(cis or trans) gives rise to which nmr signals. This is very convenient as there is no sure way, with the data at hand, to make such an assignment.[16,17] Since the energy difference between the two is so small, arguments depending on estimates of steric strain are inconclusive, even though we know the structure of the cis isomer in detail.[12] We also think it doubtful that any reliable answer could be obtained from study of how solvent polarity affects the infrared spectrum since both isomers are inherently polar (unlike the case of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ where the trans isomer is rigorously nonpolar).

Finally, we note that the activation energy here, *ca.* 20 kcal mol^{-1}, is some 8 kcal mol^{-1} higher than that for the comparable processes in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. This would be expected from the Adams and Cotton mechanism, since the replacement of one CO ligand by the very bulky $P(OPh)_3$ ligand should increase the barrier to the rotation which is required in each step of the cycle.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. 33142X and by The Robert A. Welch Foundation (Grant A494).

Registry No. $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[P(OPh)_3]$, 51056-17-8; ^{13}C, 14762-74-4.

[16] It is possible to design an experiment which can resolve this ambiguity, and such work is now in progress. If it is successful, the results will be reported later.

[17] Note Added in Proof. Although, as noted explicitly, the uncertainity as to which isomer is the predominant one in solution does not interfere at all with the kinetic analysis, we nevertheless desired to make an identification. This was done by preparing the compound $[C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4]Fe_2(CO)_3P(OPh)_3$, measuring its ir spectrum, and comparing with that of $(C_5H_5)_2Fe_2(CO)_3P(OPh)_3$. The former, which can exist only in a cis form, was prepared by reaction of $P(OPh)_3$ with $[C_5H_4CH(NMe)_2CH(NMe_2)C_5H_4]Fe_2(CO)_4$ [P. McArdle and A. R. Manning, *J. Chem. Soc. A*, 2119 (1970)]. In CS_2 the new compound, which is constrained to be cis, has bands at 1958 and 1745 cm^{-1}, of essentially equal intensities. $(C_5H_5)_2Fe_2(CO)_3P(OPh)_3$ has bands at 1961 (s), 1940 (w), 1751 (sh), and 1748 (s) cm^{-1}. These results clearly indicate that the cis isomer predominates and has bands at 1961 and 1748 cm^{-1} while the trans isomer has bands at 1940 and 1751 cm^{-1}.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Crystal and Molecular Structures of *cis*-Bis(*pentahapto*cyclopentadienyl)tricarbonyl(triphenyl phosphito)diiron

F. A. COTTON,* B. A. FRENZ, and A. J. WHITE

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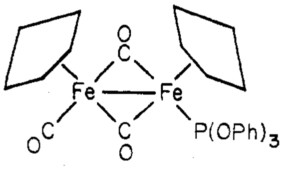
Bis(*pentahapto*cyclopentadienyl)tricarbonyl(triphenyl phosphito)diiron crystallizes in space group $P\bar{1}$ with unit cell dimensions $a = 14.331$ (5) Å, $b = 17.335$ (9) Å, $c = 12.482$ (7) Å, $\alpha = 102.12$ (4)°, $\beta = 92.02$ (4)°, $\gamma = 66.44$ (4)° and $Z = 4$. The asymmetric unit is formed by two cis molecules. The structure has been solved and refined using 3605 independent reflections with intensities greater than 3σ, where σ is the estimated standard deviation for the intensity. The cyclopentadienyl rings and the phenyl groups were refined as rigid bodies and anisotropic thermal parameters were assigned to the iron and phosphorus atoms only. Refinement converged at reliability indices of $R_1 = 0.075$ and $R_2 = 0.090$. Each molecule has the expected structure, with an Fe–Fe bond (Fe–Fe = 2.543 (3) and 2.548 (3) Å) and two bridging carbonyl groups. Aside from the replacement of one terminal CO group by $(C_6H_5O)_3P$ each molecule closely resembles the cis isomer of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. This supports our earlier assumption that the structural and dynamical behavior of the two systems should be qualitatively very similar and that information obtained on one should have relevance to the understanding of the other.

