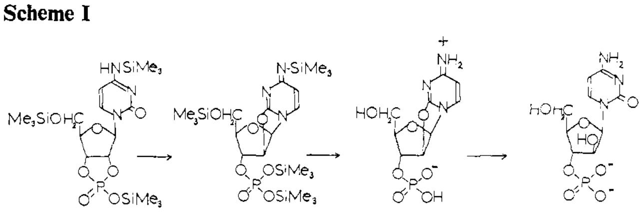
Anal. Calcd for $C_9H_{12}N_3O_7P \cdot H_2O$ (323.20): C, 33.45; H, 4.35; N, 13.01; P, 9.60. Found: C, 33.47; H, 4.44; N, 12.90; P, 9.8 (titration). The uv spectrum exhibited the characteristic features of this system:[3] λ_{max} 231 (ϵ 9550), 262.5 mμ (ϵ 10,640); λ_{min} 243 mμ (ϵ 6480) in water, pH 1–7. Characteristic ir frequencies were 1665, 1376, 1358, 1252, 1212, 1060, and 932 cm^{-1}. The nmr spectrum taken at 100 MHz in D_2O at pD 7 featured the following resonances [δ ppm (J Hz) relative to TMS]: a doublet of H-6 at 8.61 (7.5); two unresolved doublets of H-5 and H-1′ centered at 7.09 (7.5) and 7.15 (5.5), respectively; a doublet of H-2′ at 6.24 (5.5). The clear separation of the H-2′ signal is remarkable when compared with other nucleotide spectra,[7] and it must be due to the combined deshielding effect of the isourea and phosphate groups. The ORD characteristics in water ([M] at c 10^{-4} M) were: peak at 282 mμ, +6200°, trough at 239 mμ, −20,800°; crossover at 268 mμ.

Several interesting reactions of **3** are currently under study. Its hydrolysis is pH dependent and general base catalyzed above its pK_2 (5.7).[2] At pH 1 to 7 a partial conversion to cytidine 2′,3′-cyclic phosphate can take place, which can be followed by electrophoresis at pH 6. Treatment with alkali or bicarbonate gave aracytidine 3′-phosphate[8] **(4)** as the only product.

Scheme I



1 2 3 4

The identification of **4** was carried out by comparison with all published data. Its 100-MHz nmr spectrum in D_2O exhibited the following signals relative to acetone as internal standard: at pD 7: H-6, δ 5.65 (8); H-5, 3.83 (8); H-1′, 4.03 (3); at pD 4: H-6, 5.87 (8); H-5, 4.02 (8); H-1′, 3.99 (3). The nmr and uv spectra were in good agreement with those of Wechter.[9] The ORD characteristics in 0.1 M Na_2HPO_4, pH 7.8 ([M] at c 9.3 $\times$ 10^{-5} M) were: peak at 288 mμ, +15,900°; broad trough centered at 240 mμ, −18,800°; crossover at 272 mμ. We also obtained good elementary analysis from the crystalline free acid. Furthermore, alkaline phosphatase hydrolysis liberated 1-β-D-arabinosylcytosine which was identical with the commercial sample (Sigma) by all usual criteria.

The concept of a cyclic phosphate derivative as an intramolecular leaving group has already been proposed[10] as the mechanism of anhydronucleotide formation in polyphosphoric acid.[3] Our work on the alkyl[1] and silyl esters of cytidine 2′,3′-cyclic phosphate represents a direct experimental proof and a further development of the same general concept. This novel reaction provides an extremely simple and economical way to the most suitable intermediate for a direct polymerization of aracytidylic acid. The possibility of similar rearrangements should also be considered in connection with mass-spectrometric work on oligonucleotides. It is noteworthy that the trimethylsilylated uridine 2′,3′-cyclic phosphate and adenosine 3′,5′-cyclic phosphate did not show any change under the same conditions.

Acknowledgment. The author gratefully acknowledges the contribution of Dr. D. H. O'Brien in taking the nmr spectra and Mr. B. J. Henrici in performing some of the experiments. This work was supported by grants from the National Institutes of Health (GM-16213) and the Texas A&M Research Council.

