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## Crystal and Molecular Structure of (3,4-Bis(1-propynyl)-2,5-dimethylcyclopentadienone)tricarbonyliron(0), [ $\eta^4$ -C<sub>4</sub>(C<sub>3</sub>H<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>CO]Fe(CO)<sub>3</sub><sup>1</sup>

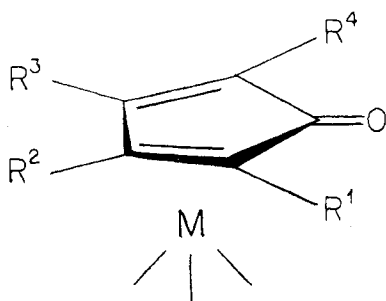
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The title compound, previously prepared from iron pentacarbonyl and 2,4-hexadiyne but identified as the incorrect isomer, has been characterized by x-ray diffraction. The structure is monoclinic, space group *I2/c*, an alternative representation of *C2/c*, with  $a = 17.981(8)$  Å,  $b = 8.830(6)$  Å,  $c = 19.667(5)$  Å,  $\beta = 95.15(4)^\circ$ ,  $V = 3109.6(25)$  Å<sup>3</sup>,  $\rho(\text{obsd}) = 1.393$  g cm<sup>-3</sup>, and  $\rho(\text{calcd}) = 1.385$  g cm<sup>-3</sup> for  $Z = 8$  and mol wt 324.12. Data were collected using Mo K $\alpha$  radiation ( $\lambda$  0.71069 Å) to a maximum  $2\theta$  of 45°. The iron atom was located on a Patterson map, and the remaining nonhydrogen atoms positions were deduced from a difference Fourier map. The structure was refined using least-squares methods to final discrepancy indices of  $R_F = 3.2\%$  and  $R_{wF} = 4.7\%$  for 1038 independent reflections. The butadiene portion of the ligand is essentially planar, with the ketonic carbonyl bent away from the iron atom by 14.1°. One of the propynyl substituents is also bent away from the iron atom.

### Introduction

Cyclopentadienone-metal complexes are among the products commonly isolated from reactions of acetylenes with group 8 metal carbonyls or their derivatives. When an unsymmetrical acetylene, RC $\equiv$ CR', is employed, there exists the possibility of isomerism in the cyclopentadienone ring (1a,b,c).



- 1a:  $R^1=R^4=R$ ,  $R^2=R^3=R'$   
 b:  $R^2=R^3=R$ ,  $R^1=R^4=R'$   
 c:  $R^1=R^3=R$ ,  $R^2=R^4=R'$

Since 1c is a racemate, one would predict upon statistical considerations alone that the isomers would be formed in the a:b:c ratio of 1:1:2. A survey of the literature reveals, however, that in actual reactions this is seldom the case. Often only a single isomer is isolated.

Unambiguous structural identification of these materials has been quite elusive. For many substituents R and R', NMR spectroscopy can distinguish the racemate from the meso compounds, but assignment of substituent positions in the meso compounds is not at all a straightforward task. It was for this reason that the present x-ray structural investigation of the single organometallic product obtained from a reaction between iron pentacarbonyl and 2,4-hexadiyne<sup>2</sup> was undertaken.

### Experimental Section

An aqueous solution of the title compound was obtained according to the published procedure.<sup>2</sup> Slow evaporation of the solution gave numerous yellow crystals. The one used for structure determination was a block measuring 0.11 × 0.13 × 0.36 mm and was mounted on a glass fiber with the long axis, later shown to be the crystallographic *b* axis, approximately parallel to the fiber.

Data were collected on a General Electric XRD-7 quarter-circle manual diffractometer using Mo K $\alpha$  radiation ( $\lambda$  0.71069 Å) out to a maximum  $2\theta$  of 45°. Intensity measurements were made for 2115 independent reflections using the stationary-crystal/stationary-counter

method with balanced zirconium and yttrium filters and a takeoff angle of 5.0°. Ten-second counts were recorded for both filters. Five strong reflections were measured periodically during data collection. Since no significant changes in these were observed, it was assumed that crystal quality and alignment were stable.