Introduction

In the preceding paper[1] the structural and dynamic behavior of cis and trans isomers of bis(cyclopentadienyl)tricarbonyl(triphenyl phosphito)diiron in solution have been reported and interpreted on the assumption that the structures are, schematically, **1** and **2**. The results help to support



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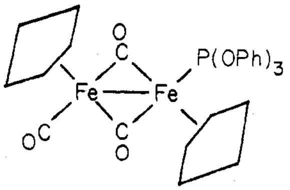

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and lend emphasis to the picture previously developed in this laboratory of the way in which binuclear metal carbonyl species undergo isomerization and carbonyl scrambling reactions.[2-7]

In connection with the solution studies we have undertaken an X-ray crystallographic study of the molecular structure. A secure knowledge of the molecular structure in the crystal lends support to the interpretation of solution spectra and demonstrates in detail the close relationship of the structure of this molecule to the structure of what we had presumed to be related species such as the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ isomers[8,9] and the several methyl isocyanide substitution products thereof.[10-12]

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[1] F. A. Cotton, L. Kruczynski, and A. J. White, *Inorg. Chem.*, 13, 1402 (1974).

[2] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 94, 6193 (1972).

[3] R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, 7, 153 (1973).

[4] F. A. Cotton, Plenary Lecture, Assemblee Annuelle, Societe Chimique de France, Marseille, May 23-25, 1973; *Bull. Soc. Chim. Fr.*, (9) 2588 (1973).

[5] F. A. Cotton, Plenary Lecture, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 13, 1973; see Abstracts, pp 1-8.

[6] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 95, 6589 (1973).

[7] R. D. Adams, M. D. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, 95, 6594 (1973).

[8] R. F. Bryan and P. T. Greene, *J. Chem. Soc. A*, 3064 (1970).

[9] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 3068 (1970).

[10] R. D. Adams and F. A. Cotton, *Inorg. Chem.*, 13, 249 (1974).

Table I. Positional, Thermal, and Group Parameters[a] for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3P(OC_6H_5)_3$

1\. Anisotropically Refined Atoms[b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			Molecule I						
Fe(1)	−0.0576 (1)	0.1343 (1)	−0.2128 (2)	45 (1)	34 (1)	55 (2)	−21 (1)	−7 (1)	8 (1)
Fe(2)	0.1232 (2)	0.0187 (1)	−0.2409 (2)	52 (1)	34 (1)	59 (2)	−16 (1)	−9 (1)	12 (1)
P	−0.0401 (3)	0.2527 (2)	−0.1912 (3)	46 (3)	36 (2)	52 (3)	−17 (2)	−4 (2)	11 (2)
			Molecule II						
Fe(1)	0.3226 (1)	0.1958 (1)	0.1780 (1)	40 (1)	30 (1)	44 (2)	−12 (1)	−5 (1)	3 (1)
Fe(2)	0.4535 (2)	0.2266 (1)	0.0812 (2)	50 (1)	40 (1)	53 (2)	−17 (1)	−1 (1)	10 (1)
P	0.3397 (3)	0.2350 (2)	0.3480 (3)	44 (3)	29 (2)	49 (3)	−13 (2)	−7 (2)	8 (2)

2\. Isotropically Refined Atoms

	Molecule I				Molecule II			
Atom	x	y	z	B, Å^2	x	y	z	B, Å^2
C(1)	0.041 (1)	0.091 (1)	−0.111 (1)	4.0 (3)	0.456 (1)	0.136 (1)	0.152 (1)	3.5 (3)
C(2)	0.035 (1)	0.088 (1)	−0.334 (1)	4.1 (3)	0.319 (1)	0.299 (1)	0.145 (1)	3.7 (3)
C(3)	0.202 (1)	0.073 (1)	−0.230 (1)	3.4 (3)	0.510 (1)	0.270 (1)	0.184 (1)	5.0 (4)
O(1)	0.0486 (7)	0.0952 (6)	−0.0140 (8)	4.5 (2)	0.5312 (7)	0.0677 (6)	0.1598 (8)	4.3 (2)
O(2)	0.0390 (7)	0.0911 (6)	−0.4300 (8)	4.5 (2)	0.2627 (8)	0.3734 (7)	0.1501 (8)	4.8 (2)
O(3)	0.2641 (7)	0.1013 (6)	−0.2267 (8)	4.7 (2)	0.5524 (9)	0.3031 (8)	0.2493 (10)	7.1 (3)
O(4)	−0.1155 (7)	0.3379 (6)	−0.1065 (7)	3.9 (2)	0.2403 (6)	0.2801 (5)	0.4334 (7)	3.1 (2)
O(5)	0.0703 (6)	0.2475 (5)	−0.1609 (7)	3.2 (2)	0.3962 (6)	0.2991 (6)	0.3803 (7)	3.5 (2)
O(6)	−0.0534 (7)	0.2993 (6)	−0.2925 (7)	3.9 (2)	0.4076 (6)	0.1628 (5)	0.4151 (7)	3.5 (2)

