material for an X-ray structural investigation.

Acknowledgment is made to the National Science Foundation for its support of this research through Grant CHE8019513 (D.L.R.). We also thank the University of South Carolina for funds used to purchase the diffractometer.

Registry No. (η^5-C_5H_5)Fe(CO)(PPh_3)[C(CO_2Et)C(Me)$_2$], 80485-08-1; (η^5-C_5H_5)Fe(CO)(PPh_3)I, 12099-18-2; MeC≡CCO_2Et, 4341-76-8; [(η^5-C_5H_5)Fe(CO)(PPh_3)(η^2-MeC≡CCO_2Et)]BF_4, 80501-96-8.

Supplementary Material Available: Listings of structural factors (28 pages). Ordering information is given on any current masthead page.

Crystal and Molecular Structure of Dicarbonyl(hexaethylbenzene)(triethylphosphine)chromium(0). A Novel Example of Conformational Variability in Hexaethylbenzene π Complexes

Geoffrey Hunter,*[1a] John F. Blount,[1b] James R. Damewood, Jr.,[1c] Daniel J. Iverson,[1c] and Kurt Mislow*[1c]

Department of Chemistry, The University, Dundee DD1 4HN, Scotland, Chemical Research Department, Hoffmann-La Roche, Inc., Nutley, New Jersey 07110, and Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received October 8, 1981

The crystal and molecular structure of the title compound, (HEB)Cr(CO)$_2$PEt$_3$ (1), has been determined: space group $P2_1/c$, a = 9.729 (4) Å, b = 18.353 (6) Å, c = 29.869 (12) Å, β = 98.26 (2)°, and Z = 8, with two different conformations (**1A** and **1B**) present in equal population. In **1A** one terminal methyl (C(31)) projects toward the complexed (proximal) side of the ring while the other five project toward the uncomplexed (distal) side. The molecule is in an eclipsed conformation, with the PEt$_3$ ligand anti to C(31); the resulting structure has near C_s symmetry. Conformation **1A** is unprecedented among HEB transition-metal complexes. In **1B** all six methyls are distal and the molecule adopts a staggered arrangement. The resulting conformation closely resembles that of the previously reported (HEB)Cr(CO)$_2$PPh$_3$ (2), and a detailed comparison of these structures has served to clarify the origin of the steric effect responsible for this conformational preference. Arguments are advanced that four diastereomeric HEB π complexes are energetically favored and that the range of stabilities spanned by these four is less than the calculated range spanned by the corresponding uncomplexed HEB conformers. Structures corresponding to three of these four isomers have been experimentally realized in this and a previous study.

Special interest in hexaethylbenzene (HEB) derives from its role as a simple representative of a class of hexaalkylbenzenes and hexaalkylbenzene analogues in which the alkyl groups point alternately up and down around the ring perimeter; such alternation is found in HEB itself and in its tricarbonylchromium and -molybdenum π complexes.[2] In a previous study[2] we had found that replacement of one carbonyl group in tricarbonyl(hexaethylbenzene)chromium(0) by triphenylphosphine leads to a striking change in the conformation of the arene moiety: whereas the conformation of the tricarbonyl complex is eclipsed, with the terminal methyl groups alternately projecting toward the complexed (proximal) and uncomplexed (distal) side of the ring, in the dicarbonyl triphenylphosphine complex the conformation is staggered and all six methyls are distal. This conformational change was found to persist in solution and was ascribed to steric effects of the triphenylphosphine group. The present work was initiated in the hope that a study of conformational preferences in dicarbonyl(hexaethylbenzene)(tri*ethyl*phosphine)chromium(0) (1) might serve to clarify the origin of this remarkable steric effect in the previously studied dicarbonyl(hexaethylbenzene)(tri*phenyl*-

Table I. Selected Bond Lengths for **1A** and **1B**[a]

atoms[b]	**1A**	**1B**
C(11)-C(12)	1.412	1.423
C(12)-C(13)	1.428	1.425
C(13)-C(14)	1.432	1.413
C(14)-C(15)	1.414	1.426
C(15)-C(16)	1.432	1.412
C(16)-C(11)	1.412	1.426
Cr-C(11)	2.224	2.184
Cr-C(12)	2.201	2.196
Cr-C(13)	2.250	2.231
Cr-C(14)	2.263	2.272
Cr-C(15)	2.232	2.256
Cr-C(16)	2.209	2.232
Cr-C(1)	1.809	1.812
Cr-C(2)	1.790	1.817
Cr-P	2.308	2.324
C(1)-O(1)	1.164	1.175
C(2)-O(2)	1.174	1.168

[a] In angstrom units. Estimated standard deviations for bond lengths are 0.002-0.009 and 0.001-0.009 Å for **1A** and **1B**, respectively. [b] Numbering as in Figures 1, 2, and 4.

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(1) (a) University of Dundee. (b) Hoffmann-La Roche, Inc. (c) Princeton University.

(2) (a) Hunter, G.; Iverson, D. J.; Mislow, K.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5942. (b) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *Ibid.* **1981**, *103*, 6073.

