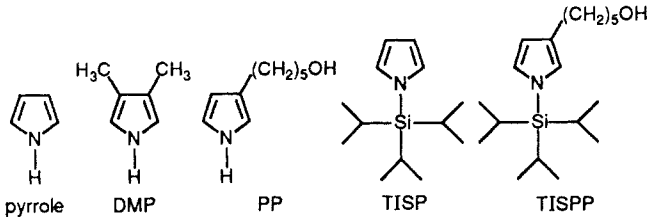
voltammetry. This also allowed by estimation of the corresponding standard potentials and lifetimes.

The following compounds[5] were investigated:



The substituents on the pyrroles were selected in an effort to make them easier to oxidize and to decrease the reactivity of their cation radicals without, however, preventing the feasibility of their anodic electropolymerization.[6] Among these substituted pyrroles, PP is of particular interest since the polymers derived from 3-substituted pyrroles constitute a class of new and promising materials.[7] Their structure is indeed much more regular than that of polypyrrole itself and of poly(N-substituted pyrroles). Figure 1 shows their cyclic voltammograms in acetonitrile. In all cases, total or partial reversibility of the cyclic voltammograms could be reached upon raising the scan rate. This is true even for pyrrole itself. It exhibits total irreversibility at 1600 V/s whereas a partial reversibility of about 20% is observed at 18 000 V/s. As expected, reversibility was easier to reach with the four substituted compounds.

The standard potentials and cation radical lifetimes[8] derived from the cyclic voltammograms are listed in Table I.

The variations of these two parameters upon changing the ring-carbon substituents are as expected from electronic inductive effects: given the N-substituent, alkyl substitution in the 3-position or in the 3- and 4-positions decreases the standard potential and increases the lifetime. The variations are about the same in the H and Si series. Passing from H to Si with the same substituents on the ring carbons slightly increases the standard potential and significantly increases the lifetime. The latter variation is likely to derive from steric hindrance to dimerization.

It was noticed that, in the cases where only partial reversibility could be reached, a further increase of the scan rate did not bring about significant improvements, whereas much higher scan rates could be used in other instances,[4g] even for the oxidation, also in acetonitrile, of a compound, *N*-methylacridane,[9a] the structure of which is not too far from the presently studied molecules (no polymerization and dimerization occur in that case, however). This is partly due to slow charge-transfer kinetics showing up at these high scan rates. However, surface effects are also likely to interfere, as in the case of the oxidation of aromatic hydrocarbons in *N,N'*-dimethylformamide.[9b]

A new route to the comprehension of the very first stages of the electropolymerization of pyrroles is thus open. Work is currently in progress to ascertain the dimerization mechanism in the most favorable case, i.e., that of TISPP, where undistorted cyclic voltammograms could be obtained in the whole range of scan rates up to complete reversibility, and to improve the responses obtained in the other cases. Variation of the reaction medium should be helpful in the latter of these purposes.

Registry No. PP, 125227-73-8; $PP^{\bullet+}$, 125227-75-0; DMP, 822-51-5; $DMP^{\bullet+}$, 125227-77-2; TISP, 87630-35-1; $TISP^{\bullet+}$, 125227-76-1; TISPP, 125227-74-9; $TISPP^{\bullet+}$, 125227-78-3; pyrrole, 109-97-7; pyrrole cation radical, 34468-30-9; triisopropylsilyl chloride, 13154-24-0; potassium pyrrolide, 16199-06-7.

(5) (a) *N*-(Triisopropylsilyl)pyrrole (TISP) was prepared by condensation of triisopropylsilyl chloride with potassium pyrrolide. The synthesis of 3,4-dimethylpyrrole (DMP) was carried out according to ref 5b, and the syntheses of 1-(pyrrol-3-yl)-pentan-5-ol (PP) and 1-[1-(triisopropylsilyl)pyrrol-3-yl]-pentan-5-ol (TISPP) are described elsewhere.[5c] (b) Farnier, M.; Fournari, P. *Bull. Soc. Chim. Fr.* **1975**, 2335. (c) Andrieux, C. P.; Audebert, P.; Merz, A.; Schwarz, R. Submitted for publication.

(6) In all cases, even with TISPP, a polymer film is formed upon setting the potential beyond the oxidation potential of the monomer. Its presence is attested by visual observation and by the typical slow scan voltammetric pattern it exhibits.

