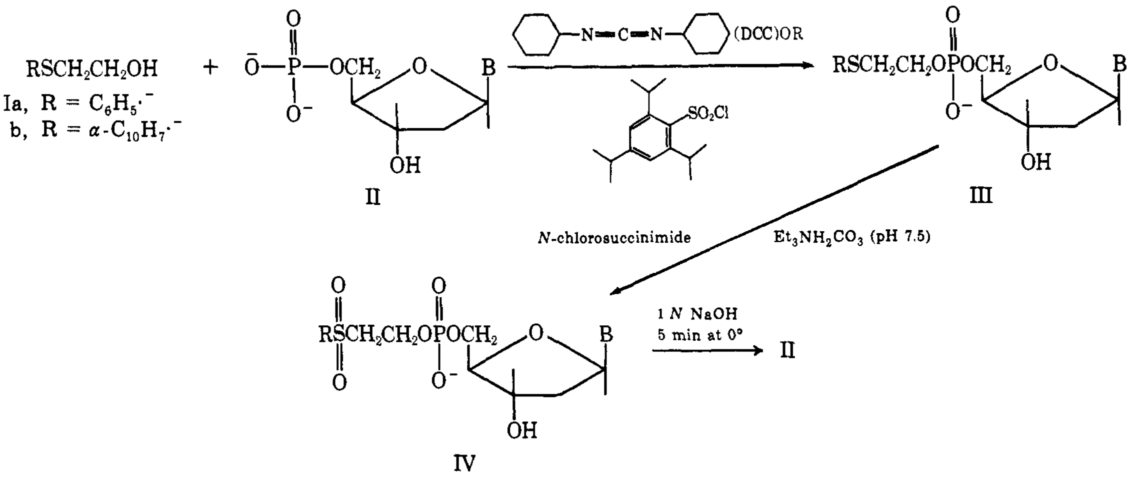

B = thymine, N-anisoylcytosine, N-isobutyrylguanine, and N-benzoyladenine

protected nucleotides and in the conditions required for their removal. In this communication, we report on the use of S-substituted mercaptoethanols (I) as a new class of phosphate protecting groups. Nucleotides can be derivatized easily in high yields using these protecting groups and their removal is achieved safely and quantitatively under very mild conditions.

The phosphate-protected derivatives (III) of all the four mononucleotides were prepared and isolated in quantitative yields. In a typical experiment Ib (5 mmol) was condensed with II (B = thymine, 1 mmol) in anhydrous pyridine, using either dicyclohexylcarbodiimide (DCC) (10 mmol) for 12 hr at room temperature or triisopropylbenzenesulfonyl chloride (TPS) (4 mmol) for 3 hr at room temperature. The reaction mixture was extracted with ether to remove unreacted Ib followed by a methylene dichloride–n-butyl alcohol (7:3, v/v) mixture which extracted III ($R = C_{10}H_7$; B = thymine) in quantitative yield. The protecting group was removed by oxidation of the sulfide ester (III, $R = C_6H_5, C_{10}H_7$) with N-chlorosuccinimide in $Et_3NH_2CO_3$ or phosphate buffer (pH 7.5) for 10 min at 0° followed by 1 N NaOH treatment for 5 min at 0°. Under these conditions, the appropriately protected mononucleotides showed no loss of the N-protecting groups or any other side reactions. Narang, *et al.*,[9] have recently described the use of Ia in a similar procedure, but the conditions used for the removal of the phosphate-protecting group are relatively severe. These authors have oxidized the sulfide ester to the sulfoxide with $NaIO_4$ and then subjected the sulfoxide ester to 2 N NaOH for 30 min at room temperature for removal. These conditions for the alkaline treatment are required for removal of the sulfoxide ester evidently due to the slow β elimination.

$$\underset{\text{III}}{C_{10}H_7SCH_2CH_2O\text{—pT—OH}} + \text{pC}^{\text{An}}\text{OAc} \longrightarrow$$

$$\underset{\text{V}}{C_{10}H_7SCH_2CH_2O\text{—pTpC}^{\text{An}}\text{OAc}} \xrightarrow[\text{2. 1 } N \text{ NaOH; 5 min at 0°}]{\text{1. 1 } N\text{-chlorosuccinimide}} \underset{\text{VI}}{\text{pTpC}^{\text{An}}\text{OH}}$$