3\. Group Parameters[c]

Group[d]	x(o)	y(o)	z(o)	δ	ϵ	η	B, Å^2
			Molecule I				
Cp(1)	−0.1791 (5)	0.1300 (5)	−0.2414 (6)	0.34 (2)	1.944 (7)	1.71 (2)	4.6 (2)
Cp(2)	0.1576 (8)	−0.0946 (6)	−0.2921 (9)	1.67 (2)	2.12 (1)	1.92 (2)	7.8 (2)
Ph(1)	−0.1997 (5)	0.3366 (4)	0.0907 (6)	−1.855 (6)	−2.817 (6)	1.075 (7)	5.1 (1)
Ph(2)	0.1495 (5)	0.3696 (4)	−0.1644 (5)	−1.944 (12)	−1.998 (6)	−3.191 (12)	4.3 (1)
Ph(3)	−0.2352 (5)	0.3674 (4)	−0.3934 (6)	−2.742 (8)	2.388 (6)	−0.747 (9)	5.1 (1)
			Molecule II				
Cp(1)	0.2271 (5)	0.1523 (5)	0.1566 (6)	2.200 (2)	−1.971 (7)	−0.14 (2)	4.0 (1)
Cp(2)	0.4854 (7)	0.1889 (6)	−0.0657 (7)	3.054 (8)	2.926 (9)	−0.258 (9)	5.8 (2)
Ph(1)	−0.0486 (5)	0.3930 (4)	0.3917 (5)	−0.448 (6)	2.740 (6)	−2.889 (6)	4.3 (1)
Ph(2)	0.4351 (5)	0.3632 (5)	0.5930 (6)	−2.248 (6)	−3.094 (6)	−1.933 (6)	5.2 (2)
Ph(3)	0.3799 (5)	0.0133 (4)	0.4155 (5)	−1.689 (5)	2.630 (6)	−0.004 (6)	4.1 (1)

[a] The numbers in parentheses are estimated standard deviations in the last significant digits in this and all other tables. [b] x, y, and z are fractional coordinates. The form of the thermal ellipsoid is $\exp[-10^4(\beta_{11}h^2 + \beta_{22}h^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] x(o), y(o), and z(o) are fractional coordinates of the ring origin; δ, ϵ and η (in radians) are group orientation angles as defined previously; B is the isotropic group temperature factor. [d] Cp = cyclopentadienyl; Ph = phenyl.

An additional point of interest in this case was raised by the observations and speculations of Haines and du Preez,[13] who originally reported this compound. They found that in the solid-state ir spectrum there are two well-separated terminal CO stretching bands, at 1945 and 1962 cm^{-1}. Effects of this sort are, of course, often found in the solid-state spectra of metal carbonyls and can usually be explained straightforwardly by taking proper account of the symmetry-governed intermolecular couplings.[14-16] Such an interpretation requires knowledge of the crystal structure, at the very least to the extent of knowing the space group and the number of molecules in the unit cell.

In this case the separation between the two terminal bands was much larger than that between the two bridging bands and appreciably larger than that (*ca.* 10 cm^{-1}) for both bridge and terminal bands in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$.[15,16] In fact, it was comparable to the separation between the two terminal CO stretching bands exhibited by this compound in solution (*ca.* 1948 and *ca.* 1971 cm^{-1}), in which case the two bands were presumed to be due to the cis and trans isomers. This led Haines and du Preez to suggest that perhaps both isomers were present in the solid state. The present work was intended, in part, to test that suggestion.

Experimental Section

The synthesis and purification of the compounds were described in the previous paper.[1] Dark red-violet crystals were grown from a 1:3 v/v benzene-hexane solvent at 3°. A crystal of dimensions 0.29 × 0.12 × 0.12 mm was mounted on a glass fiber. Data were collected on a Syntex $P\bar{1}$ automated diffractometer at a temperature of 21 ± 2° using Mo Kα radiation, monochromatized with a graphite crystal. The principal crystallographic data are as follows: space group $P\bar{1}$; $a = 14.331$ (5) Å, $b = 17.335$ (9) Å, $c = 12.482$ (7) Å; $\alpha = 102.12$ (4)°, $\beta = 92.04$ (4)°, $\gamma = 66.44$ (4)°; $V = 2775$ (2) Å^3; $d_{\text{calcd}} = 1.52$ g cm^{-3} for $Z = 4$ and mol wt 636.21. The cell constants and orientation matrix used in data collection were obtained by least-squares refinement of 15 carefully centered reflections with $0° < 2\theta < 30°$. A total of 6387 reflections up to $2\theta_{\max}$ 42.9° were collected using the θ-2θ scan technique with variable scan rates from 4.0 to 24.0°/min and a scan range from 2θ(Mo Kα_1) −0.9° to 2θ(Mo Kα_2) +0.9°. Intensities of three standard reflections measured every

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(11) F. A. Cotton and B. A. Frenz, *Inorg. Chem.*, 13, 253 (1974).

