Journal of Organometallic Chemistry, 102 (1975) 345—351

SYNTHESIS AND STRUCTURE PROOF OF A NEW RING SYSTEM FROM THE REACTION OF DIIRONNONACARBONYL AND NAPHTHO[*b*]-CYCLOPROPENE

F.A. COTTON* and J.M. TROUP

Department of Chemistry, Texas A & M University, College Station, Texas 77843 (U.S.A.)

W.E. BILLUPS*, L.P. LIN and C.V. SMITH

Department of Chemistry, Rice University, Houston, Texas 77001 (U.S.A.)

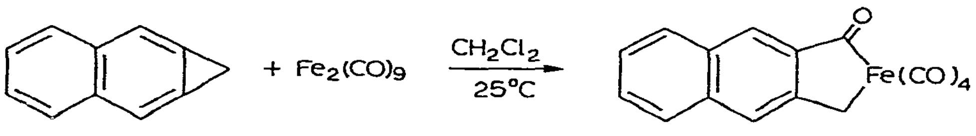
(Received January 28th, 1975)

Summary

The reaction of naphtho[*b*]cyclopropene with $Fe_2(CO)_9$ in CH_2Cl_2 at 25°C yields a yellow crystalline product, I, in 27% yield. The identity and structure of I were ascertained by spectroscopic, and especially X-ray crystallographic means. The product can be formally regarded as resulting from the addition of an Fe—C bond of $Fe(CO)_5$ across one edge of the three-membered ring of naphtho[*b*]-cyclopropene. Thus, the iron atom is coordinated in a distorted octahedral fashion by four CO groups, the carbon atom of a carbonyl group at the 2 position of naphthalene and the carbon atom of a methylene group at the 3 position of naphthalene. The product, $(C_{12}H_8O)Fe(CO)_4$, crystallizes in space group $P2_1/n$. The unit cell contains four molecules and has the dimensions $a = 9.446(3)$, $b = 6.383(2)$, $c = 23.464(4)$ Å, $\beta = 91.58(2)°$. Using a total of 1731 reflections for which $|F_0|^2$ exceeded 3 times the standard deviation of $|F_0|^2$ the structure was solved and refined to convergence using anisotropic temperature factors for all atoms to give discrepency indices of $R_1 = 0.064$ and $R_2 = 0.081$. The C—C distances in the naphthalene moiety agree very well with known values for naphthalene itself. The four Fe—CO distances are 1.815, 1.823, 1.831 and 1.844 Å, the Fe—CH_2 distance is 2.112(7) Å and the Fe—C(O) ring distance is 2.035(5) Å.

Introduction

The reactions of the iron carbonyls with strained ring systems has already been the subject of much study [1,2]. We report here the synthesis and structure of the novel product I, a compound of considerable intrinsic interest, which results from the reaction of $Fe_2(CO)_9$ with naphtho[*b*]cyclopropene (II) [3].



(II) (I)

Experimental

General. All melting points are uncorrected. Infrared spectra were recorded on a Beckman IR8 spectrometer as KBr plates. Proton magnetic resonance spectra were obtained with a Perkin—Elmer R-12 spectrometer in CCl_4 or $DCCl_3$ solution and results are expressed in parts per million downfield from internal TMS. Mass spectra were obtained with a double focusing C.E.C. 21-110B mass spectrometer.

Tetrahydrofuran was distilled from sodium-benzophenone ketyl immediately before use. Benzene was distilled from sodium wire and stored over 4A molecular sieves.

Synthesis of naphtho[b]cyclopropene (II). In a 1 l three necked flask equipped with a mechanical stirrer and nitrogen purging system was prepared a suspension of KO-t-Bu(112.2 g; 1 mol) in 400 ml of THF. 7,7-Dichloro-3,4-benzobicyclo[4.1.0]hept-3-ene [3] (26.7 g; 0.125 mol) was then added at 20-25°C over a 30 min period and the mixture stirred for an additional 17.5 h. Water was added and the aqueous layer was extracted with pentane. The combined organic layers were dried over Na_2SO_4 and the solvent removed in vacuo. The product [3] was then passed through a column of florisil (100-200 mesh) with pentane eluant. The product (11.4 g, 65% yield) was obtained as a white solid, m.p. 86-87°C.