A background correction for random scattered Mo K $\alpha$  radiation was made as a function of  $2\theta$ . A reflection was deemed significantly above background if it fulfilled the condition  $|I_{Zr} - 2\sigma(I_{Zr})| - |I_Y + 2\sigma(I_Y)| \geq 100$  counts, where  $I_{Zr}$  and  $I_Y$  are the measured counts for the designated filters and  $\sigma(I_{Zr})$  and  $\sigma(I_Y)$  are the usual standard deviations from counting statistics. A total of 1038 reflections met this criterion and were classed as observed. A weight  $w$  was assigned to each reflection where  $w = 1/[\sigma(F_o)]^2$  and

$$\sigma(F_o) = 1/2 \left[ (Lp)^{-1} \frac{I_{Zr} + I_Y + (KI_{Zr})^2}{I_{Zr} - I_Y} \right]^{1/2}$$

$Lp$  is the Lorentz-polarization factor, and  $K$ , an empirical instrument factor, was assigned the value 0.03. No corrections were made for absorption. The linear absorption coefficient,  $\mu$ , is 10.12 cm<sup>-1</sup>. Calculated minimum and maximum transmission factors are 0.69 and 0.89, respectively.

Use of diiron nonacarbonyl in place of iron pentacarbonyl in the reaction gave a mixture of products, a minor component of which was the title compound.

### Solution and Refinement of the Structure

The following computer programs were used: LSLAT (cell parameter refinement), INCON (data reduction, by R. E. Davis), NORMAL (generation of  $E'$ s and statistics, part of the MULTAN system), RAO (Fourier, by S. T. Rao), BDLR (block-diagonal least squares), NUCLS (full-matrix least squares), JIMDAP (a version of Zalkin Fourier program), ORFFE (molecular geometry with esd's, by Busing, Martin, and Levy), ORTEP (thermal ellipsoid plotting program, by C. K. Johnson), and XANADU (molecular geometry, by Roberts and Sheldrick). INCON, RAO, BDLR, and XANADU were run on a CDC 1604A computer. All other calculations were performed on the Amdahl 470V/6 at Texas A&M University.

The reflections were indexed in such a way that the space group was *I2/c* or *Ic* (systematic absences:  $hkl$ ,  $h + k + l \neq 2n$ , and  $h0l$ ,  $l \neq 2n$ ). Use of the standard *C*-centered cell would have resulted in a  $\beta$  angle of 135.2°. Statistics from NORMAL indicated a non-centrosymmetric space group, but refinement in *Ic* did not result in a significant reduction of the  $R$  factor. Using the criteria of Hamilton,<sup>3</sup> the hypothesis that *I2/c* is the correct space group cannot be rejected even at the 50% confidence level. Therefore, the centrosymmetric group was used as a matter of convenience.

The iron atom was located by means of a Patterson map. Refinement of this atom followed by a difference map indicated positions for all of the carbon and oxygen atoms except C(3). An approximate position for C(3) could be calculated, however. The positional and anisotropic thermal parameters for the nonhydrogen atoms were

Table I. Positional and Anisotropic Thermal Parameters for the Nonhydrogen Atoms<sup>a</sup>