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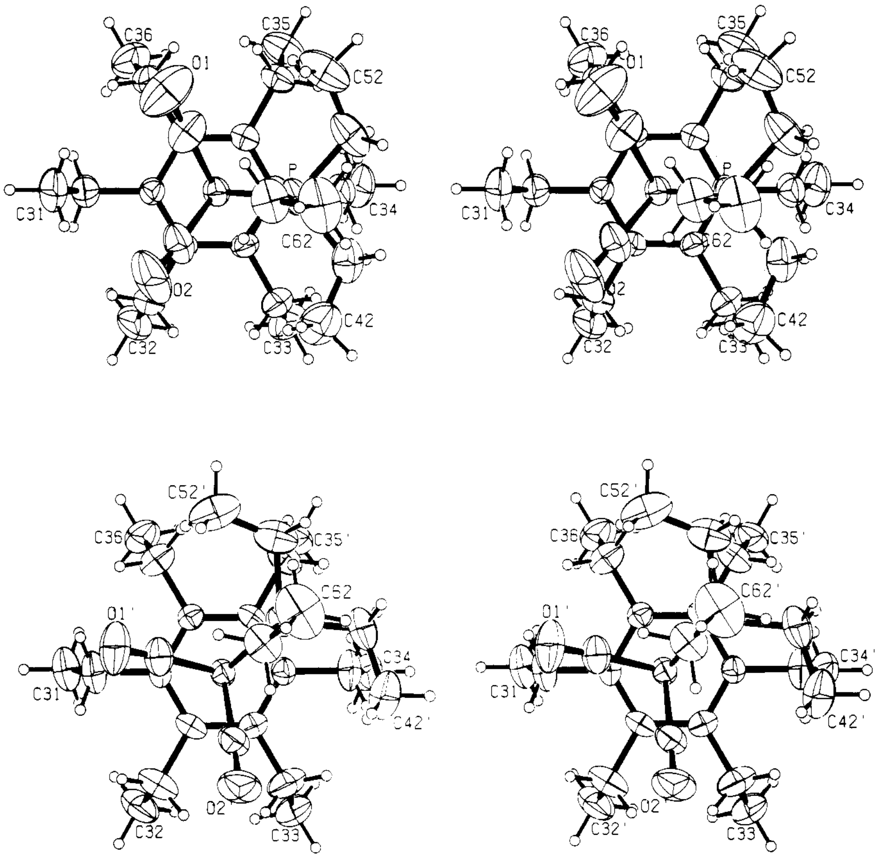

Figure 1. Stereoviews of the X-ray structures of the two conformations of dicarbonyl(hexaethylbenzene)(triethylphosphine)chromium(0) (**1**): top, **1A** (unprimed); bottom, **1B** (primed).

Table II. Selected Bond Angles for 1A and 1B[a]

atoms[b]	1A	1B
C(11)-C(12)-C(13)	121.0	119.9
C(12)-C(13)-C(14)	119.1	120.3
C(13)-C(14)-C(15)	120.3	119.6
C(14)-C(15)-C(16)	119.3	120.7
C(15)-C(16)-C(11)	121.0	119.6
C(16)-C(11)-C(12)	119.2	120.0
C(11)-C(21)-C(31)	116.6	115.2
C(12)-C(22)-C(32)	113.3	115.8
C(13)-C(23)-C(33)	114.9	115.8
C(14)-C(24)-C(34)	114.5	114.0
C(15)-C(25)-C(35)	116.5	115.1
C(16)-C(26)-C(36)	113.6	115.7
C(1)-Cr-C(2)	87.0	87.0
C(1)-Cr-P	86.0	86.5
C(2)-Cr-P	86.0	87.1
Cr-C(1)-O(1)	177.1	176.4
Cr-C(2)-O(2)	177.8	177.2

[a] In degrees. Estimated standard deviations for bond angles are 0.2-0.5°. [b] See footnote *b*, Table I.

Table III. Selected Dihedral Angles with the Least-Squares Benzene Plane for 1A and 1B[a]

atoms[b,c]	1A	1B
C(11)-C(21)-C(31)	88.7	86.7
C(12)-C(22)-C(32)	88.8	87.5
C(13)-C(23)-C(33)	88.4	84.7
C(14)-C(24)-C(34)	84.7	88.1
C(15)-C(25)-C(35)	83.8	87.9
C(16)-C(26)-C(36)	86.8	88.4

[a] In degrees. Estimated standard deviations for dihedral angles are 0.3-0.5°. [b] The atoms which define the second plane. [c] See footnote *b*, Table I.

phosphine)chromium(0) (**2**).

Results and Discussion

Ultraviolet irradiation of a pentane solution of tricarbonyl(hexaethylbenzene)chromium(0) (**3**)[2] in the presence of triethylphosphine yielded **1**, isolated as orange crystals. The structure of **1** was determined by X-ray analysis. The crystals are monoclinic, space group $P2_1/c$. The unit cell contains two independent conformers (**1A** and **1B**) in equal population, and neither conformer occupies a special position in the unit cell. Stereoviews of **1A** and **1B** are shown in Figure 1, deviations of the nonhydrogen atoms from the least-squares plane of the benzene ring are given in Figure 2, and selected bond lengths, bond angles, and dihedral angles are reported in Tables I–III. Final atomic parameters for **1A** and **1B** are listed in Table IV.