Reaction of naphtho[b]cyclopropane with $Fe_2(CO)_9$. A mixture of naphtho[*b*]cyclopropane (0.70 g; 0.005 mol) and $Fe_2(CO)_9$ (3.64 g; 0.01 mol) in 250 ml of degassed benzene was stirred under N_2 at ambient temperature for 4 h, filtered through silica gel and washed with $CHCl_3$. The solvent was then removed under reduced pressure and the resulting material dissolved in CH_2Cl_2 and purified by thin-layer chromatography on silica gel (benzene eluent) giving 0.46 g (27%) of I, m.p. $> \sim 140°$ dec., and traces of the diketone V. Other products were detected but attempts to isolate them in pure form were unsuccessful.

X-ray crystallography. The general procedures, equipment and computer programs have been described elsewhere [4]. A needle crystal 0.35 × 0.15 × 0.17 mm was mounted in a glass capillary. The space group was established from systematic absences as $P2_1/n$. The unit cell dimensions were found to be a = 9.446(3), b = 6.382(2), c = 23.464(4) Å, β = 91.58(2)°; V = 1414.0(8) Å^3.

Only those 1731 reflections for which $|F_0|^2 > 3\sigma|F_0^2|$ were used to refine the structure anisotropically to final discrepancy indices of R_1 = 0.064 and R_2 = 0.081. A table of observed and calculated structure factors is available from the authors on request.

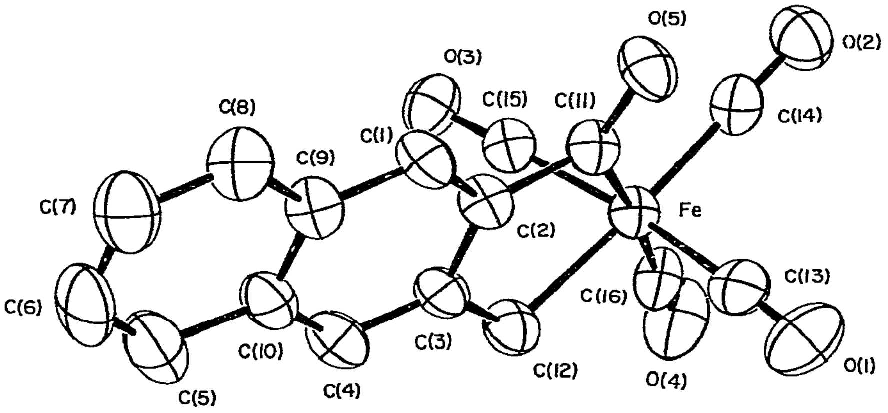


Fig. 1. An ORTEP drawing of the structure. The atoms of the $C_{12}H_8O$ group are numbered in accord with standard chemical nomenclature. Each atom is represented by its thermal vibration ellipsoid drawn to enclose 50% of the electron density.

Results

The elemental composition of I was shown by high resolution mass spectroscopy. The parent ion $C_{11}H_8Fe(CO)_5^+$ is seen at *m/e* 335.9731 (calc. 335.9719) and other major fragments were $C_{11}H_8Fe(CO)_4^+$ at *m/e* 308, $C_{11}H_8Fe(CO)_3^+$ at *m/e* 280, $C_{11}H_8Fe(CO)_2^+$ at *m/e* 252, $C_{11}H_8Fe(CO)^+$ at *m/e* 224 and $C_{11}H_8Fe^+$ at *m/e* 196 (base peak). The IR (KBr) spectrum showed terminal carbonyl absorp-

