

Synthesis and characterization of organomolybdenum and organotungsten halides containing the  $\eta^5$ -pentabenzylcyclopentadienyl ligand  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>M(CO)<sub>3</sub>X (M=Mo, W; X=Cl, Br, I). The X-ray molecular structure of  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>Mo(CO)<sub>3</sub>I

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**Abstract**

An improved synthetic procedure for pentabenzylcyclopentadiene Bz<sub>5</sub>C<sub>5</sub>H was developed. Six new organomolybdenum and organotungsten halides  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>M(CO)<sub>3</sub>X (M=Mo, W; X=Cl, Br, I) were synthesized through the reaction of  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>M(CO)<sub>3</sub>Li (derived from Bz<sub>5</sub>C<sub>5</sub>H, n-BuLi and M(CO)<sub>6</sub>) with PCl<sub>3</sub>, PBr<sub>3</sub> or I<sub>2</sub> and characterized by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy. The structure of  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>Mo(CO)<sub>3</sub>I was determined by single-crystal X-ray diffraction techniques. It crystallized in the monoclinic space group *P*2<sub>1</sub>/*c* with cell parameters *a* = 13.294(4), *b* = 15.147(4), *c* = 19.027(3) Å,  $\beta$  = 108.32(2)°, *V* = 3637(2) Å<sup>3</sup>, *Z* = 4 and *D*<sub>x</sub> = 1.50 g cm<sup>-3</sup>. The final *R* value was 0.035 for 4564 observed reflections.

**Keywords:** Crystal structures; Molybdenum complexes; Tungsten complexes; Organic complexes; Cyclopentadienyl complexes

**1. Introduction**

The  $\eta^5$ -pentabenzylcyclopentadienyl derivatives of main group elements and transition metals have received considerable attention during recent years [1–11]. This is mainly due to the special electronic and steric effects of the  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub> ligand, which might make  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub> compounds have unusual structures and properties relative to their  $\eta^5$ -Cp,  $\eta^5$ -Me<sub>5</sub>C<sub>5</sub> and  $\eta^5$ -Ph<sub>5</sub>C<sub>5</sub> analogues [1–17]. However, at present, transition metal compounds of this type are known only for Mn, Re, Fe, Co, Rh and Au [8–11], and no report has yet appeared in the literature concerning Group 6 metal compounds. Herein, we report the synthesis and some properties of the first  $\eta^5$ -pentabenzylcyclopentadienyl derivatives of Group 6 metals  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>M(CO)<sub>3</sub>X (M=Mo, W; X=Cl, Br, I), the X-ray structural analysis of one derivative  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>Mo(CO)<sub>3</sub>I, as well as an improved synthetic route to the parent organic compound pentabenzylcyclopentadiene.

**2. Experimental**

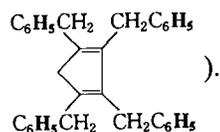
All reactions were carried out under highly purified tank nitrogen. Tetrahydrofuran (THF), diglyme, toluene and hexane were rigorously dried and deoxygenated by distillation from sodium/benzophenone ketyl. Silica gel for column chromatography was about 300–400 mesh. Silica gel for TLC was GF 254 (10–40 μ). Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub> were purchased from Strem Chemicals, Inc. n-BuLi/hexane was prepared and analyzed by published methods [18,19]. PCl<sub>3</sub>, PBr<sub>3</sub> and I<sub>2</sub> were of commercial origin. IR spectra were recorded on a Nicolet FT-IR 5 DX spectrophotometer and the <sup>1</sup>H NMR spectra on a Jeol FX 90Q NMR spectrometer. Elemental analysis and melting point determinations were performed with a Perkin-Elmer model 240C analyzer and a Yanako MP-500 apparatus, respectively.