It is immediately apparent upon examination of Figures 1 and 2 that the structures of **1A** and **1B** differ in two important respects. First, whereas in **1A** one methyl (C(31)) is proximal and five are distal, in **1B** all six methyls are distal. Second, whereas **1B** adopts an approximately staggered arrangement about the arene–metal bond axis, in **1A** the metal fragment assumes an eclipsed conformation, with the triethylphosphine ligand anti to C(31). As a result the symmetry of **1A** is close to $C_s(m)$.[3] In most other respects the structural parameters of **1A** and **1B** do not deviate markedly from each other[4] or from values

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(3) The plane formed by C(11)–C(21)–C(31) is, to a high degree of approximation, the molecular symmetry plane which contains C(24)–C(34) and C(61)–C(62) and which bisects the C(1)–Cr–C(2) and C(41)–P–C(51) angles. Deviations from C_s symmetry are, however, far from insignificant. For example, the C_{ar}–X–Cr–C_{CO} angles (X = centroid of arene ring) differ by over 10° from symmetry-related values (Figure 2).

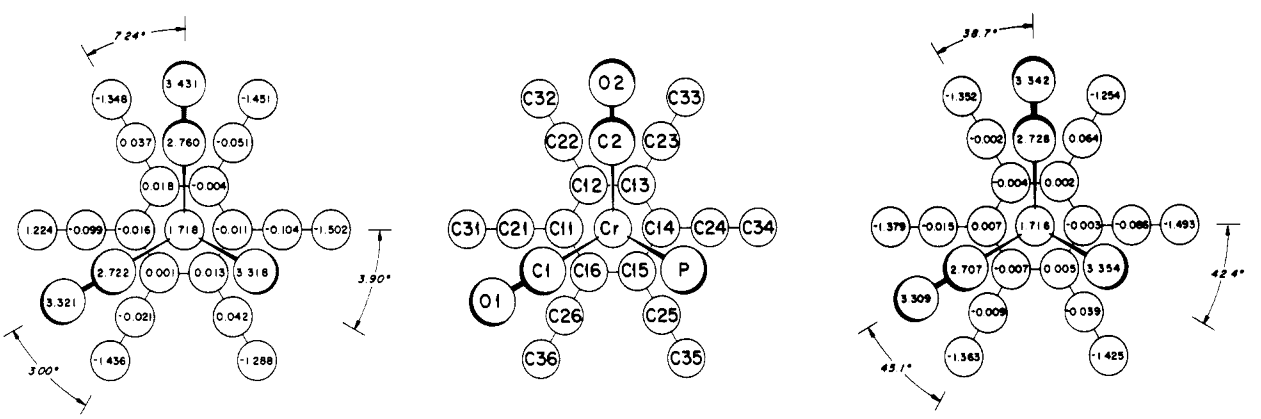

Figure 2. Dicarbonyl(hexaethylbenzene)(triethylphosphine)chromium(0) (**1**): center, numbering scheme for heavy atoms; left, deviations (in Å) of nonhydrogen atoms in **1A** from the least-squares plane of the benzene ring and selected C_{ar}–X–Cr–C_{CO} (or P) torsion angles (X = centroid of the arene ring) (a positive value indicates that the atom is proximal to the metal and a negative value that is is distal); right, the same for **1B**. Torsion angles for **1A**, obtained from parameters in Table IV, are reported as their negatives for ease of comparison with **1B**.

which might be regarded as normal for $(\eta^6\text{-arene})$chromium complexes.[5]

Conformational Variability of Stereoisomeric Hexaethylbenzene π Complexes. Among the transition-metal complexes of HEB, there is no precedent for the distal–proximal arrangement of methyl groups found in **1A**.[6] In order to place the discussion of this finding into proper perspective, we begin with an enumeration of the possible stereoisomers of such complexes.

In principle, complexation of the eight "up–down" isomers of HEB[2b] may occur on either face. Three of these isomers (**1a**, **1d**, **1f**)[2b] each have three "up" and three "down" methyls and have homotopic (equivalent) faces, whereas the other five have diastereotopic (nonequivalent) faces. Disregarding isomerism due to orientation of the metal fragment in relation to the ring, there should therefore be a total of 13 diastereomers (Figure 3).[7,8] When such orientation is taken into account, 36 diastereomers are possible, given that these $(\eta^6\text{-arene})MX_3$ complexes are either eclipsed or staggered.[5] If the metal fragment does not have threefold symmetry, this number is even larger. However, the isomer count can be drastically reduced if we postulate that *eclipsing cannot take place over carbons bearing proximal groups, and staggering is disallowed if any one of the bisected bonds is joined to a carbon atom bearing a proximal group.* Under these two constraints, which are based on the reasonable assumption that steric interactions between a normal metal fragment and proximal methyl groups play a decisive role in determining molecular stability, only one staggered (**1h**) and four eclipsed (**1a**, **1c**, **1e**, and **1h**) structures need be considered. While **1h** is a member of both sets there appears to be a preference for the staggered (i.e., **S**(6)) conformation.[2b,5] Thus, four conformational types remain.