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Fe	0.1397 (1)	-0.0116 (1)	0.1764 (1)	413 (5)	591 (6)	487 (5)	-12 (6)	41 (3)	-56 (6)
C(1)	0.2332 (4)	0.0260 (9)	0.2102 (3)	561 (46)	983 (63)	669 (47)	-46 (53)	6 (38)	-135 (49)
O(1)	0.2934 (3)	0.0483 (8)	0.2310 (3)	581 (36)	2005 (74)	1280 (55)	-108 (45)	-234 (37)	-220 (52)
C(2)	0.0998 (4)	0.1476 (10)	0.2148 (4)	600 (54)	1147 (75)	756 (63)	83 (54)	26 (46)	-448 (58)
O(2)	0.0748 (3)	0.2518 (8)	0.2370 (3)	974 (50)	1488 (62)	1413 (61)	287 (46)	20 (42)	-848 (51)
C(3)	0.1152 (4)	-0.1480 (10)	0.2383 (4)	741 (60)	1065 (71)	556 (52)	-173 (54)	12 (47)	10 (51)
O(3)	0.1003 (4)	-0.2318 (8)	0.2784 (3)	1685 (70)	1591 (68)	864 (51)	-386 (54)	180 (47)	499 (48)
C(4)	0.1953 (3)	-0.0078 (8)	0.0713 (2)	421 (37)	672 (44)	446 (35)	-83 (48)	65 (28)	18 (43)
O(4)	0.2575 (2)	0.0234 (5)	0.0535 (2)	446 (25)	662 (33)	817 (32)	-41 (26)	197 (23)	41 (28)
C(5)	0.1330 (3)	0.0946 (6)	0.0790 (3)	509 (44)	422 (40)	550 (45)	-24 (39)	78 (36)	5 (34)
C(6)	0.0681 (2)	0.0053 (7)	0.0886 (2)	408 (34)	382 (38)	463 (34)	-98 (41)	-3 (25)	36 (38)
C(7)	0.0915 (3)	-0.1501 (7)	0.0978 (2)	496 (44)	382 (41)	414 (38)	-60 (38)	5 (32)	-31 (31)
C(8)	0.1699 (3)	-0.1539 (6)	0.0964 (3)	461 (42)	396 (42)	475 (40)	56 (36)	108 (31)	49 (33)
C(9)	0.1339 (3)	0.2584 (7)	0.0606 (4)	686 (52)	447 (44)	1117 (66)	60 (40)	218 (46)	174 (44)
C(10)	-0.0080 (3)	0.0568 (6)	0.0868 (3)	435 (41)	346 (38)	580 (44)	21 (32)	-66 (34)	-18 (31)
C(11)	-0.0710 (3)	0.0922 (6)	0.0878 (3)	440 (46)	438 (40)	590 (45)	33 (36)	-74 (36)	5 (35)
C(12)	-0.1492 (3)	0.1363 (8)	0.0912 (3)	503 (47)	675 (51)	928 (59)	105 (38)	71 (41)	-15 (43)
C(13)	0.0422 (3)	-0.2737 (7)	0.1032 (3)	472 (45)	411 (43)	647 (49)	36 (39)	110 (36)	-1 (37)
C(14)	0.0001 (3)	-0.3759 (7)	0.1037 (3)	445 (42)	496 (46)	839 (55)	20 (40)	61 (40)	-82 (41)
C(15)	-0.0520 (3)	-0.5020 (8)	0.1063 (4)	632 (45)	457 (42)	1523 (79)	-124 (47)	175 (47)	60 (55)
C(16)	0.2160 (4)	-0.2934 (7)	0.0999 (3)	779 (54)	567 (48)	769 (53)	143 (41)	161 (43)	71 (42)

<sup>a</sup> The anisotropic parameters ( $\text{Å}^2, \times 10^{-3}$ ) are used in the expression  $\exp(-[2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k lb^*c^*)])$ .

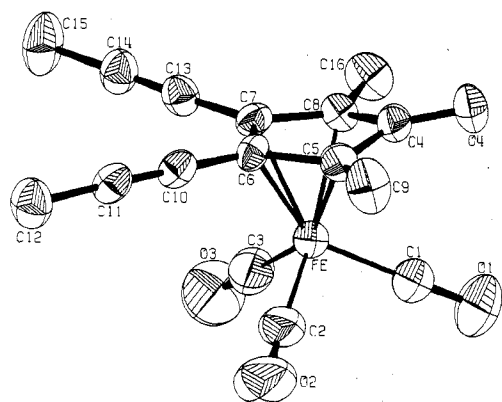


Figure 1. ORTEP drawing of  $[\eta^4\text{-C}_4(\text{C}_3\text{H}_3)_2(\text{CH}_3)_2\text{CO}]\text{Fe}(\text{CO})_3$ . The 50% probability thermal ellipsoids are shown.