**2.1. Preparation of Bz<sub>5</sub>C<sub>5</sub>H**

A 1000 ml four-necked flask was fitted with a mechanical stirrer, a nitrogen inlet tube, a ground-glass thermometer and a water collector topped with a reflux

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condenser connected to a mercury-sealed outlet tube. The flask was charged with 300 ml (313.9 g, 2.90 mol) of dried benzyl alcohol and then 23 g (1.00 mol) of sodium chips were gradually added in batches during stirring. The temperature was raised to about 80 °C and hydrogen gas was violently evolved from the outlet tube. **Caution:** the preparation should be carried out in a well-ventilated hood since hydrogen gas is highly inflammable. Stirring continued at 80 °C for 1.5 h until all the sodium was consumed. 7 ml (0.05 mol) of 95% dicyclopentadiene and 300 ml of tetralin were then added. The reaction mixture was refluxed at about 200 °C for 30 h and at this time ~ 8 ml of water remained in the water collector. The viscous liquid/solid mixture formed in the flask was extracted with 500 ml of benzene and the extracts were washed twice with 250 ml portions of distilled water and dried over anhydrous MgSO<sub>4</sub>. MgSO<sub>4</sub> was removed by filtration, benzene removed by atmospheric distillation and tetralin (with unreacted benzyl alcohol) removed by vacuum distillation to leave a yellow viscous oil. To this oil were added 250 ml of anhydrous methanol and the mixture was stirred and refluxed for 15 min, then cooled down to room temperature to give white crystals. The crystals were filtered out, washed with methanol and dried under vacuum for 5 h to give 15.0 g (29%) of Bz<sub>5</sub>C<sub>5</sub>H, which was identified by its m.p. and <sup>1</sup>H NMR spectrum. M.p.: 67–68 °C (lit. [8] 68–70 °C; lit [20] 69.2–75.7 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 3.20–3.81 (m, 11H, 5CH<sub>2</sub>, HC $\square$ ), 6.64–6.84 (m, 5H, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>- $\square$ ), 6.96–7.18 (m, 20H,



## 2.2. Preparation of $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>Mo(CO)<sub>3</sub>X (X = Cl (I), Br (II), I (III))

A 100 ml two-necked flask fitted with a magnetic stir-bar, a serum cap and a reflux condenser was charged with 0.619 g (1.2 mmol) of  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>H and 20 ml of THF. The mixture was stirred and cooled to 0 °C. Then, an equimolar aliquot of n-BuLi/hexane was added and the solution turned deep purple. After 15 min of stirring, 0.31 g (1.2 mmol) of Mo(CO)<sub>6</sub> was added and the reaction mixture was refluxed for about 24 h. The mixture turned yellow-brown and the salt of  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>Mo(CO)<sub>3</sub>Li was formed. To this salt a given amount of PCl<sub>3</sub>, PBr<sub>3</sub> or I<sub>2</sub> was added at room temperature and the mixture turned red immediately [21,22]. The reaction mixture was stirred for about 2 h. The solvent was removed at reduced pressure and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extracts were subjected to column chromatography. A red band was eluted with

50% CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether to give red solids. The red solids were further purified by TLC to give the corresponding products. All samples for C/H analysis, IR and <sup>1</sup>H NMR determinations were recrystallized from 50% CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether.

When 0.2 ml (2.30 mmol) of PCl<sub>3</sub> was added, 0.125 g of I was obtained in 15% yield; m.p. 106–108 °C. *Anal.* Found: C, 70.32; H, 4.98. Calc. for C<sub>43</sub>H<sub>35</sub>ClMoO<sub>3</sub>: C, 70.64; H, 4.82%. IR (KBr disc):  $\nu$ (C≡O), 2040.6(s), 1975.0(vs), 1958.6(s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 3.67 (s, 10H, 5CH<sub>2</sub>), 6.63–7.23 (m, 25H, 5C<sub>6</sub>H<sub>5</sub>).