(12) R. D. Adams, F. A. Cotton, and J. M. Troup, *Inorg. Chem.*, 13, 257 (1974).

(13) R. J. Haines and A. L. du Preez, *Inorg. Chem.*, 8, 1459 (1969).

(14) G. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc. A*, 471 (1970).

(15) J. G. Bullitt and F. A. Cotton, *Inorg. Chim. Acta*, 5, 637 (1971).

(16) F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Wiley-Interscience, New York, N. Y., 1971, pp 333-339.

Table II. Positional Parameters for Ring Carbon Atoms

	Molecule I			Molecule II		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
			Cyclopentadienyl Ring 1[a]			
C(1,1)	−0.143 (2)	0.0700 (6)	−0.1620 (8)	0.296 (1)	0.1023 (9)	0.0545 (7)
C(1,2)	−0.190 (1)	0.1593 (7)	−0.1176 (6)	0.222 (1)	0.1854 (5)	0.0525 (7)
C(1,3)	−0.217 (2)	0.2022 (5)	−0.2054 (9)	0.167 (1)	0.2196 (8)	0.1550 (8)
C(1,4)	−0.186 (1)	0.1394 (7)	−0.3042 (6)	0.207 (1)	0.1576 (6)	0.2203 (6)
C(1,5)	−0.140 (2)	0.0577 (5)	−0.2773 (8)	0.286 (1)	0.0851 (8)	0.1582 (8)
			Cyclopentadienyl Ring 2			
C(2,1)	0.251 (1)	−0.095 (2)	−0.232 (1)	0.5456 (8)	0.2439 (7)	−0.031 (1)
C(2,2)	0.170 (1)	−0.093 (1)	−0.170 (1)	0.4426 (9)	0.2858 (6)	−0.054 (1)
C(2,3)	0.091 (1)	−0.092 (2)	−0.242 (1)	0.4020 (7)	0.2228 (8)	−0.084 (1)
C(2,4)	0.124 (1)	−0.094 (1)	−0.348 (1)	0.4800 (9)	0.1420 (6)	−0.079 (1)
C(2,5)	0.223 (1)	−0.096 (2)	−0.342 (1)	0.5688 (7)	0.1551 (7)	−0.047 (1)
			Phenyl Ring 1[b]			
C(1)	−0.1569 (8)	0.3381 (8)	−0.0071 (7)	0.1460 (5)	0.3373 (6)	0.4123 (8)
C(2)	−0.2621 (7)	0.3795 (6)	0.0151 (8)	0.0606 (7)	0.3256 (5)	0.4428 (6)
C(3)	−0.3049 (5)	0.3780 (7)	0.1129 (9)	−0.0367 (6)	0.3813 (7)	0.4222 (8)
C(4)	−0.2425 (8)	0.3351 (8)	0.1185 (7)	−0.0487 (5)	0.4487 (6)	0.3711 (8)
C(5)	−0.1373 (7)	0.2937 (6)	0.1663 (8)	0.0367 (7)	0.4604 (5)	0.3406 (8)
C(6)	−0.0945 (5)	0.2952 (7)	0.0684 (9)	0.1340 (6)	0.4047 (7)	0.3612 (8)
			Phenyl Ring 2			
C(1)	0.106 (2)	0.3104 (11)	−0.1642 (7)	0.4152 (8)	0.3293 (7)	0.4874 (6)
C(2)	0.092 (1)	0.3763 (9)	−0.0721 (6)	0.3534 (7)	0.4135 (6)	0.5397 (8)
C(3)	0.135 (1)	0.4355 (6)	−0.0723 (6)	0.3733 (8)	0.4473 (5)	0.6453 (8)
C(4)	0.192 (2)	0.4289 (11)	−0.1646 (7)	0.4550 (8)	0.3970 (7)	0.6986 (6)
C(5)	0.206 (1)	0.3630 (9)	−0.2566 (6)	0.5168 (7)	0.3129 (6)	0.6463 (8)
C(6)	0.163 (1)	0.3038 (6)	−0.2564 (6)	0.4969 (8)	0.2790 (5)	0.4507 (8)
			Phenyl Ring 3			
C(1)	−0.1441 (7)	0.3335 (8)	−0.3421 (9)	0.3927 (8)	0.0889 (5)	0.4151 (8)
C(2)	−0.2157 (8)	0.4163 (7)	−0.2984 (8)	0.3066 (6)	0.0927 (4)	0.4685 (7)
C(3)	−0.3069 (8)	0.4502 (5)	−0.3498 (9)	0.2938 (6)	0.0171 (6)	0.4688 (7)
C(4)	−0.3263 (7)	0.4012 (8)	−0.4447 (9)	0.3671 (8)	−0.0623 (5)	0.4158 (8)
C(5)	−0.2546 (8)	0.3184 (7)	−0.4883 (8)	0.4532 (6)	−0.0061 (4)	0.3625 (7)
C(6)	−0.1635 (8)	0.2845 (5)	−0.4370 (9)	0.4660 (6)	0.0096 (6)	0.3622 (7)