The protected mononucleotides III ($R = C_6H_5$ or $C_{10}H_7$) have been used for the synthesis of dinucleotides. In a typical experiment, III (0.5 mmol; $R = C_{10}H_7$; B = thymine) was condensed in pyridine with N^6-anisoyl-3′-acetyldeoxycytidine 5′-phosphate ($\text{pC}^{\text{An}}\text{OAc}$) (0.75 mmol) in the presence of triisopropylbenzenesulfonyl chloride (1.5 mmol) for 2 hr at room temperature. The reaction mixture was subjected to tritylcellulose chromatography.[1,10] The column was first washed with 0.05 M $Et_3NH_2CO_3$ containing 10% ethyl alcohol to remove $\text{pC}^{\text{An}}\text{OAc}$ and its symmetrical pyrophosphate. Elution with 0.05 M $Et_3NH_2CO_3$ in 60% ethyl alcohol eluted a mixture of III and V which was further extracted with methylene dichloride–n-butyl alchol (7:3, v/v) to remove unreacted III. The dinucleotide V was isolated in 85% yield. Removal of the phosphate protecting group was carried out by oxidation of V to the sulfone ester followed by alkaline treatment as described for the phosphate protected mononucleotide. The dinucleotide $\text{pTpC}^{\text{An}}\text{OH}$ was isolated in 80% yield and was homogenous as judged by tlc and paper chromatography.

Acknowledgment. This work has been generously supported by the National Institutes of Health (Grants 72576 and CA 05178) and the National Science Foundation (Grants 73078 and GB-21053X1).

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Preparation, Properties, and Structure of a Diamagnetic Dimeric Diiron Compound with Three Bridge Hydrogen Bonds

Sir:

It has been reported[1,2] that the tripod-like triphosphine $MeC(CH_2PPh_2)_3$ (P_3) reacts with cobalt(II) and nickel(II) halides either alone or in the presence of sodium borohydride to give tetrahedral complexes $M(P_3)X$ in which the oxidation state of the metal is +1.

Iron(II) halides react with the triphosphine under

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(2) P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 1161 (1972).

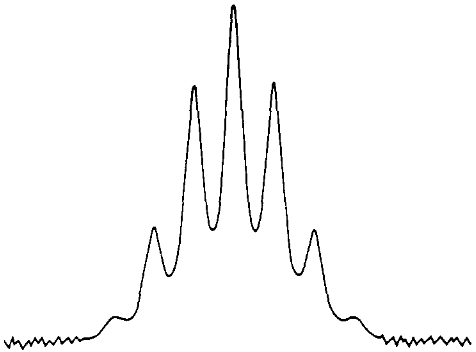

Figure 1. Hydride absorption in the nmr spectrum of $[Fe_2H_3(P_3)_2]B(Ph)_4$ complex (CH_2Cl_2 solution), at room temperature.

similar conditions to give blue crystalline compounds of the formula $[Fe_2H_3(P_3)_2]Y$ where Y = Br, I, ClO_4, PF_6, and BPh_4. When recrystallized from methylene chloride or butanol the compounds contain solvent of crystallization. The purity of the samples has been confirmed by a total elemental analysis in each case. The compounds are air stable but decompose with evolution of hydrogen when treated with iodine in boiling *sym*-tetrachloroethane. The compounds are 1:1 electrolytes in dichloroethane and nitroethane, and their solution spectra in these solvents are identical with the reflectance spectra. These results show that the anion Y is not coordinated. The compounds are all diamagnetic.

The nmr spectra can be explained on the basis that the protons are in bridging positions and are magnetically equivalent, as are the six phosphorus atoms. Thus, the ^1H spectrum shows a first-order splitting of the bridge-hydrogen resonance into a septuplet with $J_{P-H} = 8.0$ Hz, δ +21.1 (Figure 1). The ^{31}P spectrum shows a quartet at δ +50.1 (δ for the free ligand −26.7, both values referred to H_3PO_4) with $J_{P-H} = 8.0$ Hz.

The infrared spectra show no band in the region 1700–2100 cm^{-1} that can be attributed to terminally bonded Fe–H stretching absorption, but only one band at 1048 cm^{-1}. This is observed to shift to 790 cm^{-1} in the deuterated derivative, which was prepared by using $NaBD_4$ and deuterated solvents. On the basis of the literature reports[3] this can with confidence be attributed to hydrido–metal groups in which hydrogen is in bridging position.