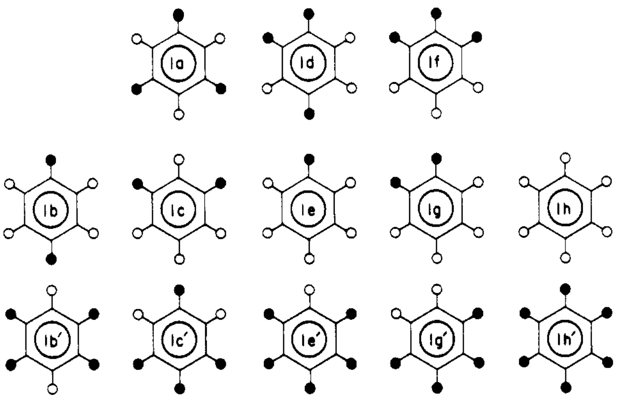

Figure 3. The 13 diastereotopic faces of hexaethylbenzene (HEB) π complexes. The metal atom is the point of reference and should be viewed as residing over the ring and above the plane of the paper. The filled (open) circles represent proximal (distal) methyl groups projecting toward (away from) the observer: top row, HEB conformers with homotopic faces; middle and bottom rows, HEB conformers with diastereotopic faces. Diastereomeric complexes derived from the same HEB conformer are given the same descriptor[7] and are differentiated by a prime.

On the premise that nonbonded repulsive interactions between a given metal fragment and η^6-HEB (i.e., the bound HEB moiety) increases with the number of proximal methyl groups, p, the destabilizing interaction for the four HEB complexes under consideration increases in the order **1h** ($p = 0$) < **1e** ($p = 1$) < **1c** ($p = 2$) < **1a** ($p = 3$). This parallels the order of *decreasing* destabilization in the corresponding free arenes, **1h** ($s = 6$) > **1e** ($s = 4$) > **1c** ($s = 2$) > **1a** ($s = 0$), where s is the number of repulsive syn interactions between ethyls in neighboring (ortho) positions whose methyls are located on the same side of the ring.[9] On the further assumption that these syn re-

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[4] See Tables I–III. For example, the average C_{ar}–C_{ar} bond distance for **1A** (**1B**) is 1.422 (1.421) Å, approximately 0.02 Å longer than found for HEB,[2b] and there is no evidence for bond length alternation. The average C_{ar}–C_{ar}–C_{ar} bond angle is 120.0° for both compounds and deviations of the aryl carbon atoms from the least-squares benzene planes are small. The benzene rings are therefore approximated well by regular hexagons. The planes formed by the C_{ar}–CH_2–CH_3 fragments are essentially perpendicular to the least-squares benzene plane with an average dihedral angle of 86.9 (87.2)°. The average Cr–C_{ar} distance is 2.230 (2.229) Å. The C_{ar}–CH_2–CH_3 bond angle involving C(31) in **1a** (116.6°) is similar to the average angle for the three proximal methyls in **3** (115.8°).[2b] However, the average C_{ar}–CH_2–CH_3 angle for the five (six) distal methyls in **1A** (**1B**), 114.6° (115.3°), is significantly larger than the average value for the three distal methyls in **3** (111.9°)[2b] and is rather close to the angles found in **2** (av 115.7°).[2b] This phenomenon probably reflects the increased steric interaction among these crowded distal groups.

[5] For comprehensive reviews and leading references to the chemistry of tricarbonyl$(\eta^6\text{-arene})$transition-metal complexes (M = Cr, Mo, W), see: Sneeden, R. P. E. "Organochromium Compounds"; Academic Press: New York, 1975; p 19 ff. Silverthorn, W. E. in Stone, F. G. A.; West, R., Eds. *Adv. Organomet. Chem.* Vol. 13; *13*, p 48 ff. Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. For recent update on the literature, see: Atwood, J. D. *J. Organomet. Chem.* **1980**, *196*, 79.

[6] In making this statement we discount a maverick methyl group (C(33B)) which is found on the proximal side as a disorder in the crystal of **2** and which is shown by a dashed bond and an open circle in Figure 4.

[7] As a matter of convenience in discussion, we retain the previously introduced[2b] configurational descriptors (**1a–h**) for the eight HEB isomers and extend them to the corresponding π complexes.

[8] Of the eight HEB isomers, one (**1d**) is chiral and exists in enantiomeric forms. The faces of the two enantiomers are enantiotopic by external comparison.

Table IV. Final Atomic Parameters for **1A** and **1B**[a-d]