[a] Cyclopentadienyl ring carbon atoms are numbered as in Figures 1 and 2. [b] Phenyl ring carbon atoms are numbered consecutively with C(1) attached to the phosphite oxygen atom.

Table III. Bond Distances

Bond	Molecule I	Molecule II	Av
Fe(1)-Fe(2)	2.543 (3)	2.548 (3)	2.545 (2)
Fe(1)-P	2.126 (4)	2.125 (4)	2.126 (3)
Fe(1)-C(1)	1.90 (2)	1.91 (1)	1.90 ± 0.02
Fe(2)-C(1)	1.92 (2)	1.91 (1)	
Fe(1)-C(2)	1.86 (2)	1.88 (2)	
Fe(2)-C(2)	1.91 (2)	1.92 (2)	
Fe(2)-C(3)	1.72 (1)	1.69 (2)	1.71 (2)
P-O(3)	1.62 (1)	1.63 (1)	1.61 (1)
P-O(4)	1.59 (1)	1.62 (1)	
P-O(5)	1.60 (1)	1.60 (1)	
C(1)-O(1)	1.20 (2)	1.20 (1)	1.21 (1)
C(2)-O(2)	1.22 (2)	1.20 (1)	
C(3)-O(3)	1.17 (1)	1.19 (2)	1.18 (1)
Cent(1)-Fe(1)[a,b]	1.76	1.76	1.76
Cent(2)-Fe(2)	1.76	1.77	
O(3)C(1)*Ph*(1)[c]	1.39	1.38	1.38
O(4)C(1)*Ph*(2)	1.38	1.39	
O(5)C(1)*Ph*(3)	1.38	1.38	

[a] *Cent* refers to the centroid of the cyclopentadienyl ring here and in Table IV. [b] Standard deviations are not available for distances involving group centroids or group atoms. [c] *Ph* refers to the phenyl rings on the appropriate phosphite oxygen here and in Table IV.

100 reflections showed no significant variation during data collection. Lorentz and polarization corrections were applied but no absorption correction ($\mu = 7.7\ \text{cm}^{-1}$) or extinction correction was deemed necessary.[17]

Solution and Refinement of Structure

The distribution of normalized structure factors as a function of $(\sin\theta)/\lambda$ strongly indicated a centrosymmetric unit cell, *i.e.*, space group $P\bar{1}$. This was confirmed by the subsequent refinement. A sharpened, three-dimensional Patterson function, with the origin removed, was calculated. All but five of the 34 highest peaks were interpretable in terms of an asymmetric unit with six heavy atoms, which could be assigned as four iron atoms and two phosphorus atoms. All structure factor calculations and least-squares refinements were executed using only those 3605 reflections for which $|F_o|^2$ exceeds 3 times the standard deviation of $|F_o|^2$, calculated in the manner previously described,[18] with $p = 0.05$. Refinement minimized $\Sigma w(|F_o| - |F_c|)^2$, with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. The discrepancy indices were defined as follows: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2)^{1/2}$. Atomic scattering factors were those of Cromer and Waber.[19] Anomalous dispersion effects were included in the calculated scattering factors for Fe and P.[20]

After locating and refining the four iron atoms and two phosphorus atoms, three successive difference electron density maps, each followed by a cycle of full-matrix least-squares refinement of all atoms so far located revealed the positions of the six carbonyl groups