The molecular structure of the compound $[Fe_2H_3(P_3)_2]PF_6 \cdot 1.5CH_2Cl_2$ has been determined by a three-dimensional X-ray analysis. The crystals are monoclinic, space group $P2/c$, with lattice constants a = 22.669 (2), b = 17.839 (2), and c = 20.106 (2) Å; β = 95.57 (1)°; $D_{measd} = 1.32$ and $D_{calcd} = 1.321$ g cm^{-3}; and $Z = 4$. Observed reflections (4284) were collected by counter methods with Mo Kα radiation using ϑ–ω scan technique. The structure was solved by direct methods and Fourier syntheses to give all nonhydrogen atoms. R has been reduced to 0.114 by full-matrix least-squares refinement, using isotropic temperature factors for all atoms except Fe, P, and F. The refinement is still in progress. A three-dimensional difference map has revealed the positions of the three bridge-hydrogen atoms. Three peaks of *ca.* 0.4 e Å^{-3} are found in a plane normal to the Fe–Fe axis, forming an equatorial triangle equidistant from the iron atoms.

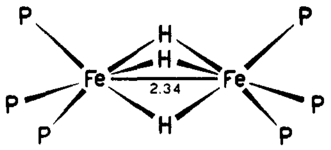

Figure 2. A schematic view of the coordination polyhedron. The average values of distances (Å) and angles (deg) are: Fe–P, 2.21 (range 2.20–2.23); Fe–H, 1.7 (1.6–1.8); P–Fe–P, 89 (87–90); P–Fe–H$_{trans}$, 171 (168–175); P–Fe–H$_{cis}$, 96 (89–103); H–Fe–H, 80 (77–83); Fe–H–Fe, 85 (83–87).

The structure consists of $[Fe_2H_3(P_3)_2]^+$ cations and PF_6^- anions with solvent molecules interspersed in a disordered manner. Each iron atom is bonded to the three phosphorus atoms of one ligand and to the three bridge hydrogens. The chromophore can be said to be formed from two octahedra sharing a face, with the three hydrogen atoms at the corners of the shared face, though it is not yet clear how great the deviations from idealized D_{3h} symmetry are. A schematic view of the chromophore with the most significant bond lengths and angles is shown in Figure 2.

The Fe–Fe distance of 2.34 Å is clear evidence of an intermetallic bond when compared with Fe–Fe distances in other organo–diiron complexes. In the complex $Fe_2(CO)_9$, with three bridging CO groups, the metal–metal bond distance is 2.46 Å;[4] in other bridged dimeric iron complexes, which supposedly contain metal–metal single bonds, the Fe–Fe distances range from 2.37 to 2.77 Å.[5] The very short Fe–Fe distance, of 2.215 Å, in the compound tetracarbonyl-μ-2,2,5,5-tetramethylhex-3-yne-diiron[6] has been considered indicative of a Fe–Fe double bond.

The electronic configuration about each iron atom can be described in simple terms as follows. Following the usual convention, the compound is considered to be formed from Fe^{2+} (d^6) and H^- ions. Each of three hydride ions and each of the six phosphorus atoms contributes two electrons (18 in total) which, with 12 electrons of the two iron ions, give a total of 30 valence electrons. Eighteen of these are accomodated in a σ framework, 12 in the six Fe–P bonds, and 6 in the three three-centered M–H–M bonding molecular orbitals. The remaining 12 electrons, six per iron atom, are located in the d orbitals whose lobes are predominantly between the σ-bond directions (in octahedral symmetry these would be denoted by the symbol t_{2g}). There are thus no unpaired electrons, and the diamagnetism of the compounds is explained.

This simple picture, however, implies that the overlap between filled t_{2g} orbitals on different atoms is negligible, which is hardly likely in view of the very short Fe–Fe distance. Therefore the following alternative electronic configuration must be considered probable. The three "nonbonding" orbitals of the three-centered systems may contain a pair of electrons each without destroying the bridge bonds. The overlap of corre-

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sponding t_{2g} orbitals on each metal atom, then, gives three Fe–Fe bonds, one σ and two π.

Concerning the evaluation of the Fe–Fe bond order in this compound, we are in agreement with Cotton[7] that any attempt to find a direct correlation of the metal–metal distance with bond order in this type of structures is meaningless. Therefore, it does not seem unreasonable to affirm that in the $[Fe_2H_3(P_3)_2]^+$ complex cation there are three Fe–Fe interactions, some or all of which are weaker than a full bonding interaction.

Acknowledgments. We wish to thank Professor L. M. Venanzi for measuring the ^{31}P spectrum of the compound.