refined to convergence, and a difference Fourier map was generated. Three peaks in the vicinity of each methyl carbon were selected as initial hydrogen atom positions. The hydrogen atoms were assigned isotropic  $B$ 's of 7.0, and the nonhydrogen atom parameters were further refined with the hydrogen parameters fixed. The hydrogen atoms were then removed, and a new difference Fourier map was generated. From this, reasonable positions were obtained for 7 of the 12 hydrogen atoms. Positions for the others were calculated assuming a C-H distance of 1.00 Å. The structure was again refined with fixed hydrogen parameters to a final unweighted  $R$ , defined as  $\sum |F_o - F_c| / \sum F_o$ , of 0.032. The weighted  $R_w$ ,  $(\sum w|F_o - F_c|^2 / \sum wF_o^2)^{1/2}$ , was 0.047, and the goodness of fit,  $[\sum w|F_o - F_c|^2 / (M - S)]^{1/2}$ , was 1.88 for  $M = 1038$  reflections and  $S = 190$  parameters. The largest shift in a positional parameter on the last cycle was  $0.06\sigma$ ; the largest shift in a thermal parameter was  $0.10\sigma$ . A final difference map showed no peak larger than  $0.22 e \text{ Å}^{-3}$ . Scattering factors used in these calculations were taken from ref 4a. Both the real and imaginary components of anomalous dispersion due to iron were included; the values used were those of Cromer and Liberman.<sup>4b</sup>

A table of observed and calculated structure factors is available.<sup>5</sup> Positional and thermal parameters with their esd's are given in Table I.

### The Molecular Structure

A view of the molecule is presented in Figure 1. Interatomic distances not involving a hydrogen atom are given in Table II along with their esd's; bond angles and their esd's are given in Table III. The cyclopentadienone skeleton consists essentially of two planes of atoms, one defined by C(5), C(6),

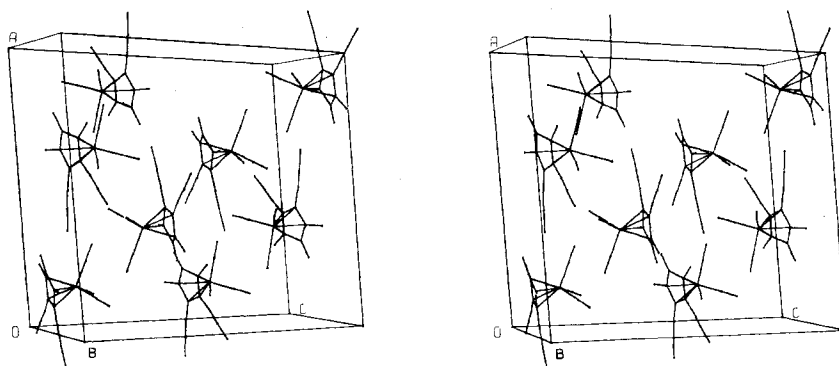
Table II. Interatomic Distances and Esd's for  $[\eta^4\text{-C}_4(\text{C}_3\text{H}_3)_2(\text{CH}_3)_2\text{CO}]\text{Fe}(\text{CO})_3$  (Å)