(7) (a) Lemaire, M.; Garreau, R.; Garnier, F.; Roncali, J. *New. J. Chem.* **1987**, *11*, 703. (b) Andrieux, C. P.; Audebert, P. *J. Electroanal. Chem.* **1989**, *261*, 443.

(8) (a) The lifetimes were estimated by adapting a working curve appropriate for the radical–radical coupling mechanism in double potential-step chronoamperometry.[8b] This does not mean that we favor this particular mechanism over other possibilities, particularly the radical–substrate coupling mechanism, but simply that the estimation of the lifetime is not critically dependent on the mechanism used to generate the working curve. (b) Amatore, C.; Hammi, M.; Pinson, J.; Savéant, J.-M. *Electroanal. Chem.* **1985**, *284*, 1.

(9) (a) Hapiot, P.; Moiroux, J.; Savéant, J.-M. *J. Am. Chem. Soc.*, in press. (b) Anxolabehere, E.; Hapiot, P.; Savéant, J.-M. *J. Electroanal. Chem.*, in press.

Template-Driven Self-Assembly of a Porphyrin-Containing Supramolecular Complex†

John S. Manka and David S. Lawrence*

Department of Chemistry, State University of New York Buffalo, New York 14214

Received July 10, 1989

Heme-dependent proteins participate in a diverse array of biochemical phenomena including oxygen transport (hemoglobin) and activation (cytochrome P-450 enzymes).[1,2] The proteinoid appendage of these species serves as a steric impediment that precludes μ-oxo oligomer formation, as a protective barrier that prevents oxidative decomposition of the porphyrin periphery, as a water-soluble carrier of the heme, and as an entity that maintains the hydrophobic nature of the active site to promote substrate binding and/or retard the oxidation of Fe^{2+} to Fe^{3+}. With these structural features in mind, we have designed and synthesized a porphyrin encased within a protective barrier that is circumscribed by a hydrophobic groove. The synthetic approach is notable in that it is a template-driven self-assembly of a multicomponent entity. We have recently employed such an approach to construct a rotaxane, and we have found that the self-assembly process, propelled by noncovalent interactions, is extremely facile.[3]

The tetraamino porphyrin **1** (prepared in three steps from *p*-hydroxybenzaldehyde)[4] forms an inclusion complex upon exposure to 10 equiv of heptakis(2,6-di-*O*-methyl)-β-cyclodextrin[5,6] ("Me-CD") (**2**) in aqueous solution at pH 6.0. The evidence for complexation is threefold: (1) the Soret band for the tetraprotonated amine porphyrin shifts from 444 to 418 nm in the presence of Me-CD; (2) the chemical shifts for the C-3 and C-5 protons in the ^{1}H NMR spectrum (300 MHz) for Me-CD move upfield (36.3 and 41.4 Hz, respectively) in the presence of the porphyrin; and (3) the tetraamino porphyrin, which is insoluble in basic (pH 14) water, is rendered freely soluble upon complexation with Me-CD. The inclusion complex was subsequently

† Dedicated to the memory of Professor Robert V. Stevens and the memory of Professor E. Thomas Kaiser.

* To whom correspondence should be directed.

(1) (a) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139. (b) Baldwin, J. E.; Perlmutter, P. *Top. Curr. Chem.* **1984**, *121*, 181. (c) Tsuchida, E.; Nishide, H. *Top. Curr. Chem.* **1986**, *132*, 63.

(2) (a) Bruice, T. C. *Ann. N.Y. Acad. Sci.* **1986**, *471*, 83. (b) Groves, J. T. *Ann. N.Y. Acad. Sci.* **1986**, *471*, 99. (c) Lee, W. A.; Lung-Chi, Y.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 4277 and references cited therein.

(3) Rao, T. V. S.; Lawrence, D. S. *J. Am. Chem. Soc.* In press.