When 0.14 ml (1.4 mmol) of PBr<sub>3</sub> was added, 0.239 g of II was obtained in 26% yield; m.p. 121–123 °C. *Anal.* Found: C, 66.60; H, 4.54. Calc. for C<sub>43</sub>H<sub>35</sub>BrMoO<sub>3</sub>: C, 66.59; H, 4.55. IR (KBr disc):  $\nu$ (C≡O), 2032.4(s), 1958.6(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 3.75 (s, 10H, 5CH<sub>2</sub>), 6.64–7.31 (m, 25H, 5C<sub>6</sub>H<sub>5</sub>).

When 0.3 g (1.2 mmol) of I<sub>2</sub> was added, 0.184 g of III was obtained in 20% yield; m.p. 110–112 °C. *Anal.* Found: C, 62.93; H, 4.30. Calc. for C<sub>43</sub>H<sub>35</sub>IMoO<sub>3</sub>: C, 62.79; H, 4.29%. IR (KBr disc):  $\nu$ (C≡O), 2024.2(s), 1950.4(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 3.82(s, 10H, 5CH<sub>2</sub>), 6.60–7.22 (m, 25H, 5C<sub>6</sub>H<sub>5</sub>).

## 2.3. Preparation of $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>W(CO)<sub>3</sub>X (X = Cl (IV), Br (V), I (VI))

A 100 ml two-necked flask fitted with a magnetic stir-bar, a serum cap and a reflux condenser, was charged with 2.476 g (4.8 mmol) of  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>H and 20 ml of diglyme. The mixture was stirred and cooled to 0 °C. An equimolar aliquot of n-BuLi/hexane was then added and the solution turned deep purple. After 15 min of stirring, 1.68 g (4.8 mmol) of W(CO)<sub>6</sub> were added and the reaction mixture was heated at ~130 °C for about 22 h. Solvent was removed at reduced pressure and 20 ml of THF were added to give a THF solution of the salt of  $\eta^5$ -Bz<sub>5</sub>C<sub>5</sub>W(CO)<sub>3</sub>Li. To this salt a given amount of PCl<sub>3</sub>, PBr<sub>3</sub> or I<sub>2</sub> was added at room temperature, and the mixture turned red immediately [21,22]. The reaction mixture was stirred for 2 h. The workup was the same as that in the preparation of I–III.

When 0.5 ml (5.73 mmol) of PCl<sub>3</sub> was added, 0.329 g of IV was obtained in 0.9% yield; m.p. 125–126 °C. *Anal.* Found: C, 63.09; H, 4.49. Calc. for C<sub>43</sub>H<sub>35</sub>ClO<sub>3</sub>W: C, 63.06; H, 4.31. IR (KBr disc):  $\nu$ (C≡O), 2032.4(s), 1966.8(vs), 1942.2(s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 3.73 (s, 10H, 5CH<sub>2</sub>), 6.63–7.22 (m, 25H, 5C<sub>6</sub>H<sub>5</sub>).

When 0.8 ml (8.41 mmol) of PBr<sub>3</sub> was added, 0.25 g of V was obtained in 6% yield; m.p. 122–124 °C. *Anal.* Found: C, 59.70; H, 4.19. Calc. for C<sub>43</sub>H<sub>35</sub>BrO<sub>3</sub>W: C, 59.81; H, 4.08. IR (KBr disc):  $\nu$ (C≡O), 2024.2(s), 1950.4(vs), cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 3.79 (s, 10H, 5CH<sub>2</sub>), 6.70–7.27 (m, 25H, 5C<sub>6</sub>H<sub>5</sub>).

When 1.2 g (4.8 mmol) of I<sub>2</sub> were added, 0.31 g of VI was obtained in 7% yield; m.p. 130–131 °C. *Anal.*

Found: C, 56.90; H, 3.78. Calc. for  $C_{43}H_{35}IO_3W$ : C, 56.72; H, 3.87. IR (KBr disc):  $\nu(C\equiv O)$ , 2024.2(s), 1934.0(vs)  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  (ppm)): 3.87 (s, 10H, 5CH<sub>2</sub>), 6.69–7.29 (m, 25H, 5C<sub>6</sub>H<sub>5</sub>).