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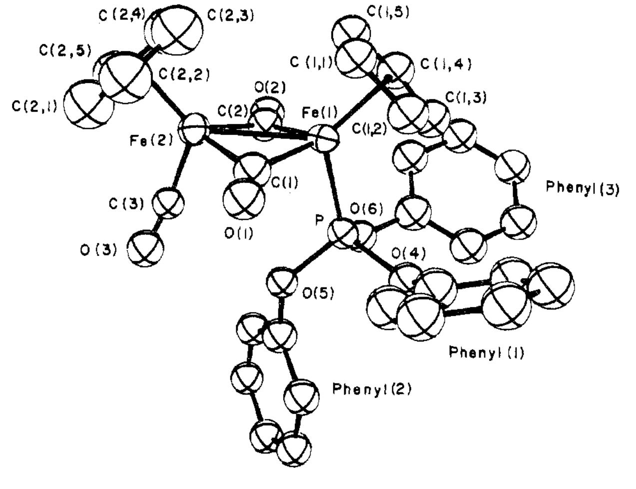
(17) The following computer programs written for the IBM 360/65 were used: DATARED, a data reduction program by Frenz; FAME, a program for calculating Wilson statistics and generating normalized structure factors originally written by Dewar and modified by Goldberg and Gaughan; FOURIER, a crystallographic Fourier summation program written by Dellaca and Robinson based on Zalkin's FORDAP; NUCLS, a least-squares program by Ibers and Doedens; RBANG, a modification of Watkins' program for the generation of group orientation angles for use in rigid group refinement; SADIAN, a program for calculating atomic distances and angles by Baur; PERFACT, a structure factor analysis program by Frenz; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen; and LIST, a data listing program by Snyder.

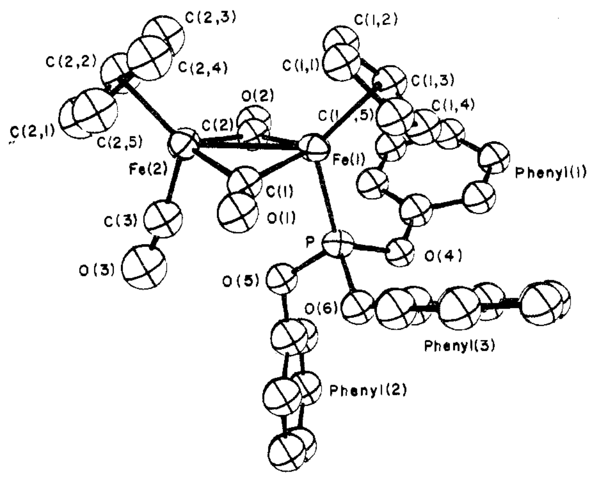
(18) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, 50, 227 (1973).

(19) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in press.

(20) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).



Molecule I



Molecule II

Figure 1. Views of the structures of the two independent molecules of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3P(OC_6H_5)_3$ showing the 50% probability ellipsoids and the atomic numbering scheme.

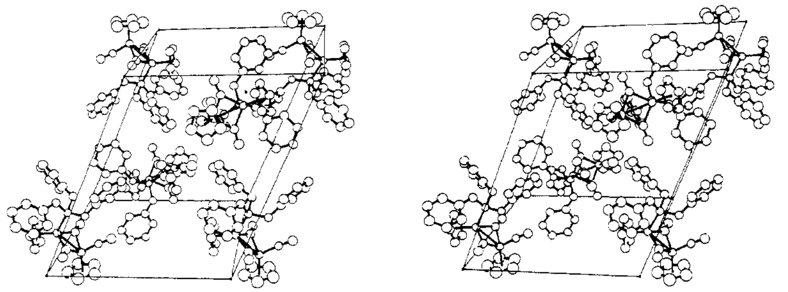


Figure 2. A stereoscopic view of the unit cell of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3P(OPh)_3$.