TABLE 1

FRACTIONAL COORDINATES FOR NON-HYDROGEN ATOMS

Atom	*x*	*y*	*z*
Fe	0.2231(1)	0.2404(1)	0.4452(1)
O(1)	0.4879(5)	0.0226(9)	0.4202(2)
O(2)	0.2030(5)	0.0551(9)	0.5605(2)
O(3)	−0.0673(5)	0.4081(7)	0.4366(2)
O(4)	0.3701(5)	0.6306(8)	0.4833(3)
O(5)	0.1061(5)	−0.1796(7)	0.4358(2)
C(1)	0.0076(7)	−0.1310(10)	0.3189(3)
C(2)	0.0904(6)	0.0098(9)	0.3487(2)
C(3)	0.1355(6)	0.2001(9)	0.3234(2)
C(4)	0.0904(7)	0.2416(11)	0.2683(3)
C(5)	−0.0494(10)	0.1464(16)	0.1812(3)
C(6)	−0.1356(9)	0.0094(16)	0.1524(3)
C(7)	−0.1742(9)	−0.1815(15)	0.1771(3)
C(8)	−0.1281(8)	−0.2268(12)	0.2310(3)
C(9)	−0.0387(6)	−0.0909(10)	0.2628(3)
C(10)	0.0026(7)	0.1048(11)	0.2371(2)
C(11)	0.1296(6)	−0.0183(8)	0.4102(2)
C(12)	0.2269(8)	0.3422(11)	0.3596(3)
C(13)	0.3866(7)	0.1036(11)	0.4304(3)
C(14)	0.2098(6)	0.1290(10)	0.5168(3)
C(15)	0.0442(7)	0.3476(9)	0.4414(3)
C(16)	0.3113(6)	0.4849(11)	0.4684(3)

TABLE 2

ANISOTROPIC THERMAL PARAMETERS[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	96(1)	146(2)	15(1)	6(1)	—4(1)	—4(1)
O(1)	122(6)	357(18)	34(1)	43(1)	10(2)	—24(4)
O(2)	165(7)	418(19)	17(1)	37(10)	—1(2)	13(4)
O(3)	109(6)	219(12)	26(1)	27(7)	—6(2)	—9(3)
O(4)	171(8)	202(14)	44(2)	—21(9)	—31(3)	—18(4)
O(5)	155(6)	155(11)	17(1)	—10(7)	—11(2)	9(3)
C(1)	135(9)	172(17)	14(1)	—1(10)	—2(3)	6(4)
C(2)	109(7)	146(14)	13(1)	—1(9)	—3(2)	—4(3)
C(3)	110(7)	159(15)	14(1)	—2(8)	0(2)	4(3)
C(4)	151(9)	192(18)	16(1)	4(12)	3(3)	10(4)
C(5)	190(13)	379(31)	17(1)	46(16)	—2(3)	16(6)
C(6)	185(12)	516(35)	12(1)	56(17)	—15(3)	—16(6)
C(7)	178(11)	367(26)	18(2)	15(15)	—16(3)	—20(5)
C(8)	139(9)	234(22)	20(1)	12(11)	—7(3)	—13(5)
C(9)	118(8)	196(16)	14(1)	21(9)	—3(2)	—7(4)
C(10)	130(8)	251(18)	12(1)	22(10)	1(3)	1(4)
C(11)	99(7)	119(14)	16(1)	9(8)	—4(2)	—4(3)
C(12)	124(9)	191(18)	18(1)	—21(11)	—6(3)	8(4)
C(13)	108(8)	234(18)	18(1)	—21(10)	—3(3)	—7(4)
C(14)	—104(8)	238(19)	16(1)	32(10)	—5(3)	—6(4)
C(15)	109(8)	153(15)	15(1)	—9(9)	—6(2)	—7(4)
C(16)	106(8)	219(18)	23(2)	19(10)	—17(3)	—5(4)

[a] The anisotropic temperature parameters are of the form $10^{-4}\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

tions at 2115, 2070 and 2020 cm^{-1} and a keto or bridging C=O at 1618 cm^{-1} The proton NMR spectrum exhibits signals at δ 3.57 (2H, —CH$_2$—) and 7.25-8.28 (6H, aromatic) ppm.

Complete and unequivocal structural characterization of I was accomplished by X-ray single-crystal analysis. The crystallographic results are summarized in Fig. 1 which shows the molecular structure and the various Tables. Atomic positional parameters and temperature parameters are given in Tables 1, 2 and 3. Bond distances and angles are listed in Tables 4 and 5, respectively. The accuracy

TABLE 3

ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE PARAMETERS FOR HYDROGEN ATOMS

