$$CF_3C\!\!=\!\!\!=\!\!CCF_3$$
$$\diagdown\!\diagup$$
$$CF_2$$

5

$$CF_3C\!\!=\!\!CCF_3$$
$$| \quad |$$
$$F_2C\!-\!CF_2$$

6

a gross redistribution of phosphine ligands occurs to give $(Ph_3P)_3Ni(C_2F_4)$.

Preparation of **1** was effected by bubbling TFE through a suspension of acetylacetonatodiethylene-rhodium in ether for 30 min. Cooling to $-78°$ gave yellow crystals of **1**, m.p. 78–79°. *Anal.* Calcd. for $C_9H_{11}F_4O_2Rh$: C, 32.8; H, 3.34; mol. wt., 330. Found: C, 33.3; H, 3.65; mol. wt., 350. The iridium–TFE complex **3** was obtained as off-white crystals by shaking a toluene solution of $(Ph_3P)_2(CO)$-IrCl with TFE at 3 atm. for 7 days. *Anal.* Calcd. for $C_{39}H_{30}ClF_4IrOP_2$: C, 53.2; H, 3.44; F, 8.63. Found: C, 53.6; H, 3.74; F, 8.85. The iridium–hexafluorobutyne complex **4** was obtained by stirring a toluene solution of $(Ph_3P)_2(CO)IrCl$ with hexafluoro-butyne at 1 atm. for 16 hr. Pyrolysis of 0.85 mmole of **4** at 105° gave 0.84 mmole of pure $(Ph_3P)_2(CO)IrCl$, 0.79 mmole of hexafluoro-2-butyne, and a trace of toluene. The infrared spectra of **1** and **3** showed two CF stretching bands at longer wave length than those of TFE. The CO absorption bands of **3** and **4** appeared at 2040 and 2025 cm.$^{-1}$, respectively, *vs.* 1965 cm.$^{-1}$ for $(Ph_3P)_2(CO)IrCl$.

Further details of the chemistry and spectral properties of these compounds will be published soon.

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A Large Solvation Enthalpy Effect in Highly Aqueous t-Butyl Alcohol Solutions[1,2]

Sir:

We wish to report an enormous change in the heat of solvation resulting from a modest composition change in a highly aqueous alcohol solution. The partial molal heat of solution at infinite dilution $(\Delta \bar{H}_s)$ of crystalline sodium tetraphenylboride in pure water is -5.2 ± 0.1 kcal./mole, while that in water containing only 0.045 mole fraction of *t*-butyl alcohol is 11.7 $\pm$ 0.1 kcal./mole. The difference of nearly 17 kcal./mole produced by adding this small amount of a hydroxylic cosolvent to water occurs at a sharp maximum (Figure 1) and may very well have implications for a number of areas of physical and biological chemistry.

Many properties of water–alcohol solvent systems go through sharp maxima in water-rich regions of the solvent spectrum. These facts have been reviewed recently by Franks[3] and interpreted in terms of an *increase(sic)* in the structuredness of the solvent occasioned by the first increments of added cosolvent; larger quantities eventually cause the expected disruption of solvent structure. *t*-Butyl alcohol is especially inter-

Figure 1. Partial molal heats of solution at infinite dilution $(\Delta \bar{H}_s)$ for several electrolytes in aqueous *t*-butyl alcohol solutions. The curve for tetraphenylarsonium chloride refers to its dihydrate. On the basis of our results in aqueous ethanol, the curve for the anhydrous salt will be identical with this, although slightly displaced in an exothermic direction.

esting for such studies because at room temperature its miscibility is just on the borderline of allowing a complete spectrum of binary solvent mixtures. Tommila[4] and co-workers have given particular attention to aqueous solutions of this alcohol and find that extrema for molal volumes, heats of mixing, and deviations from Raoult's law are generally larger than for aqueous solutions of lower alcohols and occur at higher water concentrations (on the mole fraction scale). The same may be said for ultrasonic absorption,[5] an important guide to solvent structure, and the solvent effect on enthalpy of activation.[6]