atom	x	y	z
Cr	0.56504 (7)	0.13406 (4)	0.13372 (2)
Cr′	0.85408 (7)	0.63072 (4)	0.11967 (2)
P	0.51173 (14)	0.24377 (7)	0.16488 (4)
P′	1.02267 (13)	0.71571 (7)	0.14685 (4)
O(1)	0.3558 (5)	0.0666 (3)	0.1842 (1)
O(2)	0.7690 (5)	0.1124 (2)	0.2164 (1)
O(1)′	0.8815 (4)	0.6816 (2)	0.0264 (1)
O(2)′	0.6416 (4)	0.7476 (2)	0.1210 (1)
C(1)	0.4378 (6)	0.0946 (3)	0.1652 (2)
C(2)	0.6887 (6)	0.1225 (3)	0.1837 (2)
C(11)	0.6240 (5)	0.0373 (2)	0.0959 (1)
C(12)	0.7266 (5)	0.0918 (3)	0.0961 (1)
C(13)	0.6917 (5)	0.1630 (3)	0.0789 (1)
C(14)	0.5495 (5)	0.1798 (3)	0.0628 (1)
C(15)	0.4452 (4)	0.1265 (3)	0.0643 (1)
C(16)	0.4838 (5)	0.0550 (3)	0.0807 (1)
C(21)	0.6644 (5)	−0.0404 (3)	0.1112 (2)
C(22)	0.8765 (5)	0.0725 (3)	0.1138 (2)
C(23)	0.8040 (5)	0.2199 (3)	0.0766 (2)
C(24)	0.5116 (5)	0.2539 (3)	0.0423 (2)
C(25)	0.2933 (5)	0.1450 (3)	0.0483 (2)
C(26)	0.3746 (5)	−0.0041 (3)	0.0812 (2)
C(31)	0.6635 (6)	−0.0578 (3)	0.1610 (2)
C(32)	0.9564 (6)	0.0443 (3)	0.0773 (2)
C(33)	0.8635 (6)	0.2219 (3)	0.0322 (2)
C(34)	0.5032 (6)	0.2569 (3)	−0.0084 (2)
C(35)	0.2371 (5)	0.1248 (3)	0.0001 (2)
C(36)	0.3560 (6)	−0.0521 (3)	0.0387 (2)
C(41)	0.6215 (6)	0.3236 (3)	0.1595 (2)
C(42)	0.7731 (7)	0.3158 (3)	0.1810 (2)
C(51)	0.3416 (6)	0.2861 (3)	0.1462 (2)
C(52)	0.2180 (6)	0.2403 (4)	0.1545 (2)
C(61)	0.5141 (6)	0.2387 (3)	0.2268 (2)
C(62)	0.4810 (7)	0.3074 (3)	0.2521 (2)
C(1)′	0.8748 (5)	0.6628 (3)	0.0636 (2)
C(2)′	0.7273 (5)	0.7031 (3)	0.1209 (2)
C(11)′	0.7955 (5)	0.5270 (2)	0.0865 (1)
C(12)′	0.6887 (5)	0.5483 (2)	0.1118 (2)
C(13)′	0.7218 (5)	0.5635 (2)	0.1588 (2)
C(14)′	0.8598 (5)	0.5563 (2)	0.1807 (1)
C(15)′	0.9663 (4)	0.5348 (2)	0.1553 (2)
C(16)′	0.9347 (5)	0.5193 (2)	0.1086 (2)
C(21)′	0.7609 (5)	0.5100 (3)	0.0365 (2)
C(22)′	0.5401 (5)	0.5558 (3)	0.0880 (2)
C(23)′	0.6088 (5)	0.5902 (3)	0.1854 (2)
C(24)′	0.8942 (5)	0.5678 (3)	0.2319 (2)
C(25)′	1.1146 (5)	0.5250 (3)	0.1791 (2)
C(26)′	1.0477 (5)	0.4958 (3)	0.0814 (2)
C(31)′	0.7304 (6)	0.4314 (3)	0.0253 (2)
C(32)′	0.4539 (5)	0.4877 (3)	0.0854 (2)
C(33)′	0.5238 (5)	0.5319 (3)	0.2036 (2)
C(34)′	0.8772 (5)	0.5006 (3)	0.2595 (2)
C(35)′	1.1473 (5)	0.4504 (3)	0.1995 (2)
C(36)′	1.0746 (5)	0.4152 (3)	0.0802 (2)
C(41)′	1.0478 (6)	0.7403 (3)	0.2070 (2)
C(42)′	0.9166 (7)	0.7696 (3)	0.2235 (2)
C(51)′	1.2062 (5)	0.7001 (3)	0.1400 (2)
C(52)′	1.2331 (6)	0.6934 (3)	0.0923 (2)
C(61)′	0.9923 (5)	0.8055 (3)	0.1194 (2)
C(62)′	1.0959 (7)	0.8660 (3)	0.1346 (2)

[a] Standard deviations in parentheses. [b] Atom descriptors for **1A** and **1B** are unprimed and primed, respectively. [c] Anisotropic thermal parameters are recorded in the supplementary material. [d] Parameters for hydrogen atoms are recorded in Table VII (supplementary material).

pulsions remain effective within η^6-HEB, it follows that there is a tradeoff in p and s destabilizations which leads to a decrease in the range of stabilities spanned by the four HEB complexes relative to the range (8–11 kcal mol^{-1}) calculated[2b] for the corresponding uncomplexed HEB conformers. Additionally, the magnitude of a p destabilization is a function of the steric bulk of the tripodal ligands. As a result of this dependence, the relative magnitudes of p and s destabilizations are expected to vary from system to system.

The preceding analysis is fully borne out by our present and previous[2] observations. Of the 36 or more possible isomeric HEB complexes, only three types have thus far been observed (**1a** (**3**), **1e** (**1A**), and **1h** (**1B**, **2**)), all of which belong to the set of four discussed above. Although no representative of the missing type **1c** has been reported, tricarbonyl(hexaethylborazine)chromium(0)[10] may be regarded as a close relative since HEB and hexaethylborazine are isosteric. Furthermore, the coexistence of two conformational isomers in the unit cell of **1** indicates that **1A** and **1B** do not differ appreciably in stability; this supports our argument that compensatory destabilization tends to equalize the internal energies of stereoisomeric HEB complexes, as in **1A** ($p = 1$, $s = 4$) vs. **1B** ($p = 0$, $s = 6$). Indeed, the observation (NMR) that **1A** and **1B** also coexist in comparable quantities in solution[11,12] indicates that the two conformers are virtually isoenergetic.