C(1)-O(1)	1.138 (8)	C(6)-C(10)	1.439 (8)
C(2)-O(2)	1.129 (8)	C(7)-C(8)	1.412 (8)
C(3)-O(3)	1.132 (9)	C(7)-C(13)	1.416 (9)
C(4)-O(4)	1.232 (7)	C(8)-C(16)	1.483 (9)
C(4)-C(5)	1.458 (9)	C(10)-C(11)	1.176 (8)
C(4)-C(8)	1.469 (9)	C(11)-C(12)	1.466 (9)
C(5)-C(6)	1.435 (8)	C(13)-C(14)	1.178 (9)
C(5)-C(9)	1.492 (9)	C(14)-C(15)	1.459 (10)
C(6)-C(7)	1.442 (8)		
Fe-C(1)	1.783 (8)	Fe-C(5)	2.126 (6)
Fe-C(2)	1.777 (9)	Fe-C(6)	2.066 (5)
Fe-C(3)	1.793 (10)	Fe-C(7)	2.097 (6)
Fe-C(4)	2.376 (6)	Fe-C(8)	2.123 (6)

Table III. Bond Angles and Esd's for  $[\eta^4\text{-C}_4(\text{C}_3\text{H}_3)_2(\text{CH}_3)_2\text{CO}]\text{Fe}(\text{CO})_3$  (deg)

C(1)-Fe-C(2)	95.6 (4)	C(6)-C(5)-C(9)	126.3 (6)
C(1)-Fe-C(3)	98.8 (4)	C(5)-C(6)-C(7)	107.9 (5)
C(2)-Fe-C(3)	96.4 (4)	C(5)-C(6)-C(10)	127.3 (6)
C(5)-Fe-C(6)	40.0 (2)	C(7)-C(6)-C(10)	124.8 (5)
C(6)-Fe-C(7)	40.5 (2)	C(6)-C(7)-C(8)	107.5 (5)
C(7)-Fe-C(8)	39.1 (2)	C(6)-C(7)-C(13)	124.4 (6)
Fe-C(1)-O(1)	178.8 (7)	C(8)-C(7)-C(13)	128.0 (6)
Fe-C(2)-O(2)	177.4 (9)	C(4)-C(8)-C(7)	109.1 (5)
Fe-C(3)-O(3)	178.4 (8)	C(4)-C(8)-C(16)	123.7 (6)
O(4)-C(4)-C(5)	128.1 (7)	C(7)-C(8)-C(16)	125.0 (6)
O(4)-C(4)-C(8)	127.6 (7)	C(6)-C(10)-C(11)	176.2 (7)
C(5)-C(4)-C(8)	104.1 (5)	C(10)-C(11)-C(12)	178.3 (8)
C(4)-C(5)-C(6)	108.4 (5)	C(7)-C(13)-C(14)	176.1 (8)
C(4)-C(5)-C(9)	123.4 (6)	C(13)-C(14)-C(15)	178.4 (8)

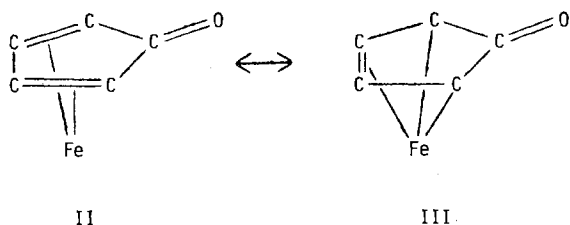
C(7), and C(8), and the other defined by C(4), O(4), C(5), and C(8). The dihedral angle between these two planes is  $14.1^\circ$ . This is somewhat less than the  $20.1^\circ$  reported for tetrakis(trifluoromethyl)cyclopentadienonetricarbonyliron(0)<sup>6</sup> and the  $21.3^\circ$  reported for  $\pi$ -cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonecobalt(I)<sup>7</sup> but greater than the  $9^\circ$  reported for  $\pi$ -cyclopentadienyltetramethylcyclopentadienonecobalt(I).<sup>8</sup> One might infer from this that the presence of electron-donating substituents on the ring favors resonance interaction with the carbonyl group and causes that group to approach the ring plane, while electron-withdrawing substituents disfavor such interaction and cause the carbonyl group to depart from the ring plane. More structural studies are needed to confirm or refute this, however.