Atom	x	y	z	B_{iso}
H(1)	—0.026(7)	—0.240(10)	0.338(3)	5(2)
H(2)	0.109(8)	0.364(14)	0.256(3)	6(2)
H(3)	—0.012(14)	0.252(22)	0.171(7)	7(5)
H(4)	—0.175(7)	0.042(11)	0.116(3)	5(2)
H(5)	—0.238(8)	—0.265(12)	0.155(4)	6(2)
H(6)	—0.150(7)	—0.342(12)	0.246(3)	4(2)
H(7)	0.324(8)	0.337(12)	0.351(3)	5(2)
H(8)	0.193(8)	0.498(15)	0.358(3)	7(2)

TABLE 4

BOND DISTANCES (Å)

Fe—C(13)	1.815(7)	C(1)—C(2)	1.371(8)
Fe—C(14)	1.844(7)	C(1)—C(9)	1.397(8)
Fe—C(15)	1.823(7)	C(2)—C(3)	1.422(8)
Fe—C(16)	1.831(7)	C(2)—C(11)	1.492(8)
Fe—C(11)	2.035(5)	C(3)—C(4)	1.376(9)
Fe—C(12)	2.112(7)	C(3)—C(12)	1.499(9)
O(1)—C(13)	1.120(7)	C(4)—C(10)	1.398(9)
O(2)—C(14)	1.133(8)	C(5)—C(6)	1.362(12)
O(3)—C(15)	1.125(7)	C(5)—C(10)	1.412(9)
O(4)—C(16)	1.132(8)	C(6)—C(7)	1.403(13)
O(5)—C(11)	1.215(7)	C(7)—C(8)	1.358(10)
		C(8)—C(9)	1.410(9)
C(1)—H(1)	0.89(7)	C(9)—C(10)	1.446(9)
C(4)—H(2)	0.86(8)		
C(5)—H(3)	0.80(14)		
C(6)—H(4)	0.94(7)		
C(7)—H(5)	0.95(8)		
C(8)—H(6)	0.84(7)		
C(14)—H(7)	0.95(7)		
C(12)—H(8)	1.05(9)		

of the structure is indicated by a comparison of the C—C distances in the naphthalene group with the accepted best values for the naphthalene molecule [5].

The five-membered chelate ring deviates from planarity with a bend along the C(11) · · · C(12) line of 15°. About half of the difference in the Fe—CH$_2$ and Fe—C(O) bond lengths, $\sim$0.07 Å can be attributed to the difference in covalent radii for sp^2 and sp^3 hybridized carbon atoms. The rest probably results from a slight π interaction of Fe with the CO group.

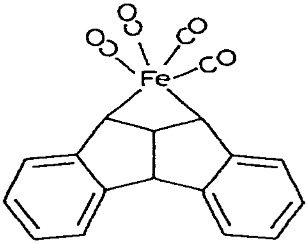
TABLE 5

BOND ANGLES (Deg)

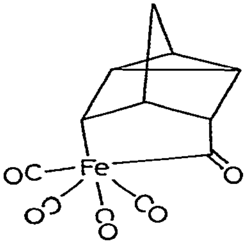
C(11)—Fe—C(12)	83.4(2)	C(2)—C(1)—C(9)	121.3(6)
C(11)—Fe—C(13)	84.0(2)	C(1)—C(2)—C(3)	121.4(5)
C(11)—Fe—C(16)	173.3(3)	C(1)—C(2)—C(11)	122.6(5)
C(11)—Fe—C(15)	83.9(2)	C(2)—C(3)—C(4)	117.8(6)
C(11)—Fe—C(14)	90.9(3)	C(2)—C(3)—C(12)	117.1(5)
C(12)—Fe—C(13)	86.0(3)	C(3)—C(4)—C(10)	122.5(6)
C(12)—Fe—C(16)	90.0(3)	C(6)—C(5)—C(10)	121.9(9)
C(12)—Fe—C(15)	83.0(3)	C(5)—C(6)—C(7)	120.7(7)
C(12)—Fe—C(14)	174.2(3)	C(6)—C(7)—C(8)	119.4(8)
C(13)—Fe—C(16)	94.8(3)	C(7)—C(8)—C(9)	122.3(8)
C(13)—Fe—C(15)	164.4(3)	C(1)—C(9)—C(8)	123.5(6)
C(13)—Fe—C(14)	93.9(3)	C(1)—C(9)—C(10)	118.1(6)
C(14)—Fe—C(15)	96.2(3)	C(4)—C(10)—C(5)	123.8(7)
C(14)—Fe—C(16)	95.7(3)	C(4)—C(10)—C(9)	118.9(5)
C(15)—Fe—C(14)	96.0(3)	Fe—C(11)—C(2)	112.7(4)
Fe—C(13)—O(1)	178.2(6)	Fe—C(11)—O(5)	124.8(4)
Fe—C(14)—O(2)	178.1(6)	C(2)—C(11)—O(5)	122.4(5)
Fe—C(15)—O(3)	176.5(5)	Fe—C(12)—C(3)	109.1(4)
Fe—C(16)—O(4)	177.3(5)		