Steric Effects of PR_3 Groups on the Conformations of Hexaethylbenzene Complexes 1 and 2. We now turn to a consideration of the question which motivated this study. That the conformation of **1B** is strikingly similar to that of **2** is obvious by comparison of Figures 1 and 2 in the present paper with Figure 8 and 9 in reference 2b. In both molecules the six methyls are distal and the expected staggered[5] conformation is adopted. The resemblance between the two compounds extends to a close similarity in bonding parameters for η^6-HEB as well as for the Cr–P (**1B** (**2**): 2.324 (2.320) Å) and average Cr–C_{ar} (**1B** (**2**): 2.229 (2.241) Å) distances, for the chromium atom distances from the least-squares plane (**1B** (**2**): 1.716 (1.729) Å), and for the chromium tilt angles (**1B** (**2**): 2.3 (2.5)°).[13]

At first sight this result might seem surprising, since PEt_3 is presumably less sterically demanding than PPh_3.[14] However, detailed examination of the two structures reveals that the relevant portions of the two PR_3 ligands are closely similar. As shown in Figure 4, one of the three ethyl groups in **1B** (C(61)′-C(62)′) and one of the three phenyl rings in **2** (C(41)–C(46)) points directly away from η^6-HEB and therefore has only a small, if any, direct effect on the arene conformation. In contrast, the remaining PEt_2 fragment in **1B**, whose nonhydrogen atoms (P′, C(41)′, C(42)′, C(51)′, C(52)′) are shaded in Figure 4, zig-zags across almost half of the face of the ring in an arc that extends virtually from C(13)′–Et to C(16)′–Et. Likewise, the lower edge of the remaining PPh_2 fragment in **2**, whose nonhydrogen atoms (P, C(51), C(52), C(61), C(66)) are

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[9] The calculated[2b] order of stability among the eight HEB conformers seems to be qualitatively related to s. According to this criterion, the isomers of HEB may be partitioned into four sets: **1a** (s = 0), **1b–d** (s = 2), **1e–g** (s = 4), and **1h** (s = 6). The relative energies, in kcal mol^{-1}, within each set are (EFF, EFF-EHMO): **1a** (0.0, 0.0), **1b–d** (3.5–3.7, 3.6–5.0), **1e–g** (5.9–7.2, 8.0–9.3), and **1h** (8.2, 11.5).

[10] Huttner, G.; Krieg, B. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 512; *Chem. Ber.* **1972**, *105*, 3437.

[11] Preliminary results on **1** in CD_2Cl_2 at −87 °C (360 MHz). Interconversion of the conformers takes place by ethyl group rotation, with $\Delta G^* \approx 9.4$ kcal mol^{-1} at −73 °C. Further details will be reported elsewhere.

[12] In view of the other similarities between **1B** and **2**, it is somewhat surprising that only one conformation of **2**, i.e., **2B**, was observed in the solid state and in solution at low temperatures.[2,6]

[13] The chromium tilt angle is the angle between the X–Cr vector and the normal to the arene least-squares plane. In both compounds this tilt is caused by a movement of the chromium atom toward the side of the benzene ring which is anti to the phosphorus atoms, i.e., toward C(11)′ and C(12)′ in **1B**.

[14] However, the cone angles of PEt_3 and PPh_3 ligands are quite similar: Clark, H. C. *Isr. J. Chem.* **1976**, *15*, 210.