**Figure 2.** Stereoscopic view of the crystal packing of  $[\eta^4\text{-C}_4(\text{C}_6\text{H}_5)_2(\text{CH}_3)_2\text{CO}]\text{Fe}(\text{CO})_3$ .

The deviations of the propynyl atoms from the best least-squares plane defined by C(5), C(6), C(7), and C(8) are as follows: C(10), 0.00; C(11), 0.03; C(12), 0.10; C(13), -0.11; C(14), -0.27; C(15), -0.43 Å, where negative numbers indicate displacement away from the iron atom. Neither intramolecular nor intermolecular effects seem to provide a ready explanation for the relatively large displacement of the one propynyl group away from iron. Figure 2, which provides a stereoscopic view of the crystal packing, does not clarify the situation.

The nearly equal lengths of the C(5)–C(6), C(6)–C(7), and C(7)–C(8) bonds imply approximately equal contributions from II and III. In the two other metal–cyclopentadienone



studies for which the relevant data were reported,<sup>6,7</sup> this was also the case.

### Discussion

Formation of the cyclopentadienone ring from an unsymmetric alkyne,  $\text{RC}\equiv\text{CR}'$ , often occurs in a stereoselective way. The following three factors have been suggested<sup>9</sup> to contribute to this phenomenon: (1) in cases in which R and R' have very different effective electronegativities, Coulombic interaction in an intermediate or transition state might cause the two alkyne units to join in a head-to-tail fashion, thus favoring formation of the racemate; (2) in cases in which R and R' are of very different steric bulk, the formation of the meso compound with the sterically larger groups in the 3 and 4 positions might be impeded; (3) differences in the  $\pi$ -electron density at the alternative substituent sites would influence the relative energies of the transition states for carbonyl insertion leading to the various isomers.

The first of these seems to be operative in the reaction between methyl phenylpropiolate and diiron nonacarbonyl, from which the only cyclopentadienone complex isolated was the racemate.<sup>10</sup> A similar result was obtained in the reaction of 1-propynyldiethylamine with iron pentacarbonyl.<sup>11</sup> The effect is not seen in reactions involving terminal alkynes, however. Symmetric isomers are the predominant products obtained from 1,1,1-trifluoropropyne<sup>9,12</sup> or pentafluorophenylacetylene.<sup>13</sup>

When mesitylphenylacetylene (2,4,6-( $\text{CH}_3$ )<sub>3</sub> $\text{C}_6\text{H}_2\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$ ) is allowed to react with  $\pi$ -cyclopentadienyldicarbonylcobalt(I), the only cyclopentadienone complex formed is the racemate.<sup>14</sup> This result might be attributable to steric

factors, since even the racemate is so crowded that all four ortho methyl groups are resolved in the room-temperature <sup>1</sup>H NMR spectrum and since the cyclobutadiene complex formed in the same reaction is the isomer resulting from head-to-tail fusion of the alkynes.

The third factor, which involves differences in  $\pi$ -electron density, was proposed to account for the exclusive formation of 2,5-diphenylcyclopentadienonetricarbonyliron(0) from phenylacetylene and iron pentacarbonyl.<sup>15</sup> A later study showed that a small amount of the 3,4 isomer is also formed,<sup>16</sup> but the argument is still the same. The same argument might apply to the analogous reaction of pentafluorophenylacetylene, from which the analogous product is obtained.<sup>13</sup>