Table IV. Bond Angles

Angle	Molecule I	Molecule II
P–Fe(1)–Fe(2)	104.9 (1)	104.7 (1)
P–Fe(1)–C(1)	94.1 (5)	93.4 (4)
P–Fe(1)–C(2)	90.4 (5)	91.2 (4)
P–Fe(1)–*Cent*(1)[a]	124.4	123.1
C(1)–Fe(1)–Fe(2)	48.6 (5)	48.3 (4)
C(1)–Fe(1)–C(2)	94.9 (6)	94.7 (6)
C(1)–Fe(1)–*Cent*(1)	121.6	123.3
C(2)–Fe(1)–Fe(2)	48.4 (5)	48.5 (4)
C(2)–Fe(1)–*Cent*(1)	123.1	122.7
C(3)–Fe(2)–Fe(1)	106.0 (5)	104.8 (5)
C(3)–Fe(2)–C(1)	94.1 (6)	92.8 (7)
C(3)–Fe(2)–C(2)	92.7 (6)	92.1 (7)
C(3)–Fe(2)–*Cent*(2)	121.3	123.0
C(1)–Fe(2)–Fe(1)	48.0 (5)	48.1 (4)
C(1)–Fe(2)–C(2)	92.7 (6)	93.5 (6)
C(1)–Fe(2)–*Cent*(2)	122.9	123.1
C(2)–Fe(2)–Fe(1)	46.7 (4)	47.4 (4)
C(2)–Fe(1)–*Cent*(2)	124.7	123.6
Fe(1)–P–O(4)	120.9 (4)	120.1 (3)
Fe(1)–P–O(5)	115.1 (4)	116.6 (4)
Fe(1)–P–O(6)	120.0 (4)	118.9 (4)
O(4)–P–O(5)	103.8 (5)	102.4 (5)
O(4)–P–O(6)	98.0 (5)	96.8 (5)
O(5)–P–O(6)	95.0 (5)	98.0 (5)
Fe(1)–C(1)–Fe(2)	83.4 (6)	83.6 (6)
Fe(1)–C(1)–O(1)	140 (1)	141 (1)
Fe(2)–C(1)–O(1)	135 (1)	135 (1)
Fe(1)–C(2)–Fe(2)	84.9 (6)	84.1 (6)
Fe(1)–C(2)–O(2)	140 (1)	140 (1)
Fe(2)–C(2)–O(2)	135 (1)	135 (1)
Fe(2)–C(3)–O(3)	173 (1)	174 (1)
P–O(1)–C(1)*Ph*(1)	124.9	125.3
P–O(2)–C(1)*Ph*(2)	125.6	123.8
P–O(3)–C(1)*Ph*(3)	124.2	123.4

[a] Standard deviations are not available for angles involving group centroids or group atoms.

and the six phosphite oxygen atoms. The carbon atoms of the four cyclopentadienyl groups and six phenyl groups were then located in difference maps, but for refinement each ring was treated as a rigid body, with symmetries D_{5h} and D_{6h}, respectively. The variable parameters for a given ring were the three coordinates of its center, three orientation angles and an overall isotropic thermal parameter.[21]

In the final two cycles of refinement the iron and phosphorus atoms were given anisotropic thermal parameters. The last cycle converged with $R_1 = 0.075$ and $R_2 = 0.090$. The only significant features in the difference electron density map were five peaks with heights of 1.2–1.4 e Å^{-3} lying between the atoms of ring 2 of molecule I; the accepted atoms of that ring had peak heights of 2.7–3.1 e Å^{-3}. Evidently this ring is partially disordered. No other peaks higher than 0.9 e Å^{-3} were found. Shifts of positional parameters in the last cycle of refinement were all less than 0.5 times their esd's. The error in an observation of unit weight was 1.84.

A table of observed and calculated structure factors for the data used in refinement is available.[22]

Results and Discussion

The compound crystallizes in space group $P\bar{1}$ with two independent cis molecules constituting the asymmetric unit. The independent molecules are depicted in Figure 1, which also defines the atom-numbering scheme. These figures are drawn so as to afford essentially the same view of each mole-

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(21) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

(22) See paragraph at end of paper regarding supplementary material.

cule. Figure 2 shows the molecular packing. The positional and thermal vibration parameters are listed in Tables I and II. Bond distances are given in Table III and bond angles in Table IV. There are no abnormal intermolecular contacts.

The corresponding dimensions of the two independent molecules agree throughout to within the uncertainties, thus indicating that both are representative of the inherent, unperturbed structure which the cis isomer might be expected to have when dissolved in a solvent of low polarity.

On nearly all points where comparisons can be made the present structure is closely similar to that of *cis*-$(\eta^5\text{-}C_5H_5)$-$Fe_2(CO)_4$, **3**. Thus, the Fe-Fe distance in **3** is 2.531 (2) Å which is only about 0.015 Å different from the average value for the present case. The iron to bridging carbonyl distances in **3** have an average value of 1.92 Å, while the average of those found here is 1.90 ± 0.02 Å. In **3**, the central four-membered ring is folded along the Fe-Fe line to give a dihedral angle of 164°, and angles in the range of 160-164° have been found in other cases. In the present compound the average value of this angle is 159 (1)°. All other bond lengths have values which may be considered normal.

