

the significantly shorter Os—N than Os—C bond lengths, the low-temperature <sup>13</sup>C NMR spectrum, and the electron count required for neutral Os atoms under the 18-electron rule. Ignoring the phosphite and nitrosyl substituents, the molecule possesses approximate *mm* symmetry; the P atom lies 0.14 Å from the Os<sub>3</sub> plane and the nitrosyls are approximately equidistant on opposite sides of it. The (OC)<sub>4</sub>Os—Os(CO)<sub>4</sub> distance [2.860 (6) Å] is close to the mean value in Os<sub>3</sub>(CO)<sub>12</sub> [2.877 (3) Å; Churchill & De Boer, 1977] but the other two Os—Os bonds are appreciably shorter. Although the molecular symmetry does not require the Os—N bonds to be equal, the apparent discrepancy is probably simply a reflexion of the relatively large uncertainties, since almost identical *R* indices (*R* 0.0615, *R'* 0.0620) were obtained in a separate refinement in which both Os—N, and both N—O, distances were constrained to be equal.

We thank Dr C. Zuccaro for providing the crystals, the Universidad de Los Andes for a Fellowship to AVR, and the SRC for the diffractometer. Calculations were performed on the Cambridge University IBM 370/165 computer with programs written by GMS.

#### References

- BHADURI, S., JOHNSON, B. F. G., LEWIS, J., WATSON, D. J. & ZUCCARO, C. (1977). *J. Chem. Soc. Chem. Commun.* pp. 477–478.  
 BHADURI, S., JOHNSON, B. F. G., LEWIS, J., WATSON, D. J. & ZUCCARO, C. (1978). *J. Chem. Soc. Dalton Trans.* In the press.  
 CHURCHILL, M. R. & DE BOER, B. G. (1977). *Inorg. Chem.* **16**, 878–884.

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### Tricarbonyl{3-4:6-7-η-(2-isopropylthio-8-benzoylbicyclo[3.2.1]octadiene)}iron

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**Abstract.** C<sub>21</sub>H<sub>20</sub>FeO<sub>4</sub>S, triclinic, *P* $\bar{1}$ , *a* = 9.437 (6), *b* = 10.249 (5), *c* = 11.545 (6) Å,  $\alpha$  = 84.67 (5),  $\beta$  = 71.44 (4),  $\gamma$  = 67.54 (5)°, *U* = 977.7 Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.441 g cm<sup>-3</sup>,  $\mu$ (Mo *K*α) = 8.39 cm<sup>-1</sup>. The structure was solved by direct methods and refined to an *R* of 0.030 for 2045 diffractometer data. The bicyclo[3.2.1]octadiene ligand has *M-exo* stereochemistry at C(2), and coordinates the Fe atom *via* two π-alkene bonds.

**Introduction.** Yellow crystals of the title compound were obtained from the reaction of the {2-4:6-7-η-(8-benzoylbicyclo[3.2.1]octadienylum)}tricarbonyliron cation with the nucleophile 2-propanethiol by Charles (1977). The crystal structure has been determined in order to establish the orientation of the substituents on the bicyclic diene.

2539 intensities were measured on a Syntex P<sub>2</sub>, four-circle diffractometer with graphite-monochromated Mo *K*α radiation. After application of Lp but not absorption corrections, equivalent reflexions were averaged to give 2045 unique reflexions with *F* > 4σ(*F*) based on counting statistics. Unit-cell dimensions were determined from the diffractometer angles of 15 reflexions. The Fe and S atoms were located by multi-

