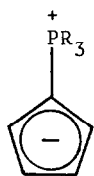


A NEW TRIPOLAR MESOMERIC SYSTEM  
 BIS-(TRIS-DIMETHYLAMINOPHOSPHONIUM) CYCLOPENTADIENYLIDE

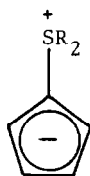
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(Received in Japan 13 January 1973; received in UK for publication 6 February 1973)

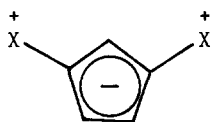
We have carried out extensive study on the dipolar mesomeric systems having  $5C6\pi$  ring i.e. phosphonium (I)<sup>1-3</sup> and sulfonium (II)<sup>4</sup> cyclopentadienylides. These studies directed our interest to a quite new tripolar mesomeric system (III). In this system, both the hetero-atoms, for instance phosphorus atoms, seem to stabilize III by the (p-d) $\pi$  resonance effect. Here we wish to report the successful synthesis of one such system, bis-(tris-dimethylaminophosphonium) cyclopentadienylide (IV) as the form of bromide.



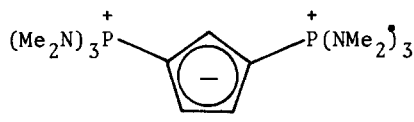
I



II



III (X=P or S)



IV

To a stirred solution of cis-3,5-dibromocyclopentene in chloroform was added a solution of tris-dimethylaminophosphine in chloroform at 0° under nitrogen atmosphere. Temperature was gradually elevated to 40° and stirring was continued for 24 hours. After concentration of the reaction mixture by evaporation and filtration of dimethylamine hydrobromide, the filtrate was chromatographed on silica gel, and recrystallized from methylene chloride-ether to afford colorless crystalline solid in 20 % yield, mp 209.5°. The elemental

analysis of IV showed a good accord with the assigned formula. Found: C, 43.50; H, 8.37; N, 17.90; P, 13.20; Br, 17.07. Calcd for  $C_{17}H_{39}N_6P_2Br_2$ : C, 43.61; H, 8.54; N, 17.89; P, 13.34; Br, 17.29. The pmr spectrum of IV in deuteriochloroform showed three peaks centered at  $\tau$  3.38 (tripl t of triplet,  $J_{p-H} = 5.0$  Hz,  $J_{H-H} = 2.0$  Hz; 1H, ring),  $\tau$  3.62 (triplet of doublet,  $J_{p-H} = 5.0$  Hz,  $J_{H-H} = 2.0$  Hz; 2H, ring), and at  $\tau$  7.24 (d.  $J_{p-H} = 10.0$  Hz; 36 H, methyl). No change in spectrum was observed at  $-63^\circ$ . Since two methyl groups are equivalent and the ring protons couple equally with two  $^{31}P$  nuclei, it is evident that the two phosphorus atoms are quite equivalent and IV has  $C_{2v}$  symmetry.

The ultraviolet spectrum of IV in acetonitrile exhibited two absorption bands at 217 nm ( $\epsilon=35,600$ ) and at 255 nm ( $\epsilon=15,600$ ). The latter absorption band was shifted to shorter wave-length by changing a solvent from nonpolar to polar; 258 nm in chloroform, 255 nm in methanol and 255.5 nm in water. Since this tendency is similar to those of I and II<sup>5</sup>, the band can be assigned to the intramolecular charge-transfer band.

The pKa values of I, II, IV and bis-(tris-dimethylaminophosphonium) methylenide bromide (V)<sup>6</sup> are listed in Table 1.

Table 1. pKa Values of I, II, IV, and V.

Solvent	I	II	IV	V <sup>a</sup>
Water		7.89	1.52	9.67
50 % EtOH-water	4.69	7.53	1.05	7.44

a) V was prepared from methylene bromide and tris-dimethylaminophosphine in dioxane<sup>6</sup>.

It seemed probable that the pKa value of IV is smaller than those of I and II, because the two positively-charged phosphorus atoms are able to conjugate with the cyclopentadienyl ring by  $p\pi-d\pi$  overlap. On the other hand, the difference of pKa values (8.15 in water) between IV and V is ascribed to an aromatic stabilization of the five-membered ring of IV.