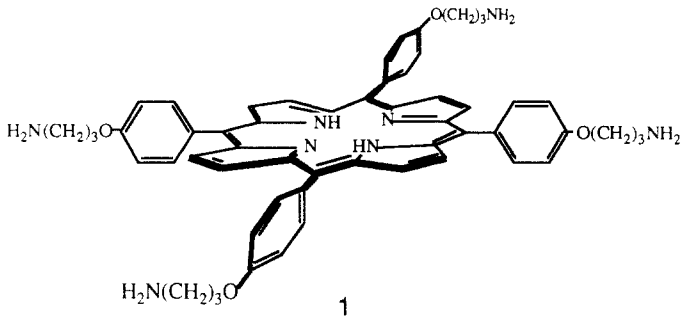
(4) From the O-alkylation of *p*-hydroxybenzaldehyde with *N*-(3-bromopropyl)phthalimide (86.8%), Rothemund cyclization in the presence of pyrrole (16%) [Lindsey, J. B.; Hsu, H. C.; Schreiman, I. C. *Tetrahedron Lett.* **1986**, *27*, 4969), and hydrazinolysis of the phthalimide (100%).

(5) Szejtli, J.; Jodal, I.; Fugedi, P.; Neszmelyi, A. *Starch* **1980**, *32*, 165.

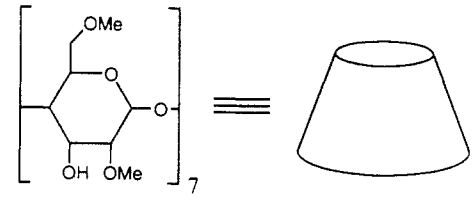
(6) Several reports of porphyrins that are covalently linked to cyclodextrins have appeared: (a) Kobayashi, N.; Akiba, U.; Takatori, K.; Ueno, A.; Osa, T. *Heterocycles* **1982**, *19*, 2011. (b) Wife, R. L.; Creed, D. E.; Volger, H. C. In *Proceedings of the First International Symposium on Cyclodextrins*; Szejtli, J., Ed.; Reidel Publishing Co.: Dordrecht, 1981; p 289. (c) Gonzalez, M. C.; Weedon, A. C. *Can. J. Chem.* **1984**, *63*, 602. (d) Kato, T.; Nakamura, Y. *Heterocycles* **1988**, *27*, 973. (e) Kuroda, Y.; Hiroshige, T.; Takashi, S.; Shiroiwa, Y.; Tanaka, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1989**, *111*, 1912.

0002-7863/90/1512-2440$02.50/0

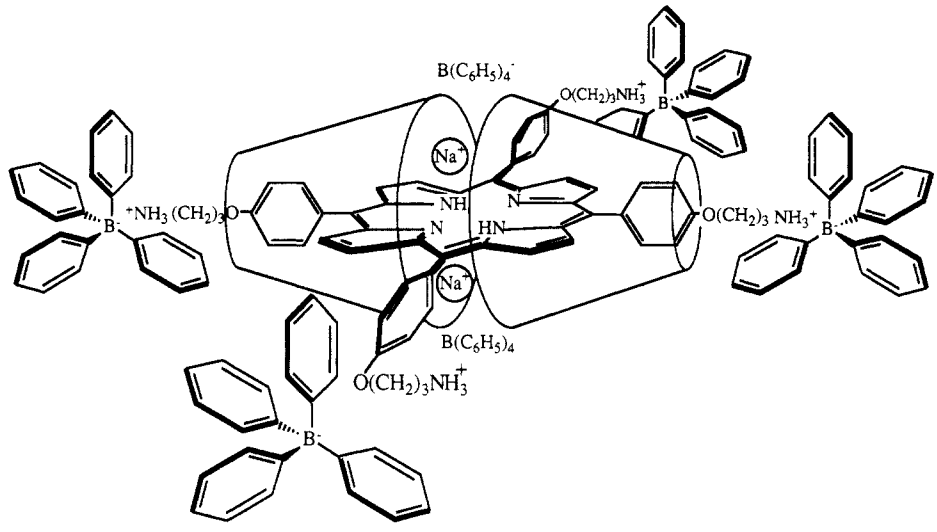
Chart I



1



2



3

sequestered by addition of an aqueous solution of sodium tetraphenylboron to produce the supramolecular entity **3**, which instantaneously precipitated out of solution. This complex was purified on a cellulose gravity column (40% acetone/60% benzene) and obtained in an isolated yield of 85.3%.