The measurements of Moss and Wolfenden[7] and Slansky[8] for partial molal heats of solution of various low molecular weight salts in aqueous methanol also exhibit small endothermic maxima about 0.80 mole fraction of water, and recent measurements from this laboratory[9,10] show clearly that in water–ethanol mixtures a number of salts *and nonelectrolytes* of varying molecular size give endothermic maxima (relative to water) for $\Delta \bar{H}_s$ in solutions of the same composition where physical properties[3–5] and heats of activation[6,11] pass through maxima or minima. Of more importance is the fact that the size of the maximum is roughly proportional to the size of the molecular (or ionic) particles of the solute, an extreme case being sodium tetraphenylboride, which gives a maximum (relative to its value in water) of 10.7 kcal./mole in a solution of 0.88 mole fraction of water. The above facts immediately

(1) Solvent Effects in Organic Chemistry. VI. Contribution 1265 from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa. 15213.

(2) This research was made possible through a grant provided by the National Science Foundation (G-14583 and GP-2014).

(3) F. Franks, *Quart. Rev.* (London), in press. We are grateful to Professor Franks for helpful discussions and allowing us to use his manuscript.
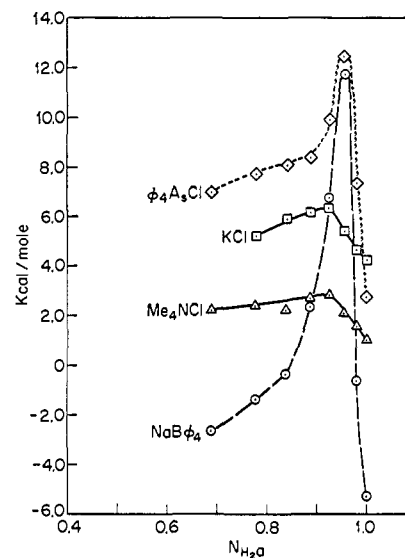
(4) J. Kenttammaa, E. Tommila, and M. Martin, *Ann. Acad. Sci. Fennicae, AII.*, No. 93 (1959).

(5) W. G. Schneider, *Colloq. intern. centre natl. rech. sci.* (Paris), 77, 529 (1959).

(6) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, 34, 931 (1956).

(7) R. L. Moss and J. H. Wolfenden, *J. Chem. Soc.*, 118 (1939).

(8) C. M. Slansky, *J. Am. Chem. Soc.*, 62, 2430 (1940).

(9) E. M. Arnett, P. M. Duggleby, and J. J. Burke, *ibid.*, 85, 1350 (1963).

(10) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, in press.

(11) S. Winstein and A. H. Fainberg, *ibid.*, 79, 5937 (1957).

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).[10] 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 $25 \pm 1°$ with a special solution calorimeter, which will presently be described in detail.[10] 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,[10] 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[3] that aqueous solutions of glycols and polyols will give much smaller effects, although the miscibility problem will be greatly reduced.

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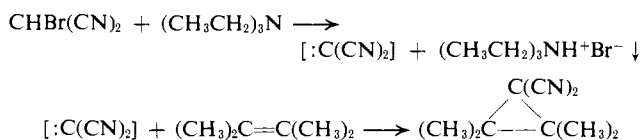*Received January 30, 1965*

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.[1,2] 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

$$CHBr(CN)_2 + (CH_3CH_2)_3N \longrightarrow$$
$$[:C(CN)_2] + (CH_3CH_2)_3NH^+Br^- \downarrow$$

$$[:C(CN)_2] + (CH_3)_2C{=}C(CH_3)_2 \longrightarrow (CH_3)_2C{-}C(CH_3)_2 \text{ with } C(CN)_2 \text{ ring}$$

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 $-8°$ 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 ($57°$ 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 51.5–52.0°. The n.m.r. spectrum of the product in carbon tetrachloride shows only a single sharp peak due to the 12 equivalent methyl hydrogens (τ 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 cm.$^{-1}$).

Anal. Calcd. for $C_9H_{12}N_2$ (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 247–248°. Decomposition of the salt with sodium hydroxide released the triethylamine which formed a yellow picrate melting at 170–172°.

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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Received January 9, 1965

A New Type of Bis Arene–Metal Complex

Sir:

Bis arene–metal complexes so far known contain a single atom between the sandwich arenes.[1] 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 $[PdAl_2Cl_7(C_6H_6)]_2$ (I) and has been obtained by allowing $AlCl_3$, Al, and

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