Joseph Nagyvary
Department of Biochemistry & Biophysics
Texas A & M University
College Station, Texas 77843
Received May 15, 1969

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A New Class of Triptycene-Like Binuclear Ions Containing Three 1,2-*Dihapto*pyrazolide Bridges

Sir:

We wish to report a new class of binuclear ions of triptycene-like structure which contain an array of three 1,2-*dihapto*pyrazolide[1] units acting as one trinegative bistridentate ligand of D_{3h} symmetry.

Instances of three identical ligands bridging two like nuclei have been scarce. They include the old example of $Fe_2(CO)_9$ containing three carbonyl bridges, the trihalo-bridged molybdenum carbonyl species [π-$C_3H_5(CO)_2Mo(X)_3Mo(CO)_2$-$\pi$-$C_3H_5$]$^-$ reported by Murdoch,[2] the alkoxy and alkylthio analogs derived therefrom,[3] as well as the more recent examples of tri-μ-hydrido- and tri-μ-alkoxy-dirhenate(I) ions.[4] In each of these cases the two metals are bridged by the same atom. It was thought that pyrazolide ion (of C_{2v} symmetry) should be capable of acting similarly as a tris-bridging 1,2-*dihapto* ligand, especially since bridging of two unlike nuclei by what may be formally regarded as pyrazolide ions has been demonstrated in the special case of transition metal tris(1-pyrazolyl)borates.[5]

This expectation has been realized and the new class of complexes is illustrated by the following two examples of a cationic, tetrahedral species I and an anionic, octahedral species, II.

I was synthesized in 22% yield by the reaction of pyrazolide ion with ethylborylene bis-p-toluenesulfonate[6] and was isolated as the hexafluorophosphate, mp 299–301°.

The structure of this salt was established by analysis (*Anal.* Calcd for $C_{13}H_{19}B_2F_6N_6P$: C, 36.7; H, 4.47; F, 26.8; N, 19.7; P, 7.28. Found: C, 36.9; H, 4.54; F, 26.9; N, 20.1; P, 7.31) and particularly by the nmr spectrum which had a doublet (J = 2.5 cps)

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(6) Ethylborylene bis-p-toluenesulfonate was prepared *in situ* in a manner analogous to that used for making dialkylboryl sulfonates,[7] except that the triethylborane:p-toluenesulfonic acid ratio was 1:2 and longer heating was required to complete the evolution of 2 equiv of ethane.
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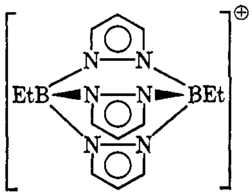
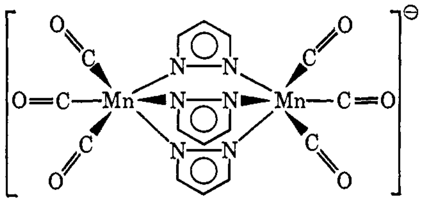


I



II

at τ 2.14, a triplet (J = 2.5 cps) at τ 3.89, and a distorted B-ethyl multiplet around τ 9 in 6:3:10 ratio. These data are consistent with structure I where both borons are tetrahedral and the ion is of local D_{3h} symmetry.[8] The ion I is also of interest in that it provides, formally at least, the first example of a boronium ion containing a formal charge of $+^1/_2$ per boron. Boronium ions with integral charges of +1 to +3 have been reported previously.[9,10]