Table 1. *Atom coordinates* (× 10<sup>4</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>
Fe	7948 (1)	3545 (1)	3441 (1)
S	11501 (1)	-1181 (1)	2754 (1)
O(9)	12279 (3)	2965 (2)	-562 (2)
C(1)	10218 (3)	1253 (3)	1456 (2)
C(2)	9950 (3)	561 (3)	2698 (2)
C(3)	9857 (3)	1579 (3)	3620 (2)
C(4)	10507 (3)	2603 (3)	3278 (2)
C(5)	11078 (3)	2935 (3)	1945 (2)
C(6)	9491 (3)	3737 (3)	1720 (2)
C(7)	8891 (3)	2725 (3)	1589 (2)
C(8)	11768 (3)	1591 (2)	1172 (2)
C(9)	12496 (3)	1797 (3)	-171 (3)
C(10)	13486 (3)	515 (3)	-1005 (2)
C(11)	14213 (4)	709 (3)	-2230 (3)
C(12)	15119 (4)	-442 (4)	-3028 (3)
C(13)	15324 (4)	-1779 (4)	-2627 (3)
C(14)	14644 (4)	-1976 (3)	-1424 (3)
C(15)	13720 (3)	-839 (3)	-603 (3)
C(16)	10764 (5)	-2286 (3)	2116 (3)
C(17)	9425 (6)	-2587 (4)	3070 (5)
C(18)	12167 (6)	-3625 (4)	1564 (4)
C(19)	6725 (4)	2607 (3)	4330 (3)
O(19)	5914 (3)	2054 (3)	4929 (2)
C(20)	7842 (4)	4688 (3)	4563 (3)
O(20)	7764 (3)	5415 (3)	5293 (2)
C(21)	6344 (4)	4874 (4)	3031 (3)
O(21)	5318 (3)	5696 (3)	2746 (3)

Table 2. Hydrogen atom coordinates ( $\times 10^3$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(1)	1023 (3)	70 (2)	84 (2)	37 (6)
H(2)	893 (3)	43 (2)	290 (2)	36 (6)
H(3)	970 (3)	134 (3)	436 (2)	53 (6)
H(4)	1078 (3)	291 (2)	387 (2)	42 (6)
H(5)	1175 (3)	339 (2)	175 (2)	43 (6)
H(6)	923 (3)	458 (3)	137 (2)	53 (6)
H(7)	819 (3)	285 (3)	118 (2)	51 (6)
H(8)	1249 (3)	97 (2)	142 (2)	33 (5)
H(11)	1396 (4)	163 (3)	-249 (3)	92 (8)
H(12)	1565 (4)	-28 (3)	-383 (3)	71 (7)
H(13)	1599 (3)	-263 (3)	-317 (3)	70 (7)
H(14)	1477 (3)	-273 (2)	-117 (2)	28 (5)
H(15)	1331 (3)	-100 (3)	12 (2)	45 (6)
H(16)	1042 (3)	-173 (3)	146 (3)	70 (7)
H(171)	845 (4)	-165 (3)	353 (3)	71 (7)
H(172)	902 (5)	-294 (4)	273 (4)	130 (9)
H(173)	986 (4)	-317 (3)	367 (3)	93 (8)
H(181)	1258 (5)	-427 (4)	235 (4)	121 (9)
H(182)	1191 (4)	-423 (3)	121 (3)	80 (8)
H(183)	1295 (4)	-351 (3)	111 (3)	88 (8)

solution  $\sum_2$  sign expansion, and the C, O and H atoms from difference syntheses. The structure was refined by a blocked-cascade\* least-squares method, with isotropic H atoms and the remaining atoms anisotropic to an *R* of 0.030 and  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.033$ . Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974); the weighting scheme employed was  $w = [\sigma^2(F) + 0.00189F^2]^{-1}$ . Positional and H thermal parameters are given in Tables 1 and 2, and the derived interatomic distances and angles in Tables 3 and 4.†

**Discussion.** The molecular structure (Fig. 1) confirms the *M-exo* stereochemistry at C(2) predicted by Charles, Diversi, Johnson, Karlin, Lewis, Rivera & Sheldrick (1977). There is a  $\pi$ -alkene interaction between the two isolated double bonds of the bicyclic diene and the Fe atom. The Fe–C(6) and Fe–C(7) distances [2.100 (4) and 2.150 (5) Å] are appreciably shorter than the corresponding distances in the {2-4 : 6-7- $\eta$ -(8-acetylbicyclo[3.2.1]octadienyl)tricarboxyl-iron cation [2.230 (8) and 2.226 (9) Å; Rivera & Sheldrick, 1978], with a concomitant lengthening of the C(6)–C(7) bond [1.397 (6) compared with 1.349 (12)

\* In this procedure full-matrix blocks of about 55 parameters are selected automatically. The parameter shifts from one block are applied before the derivatives used in the next block are calculated. Since partial structure factors are saved it is only necessary to recalculate contributions from atoms which are refined in the present or previous block, which makes the method computationally highly efficient.

† Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33704 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å)

Fe–C(3)	2.176 (4)	Fe–C(4)	2.182 (5)
Fe–C(6)	2.100 (4)	Fe–C(7)	2.150 (5)
Fe–C(19)	1.794 (6)	Fe–C(20)	1.781 (6)
Fe–C(21)	1.769 (5)	S–C(2)	1.838 (4)
S–C(16)	1.842 (7)	O(9)–C(9)	1.205 (4)
C(1)–C(2)	1.530 (5)	C(1)–C(7)	1.532 (5)
C(1)–C(8)	1.559 (6)	C(2)–C(3)	1.518 (6)
C(3)–C(4)	1.376 (5)	C(4)–C(5)	1.514 (6)
C(5)–C(6)	1.501 (6)	C(5)–C(8)	1.513 (6)
C(6)–C(7)	1.397 (6)	C(8)–C(9)	1.514 (6)
C(9)–O(9)	1.205 (4)	C(9)–C(10)	1.500 (4)
C(10)–C(11)	1.395 (5)	C(11)–C(12)	1.379 (5)
C(12)–C(13)	1.366 (6)	C(13)–C(14)	1.364 (6)
C(14)–C(15)	1.386 (5)	C(15)–C(10)	1.378 (5)
C(16)–C(17)	1.501 (8)	C(16)–C(18)	1.510 (6)
C(19)–O(19)	1.143 (6)	C(20)–O(20)	1.143 (6)
C(21)–O(21)	1.133 (5)		

Table 4. Bond angles (°)

C(3)–Fe–C(4)	36.8 (1)	C(3)–Fe–C(6)	88.0 (2)
C(4)–Fe–C(6)	65.4 (2)	C(3)–Fe–C(7)	80.1 (2)
C(4)–Fe–C(7)	80.6 (2)	C(6)–Fe–C(7)	38.4 (1)
C(3)–Fe–C(19)	81.2 (2)	C(4)–Fe–C(19)	116.2 (2)
C(6)–Fe–C(19)	146.2 (1)	C(7)–Fe–C(19)	107.9 (2)
C(3)–Fe–C(20)	103.0 (2)	C(4)–Fe–C(20)	84.6 (2)
C(6)–Fe–C(20)	111.5 (2)	C(7)–Fe–C(20)	149.9 (1)
C(19)–Fe–C(20)	102.2 (3)	C(3)–Fe–C(21)	165.2 (2)
C(4)–Fe–C(21)	149.3 (1)	C(6)–Fe–C(21)	88.1 (2)
C(7)–Fe–C(21)	88.0 (2)	C(19)–Fe–C(21)	94.4 (3)
C(20)–Fe–C(21)	91.7 (3)	C(2)–S–C(16)	99.4 (3)
C(2)–C(1)–C(7)	108.3 (3)	C(2)–C(1)–C(8)	108.4 (3)
C(7)–C(1)–C(8)	102.6 (3)	S–C(2)–C(1)	114.9 (2)
S–C(2)–C(3)	110.0 (3)	C(1)–C(2)–C(3)	106.9 (3)
Fe–C(3)–C(2)	104.5 (3)	Fe–C(3)–C(4)	71.9 (2)
C(2)–C(3)–C(4)	122.3 (3)	Fe–C(4)–C(3)	71.3 (3)
Fe–C(4)–C(5)	95.1 (3)	C(3)–C(4)–C(5)	120.6 (4)
C(4)–C(5)–C(6)	100.4 (3)	C(4)–C(5)–C(8)	109.2 (3)
C(6)–C(5)–C(8)	104.0 (4)	Fe–C(6)–C(5)	98.9 (3)
Fe–C(6)–C(7)	72.7 (2)	C(5)–C(6)–C(7)	106.1 (3)
Fe–C(7)–C(1)	111.6 (3)	Fe–C(7)–C(6)	68.9 (2)
C(1)–C(7)–C(6)	109.5 (3)	C(1)–C(8)–C(5)	99.4 (3)
C(1)–C(8)–C(9)	113.6 (4)	C(5)–C(8)–C(9)	113.0 (3)
O(9)–C(9)–C(8)	120.7 (3)	O(9)–C(9)–C(10)	120.7 (3)
C(8)–C(9)–C(10)	118.6 (3)	C(9)–C(10)–C(11)	118.3 (3)
C(9)–C(10)–C(15)	122.6 (3)	C(11)–C(10)–C(15)	119.1 (3)
C(10)–C(11)–C(12)	120.0 (4)	C(11)–C(12)–C(13)	120.5 (4)
C(12)–C(13)–C(14)	119.7 (4)	C(13)–C(14)–C(15)	121.0 (4)
C(10)–C(15)–C(14)	119.6 (4)	S–C(16)–C(17)	111.3 (4)
S–C(16)–C(18)	108.6 (5)	C(17)–C(16)–C(18)	111.9 (4)
Fe–C(19)–O(19)	177.3 (3)	Fe–C(20)–O(20)	179.2 (3)
Fe–C(21)–O(21)	177.9 (4)		