Few accurate crystal structures of compounds containing coordinated triphenyl phosphite have been reported.[23] A very accurate structure of a presumably representative compound is that of $Cr(CO)_5[P(OPh)_3]$. The mean values of the P-O distance, the O-C distance, and the P-O-C angle are 1.598 Å, 1.399 Å and 127°. These may be compared with the following values for the present compound: 1.61 Å, 1.38 Å, and 125°. Clearly, the dimensions of the $P(OPh)_3$ ligand found here are quite normal.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. 33142X, and by The Robert A. Welch Foundation (Grant A494).

Registry No. *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[P(OPh)_3]$, 51108-08-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1407.

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[23] H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 12, 265 (1973), and references therein.

Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

X-Ray Crystallographic Elucidation of the Structure of (*Pentahapto*cyclopentadienyl)(7,8,9,10,11,12-*hexahapto*dodecahydro-7,9-dicarba-*nido*-dodecaborato)cobalt(III), a Fluxional Molecule Containing a Triangulated 13 Vertex (1,5,6,1) Docosahedral Cage

MELVYN ROWEN CHURCHILL* and BARRY G. DeBOER

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The "red" isomer of $(\pi\text{-}C_5H_5)Co(B_{10}C_2H_{12})$, synthesized and found to be "fluxional" by Hawthorne and coworkers, has been subjected to a single-crystal X-ray diffraction study. The species crystallizes as dark red rhombic plates in the noncentrosymmetric orthorhombic space group $Pca2_1$ [C_{2v}^5; No. 29] with $a = 13.744$ (4) Å, $b = 7.047$ (2) Å, $c = 13.620$ (3) Å, $\rho_{\text{obsd}} = 1.348$ (5) g cm^{-3}, and $\rho_{\text{calcd}} = 1.351$ g cm^{-3} for $Z = 4$. X-Ray data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer. All atoms, including hydrogen atoms, have been located, the final discrepancy indices being $R_F = 3.02\%$ and $R_{wF} = 3.81\%$ for 2344 *hkl* and *hkl* reflections. The π-cyclopentadienyl ligand is bound symmetrically to the cobalt(III) atom, with individual Co-C distances ranging from 2.020 (5) to 2.057 (3) Å and averaging 2.038 Å. The $B_{10}C_2Co$ fragment defines a triangulated (1,5,6,1) 13-apex docosahedron (22-sided figure) in which the equatorial (C-B-C-B-B-B) hexagonal belt is bonded to the cobalt(III) atom, individual distances (taken cyclically) being Co-C(7) = 2.032 (4) Å, Co-B(8) = 2.199 (6) Å, Co-C(9) = 2.150 (3) Å, Co-B(10) = 2.093 (3) Å, Co-B(11) = 2.165 (3) Å, and Co-B(12) = 2.203 (4) Å. The linking together of five- and six-membered equatorial rings in forming the (1,5,6,1) 13-apex triangulated cage necessarily causes some severe abnormalities in the environments of individual atoms. Thus, atom C(7) is linked to only five other atoms and is associated with two very short bonds [C(7)-B(8) = 1.429 (10) Å and C(7)-B(12) = 1.527 (6) Å], while atom B(2) is linked to *seven* other atoms and is associated with some very long bonds [B(2)-B(8) = 2.081 (10) Å and B(2)-B(12) = 1.947 (6) Å]. The four-membered systems B(2)-B(3)-B(8)-C(7) and B(2)-B(6)-B(12)-C(7) are not symmetrically triangulated but are perturbed toward open squares.

Introduction

The reduction of the icosahedral $B_{10}C_2H_{12}$ carboranes to produce the $B_{10}C_2H_{12}^{2-}$ dianions[1-4] and the protonation of these species to $B_{10}C_2H_{13}^-$ anions[2-6] are well-known reactions (see Scheme I).

Scheme I

$$B_{10}C_2H_{12} \xrightarrow{+2e^-} B_{10}C_2H_{12}^{2-} \xrightarrow{H^+} B_{10}C_2H_{13}^-$$

While X-ray crystallographic studies of $[Me_4N^+][B_{10}C_2H_{11}$-

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[1] D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2, 1128 (1963).

[2] L. Zakharkin, V. Kalinin, and L. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2310 (1967).

[3] L. Zakharkin and V. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 194 (1969).

[4] V. Stanko, Yu. V. Gol'tyapin, and V. Brattsev, *Zh. Obshch. Khim.*, 39, 1175 (1969).

[5] G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 899 (1972).

[6] G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 3174 (1973).