Several features of **3** are noteworthy:

(1) Porphyrin encapsulation occurs via the secondary alcohol face of the Me-CD, as demonstrated by one-dimensional NOE experiments. This appears to be a consequence of the sterically hindered nature of the methylated primary face,[7] which should obstruct the passage of substituents the size of phenyl or larger. In contrast, CPK models reveal that relatively small linear substituents, such as the alkylamino[8] side chain of the porphyrin, can easily thread through this barrier.

(2) The Me-CD moieties are bound opposed to one another about the porphyrin molecule. CPK models suggest that it is not sterically possible for the cyclodextrins to encapsulate adjacent phenyl groups. This structural analysis was confirmed by ^{13}C NMR. The splitting of the pyrrole α-carbons (145.79 and 145.73 ppm) of the porphyrin (in the presence of a trace of trifluoroacetic acid) is indicative of a symmetry consistent with the Me-CD moieties associated with nonadjacent phenyl groups.[9] The Me-CD moieties, bound in this fashion, create a hydrophobic groove (14 methyl substituents line the groove), which circumscribes the metal binding site of the porphyrin. In addition, since the cyclodextrins are cylindrical entities, both faces of the porphyrin nucleus are ensconced within a protective cavity.

(3) NMR experiments indicate that complex **3** contains six tetraphenylboron gegenions. Two of these appear to be associated with sodium ions that are complexed to the metal binding site of the *free base* porphyrin.[10] We have recently demonstrated that alkali metal salts form 2:1 complexes with the free base of 5,10,15,20-tetraphenylporphine.[11] This type of interaction induces two effects which can be observed by NMR. First, addition of a trace of trifluoroacetic acid to **3** produces a 20% decrease in the line width of the ^{23}Na NMR signal [as a control, we have found that trifluoroacetic acid induces only a slight increase in the ^{23}Na line width of $NaB(C_6H_5)_4$ in the absence of porphyrin]. This suggests that, as expected, protonation of the pyrrole nitrogens disrupts the interaction between the sodium ions and the porphyrin. Second, addition of 6 equiv of 18-crown-6 produces an upfield chemical shift ($\Delta\delta$ = 0.129 ppm) of the pyrrole NH hydrogens. We have previously shown that coordination of positively charged alkali salts to a free base porphyrin produces a downfield chemical shift of these protons and that this behavior can be reversed in the presence of crown ether.[11]

(4) The complex **3**, which precipitates out of aqueous solution, contains 11 separate components [tetraphenylboron (six subunits), Me-CD (two subunits), sodium ions (two subunits), tetraammonium porphyrin (one subunit)]. Its molecular weight is 5535 g/mol. Interestingly, several studies have demonstrated that, in polar aprotic solvents, ammonium tetraphenylboron salts are only loosely associated (i.e., solvent separated or free ions).[12] If the

(7) Breslow, R.; Czarniecki, M. F.; Emert, J.; Hamaguchi, H. *J. Am. Chem. Soc.* **1980**, *102*, 762.

(8) Due to extensive solvation of ammonium salts in aqueous solution, we suspect that the alkylamino side chain threads through the Me-CD as the free amine.

(9) Milgrom, L. R. *J. Chem. Soc., Perkin Trans 1* **1984**, 1483.

(10) ^1H NMR and UV-vis confirm that the porphyrin moiety in **3** exists as the free base form. The tetraphenylboron moieties associated with the sodium cations are indicated in **3** by molecular formula only for the sake of clarity. CPK models reveal that at least one phenyl group from each tetraphenylboron can occupy the hydrophobic groove. Nuclear Overhauser experiments support this analysis.

(11) Manka, J. S.; Chugh, D. B.; Lawrence, D. S. Submitted for publication. The association constants obtained for the formation of the 2:1 alkali metal–porphyrin complexes are small. We suspect that, due to the extreme solubility of Me-CD, at least six tetraphenylboron gegenions are required to precipitate **3** out of aqueous solution. Indeed, the corresponding Fe^{3+} metalloporphyrin–$(Me\text{-}CD)_2$ complex, which can bind only five tetraphenylboron moieties, is completely soluble in aqueous solution. In other words, precipitation serves as a driving force for the association of two sodium ions.

tetraphenylboron gegenions are not intimately paired with the ammonium functional groups, one might expect that the Me-CD moieties would dissociate from the phenyl substituents of the porphyrin. Nevertheless, as assessed by TLC, the complex is stable in acetone and in 60% benzene/40% acetone (the latter is the eluent employed for the purification of **3**). We have recently demonstrated in a related system that a barrier does exist for the dissociation of the Me-CD moiety and that this barrier appears to be associated with solvation of the ammonium salt. Indeed, upon heating **3** to reflux in acetone, we begin to observe the formation of uncomplexed porphyrin. This process can be accelerated by treating the complex in acetone at room temperature with a trace of triethylamine.