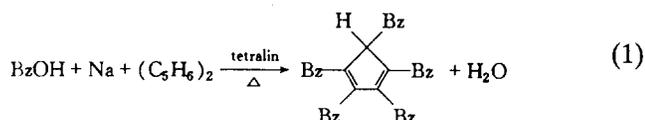
#### 2.4. Single-crystal structural determination of III

Crystals of **III** suitable for X-ray diffraction were obtained by recrystallization from 50%  $CH_2Cl_2$ /petroleum ether in refrigerator. A red crystal measuring  $0.8 \times 0.4 \times 0.2$  mm was mounted on a glass fiber and placed on a Rigaku-AFC 5R diffractometer equipped with a graphite monochromator. A total of 6671 independent reflections was collected at room temperature with Mo  $K\alpha$  ( $\lambda = 0.71069$  Å) radiation by  $\omega$ -2 $\theta$  scan mode and in the range of  $3 \leq 2\theta \leq 50^\circ$ . Of the total reflections 4564 independent reflections with  $I \geq 3\sigma(I)$  were considered to be observed and used in the subsequent refinement. Data were corrected for  $L_p$  factors. The crystal belongs to the monoclinic, space group  $P2_1/c$ , with  $a = 13.294(4)$ ,  $b = 15.147(4)$ ,  $c = 19.027(3)$  Å,  $\beta = 108.32(2)^\circ$ ,  $V = 3637(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.50$  g  $cm^{-3}$ ,  $\mu = 12.28$   $cm^{-1}$ ,  $F(000) = 1648$ .

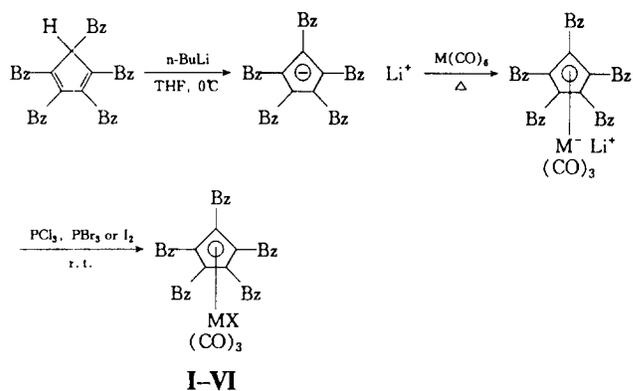
The positions of the molybdenum and iodine atoms were found in an  $E$ -map by direct methods and the remaining non-hydrogen atoms found in the succeeding difference Fourier syntheses. The final refinement by full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms converged to unweighted and weighted agreement factors of 0.035 ( $R$ ) and 0.045 ( $R_w$ ). The highest peak on the final difference Fourier map had a height of  $0.88 e \text{ \AA}^{-3}$ . All calculations were performed on a MICRO-VAX I computer using the TEXSAN system of programs.

### 3. Results and discussion

The synthesis of pentabenzylcyclopentadiene described in this paper is another improved method, following the first modification [8] of the original preparation reported by Hirsch and Bailey [20]. We found that the diisopropylbenzene could be replaced by more easily available tetralin and the treatment of the crude oil product with a given amount of methanol could, without further recrystallization, afford the pure product as white crystals in 29% yield (Eq. (1)).



$\eta^5$ -Pentabenzylcyclopentadienyl molybdenum and tungsten halides  $\eta^5\text{-Bz}_5\text{C}_5\text{M}(\text{CO})_3\text{X}$  (**I–VI**) were prepared from a one-pot reaction including three continuous steps as shown in Scheme 1.



	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>	<b>VI</b>
M	Mo	Mo	Mo	W	W	W
X	Cl	Br	I	Cl	Br	I

Scheme 1.