Å]. This is consistent with a more effective back-donation of Fe *d* electrons into the alkene antibonding  $\pi$ -orbital when the effective charge on the Fe atom is lower. The plane through O(9), C(9) and C(8) is almost parallel (the interplanar angle is 2.5°) to the plane of the phenyl ring, and the C(5)–C(8)–C(9)–O(9) dihedral angle is -11.3°. The two C–S bonds are equal (mean 1.840 Å) and relatively long for S–C(*sp*<sup>3</sup>)

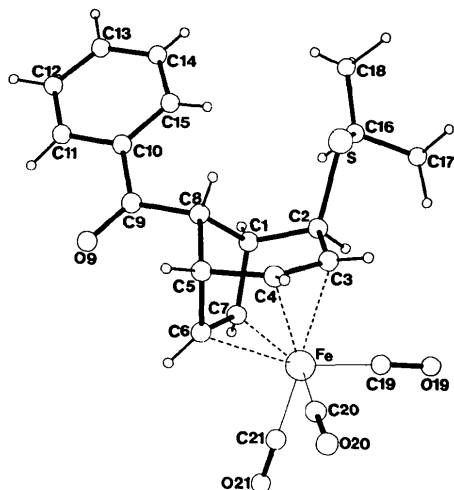


Fig. 1. Perspective view of the molecule, showing the labelling scheme.

bonds, *cf.* 1.81 (1) and 1.80 (1) Å in thiodilactic acid (Martuscelli, Mazzarella & Zagari, 1973) and 1.80 (1) Å in thiodiglycollic acid (Sukla, 1967).

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## Bis(triphenylphosphine)iminium Pentadecacarbonyliodopentaosmate

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**Abstract.**  $C_{51}H_{30}INO_{15}Os_5P_2$ , monoclinic,  $P2_1/c$ ,  $a = 18.176$  (7),  $b = 18.540$  (7),  $c = 17.317$  (7) Å,  $\beta = 106.93$  (8)°,  $U = 5583$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.423$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 115.5$  cm<sup>-1</sup>. The structure was refined to an  $R$  of 0.040 for 3500 unique diffractometer data. The anion geometry may be derived from that of  $Os_5(\text{CO})_{16}$  by replacing one carbonyl of the equatorial  $Os(\text{CO})_4$  group by iodide, and shows a similar pattern of Os–C(O)···Os incipient bridge bonds.

**Introduction.** Purple crystals of  $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{IOs}_5(\text{CO})_{15}]^-$  were prepared by Eady & Malatesta (1977). 11 586 data were measured on a Nonius CAD-4 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation and a crystal  $0.06 \times 0.13 \times 0.20$  mm.  $L_p$  and numerical absorption corrections were applied, and equivalent reflexions averaged to give 3500 unique

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### References

- CHARLES, A. D. (1977). Personal communication.  
 CHARLES, A. D., DIVERSI, P., JOHNSON, B. F. G., KARLIN, K., LEWIS, J., RIVERA, A. V. & SHELDRIK, G. M. (1977). *J. Organomet. Chem.* **128**, C31–C34.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 MARTUSCELLI, E., MAZZARELLA, L. & ZAGARI, A. (1973). *Gazz. Chim. Ital.* **103**, 563–567.  
 RIVERA, A. V. & SHELDRIK, G. M. (1978). *Acta Cryst.* **B34**, 1716–1718.  
 SUKLA, P. (1967). *Acta Cryst.* **23**, 491–494.

reflexions with  $F > 6\sigma(F)$  based on counting statistics. Os and I atoms were located by multisolution  $\sum_2$  sign expansion, and P, C, N and O from successive difference syntheses. The structure was refined by blocked-cascade least squares (Rivera & Sheldrick, 1978) with anisotropic Os, I and P, complex neutral-atom scattering factors and weights  $w = 1/\sigma^2(F)$  to  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.033$  and  $R = 0.040$ . H atoms were not included. Final atomic coordinates and thermal parameters are given in Table 1, with bond lengths and angles in Tables 2, 3 and 4.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33705 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.