The anion II was prepared in 69% yield by the reaction of $BrMn(CO)_5$ with 1.5 equiv of pyrazolide ion, and it was isolated as the yellow, fairly air-stable tetraethylammonium salt, mp 380–382°, the salt turning red around 290°. Elemental analysis (*Anal.* Calcd for $C_{23}H_{29}Mn_2N_7O_6$: C, 45.2; H, 4.77; Mn, 18.0; N, 16.1. Found: C, 45.2; H, 4.60; Mn, 17.7; N, 16.1) and the nmr spectrum [d (J = 1.9 cps) τ 2.55, t (J = 1.9 cps) 4.20, quartet (J = 7.0 cps) 7.27, and triplet of triplets (J = 7.0 and 1.8 cps) 9.21 in the correct 6:3:8:12 ratio] supported the assigned structure. In particular, the nmr spectrum not only showed the three pyrazolyl groups present to be identical, but also indicated equivalence of the 3 and 5 positions as would be anticipated on the basis of octahedral coordination for Mn and over-all D_{3h} symmetry for the ion. The ν_{CO} at 2016 and 1917 cm^{-1} reflects a higher M–C bond order as compared with the related uncharged species[11] $HB(1\text{-pyrazolyl})_3Mn(CO)_3$ which has ν_{CO} at 2041 and 1941 cm^{-1} and the cation[12] $[HC(1\text{-pyrazolyl})_3Mn(CO)_3]^+$ with ν_{CO} at 2059 and 1961 cm^{-1}.

The above examples underscore the versatility of pyrazolide ion as a ligand in organometallic chemistry, and the usefulness of the pyrazolide hydrogens for nmr probing of molecular symmetry.

(8) This does not exclude an equilibration, fast on the nmr time scale, between instantaneous structures of lesser symmetry containing one of the B–N bonds detached, although this is regarded as unlikely. Some ring opening may be indicated from the fact that prolonged boiling in alcohol degrades this cation. The salt may, nevertheless, be recrystallized from ethanol.

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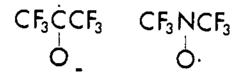
S. Trofimenko
Contribution No. 1589, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898
Received June 30, 1969

The Structure of Ketyl Radicals. Carbon-13 Splitting in Electron Spin Resonance Spectrum of Hexafluoroacetone Ketyl[1]

Sir:

Recently Janzen and Gerlock[2] reported an electron spin resonance spectrum of the hexafluoroacetone ketyl I. Their results are very unusual in that a very large (~35 G) fluorine hyperfine splitting (hfs) was observed. This is in contrast to a fluorine hfs of ~8 G for the isoelectronic bis(trifluoromethyl)nitroxide radical II.[3]



I II

The carbonyl ^{13}C hyperfine splittings in ketyl radicals have recently been discussed in terms of the structure of ketyl radicals.[4] The large ^{13}C carbonyl splitting in hexamethylacetone ketyl ($a^C_{C=O}$ = 49–53 G)[5] cannot be predicted by the Karplus–Fraenkel theory[6] if the unpaired electron is in a pure p orbital, *i.e.*, if the radical has a planar structure. Assuming a spin density of ρ^π_C = 0.8 on the carbonyl carbon, a maximum splitting of 20.3 G is calculated for a planar hexamethylacetone ketyl.[4] Thus it has been proposed that this radical is distorted out of the plane. We originally thought that the large difference between the fluorine hfs of I and II could be due to a difference in structure. Thus, we investigated the ^{13}C splittings for both the carbonyl and trifluoromethyl carbon atoms of I.

The ketyl I was generated by *in vacuo* electrolysis *intra muros*[7] with acetonitrile as the solvent.[2] The spectrum was recorded on a Varian E-3 spectrometer using Wurster's blue to calibrate the field sweep.[8] The assignments of the ^{13}C splittings were made on the basis of the intensities of the lines; the lines of the trifluoromethyl carbon splitting are about twice as intense as those of the carbonyl carbon splitting. Because the radical is unstable and the concentration was slowly changing while the spectrum was recorded, it was not possible to obtain the sign of the ^{13}C splitting by line-width variation.[9] The spectrum (Figure 1) was recorded over a period of 45 min. The ^{13}C hyperfine splittings are $a^C_{C=O} = 23.3 \pm 0.3$ G and $a^C_{CF_3} = 8.0 \pm 0.3$ G. No temperature dependence of the fluorine splitting was observed in acetonitrile in contrast to the temperature dependence found for the nitroxide.[3]

For a carbonyl carbon bonded to two carbon atoms that each have negligible π-spin density, the Karplus–Fraenkel theory predicts that

$$a^C_{C=O} = (S^C + 2Q^C_{CCF_3} + Q^C_{CO})\rho^\pi_C + Q^C_{OC}\rho^\pi_O \quad (1)$$

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