>1</sup> and alkyl migration may be inferred to be a key step in the formation of  $\sigma$ -alkyl- $\eta$ -cyclopentadienyl transition metal compounds in the reaction between spirodienes and transition metal carbonyls [*i.e.* reaction (1)].<sup>2</sup>



Eilbracht has shown reaction (1) to be quite general for spiro[4.4]nona-1,3-diene (1) and spiro[2.4]hepta-4,6-diene (2), using a variety of metal carbonyls.<sup>2</sup> Cocondensation of iron atoms with (2) gives rise to substituted ferrocene derivatives.<sup>3</sup>

We were interested in preparing bent bis- $\eta$ -cyclopentadienyl transition metal compounds which had functional groups on the cyclopentadienyl ring. Accordingly, the synthesis shown in equation (2) was proposed. Cocondensation of (1) and (2) with molybdenum atoms gave, after chromatography, the compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4[\text{CH}_2]_3\text{CH}_2)_2]$  (3) and  $\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2$  (4), respectively. In a typical experiment 2–3 g of molybdenum atoms were condensed at 77 K with *ca.* 50 cm<sup>3</sup> of (1) or (2), giving the compounds (3) or (4) in 15–25% yield. Compounds (3) and (4) form yellow-orange, air-sensitive crystals; they are volatile and may be sublimed *in vacuo* at *ca.* 110 °C. Treatment of (4) with iodine caused immediate reaction, giving a deep green compound (5).



The crystal structures of (4) and (5) were determined. The latter complex was shown to be  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{-I})_2\text{I}_2]$ , a result in agreement with microanalytical and <sup>1</sup>H n.m.r. data. <sup>1</sup>H n.m.r. of (4), ( $\text{C}_6\text{D}_6$ ),  $\delta$ : 4.71 [2H, m (6 lines)], 4.41 [2H, m (6 lines)], 4.07 [2H, m (6 lines)], and 3.88 [2H, m (4 lines)] (2  $\eta\text{-C}_5\text{H}_4$ ); 2.81 [2H, m (8 lines)], 2.52 [2H, m (8 lines)] (2 C-H<sub>2</sub>); -0.37 [2H, m (8 lines)], and -1.42 [2H, m (8 lines)] (2 CH<sub>2</sub>-Mo); <sup>1</sup>H n.m.r. of (5), ( $\text{C}_6\text{D}_5\text{CD}_3$ ),  $\delta$ : 5.49 (8H, s br, 2  $\eta\text{-C}_5\text{H}_4$ ), 3.48 [4H, t ( $J$  7 Hz), 2 C-CH<sub>2</sub>], and 2.91 [4H, t ( $J$  7 Hz), 2 CH<sub>2</sub>I].

*Crystal data* for (4):  $\text{C}_{14}\text{H}_{16}\text{Mo}$ ,  $M$  280.2, monoclinic, space group  $P2_1/a$ ,  $a = 12.259(2)$ ,  $b = 6.372(6)$ ,  $c = 17.550(3)$  Å,  $\beta = 126.62(2)^\circ$ ,  $U = 1100$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.69$  g cm<sup>-3</sup>, 2631 independent reflections with  $I > 3\sigma(I)$ . *Crystal data* for (5):  $\text{C}_{14}\text{H}_{16}\text{I}_4\text{Mo}$ ,  $M$  787.8, monoclinic, space group  $C2/c$ ,  $a = 22.260(3)$ ,  $b = 7.165(7)$ ,  $c = 13.155(4)$  Å,  $\beta = 118.03(8)^\circ$ ,  $U = 1852$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.86$  g cm<sup>-3</sup>, 1883 reflections with  $I > 3\sigma(I)$ , corrected for absorption,  $\mu = 74$  cm<sup>-1</sup>.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

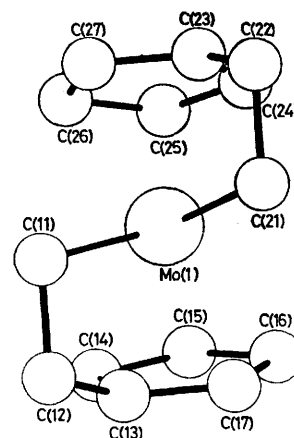


FIGURE 1. Generalized view of the molecule (4) obtained from crystallographic atomic co-ordinates.