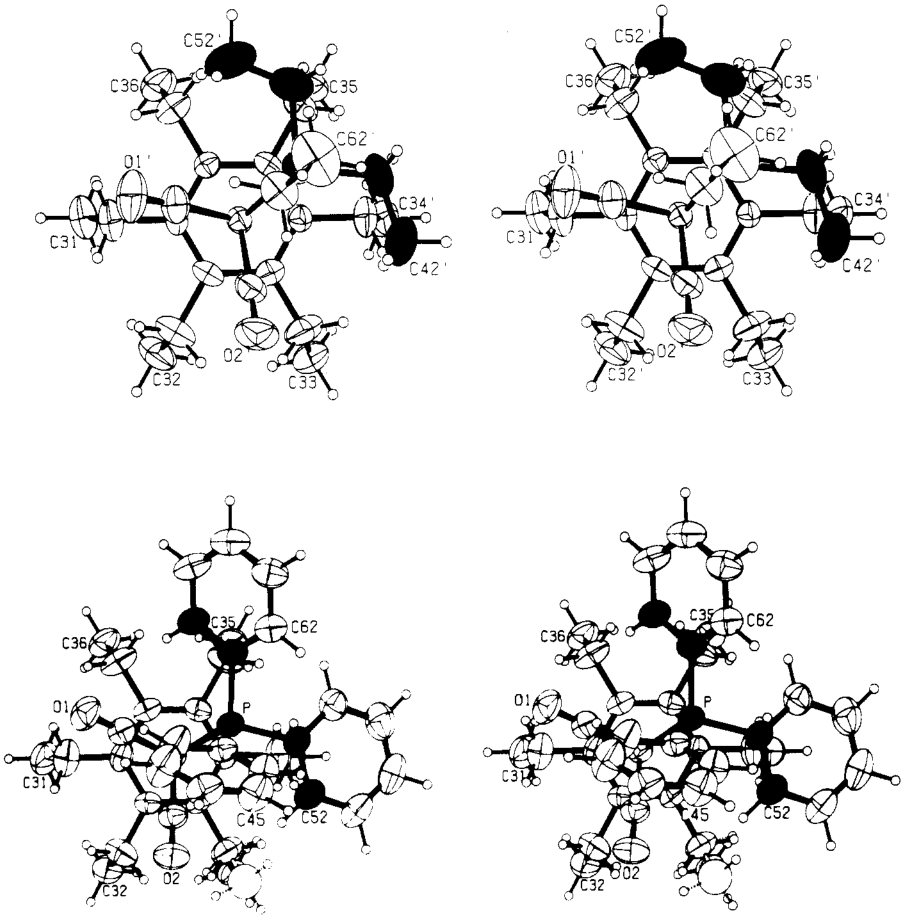

Figure 4. Stereoviews of the X-ray structures of dicarbonyl(hexaethylbenzene)(triethylphosphine)chromium(0) (1) and dicarbonyl(hexaethylbenzene)(triphenylphosphine)chromium(0)(2): top, the S(6) of 1 (1B) with atoms P′, C(41)′, C(42)′, C(51)′, and C(52)′ shaded; bottom, 2 with atoms P, C(51), C(52), C(61), and C(66) shaded. Views are perpendicular to the least- squares benzene planes.

shaded in Figure 4, extends over a similar region of η_6-HEB. The least-squares planes formed by the shaded atoms are essentially parallel to the least-squares planes of the benzene rings, making angles of only 2.0° (**1B**) and 4.9° (**2**).[15] Nonbonded interactions with the shaded atoms and the attached hydrogens are evidently responsible for forcing the terminal methyl groups to the distal side. In short, the present study clearly reveals that the conformational change induced by substitution of a triphenylphosphine ligand for a carbonyl group in **3** is almost entirely due to the interaction of η^6-HEB with a phosphorus atom and two CH–CH fragments belonging to two phenyl rings and that the remaining portions of these two rings, as well as the entire third phenyl ring, have little or no direct effect on the molecular conformation.

This interpretation nicely accounts for the distal conformation of those methyl groups which are located in the region covered by the sterically effective portion of the PR_3 ligand, i.e., the region under the arc spanned by the shaded atoms. As may be seen by inspection of Figure 1, the PEt_2 fragment which is responsible for the steric effect in **1B** performs a similar function in **1A**.[16] Specifically, the terminal methyl groups in that fragment, C(42) and C(52), are located above methyl groups C(33) and C(35) and force the latter into distal positions. In **3**, where the phosphine ligand is replaced by carbonyl, this effect is absent and the same two methyl groups are therefore able to assume proximal positions and thus relieve four syn interactions.

The steric effect of the PR_2 fragment cannot of course account for the disposition of groups, such as C(31)′ and C(32)′ in **1B**, which are on the far side of the ring and anti to the phosphorus atom and which are therefore not covered by the shaded atoms. An explanation for this conformational preference in **1B** and **2** can however be found by considering the staggered arrangement of the metal fragment in these two molecules: according to our postulated constraint, such an arrangement is only compatible with the observed all-distal conformation (**1h**).

We conclude by noting that in this as in the preceding section, our interpretations of conformational preferences in HEB transition-metal complexes have been predicated on the simplifying assumption that steric effects are exclusively responsible for the observed structures: although we recognize that electronic effects of the tripodal ligands, e.g. bonding involving phosphorus, might also play an indirect role, there has been no need thus far to invoke such effects in order to rationalize any reported observations.[17]

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(15) Although only moderate agreement might have been expected between the structural parameters about the phosphorus atom in **1B** and in **2**, because of inherent P–C$_{alk}$ and P–C$_{ar}$ bonding differences, the dissimilarities are in fact not pronounced. For example, in the shaded region the C–P–C angles for **1B** (**2**) are 98.7 (104.1)°, the average P–C distances are 1.841 (1.838) Å and the average P–C–C angles are 114.3 (118.2)°. The bond angles are larger in **2** than in **1B** and the expansion occurs parallel to the least-squares benzene plane; this results in a somewhat larger arc in **2**. The distances of the shaded atoms from their respective least-squares benzene planes show, in general, only moderate scatter and average 3.516 and 3.331 Å for **1B** and **2**.

(16) The nonhydrogen atoms of the PEt_2 fragment in **1A** are an average distance of 3.462 Å from, and form a least-squares plane of 3.0° with, the least- squares benzene plane. The values of the average P–C distance (1.837 Å), P–C–C angle (115.0°), and C–P–C angle (98.4°) are similar to the corresponding values in **1B**.[15]

Experimental Section

The infrared spectrum was recorded on a Perkin-Elmer 521 spectrometer. NMR spectra were recorded at 15.08 MHz in the Fourier transform mode on a Bruker WP60 spectrometer. All reported shifts are downfield relative to tetramethylsilane. The mass spectrum were measured on an AEI MS-9 high-resolution mass spectrometer with a DS-30 data system. An ionizing voltage of 70 eV was used. Reagents obtained from the indicated sources were used without further purification: hexaethylbenzene, $Cr(CO)_6$ (Pfaltz & Bauer); PEt_3 (Fluka).