The foregoing are reasonable factors that doubtless exert some influence over product distribution. The problem is that they predict different results, and it is not at all clear which one will predominate. A particularly intriguing set of reactions is the following: Reaction of 2,3,4,5,6-pentafluorodiphenylacetylene ( $\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{H}_5$ ) with  $\pi$ -cyclopentadienyldicarbonylcobalt(I) at 120 °C (hexane, sealed tube) gave as the only product a 46% yield of the racemic cyclopentadienone complex.<sup>17</sup> A reaction under similar conditions, but in which the acetylene was 2,3,4,5-tetrafluorodiphenylacetylene, gave all three isomers in an approximate ratio of 1:1:3 (racemate most abundant).<sup>18</sup> The total yield of cyclopentadienone complex was almost exactly the same (45%). The presence of the fifth fluorine atom does not render the symmetric isomers sterically inaccessible, since bis(pentafluorophenyl)acetylene gives the tetrakis(pentafluorophenyl) compound in the analogous reaction,<sup>17</sup> and it does not seem reasonable that addition of the fifth fluorine atom would so change the electronic structure of the acetylene that the Coulombic interaction factor could account for the observed results. Furthermore, the pentafluoro compound also produces all three isomers when the reaction medium is refluxing xylene.<sup>19</sup>

Finally, one expects as a general phenomenon that when two or more factors might reasonably predict the product distribution of a reaction and when the predictions are mutually exclusive, mixtures of products will be observed in actual experiments. While this is often the case with the formation of cyclopentadienone–metal complexes, it is also often not the case. There are clearly factors involved in these reactions which have not yet been adequately investigated.

The present compound provides a rather clear-cut example. Since the steric and Coulombic factors predict formation of the racemate, they are not applicable here. The isomer obtained, however, is the one least favored by the  $\pi$ -electron density argument.<sup>2</sup> In any case, one would not expect the electron densities of the alternative sites to be different enough to suppress the formation of all but one isomer. Indeed, a thermal reaction of 2,4-hexadiyne with  $\pi$ -cyclopentadienyldicarbonylcobalt(I) gave all three isomers in approximately the statistically expected ratio.<sup>20</sup> Even allowing for the

possibility that small amounts of the other two isomers may have been formed and escaped detection, an adequate explanation of the preference for the title compound is not apparent at this time.

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**Registry No.**  $[\eta^4-C_4(C_3H_3)_2(CH_3)_2CO]Fe(CO)_3$ , 65120-33-4;  $[\eta^4-C_4(C_3H_3)_2(CH_3)_2CO]Fe(CO)_3$ -(previous formulation), 65120-32-3.

**Supplementary Material Available:** Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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## Preparation and Molecular and Crystal Structures of Uranium(IV) Borohydride-Dimethyl Ether and Uranium(IV) Borohydride-Diethyl Ether<sup>1</sup>

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Uranium(IV) borohydride reacts with dimethyl ether and diethyl ether to form  $U(BH_4)_4 \cdot O(CH_3)_2$  and  $U(BH_4)_4 \cdot O(C_2H_5)_2$ , respectively. The yields are >90%. The latter compound can also be prepared by reacting  $UF_4$  and  $LiBH_4$  in diethyl ether for 1 week. Both compounds are green, crystalline solids that can be sublimed in bulk at 50 °C and  $10^{-5}$  mm. Single-crystal x-ray diffractometry has shown both of these materials to be monoether complexes in the solid state.  $U(BH_4)_4 \cdot O(CH_3)_2$  is orthorhombic, *Pnma*, with  $a = 11.423$  (5) Å,  $b = 10.120$  (4) Å,  $c = 9.915$  (4) Å, and  $Z = 4$ .  $U(BH_4)_4 \cdot O(C_2H_5)_2$  is monoclinic, *P2<sub>1</sub>*, with  $a = 7.95$  (1) Å,  $b = 15.24$  (1) Å,  $c = 5.74$  (1) Å,  $\beta = 106.0$  (1)°, and  $Z = 2$ . The structure of each complex consists of infinite linear chains of alternating uranium and boron atoms joined by double-hydrogen-bridge bonds. The remaining borohydrides are attached to the uranium atom by triple-hydrogen-bridge bonds. The ether moieties are associated to the uranium by the oxygen atoms. In the dimethyl ether adduct successive ether molecules along the chain are trans, whereas in the diethyl ether compound they are all cis. The total coordination about the uranium atom is 14, i.e., 1 oxygen atom and 13 hydrogen atoms. The average U-B distances for the triple-bridge and double-bridge bonds are 2.53 (2) and 2.89 (1) Å, respectively. The average U-O bond length is 2.46 (3) Å. A refinement of the anomalous dispersion term  $f''$  for uranium in the ethyl compound shows that the crystal was twinned, containing unequal fractions of the enantiomeric configurations.