These new compounds **I–VI** were fully characterized by elemental analysis, IR and  $^1H$  NMR spectroscopy. In their IR spectra there are two or three absorption bands in the range  $1934\text{--}2041$   $cm^{-1}$ , exhibiting the terminal carbonyls present in these molecules. The  $\nu(C\equiv O)$  values decrease in the order: chloride > bromide > iodide for both the molybdenum and tungsten series. This is obviously due to the decreasing electronegativity of the halogens in the same order and in turn the increasing  $\pi$ -backbonding between metal and terminal carbonyls [23]. The  $^1H$  NMR spectrum for each complex **I–VI** is quite simple and a single peak of  $\delta$  3–4 ppm is characteristic of the methylene group. The overall yields for **I–VI** are rather low, particularly for the tungsten compounds **IV–VI**. This is probably due to severe decomposition of  $\eta^5\text{-Bz}_5\text{C}_5\text{Li}$  during its reaction both with  $\text{Mo}(\text{CO})_6$  in refluxing THF and with  $\text{W}(\text{CO})_6$  in diglyme at about  $130^\circ\text{C}$ .

In order to further confirm the structure of **I–VI**, an X-ray single-crystal diffraction analysis of **III** was undertaken. The fractional coordinates and thermal parameters are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. Fig. 1 shows its molecular structure viewed from the direction parallel to the cyclopentadienyl ring.

From Fig. 1 it can be seen that this molecule, if observed by ignoring all the benzyl substituents attached to the cyclopentadienyl ring, is like a four-legged piano-stool. It is interesting to note that four of the phenyls attached to C(10), C(30), C(40) and C(50) of the benzyl substituents are all situated above the cyclopentadienyl ring and away from the molybdenum atom, while one phenyl attached to C(20) of the benzyl group is situated below the cyclopentadienyl ring and approaches the molybdenum atom. This was also observed in the cobalt compound containing the  $\eta^5\text{-Bz}_5\text{C}_5$  ligand [8] and is probably due to the small gap between the two phenyl groups attached to C(10) and C(30), which precludes

