

suggested the experiment described here—measurement of  $\Delta\bar{H}_s$  of sodium tetraphenylboride in aqueous *t*-butyl alcohol mixtures—since this should magnify the effect and cause it to come at a higher water content than in aqueous ethanol.

In Figure 1, it is seen that  $\Delta\bar{H}_s$  for several salts do indeed give sharp endothermic maxima at about 0.96 mole fraction of water (the corresponding maxima in aqueous ethanol appeared at about 0.85 mole fraction of water and were uniformly smaller).<sup>10</sup> Again, the size of the peak is roughly related to the size of the ions, although in both solvent systems there is a distinct difference between sodium tetraphenylboride and tetraphenylarsonium chloride, suggesting that the sign of the charge on a large ion is important. We also find similar behavior for nonelectrolytes, although large molecules, such as tetraphenylmethane, are too insoluble for accurate study at present. All of the heat measurements were made at  $25 \pm 1^\circ$  with a special solution calorimeter, which will presently be described in detail.<sup>10</sup> These results imply that the main effect of adding the solute to highly aqueous alcohol solutions is to reorganize the solvent structure in the neighborhood of the solute particles. It would be very difficult to explain the effect of size and charge (or lack of charge) in terms of solvation by coordination or solvent sorting. We will present a simple phenomenological interpretation of such behavior soon,<sup>10</sup> including its application to solvent effects on activation parameters. The present case is presented here as a dramatic example of the unexpected behavior of cosolvents in highly aqueous systems and to encourage the use of *t*-butyl alcohol rather than ethanol in future studies of aqueous alcohol systems. There is every reason to believe<sup>3</sup> that aqueous solutions of glycols and polyols will give much smaller effects, although the miscibility problem will be greatly reduced.

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## Dicyanocarbene

Sir:

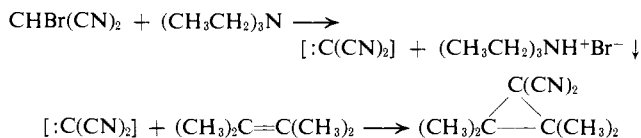
We wish to report the preparation of dicyanocarbene with evidence for its existence as an intermediate. In an earlier reference to the possible formation of dicyanocarbene, Cairns and co-workers proposed that dicyanocarbene may be an intermediate in the preparation of tetracyanoethylene from dibromomalononitrile and copper powder in boiling benzene.<sup>1,2</sup> However, they were unable to obtain direct evidence for the existence of dicyanocarbene as an intermediate having failed to obtain the expected 7,7-dicyanobicyclo[4.1.0]heptane by trapping dicyanocarbene with cyclohexene.

We have prepared dicyanocarbene from bromomalononitrile by the abstraction of hydrogen bromide with triethylamine. The dicyanocarbene was trapped with

(1) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(2) NOTE ADDED IN PROOF. E. Ciganek has recently reported the generation of dicyanocarbene from dicyanodiazomethane in the preparation of 7,7-dicyanonorcaradienes: E. Ciganek, *ibid.*, **87**, 652 (1965).

2,3-dimethyl-2-butene (tetramethylethylene), employed as the solvent in the reaction, to produce the expected 1,1-dicyanotetramethylcyclopropane. The proposed reaction sequence is



In a typical reaction, 10.0 g. (0.069 mole) of bromomalononitrile dissolved in 600 ml. of tetramethylethylene and 7.7 g. (0.076 mole) of triethylamine in 660 ml. of tetramethylethylene were added simultaneously (12 hr.) to 4.8 l. of tetramethylethylene with stirring at  $-8^\circ$  in a nitrogen atmosphere. The triethylamine hydrogen bromide salt which precipitated during the reaction was removed by filtration and the tetramethylethylene was stripped off at 50 mm. in a rotary vacuum evaporator leaving a yellow oil. The 1,1-dicyanotetramethylcyclopropane was recovered, by fractional distillation ( $57^\circ$  at 0.04 mm.), as a colorless oil which solidified and was recrystallized from ligroin to yield 2.5 g. (24%) of white needles melting at  $51.5\text{--}52.0^\circ$ . The n.m.r. spectrum of the product in carbon tetrachloride shows only a single sharp peak due to the 12 equivalent methyl hydrogens ( $\tau$  8.62 p.p.m.); the infrared spectrum of the product in carbon tetrachloride has a strong single peak due to the nitrile groups ( $2265\text{ cm.}^{-1}$ ).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{12}\text{N}_2$  (148.23): C, 72.92; H, 8.18; N, 18.90. Found: C, 72.84; H, 8.33; N, 18.71.