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Direct Observation of Chair and Boat Conformations for Dibenzocycloocta-1,5-diene by Nuclear Magnetic Resonance

Sir:

Although the conformational properties of 1,5-cyclooctadiene and some of its derivatives have been the subject of several important studies,[1–10] information regarding the nature of the most stable conformation in solution and the modes of interconversion of conformational isomers has been, heretofore, inconclusive or contradictory. Under favorable circumstances, when molecules have relatively high free energy barriers to conformational changes, the "DNMR" method[11] is particularly well suited to this area of investigation. Using this technique, we have studied the behavior of dibenzocycloocta-1,5-diene (**1**), and we wish to report observations which, we feel, make a significant contribution to the understanding of this conformational problem.

The 100-MHz pmr spectra of **1**, dissolved in a mixture of methylene-d_2 chloride and propene (2:1), are shown in Figure 1 for various temperatures. A spectral change occurs whereby the aromatic signal (δ 6.96 at $-40°$) splits into two peaks below $-72°$ (the coalescence temperature, T_c); the separation between the peaks at $-100°$ is 24 Hz, and their relative areas are in the ratio 87 : 13. On the other hand, the methylene singlet (δ 3.09 at $-40°$) remains essentially unchanged down to about $-90°$. Below this temperature it broadens and at $-115°$ (T_c) changes into an AA′BB′ spectrum whose form closely resembles an AB quartet ($\Delta\nu \approx 48$ Hz) because of the particular magnitudes of the coupling constants.[12]

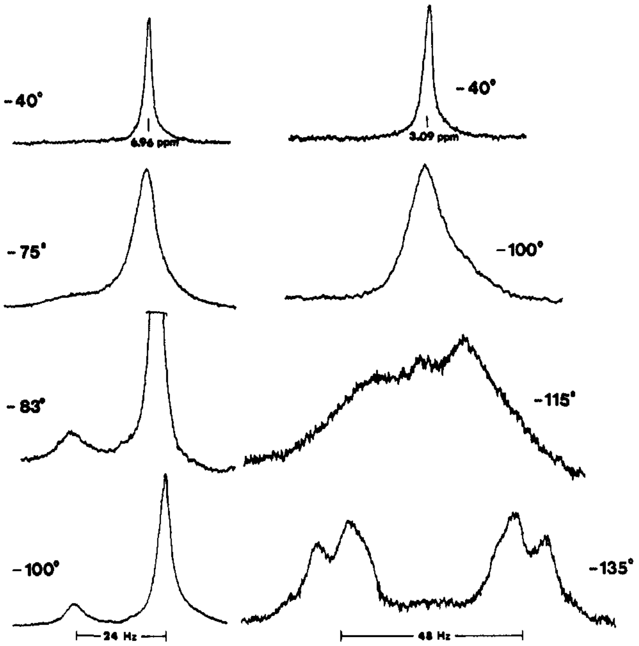

Figure 1. Typical 100-MHz pmr spectra of the aromatic (left) and methylene (right) protons of dibenzocycloocta-1,5-diene at several temperatures.

Solubility problems at low temperatures greatly limit the choice of solvents. Nevertheless it was found that a solution of **1** in a mixture of toluene-d_8 and propene (1 : 1) also revealed similar changes in both the aromatic and methylene regions of the spectrum. Unfortunately, the spectral change in the aromatic region is obscured partly by overlap with peaks from residual protons in the deuterated toluene solvent. Integrations at -40 and $-100°$ can account for these impurities and show that the low field component has increased to about 40% of the total area of the aromatic signal at $-100°$.

Approximate values for $\Delta G^{\ddagger}$ characteristic of the processes underlying the spectral changes can be obtained from standard equations.[13] Estimates of 10.2 $\pm$ 1 and 7.5 $\pm$ 1 kcal/mol were calculated for the changes at -72 and $-115°$, respectively.

The above results can most readily be interpreted in terms of a mixture of chair and boat (presumably twisted to relieve eclipsing about the CH_2–CH_2 bonds) conformations for dibenzocycloocta-1,5-diene. The spectral change near $-72°$ is then attributed to a chair to boat equilibration (**2** $\rightarrow$ **3**) while that near $-115°$ is due to an equilibration of equivalent conformations of the boat family (represented by **3** $\rightarrow$ **4**); the latter process may be called most simply a boat inversion.

Twist boat forms are presumably more stable than boat forms. However, interconversion (or rocking) between two twist boats such as **5** and **6** is expected to have a very low energy barrier such that it should be rapid on the nmr time scale at $-135°$ and should result

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