Table 1  
Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms of **III**

Atom	x	y	z	$B_{eq}^a$ (Å <sup>2</sup> )
I(1)	0.56459(2)	0.22939(3)	0.63081(2)	5.61(2)
Mo(1)	0.37868(3)	0.15871(2)	0.52621(2)	3.06(1)
O(1)	0.5567(4)	0.1595(3)	0.4491(3)	7.5(2)
O(2)	0.3330(3)	-0.0129(3)	0.4311(2)	6.2(2)
O(3)	0.4459(3)	0.0092(3)	0.6458(2)	6.7(2)
C(1)	0.4923(4)	0.1609(3)	0.4769(3)	5.0(2)
C(2)	0.3487(4)	0.0499(4)	0.4648(3)	4.4(2)
C(3)	0.4257(4)	0.0642(3)	0.6020(3)	4.5(2)
C(01)	0.1975(3)	0.1805(3)	0.4667(2)	3.0(2)
C(02)	0.2480(3)	0.2599(3)	0.4538(2)	3.1(2)
C(03)	0.2991(3)	0.2996(3)	0.5238(2)	3.0(2)
C(04)	0.2762(3)	0.2453(3)	0.5799(2)	2.9(2)
C(05)	0.2130(3)	0.1726(3)	0.5448(2)	3.0(2)
C(10)	0.1239(4)	0.1252(3)	0.4057(3)	4.0(2)
C(11)	0.0141(4)	0.1639(3)	0.3733(2)	3.8(2)
C(12)	-0.0595(5)	0.1169(4)	0.3192(4)	7.0(3)
C(13)	-0.1589(6)	0.1483(7)	0.2874(5)	11.0(5)
C(14)	-0.1894(5)	0.2272(7)	0.3105(5)	9.8(5)
C(15)	-0.1185(5)	0.2760(4)	0.3629(4)	6.3(3)
C(16)	-0.0171(4)	0.2434(3)	0.3940(3)	4.6(2)
C(20)	0.2287(4)	0.2990(4)	0.3771(2)	4.6(2)
C(21)	0.3154(4)	0.3455(4)	0.3582(2)	4.4(2)
C(22)	0.3963(5)	0.2983(4)	0.3456(3)	5.7(3)
C(23)	0.4776(6)	0.3384(7)	0.3263(3)	8.3(4)
C(24)	0.4749(8)	0.4295(8)	0.3190(4)	9.3(5)
C(25)	0.3952(8)	0.4791(6)	0.3296(4)	9.0(4)
C(26)	0.3159(6)	0.4356(4)	0.3494(3)	6.6(3)
C(30)	0.3564(3)	0.3869(3)	0.5375(2)	3.5(2)
C(31)	0.2870(4)	0.4671(3)	0.5160(2)	3.7(2)
C(32)	0.3332(4)	0.5480(3)	0.5085(3)	5.1(2)
C(33)	0.2708(6)	0.6228(4)	0.4864(4)	6.7(3)
C(34)	0.1648(6)	0.6191(4)	0.4720(4)	7.4(3)
C(35)	0.1174(5)	0.5412(4)	0.4784(4)	6.8(3)
C(36)	0.1780(4)	0.4656(3)	0.5008(3)	4.9(2)
C(40)	0.3093(4)	0.2660(3)	0.6615(2)	3.8(2)
C(41)	0.2577(4)	0.3454(3)	0.6826(2)	3.6(2)
C(42)	0.3200(4)	0.4109(4)	0.7262(3)	5.0(2)
C(43)	0.2757(7)	0.4820(4)	0.7492(4)	7.4(4)
C(44)	0.1683(8)	0.4903(4)	0.7297(4)	7.4(4)
C(45)	0.1042(5)	0.4271(5)	0.6866(3)	6.4(3)
C(46)	0.1492(4)	0.3547(3)	0.6631(3)	4.7(2)
C(50)	0.1712(3)	0.0989(3)	0.5821(2)	3.7(2)
C(51)	0.0694(4)	0.1191(3)	0.5986(3)	3.6(2)
C(52)	-0.0273(4)	0.1175(3)	0.5442(3)	4.3(2)
C(53)	-0.1195(4)	0.1372(4)	0.5600(4)	5.4(3)
C(54)	-0.1153(5)	0.1580(4)	0.6311(4)	6.1(3)
C(55)	-0.0191(6)	0.1602(4)	0.6859(4)	6.5(3)
C(56)	0.0720(4)	0.1396(4)	0.6698(3)	5.3(2)

<sup>a</sup> Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:  $(4/3)[a^2 - B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

placement of the phenyl group attached to C(20) above the cyclopentadienyl ring. This reasoning from steric effects is in good agreement with the shortest non-bonding distance of C(11)...C(31) (5.952 Å), compared to the relevant non-bonding distances of C(11)...C(41) (6.38 Å) and C(31)...C(51) (6.441 Å). It should be pointed out that the average bond length

Table 2  
Bond lengths (Å) involving the non-hydrogen atoms of **III**

I(1)-Mo(1)	2.8501(8)	O(1)-C(1)	1.139(6)
Mo(1)-C(2)	1.988(5)	O(2)-C(2)	1.129(6)
Mo(1)-C(3)	1.988(6)	O(3)-C(3)	1.149(6)
Mo(1)-C(1)	2.014(5)	C(01)-C(10)	1.514(6)
Mo(1)-C(01)	2.341(4)	C(02)-C(20)	1.520(6)
Mo(1)-C(04)	2.345(4)	C(02)-C(03)	1.426(6)
Mo(1)-C(05)	2.348(4)	C(03)-C(30)	1.508(6)
Mo(1)-C(03)	2.376(4)	C(04)-C(40)	1.507(6)
Mo(1)-C(02)	2.400(4)	C(05)-C(50)	1.519(6)
C(03)-C(04)	1.453(6)	C(10)-C(11)	1.513(6)
Mo-Cp*	2.0220		

Cp\* = centroid of the substituted cyclopentadienyl ring.