The triethylamine hydrogen bromide salt was washed with acetone and recrystallized from ethanol to give white needles melting at  $247\text{--}248^\circ$ . Decomposition of the salt with sodium hydroxide released the triethylamine which formed a yellow picrate melting at  $170\text{--}172^\circ$ .

We are continuing to study the reactions of dicyanocarbene in a number of different systems and will report our findings in future papers.

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## A New Type of Bis Arene-Metal Complex

Sir:

Bis arene-metal complexes so far known contain a single atom between the sandwich arenes.<sup>1</sup> We wish to report an example of a new type of bis arene-metal complex in which two metal atoms are contained between the two arene rings.

The new complex has the formula  $[\text{PdAl}_2\text{Cl}_7(\text{C}_6\text{H}_6)]_2$  (I) and has been obtained by allowing  $\text{AlCl}_3$ , Al, and

(1) See, e.g., H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 380-425.

$\text{PdCl}_2$  to react in benzene according to Fischer's method.<sup>2</sup>

In a typical preparation, 1 g. of  $\text{PdCl}_2$ , 1.05 g. of freshly sublimed  $\text{AlCl}_3$ , and 0.5 g. of Al were suspended in 50 ml. of anhydrous benzene and boiled for about 15 min. The brown suspension was then filtered hot ( $\text{N}_2$ ), and the filtered solution was allowed to cool very slowly to room temperature. After 1–2 days, big crystals of I having a brown-black color were found on the walls of the container. I is practically insoluble in the hydrocarbon solvents at room temperature.

*Anal.* Calcd. for  $\text{PdAl}_2\text{Cl}_7\text{C}_6\text{H}_6$ : Pd, 21.91; Al, 11.08; Cl, 50.97; C, 14.85; H, 1.24. Found: Pd, 20.9; Al, 11.7; Cl, 51.4; C, 14.6; H, 1.13.

Complex I reacts at room temperature with tetrahydrofuran giving  $\text{PdCl}_2$  and metallic Pd (in equivalent amounts),  $\text{AlCl}_3$ , and  $\text{C}_6\text{H}_6$ . Gas chromatographic determinations of benzene in the tetrahydrofuran solution gave values corresponding to the theoretical.

The crystal and molecular structure of I is being investigated by single crystal X-ray methods. After correction for absorption, the intensities of about 900 observable reflections, taken with the Cu  $K\alpha$  radiation, have been visually estimated for the ( $hk0$ ) and ( $hkl$ ), ( $hk2$ ), and ( $h0l$ ) and ( $0kl$ ) reciprocal layers.

The triclinic unit cell of I has the following dimensions:  $a = 9.42 \pm 0.04$ ,  $b = 9.24 \pm 0.04$ ,  $c = 9.56 \pm 0.04$  Å.;  $\alpha = 77.9 \pm 0.7^\circ$ ,  $\beta = 96.2 \pm 0.7^\circ$ ,  $\gamma = 108.1 \pm 0.7^\circ$ .

The experimental density of 2.07 g./cm.<sup>3</sup> is in good agreement with the calculated value of 2.09 g./cm.<sup>3</sup> based on one molecule per unit cell. The space group has been found to be  $\text{P}\bar{1}$ ; the molecule is therefore centrosymmetrical.

The crystal structure has been roughly deduced by application of the usual heavy atom technique on three two-dimensional projections, in which all the higher atoms were introduced stepwise. The atomic coordinates and isotropic thermal factors have been refined by normal and modulated difference Fourier syntheses until the agreement factor over all the observed reflections has dropped to the value  $R = 0.152$ . A three-dimensional refinement of the structure is now in progress in our laboratory.

We will expose in the following the preliminary results of our X-ray analysis.

The molecular structure (Figure 1) consists of a central nucleus in which two palladium atoms are bonded together and two benzene rings are symmetrically disposed around the Pd–Pd axis, so as to give rise to a sandwich coordination around the two central atoms; the two ( $\text{Al}_2\text{Cl}_7$ ) groups are symmetrically coordinated to the nucleus, via Cl–Pd bonds. The Pd–Pd distance of  $2.58 \pm 0.01$  Å. represents the shortest value so far found for this intermetallic bond.<sup>3</sup>

The  $\text{Pd}^{\text{I}}\text{--Cl}^{\text{I}}$ ,  $\text{Pd}^{\text{I}}\text{--Cl}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}\text{--Cl}^{\text{IV}}$ , and  $\text{Pd}^{\text{II}}\text{--Cl}^{\text{V}}$  distances are 2.34 Å. on the average; no significant difference between them may be deduced from the actually available data.