Discussion

The remarkable stability of zero-valent iron compounds with two Fe—C σ bonds such as those present in I is at first surprising. The stability is probably kinetic in origin, since metal—alkyl decomposition pathways such as carbon—carbon bond reorganization or β-elimination are not available [6]. Compound III [1b], which results from the reaction of $Fe_2(CO)_9$ and dibenzosemibullvalene, is to our knowledge the only other well characterized material with two Fe—C σ bonds, and it also exhibits remarkable chemical and thermal stability. Very recently a compound assumed to have structure IV has been described but X-ray proof of structure was not yet available [2].

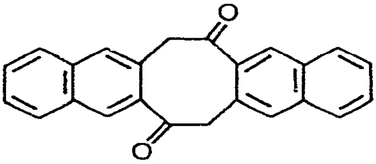


(III)



(IV)

Finally, structures similar to the one reported here have been proposed in several recent reports by Collman and his co-workers [7] as intermediates in their synthesis of aliphatic ketones from $Na_2Fe(CO)_4$ and alkyl halides. A similar decomposition of I would give naphtho[*b*]cyclobutenone. Although this compound was not observed, its dimer V was produced in low yield. In fact, I might owe its stability to the difficulty in forming the four-membered ring. The origin of diketone V is not clear; however, the thermal stability of I would seem to eliminate it as a precursor of V.



(V)

Acknowledgements

We are grateful to the Robert A. Welch Foundation for support under Grants A494 and C490.

References

1 (a) S. Sarel, R. Ben-Shoshan and B. Krison, J. Amer. Chem. Soc., 87 (1965) 2517; R. Ben-Shoshan and S. Sarel, Chem. Commun., (1969) 883; R. Victor, R. Ben-Shoshan and S. Sarel, Tetrahedron Lett.,

(1970) 4253; (b) R.M. Moriarty, R.M. Chem, K.N. Yen, J.L. Flippen and J. Karle, J. Amer. Chem. Soc., 94 (1972) 8944; (c) R.M. Moriarty, C.L. Yeh and K.C. Ramey, ibid., 93 (1971) 6709; (d) R. Noyori, T. Nishimura and H. Takya, Chem. Commun., (1969) 89; (e) T. Shirafuji and H. Nozaka, Tetrahedron, 29 (1973) 77; (f) C.H. Depuy, V.M. Kobal and D.H. Gibson, J. Organometal. Chem., 13 (1958) 266; (g) W.E. Billups, L.P. Lin and O.A. Gansow, Angew. Chem., 84 (1972) 684; Angew. Chem. Int. Ed., 11 (1972) 522; (h) W.E. Billups, L.P. Lin and B.A. Baker, J. Organometal. Chem., 61 (1973) C55.

2 V. Heil, B.F.G. Johnson, J. Lewis and D.J. Thompson, J. Chem. Soc. Chem. Commun., (1974) 270.

3 W.E. Billups and W.Y. Chow, J. Amer. Chem. Soc., 95 (1973) 4099.

4 F.A. Cotton and J.M. Troup, J. Organometal. Chem., 77 (1974) 369.

5 D.W.J. Cruickshank and R.A. Sparks, Proc. Roy. Soc., A, 258 (1960) 270.

6 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., Wiley-Interscience, New York, N.Y., 1972, p. 756-761.

7 J.P. Collman, S.R. Winter and D.R. Clark, J. Amer. Chem. Soc., 94 (1972) 1788; M.P. Cooke, Jr., ibid., 92 (1970) 7080; W.O. Siegl and J.P. Collman, ibid., 94 (1972) 2516.