Table 3  
Bond angles (°) involving the non-hydrogen atoms of **III**

C(2)-Mo(1)-C(3)	77.8(2)	C(02)-C(01)-C(10)	123.8(4)
C(2)-Mo(1)-C(1)	77.3(2)	C(05)-C(01)-C(10)	126.4(4)
C(2)-Mo(1)-I(1)	133.8(1)	C(10)-C(01)-Mo(1)	127.7(3)
C(3)-Mo(1)-I(1)	76.0(1)	C(03)-C(02)-C(20)	128.4(4)
C(1)-Mo(1)-I(1)	72.9(2)	C(01)-C(02)-C(20)	123.0(4)
C(02)-C(03)-C(30)	126.7(4)	C(20)-C(02)-Mo(1)	132.3(3)
C(04)-C(03)-C(30)	125.5(4)	C(40)-C(04)-Mo(1)	122.9(3)
C(30)-C(03)-Mo(1)	125.9(3)	C(04)-C(05)-C(01)	107.0(3)
C(05)-C(04)-C(03)	108.8(3)	C(04)-C(05)-C(50)	126.9(4)
C(05)-C(04)-C(40)	125.8(4)	C(01)-C(05)-C(50)	126.0(4)
C(03)-C(04)-C(40)	125.3(4)	C(50)-C(05)-Mo(1)	120.2(3)
O(1)-C(1)-Mo(1)	178.0(5)	C(1)-Mo(1)-Cp*	133.4
O(2)-C(2)-Mo(1)	178.5(5)	C(2)-Mo(1)-Cp*	112.2
O(3)-C(3)-Mo(1)	175.4(5)	C(3)-Mo(1)-Cp*	122.8
		I-Mo(1)-Cp*	114.0

Cp\* = centroid of the substituted cyclopentadienyl ring.

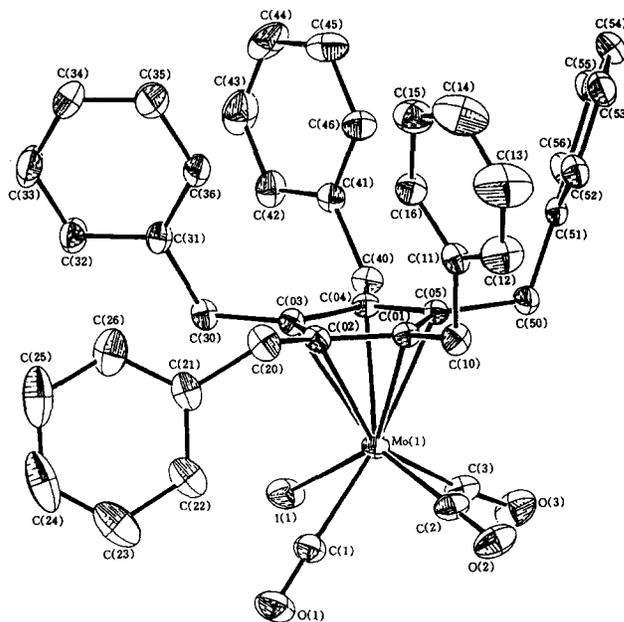


Fig. 1. Structure of  $\eta^5\text{-Bz}_5\text{C}_5\text{Mo}(\text{CO})_3\text{I}$  showing the atom-labeling scheme.

from the molybdenum atom to the five carbon atoms of the pentabenzylcyclopentadienyl ring is 2.362(4) Å, which is slightly larger than the corresponding values in its analogs of  $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$  (2.348 Å) [24] and  $\eta^5\text{-C}_9\text{H}_7\text{Mo}(\text{CO})_3\text{I}$  (2.346 Å) [25]. In addition, the bond length of Mo(1)–C(02) (2.400(4) Å) is the longest of the five bond lengths between the molybdenum atom and the five carbon atoms of the pentabenzylcyclopentadienyl ring; this is possibly caused by the special repulsion between the phenyl group attached to C(20) and the metal fragment of Mo(CO)<sub>3</sub>I.

#### 4. Supplementary material

A complete list of bond lengths and angles, and lists of structure factors are available from the authors.

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