The synthetic methodology described herein offers unusual flexibility in the construction of a range of heme-dependent protein mimics. Replacement of the Me-CD moieties with other hosts should provide a means to alter the size, shape, and hydrophobicity of the groove that circumscribes the porphyrin moiety. Since the groove has clear potential as a substrate binding site, such alterations may be useful in controlling substrate specificity. In addition, charged subunits of appropriate steric bulk can be used to covalently modify the primary amines of the porphyrin and thereby render the entire complex water soluble. These, as well as related studies, are currently in progress.

Acknowledgment. We thank Dr. Dinesh Sukumaran for helpful advice and Professor Dabney Dixon for bringing the paper cited in ref 9 to our attention. The National Science Foundation provided funds for the purchase of the NMR (CHE-8613066) and mass spectrometers (CHE-8509862) employed in this study. We thank the American Heart Association, National Center, for support of this research.

Supplementary Material Available: NMR data (^{1}H, ^{11}B, ^{13}C, ^{23}Na, NOE experiments), FAB MS data, combustion analysis, and the experimental protocol for compound **3** (1 page). Ordering information is given on any current masthead page.

(12) (a) Handy, P. R.; Popov, A. I. *Spectrochim. Acta* **1972**, *28A*, 1545. (b) Buxton, T. L.; Caruso, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 6033. (c) Barker, B. J.; Sears, P. G. *J. Phys. Chem.* **1974**, *78*, 2687.

Dichloromethane: A Bridging Ligand

Mark Bown and Joyce M. Waters*

Department of Chemistry and Biochemistry
Massey University, Palmerston North, New Zealand
Received October 27, 1989

Recently, the first account of dichloromethane acting as a ligand was published.[1] We now report[2] a second example of the binding of this molecule to a metal. The compound $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2]$[2,3] was prepared in 18% yield (based on Ru) by refluxing $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$[4] and phenylacetylene in CH_2Cl_2 under an atmosphere of dry N_2 for 43 h. Purification was effected by repeated preparative thin-layer chromatography on silica with CH_2Cl_2 as the eluting solvent (green band, R_f = 0.28).

The idealized stoichiometry is given by the equation

$$[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2] + CH_2Cl_2 \rightarrow \underset{\mathbf{1}}{} [\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2] + H_2$$
2

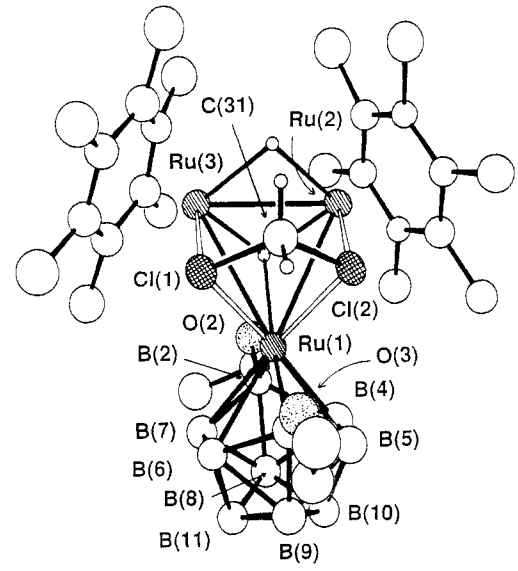


Figure 1. Diagram of the molecule $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2]$. Thermal ellipsoids are drawn at the 50% probability level. Ru–C distances average at 2.24 Å; Ru–B distances lie in the range 2.10 (1)–2.36 (1) Å; other dimensions within the closo-type RuB_{10} cluster are similar to those already reported (ref 4). Proton and ^{11}B NMR data are as follows (ordered as $\delta(^{11}B)$/ppm (relative intensities in parentheses) [with directly bound $\delta(^1H)$/ppm in square brackets (relative intensities in parentheses)]}: +99.0 (1 B) [OEt], +93.9 (1 B) [OEt], +1.4 (2 B) [+1.78 (2 H)], −1.3 (3 B) [+3.59 (1 H), +1.41 (2 H)], −4.0 (1 B) [+2.61 (1 H)], −6.5 (2 B) [+0.61 (2 H)]; also $\delta(^1H)$ (η^6-C_6Me_6) +2.17 ppm; CD_2Cl_2 solution at 297 K.