The electronic structure of IV might be better understood by the results

of Hückel MO treatment. The electronic charges and the  $\pi$ -bond orders obtained from HMO calculation are illustrated in Fig.1. It is shown that the negative charge migrates to the phosphorus atoms and the remainder equally delocalizes over the cyclopentadienyl ring. The  $\pi$ -bond orders of the C-C bond in the cyclopentadienyl ring are included in the aromatic range (0.5-0.7) proposed

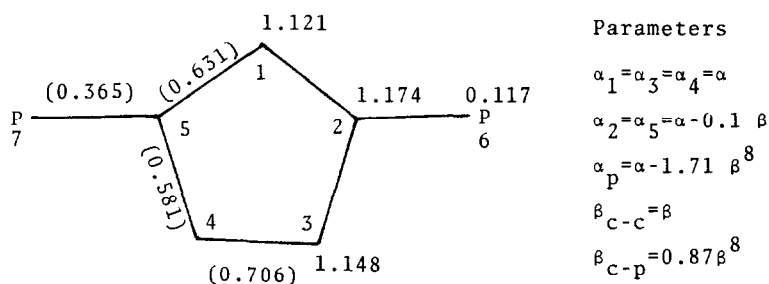
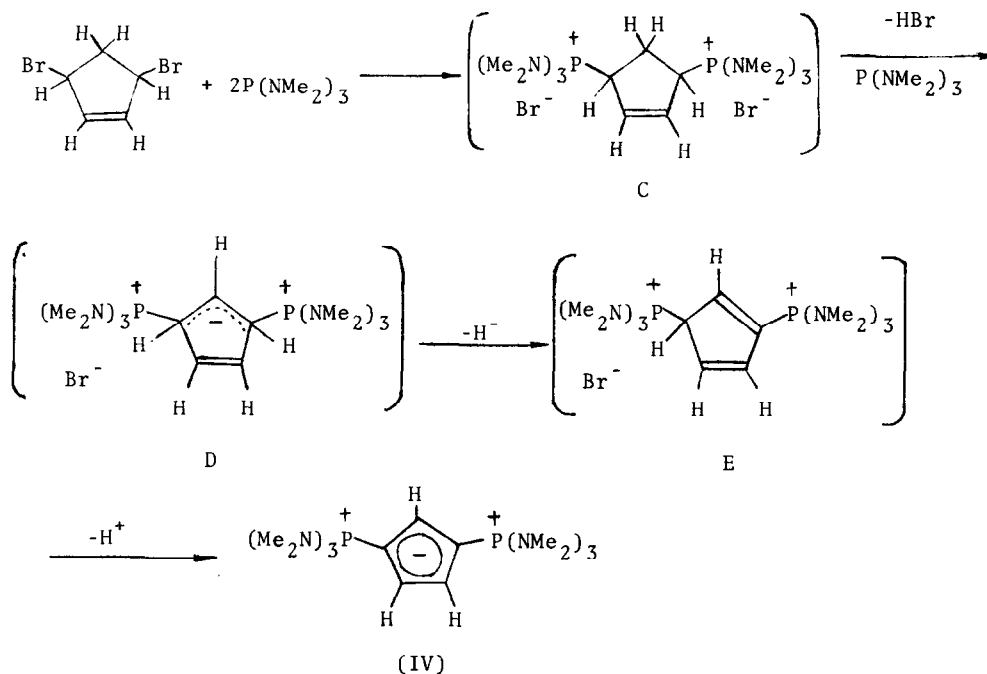


Fig. 1. Molecular diagram of IV.

Scheme 1.



by Streitwieser.<sup>7</sup> The considerable large value (0.365) of the P-C  $\pi$ -bond order suggests a significant (p-d) $\pi$  conjugation between both the atoms.

The formation of IV can be explained by the reaction route given in Scheme 1. It was unsuccessful to isolate the diphosphonium salt (A), probably because the following steps (C→D→E→IV) are fast, and isolated products were only IV and dimethylamine hydrobromide. The hydride ion abstraction (D→E) might occur by a carbonium ion such as 3-bromocyclopentyl cation generated from 3,5-dibromocyclopentene. It was confirmed that the addition of sodium borohydride inhibits the elimination of the hydride ion and interrupt the formation of IV. Such an abstraction of the hydride ion does not occur in preparing triphenylphosphonium<sup>9</sup> and dimethylsulfonium<sup>10</sup> cyclopentadienylides by similar condition. In latter case, the elimination of triphenylphosphine and dimethyl sulfide took place instead of hydride abstraction. Although the reaction behavior of IV is now under investigation, electrophilic substitutions such as diazo-coupling reaction on the cyclopentadienyl ring were found to occur.

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