## Introduction

Uranium(IV) borohydride, a volatile, dark green, crystalline compound obtained by treating  $UF_4$  with  $Al(BH_4)_3$  at room temperature, was first synthesized by Schlesinger and Brown during the Manhattan project and reported in 1953.<sup>2,3</sup> In an attempt to prepare  $U(BH_4)_4$  by another route, they treated  $UF_4$  with  $LiBH_4$  in the presence of ether to form a green, ether-soluble product but were unable to completely separate this material from the solvent.  $U(BH_4)_4$  formed a 1:1 complex with ethyl ether which was stable at -80 °C, but pure  $U(BH_4)_4$  could not be recovered by high-vacuum fractional distillation.

Recently, Russian workers<sup>4</sup> have published a new synthesis of  $U(BH_4)_4$  by the reaction of finely powdered  $UCl_4$  and  $LiBH_4$  (in a vacuum vibration ball mill). This synthesis parallels the well-known method for producing  $Hf(BH_4)_4$  and  $Zr(BH_4)_4$ <sup>5</sup> and avoids the use of  $Al(BH_4)_3$ , a liquid explosive to oxygen or water.

Hoekstra and Katz<sup>6</sup> have reported the synthesis of the isomorphous but much less volatile actinide compound  $Th(BH_4)_4$  by treating  $ThF_4$  with  $Al(BH_4)_3$ . Subsequently, Ehemann and Nöth<sup>7</sup> synthesized  $Th(BH_4)_4$  by the reaction of  $ThCl_4$  with  $LiBH_4$  in diethyl ether. Here, an etherate complex was formed as an intermediate, but the solvent could be completely removed by vacuum distillation. Consistent with this synthesis

was the isolation by Hoekstra and Katz<sup>6</sup> of  $Th(BH_4)_4 \cdot 2(C_2H_5)_2O$  by dissolution of  $Th(BH_4)_4$  in diethyl ether with partial recovery of the  $Th(BH_4)_4$  after heating under vacuum. Ehemann and Nöth<sup>7</sup> also treated  $Th(BH_4)_4$  with  $LiBH_4$  in diethyl ether and reported the synthesis of the salts  $LiTh(BH_4)_5$  and  $Li_2Th(BH_4)_6$ . Etherates were again formed as intermediates, but the diethyl ether was easily removed.

In our search for new volatile actinide compounds, we have prepared a number of Lewis-base adducts of uranium(IV) borohydride by direct combination of  $U(BH_4)_4$  and the Lewis base.<sup>8</sup> Many of these materials are volatile, among them  $U(BH_4)_4 \cdot O(CH_3)_2$  and  $U(BH_4)_4 \cdot O(C_2H_5)_2$ . We have also repeated the work of Schlesinger and Brown<sup>2</sup> and have shown their "etherate unstable at room temperature" is actually the stable compound  $U(BH_4)_4 \cdot O(C_2H_5)_2$ .

## Experimental Section

**Materials and Chemical Techniques.**  $U(BH_4)_4$  was prepared by the method of Schlesinger and Brown<sup>2</sup> and purified by sublimation at 30-40 °C and  $10^{-5}$  mm.  $UF_4$  (Alfa) was vacuum-dried at 300 °C for 3 days. Dimethyl ether (Matheson) was purified by passage through a -78 °C trap until its vapor pressure was 283 mm.<sup>9</sup> Diethyl ether (Mallinckrodt) was doubly distilled from sodium/benzophenone under argon. All manipulations were performed in mercury-, oil-, and grease-free Pyrex high-vacuum lines or in argon-filled dryboxes.<sup>9</sup>