The  $\text{Pd}^{\text{I}}\text{--Cl}^{\text{III}}$ ,  $\text{Pd}^{\text{I}}\text{--Cl}^{\text{VI}}$ ,  $\text{Pd}^{\text{II}}\text{--Cl}^{\text{III}}$ , and  $\text{Pd}^{\text{II}}\text{--Cl}^{\text{VI}}$  distances also are similar, with an average value of 2.94 Å. No significant deviation from the regular hexagonal symmetry has been assessed hitherto for the

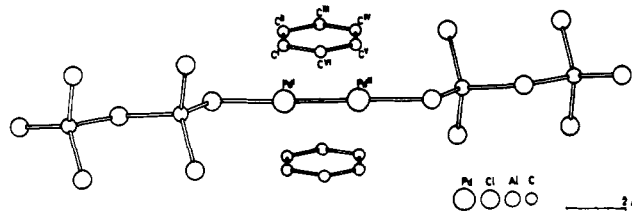


Figure 1. Side view of the  $[\text{PdAl}_2\text{Cl}_7(\text{C}_6\text{H}_6)_2]_2$  molecule as it results from the present state of structural refinement. The black spot between the two palladium atoms represents the molecular and also crystallographic center of symmetry.

benzene rings ( $d_{\text{C-C}} \cong 1.41$  Å.). The Pd–Cl distance has been found to be  $2.46 \pm 0.02$  Å., while the Cl–Pd–Pd–Cl group is approximately on a straight line ( $\angle \text{Cl–Pd–Pd} = 176 \pm 1^\circ$ ).

The resulting geometrical structure of the ( $\text{Al}_2\text{Cl}_7$ ) ligands is in substantial agreement with the X-ray results quoted for other compounds of aluminum in tetrahedral coordination, containing bridge bonds.<sup>4</sup> The bridge (Al–Cl) distances are longer (2.25 Å., av.) than the nonbridge distances (2.08 Å., av.); the  $\angle \text{Cl–Al–Cl}$  bond angles appear to deviate by  $\pm 10^\circ$  with respect to the normal tetrahedral value ( $109.5^\circ$ ) so as to give rise to fairly close distances between chlorine atoms linked to the same aluminum atom.

As it has been pointed out previously, a completely new feature which results from the present picture is the binuclear sandwich coordination of the two Pd atoms by benzene rings.

It may be interesting to observe that, assuming the Pd–Pd and Cl–Pd to be purely single bonds, the xenon electronic configuration is attained if each benzene ring is formally assumed to contribute three  $\pi$ -electrons to each of the two palladium atoms; this qualitative picture is in agreement with the observed diamagnetism of the substance.

(4) P. H. Lewis, and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953); G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chem.*, **61**, 69 (1963).

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## The Crystal Structure of Monoclinic ( $\beta$ ) Sulfur

Sir:

Above  $95.39^\circ$  the stable crystalline form of elemental sulfur is the monoclinic ( $\beta$ ) phase. The unit cell dimensions obtained at  $103^\circ$  by Burwell<sup>1</sup> are  $a = 11.02$ ,  $b = 10.96$ ,  $c = 10.90$  Å.,  $\beta = 96.7^\circ$ . The space group suggested by systematic extinctions is  $\text{P}2_1/c$ . The observed density of 1.96 g./cc. indicates that there are 48 atoms per unit cell. The predominant molecular species below the melting point is the  $\text{S}_8$  ring, which in orthorhombic sulfur has the crown configuration of ideal symmetry  $\text{D}_{4d}\text{--}\bar{8}2\text{m}$ .<sup>2</sup> Six  $\text{S}_8$  molecules can be accommodated in a unit cell of space group  $\text{P}2_1/c$  by placing four in general positions and two in special positions or by using three sets of special positions. The

(2) E. O. Fischer, and W. Hafner, *Z. Naturforsch.*, **10b**, 655 (1955).

(3) R. S. Nyholm, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, Sept. 1964.

(1) J. T. Burwell, *Z. Krist.*, **97**, 123 (1937).

(2) B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).