Tricarbonyl(hexaethylbenzene)chromium(0) (3) was prepared as described previously.[2]

Dicarbonyl(hexaethylbenzene)(triethylphosphine) chromium(0) (1) was prepared by UV irradiation for 1 h of a freeze–thaw degassed pentane (30 ml) solution of **3** (0.18 g, 0.47 mmol) and PEt_3 (0.1 g, 0.68 mmol) contained in a quartz vessel. The pentane solution was filtered under a nitrogen atmosphere and the solvent removed. The solid residue was recrystallized from pentane to give orange crystals of 1: IR (KBr) 1789, 1846, 1857, 1948 cm^{-1}; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ambient temperature) δ 6.5, 15.2, 16.1, 21.2, 22.5 (ethyl),[18] 106.9 (C_{ar}), 244.3 (CO, $^2J_{PC}$ = 22 Hz); mass spectrum, m/e (relative intensity) 472 (M^+, 8), 416 ($M^+ - 2CO$, 45), 326 ($M^+ - CO - PEt_3$, 7), 298 ($M^+ - 2CO - PEt_3$, 57), 246 ($M^+ - 2CO - PEt_3 - Cr$, 100); mass spectrum (high resolution), m/e 472.2560 (472.2562 calcd for $C_{26}H_{45}{}^{52}CrO_2P$).

Crystallography. Crystals of 1, obtained by slow evaporation of a pentane solution, are monoclinic: $P2_1/c$; a = 9.729 (4) Å, b = 18.353 (6) Å, c = 29.869 (12) Å, β = 98.26 (2)°; d_{calcd} = 1.189 g cm^{-3} for Z = 8 ($C_{26}H_{45}CrO_2P$, mol wt 472.61). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.15 × 0.15 × 0.5 mm; the data were corrected for absorption (μ = 44.4 cm^{-1}). A total of 4951 independent reflections were measured for $\theta < 48°$, of which 4015 were considered to be observed ($I > 2.5\sigma(I)$). The structure was solved by the heavy-atom method after the positions of the four chromium and phosphorus atoms had been obtained from an E map. A block-diagonal least-squares, in which the matrix was partitioned into two blocks, was used for the final refinement. Two reflections which were strongly affected by extinction were excluded from the final refinement and difference map. Anisotropic thermal parameters were used for nonhydrogen atoms and isotropic temperature factors were used for hydrogen atoms in the final refinement. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.041 and R_w = 0.044 for the 4013 observed reflections. The final difference map has no peaks greater than ±0.5 e $Å^{-3}$.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8009670) for support of this work and Stella Denman[1a] for experimental and technical assistance.

Registry No. 1, 80462-12-0; 3, 47378-46-1.

Supplementary Material Available: Final anisotropic thermal parameters and atomic parameters for hydrogen atoms, with standard deviations for **1A** and **1B** and a structure factor table for 1 (20 pages). Ordering information is given on any current masthead page.

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[17] Crystal packing effects are also unlikely to play a significant role in determining the conformations of 1 and 2, since there are no intermolecular H···H contacts shorter than 2.3 Å.

[18] Absorptions from the ethyl groups of HEB overlap with those of triethylphosphine, and no attempt was made to assign individual CH_3 and CH_2 signals.

The Series $Ru(CO)_{5-n}[P(OMe)_3]_n$ (n = 1–5). Methyl Migration in $Ru[P(OMe)_3]_5$

Randy F. Alex and Roland K. Pomeroy*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Received August 14, 1981

Pentakis(trimethyl phosphite)ruthenium, $Ru[P(OMe)_3]_5$ (5), has been prepared by the ultraviolet irradiation of a hexane solution of $Ru_3(CO)_{12}$ and excess $P(OMe)_3$. When the reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy, the stepwise formation of $Ru(CO)_{5-n}[P(OMe)_3]_n$ (n = 1–5) was indicated. Alternative syntheses for the derivatives with n = 1–4 are reported. As previously found for $Ru(CO)_4[P(OMe)_3]$, $Ru(CO)_{5-n}[P(OMe)_3]_n$ (n = 3, 4) are probably fluxional, on the NMR time scale, in solution. When **5**, in hexane solution, was heated to 120 °C, it isomerized to $Ru[P(OMe)_3]_4(CH_3)[P(O)(OMe)_2]$ (**5i**). Treatment of either **5** or **5i** with MeI gave $\{Ru[P(OMe)_3]_5(CH_3)\}I$. The preparation of the ortho-metalated compound, $(H)\overline{Ru[(C_6H_4O)P}(OPh)_2][P(OMe)_3]_3$, from $Ru(CO)_2[P(OMe)_3]_3$ and $P(OPh)_3$ is also described.

Introduction

In the past several years it has become apparent that phosphites, and trimethyl phosphite in particular, are able to stabilize transition metals in low, or formally zero, oxidation states. These complexes (e.g., $Cr[P(OMe)_3]_6$,[1] $W[P(OMe)_3]_6$,[2] $Co[P(OPh)_3]_4H$[3]) have stoichiometries that resemble the corresponding carbonyl derivatives. However, due to the different electronic and steric properties of the CO and $P(OR)_3$ ligands, it would be expected that the two types of compounds would have different chemical properties.

Two groups have reported the synthesis of $Fe[P(OMe)_3]_5$ and described aspects of its chemistry.[4,5] The preparation of the ruthenium analogue, $Ru[P(OMe)_3]_5$ (5), has also been mentioned together with its temperature-dependent $^{31}P\{^1H\}$ NMR spectrum.[6] The preparation involved the sodium amalgam reduction of $Ru[P(OMe)_3]_4Cl_2$ in the

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