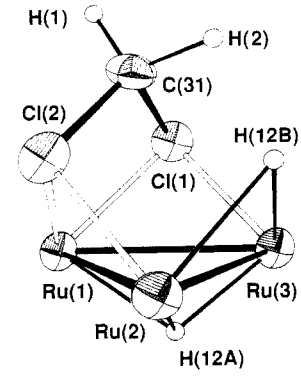


Figure 2. Diagram showing the binding of the dichloromethane molecule to the Ru_3 triangle in $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2]$. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (angstroms) and angles (degrees) are as follows: Ru(1)–Ru(2), 3.100 (1); Ru(2)–Ru(3), 2.869 (1); Ru(1)–Ru(3), 3.106 (1); Ru(1)–Cl(1), 2.403 (3); Ru(1)–Cl(2), 2.396 (2); Ru(2)–Cl(2), 2.315 (3); Ru(3)–Cl(1), 2.319 (3); Ru(1)–H(12A), 2.19 (8); Ru(2)–H(12A), 1.92 (7); Ru(3)–H(12A), 1.88 (7); Ru(2)–H(12B), 2.20 (7); Ru(3)–H(12B), 2.20 (7); C(31)–Cl(1), 1.803 (9); C(31)–Cl(2), 1.827 (9); Ru(1)–Cl(1)–Ru(3), 82.2 (1); Ru(1)–Cl(2)–Ru(2), 82.3 (1); Cl(1)–C(31)–Cl(2), 102.4 (5). Proton NMR data are as follows: $\delta(^1H)$ (H(1)) +2.49 ppm (d), $\delta(^1H)$ (H(2)) +4.89 ppm (ddd), $\delta(^1H)$ (H(12A)) −14.74 ppm (dd), $\delta(^1H)$ (H(12B)) −22.40 ppm (dd); ^2J(H(1)–H(2)) 10.1 Hz, ^4J(H(2)–H(12A)) 1.2 Hz, ^4J(H(2)–H(12B)) 5.3 Hz, ^2J(H(12A)–H(12B)) 4.9 Hz.

(1) Newbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762.

(2) 1-(6′,9′-Diethoxy-*nido*-octahydrodecaborato)-2,3-bis(η^6-hexamethylbenzene)-μ_3-hydrido-2,3-μ-hydrido-1,2-μ:1,3-μ-(dichloromethane)-*triangulo*-triruthenium.

(3) Crystallographic data: Green crystal of $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2]$, size 0.2 × 0.2 × 0.25 mm, monoclinic $P2_1/n$, a = 11.114 (2) Å, b = 17.748 (3) Å, c = 19.510 (5) Å, β = 103.18 (2)°, U = 3750 (2) Å^3, Z = 4, T = 20 °C, D_{calcd} = 1.63 g cm^{-1}, $F(000)$ = 1856.0, Enraf-Nonius CAD4 diffractometer, graphite monochromator, $\omega/2\theta$scans, θ_{max} = 25°, 6553 unique data measured. Lorentz and polarization corrections, empirical absorption corrections, maximum and minimum values of 0.9992 and 0.9539 respectively, μ(Mo Kα) = 93.3 cm^{-1}. Weighted least-squares refinement on F with neutral atom scattering factors and anomalous dispersion, anisotropic thermal parameters for all non-H atoms. Positional and thermal parameters refined for H attached to B atoms and those associated with the Ru triangle; H atoms attached to C in fixed positions with U = 0.05 e Å^{-2}. R = 0.040, R_w = 0.041 for 488 variables and 3512 data for which $F^2 > 2.5\sigma(F^2)$; weight = $3.2739/(\sigma^2(F) + 0.000318F^2)$.

(4) Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; MacKinnon, P.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2781.

0002-7863/90/1512-2442$02.50/0