The reflections were measured by four-circle diffractometry using Mo- $K_\alpha$  radiation ( $\lambda = 0.71069$  Å). The structures were solved by Patterson and Fourier methods and refined by large-block least-squares to current  $R$ -values of 0.034 for (4) and 0.048 for (5).†

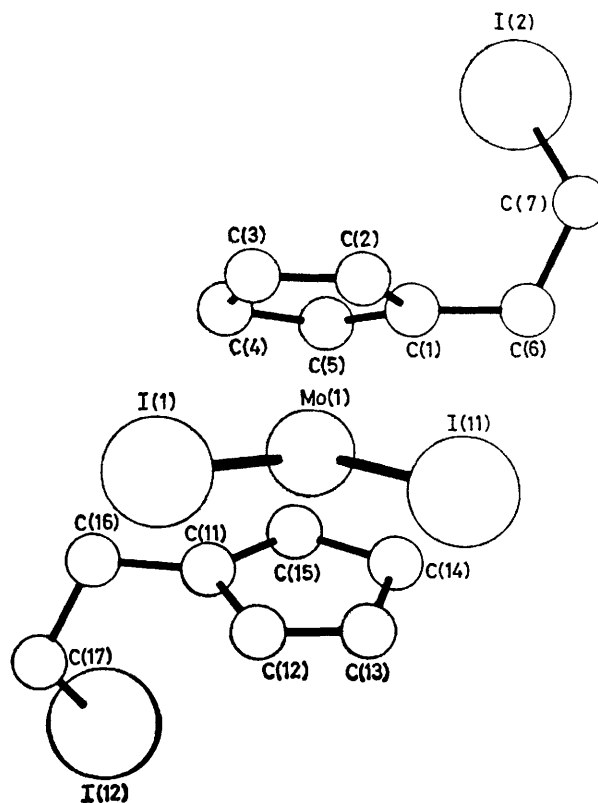


FIGURE 2. Generalized view of the molecule (5) obtained from crystallographic atomic co-ordinates. The atoms labelled  $n$  and  $n + 10$  are related by a crystallographic two-fold axis.

The unit cell of (5) contains four molecules (Figure 2), each with a crystallographic two-fold axis. The cyclopentadienyl ring centroids are at 1.97 Å from the molybdenum atom, the angle between ring normals is 128.1°, the distance Mo-I is 2.849(1) Å and the angle I(1)-Mo-I(11) is 84.91(5)°, all in agreement with the expected values.<sup>4</sup>

In (4) (Figure 1) the molecules are substantially distorted to accommodate the Mo-C  $\sigma$ -bond from the molybdenum atom to the alkyl side chain. In this highly strained system, the angle between the ring normals is increased to 149° and C(12) and C(22) of the side chains are bent 23° away from the planes of the cyclopentadienyl rings towards the metal atom {compare the M-C  $\sigma$ -bonds to the cyclopentadienyl group in the strained complexes di- $\mu$ -( $\sigma$ :1-5- $\eta$ -cyclopentadienyl)-bis[( $\eta$ -cyclopentadienyl)dimolybdenum] (*Mo-Mo*)<sup>5</sup> and niobocene<sup>6</sup>}. In addition the angle between the plane containing Mo(1), C(11), and C(21) and the plane defined by the molybdenum atom and the ring centroids is 77°.

However the Mo(1)-cyclopentadienyl carbon distances are in the range 2.249(1)—2.315(4) Å and the normal to the rings at the molybdenum atom is shorter than in (5) (1.93 Å). The distances Mo-C(11) and Mo-C(21) are respectively 2.271(5) and 2.268(5) Å. The angle C(11)-Mo-C(21) is 82.1(2)°, which is in agreement with the existence of two non-bonding d-electrons.<sup>4</sup>

In conclusion, we have exemplified what may be presumed to be a general synthetic route to ring-functionalised bis- $\eta$ -cyclopentadienyl derivatives.

We thank the Royal Society (A. B. and A. F.) and the S.R.C. (A. G.) for support, the Ramsey Memorial Trust for a fellowship (to F. G. N. C.), and the Petroleum Research Fund administered by the American Chemical Society for partial support.

(Received, 3rd November 1980; Com. 1183.)

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