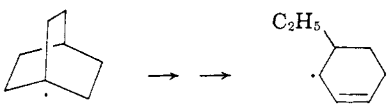
potential of 7.5 v. The concurrent pyrolysis of *t*-butyl perbenzoate gave a phenyl addition product whose 157/186 and 130/186 peak ratios were 1.2 and 0.6. For an authentic sample of 1-phenylbicyclo[2.2.2]octane,[10] these ratios were 0.55 and 1.05, respectively. It seems clear, therefore, that the C_8H_{13} radical observed was also a rearrangement product and not the 1-bicyclo[2.2.2]-octyl radical. A possible rearrangement is



There is some experimental evidence that the identity of the rearranged monocyclic radical is as shown. At higher furnace temperatures, the C_8H_{13} radical decomposed further by loss of a unit of mass 29, giving a compound whose ionization potential was the same as that of 1,3-cyclohexadiene. Moreover, the observed ionization potential of the C_8H_{13} radical is the same as that found recently[11] for 3- and 4-cyclohexenyl radicals. The change in ionization potential resulting from ethyl substitution (as in the radical above) would be expected to be negligibly small.

Although the attempted preparation of the desired radicals apparently was unsuccessful, this failure is instructive in that it shows that these bicyclic radicals are appreciably less stable toward ring rupture than monocyclic alkyl[8] and alkenyl[11] radicals, which could be produced in fair to good yields under the same conditions. Since the radicals themselves decompose faster than the nitrite esters at the temperatures employed, the activation energy for ring rupture in the radicals appears to be less than the 36 kcal/mole characteristic of nitrite decompositions.[12] Although it would be very desirable to obtain estimates for the energies of bridgehead free radicals in the gas phase by some other method,[1] the present work indicates not only that difficulties are to be anticipated, but that it will be highly important to establish that the radical studied is truly a bridgehead one and not some rearranged species.

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[10] Prepared by Dr. E. Wiskott by a Friedel–Crafts reaction on 1-hydroxymethylenenorbornane, using benzene as a solvent-reactant and $AlCl_3$ as the catalyst. The product, mp 72–74° (80% yield), gave only two sharp nmr peaks, at δ 1.75 (area 13) and at δ 7.27 (area 5).

[11] S. Pignataro, A. Cassuto, and F. P. Lossing, *J. Am. Chem. Soc.*, **89**, 3693 (1967).

[12] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co., Ltd., London, 1958.

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Two Different Tetrahedral–Octahedral Coordination Equilibria for Nickel(II) in Molten Zinc Chloride–Cesium Chloride Mixtures

Sir:

It has long been known that nickel(II) and some other transitional metal ions contained in certain binary molten chloride salt solvents may occur as an equilibrium mixture of two coordination forms.[1] In the case of nickel(II), one of these forms has a distribution of coordination geometries that on the average is more or less tetrahedral, while the other is more or less octahedral. We report here the novel fact that solute nickel(II) in molten mixtures of zinc chloride and cesium chloride has two such tetrahedral–octahedral coordination equilibria, one of which occurs in melts containing about 50–70 mole % zinc chloride and the other in about 92–100 mole % zinc chloride.

Figure 1a shows the large change in formal absorptivity of dilute solutions of nickel chloride in molten zinc chloride–cesium chloride mixtures as the solvent composition is progressively varied from 50 to 72 mole % zinc chloride. At 50 mole % the spectrum is mostly that for a more or less tetrahedral coordination geometry. Upon increasing the zinc chloride content of the solvent, however, the tetrahedral bands decrease in intensity while octahedral bands grow in. At 72 mole % zinc chloride the spectrum is mostly that of a more or less octahedral coordination, and only traces of the strongest tetrahedral bands remain.

For the above spectra the formal absorptivity, ϵ_f, at any solvent composition is approximately the sum of a purely tetrahedral spectrum, ϵ_T, and a purely octahedral spectrum, ϵ_O, over the wavenumber range 5000–21,000 cm^{-1}. That is, $\epsilon_f = x\epsilon_T + (1 - x)\epsilon_O$, where x is a function of solvent composition but not wavelength, while ϵ_T and ϵ_O are composition invariant. Such a set of spectra is said to be internally linear. Exact internal linearity in the present case would signify that there are only two coordination geometries and that the spectrum of each is unaffected by solvent composition. The small deviations from internal linearity which were observed mean either that the spectra of the components are slightly sensitive to solvent composition or else that there are small amounts of additional species. Clearly we are dealing here with what is mostly a two-species tetrahedral–octahedral equilibrium in which octahedral geometry is favored by increasing the zinc chloride content of the solvent.

Between 72 and 92 mole % zinc chloride, the nickel(II) spectrum (not shown) changes only in minor ways, but as the zinc chloride content increases from 92–100 mole % (shown in Figure 1b) the octahedral bands reverse their direction of change and grow progressively weaker while simultaneously a new set of tetrahedral bands grows in. As before, this set of spectra is nearly internally linear so that we are dealing with a tetrahedral–octahedral equilibrium except that now tetrahedral geometry rather than octahedral geometry is favored by increasing the zinc chloride content of the

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[1] See, for example, C. R. Boston and G. P. Smith, *J. Phys. Chem.*, **62**, 409 (1958); C. K. Jørgensen, *Mol. Phys.*, **1**, 410 (1958); D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962); H. A. Øye and D. M. Gruen, *Inorg. Chem.*, **4**, 1173 (1965); C. A. Angell and D. M. Gruen, *J. Phys. Chem.*, **70**, 1601 (1966).

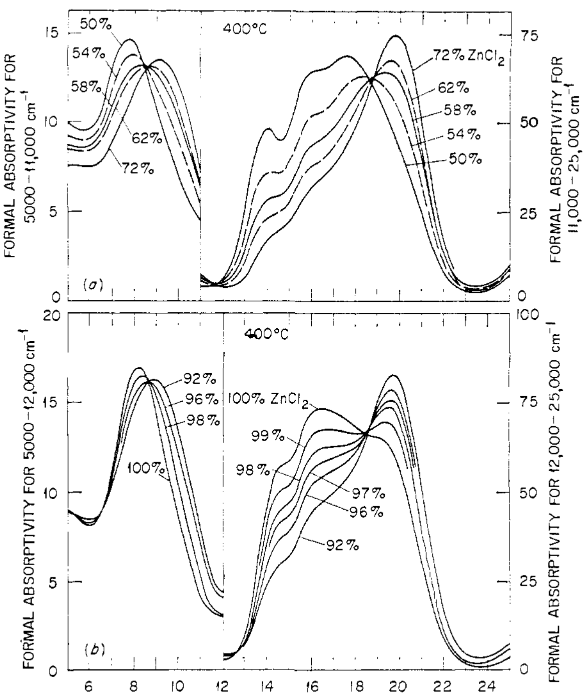

Figure 1. Spectra of dilute solutions of nickel(II) ions in molten $ZnCl_2$–CsCl mixtures at 400°. Each spectrum is labeled with the mole percentage of zinc chloride in the solvent salt.

solvent. In the limit of pure zinc chloride as solvent there is a mixture of tetrahedral and octahedral entities.

The tetrahedral spectra in the two ranges, 50–72 and 92–100 mole % zinc chloride, have significantly different band energies and correspond to different entities.

The tetrahedral–octahedral equilibrium that occurs between about 50 and 70 mole % $ZnCl_2$ appears to be of the same type as is found for solute nickel(II) in lithium chloride–potassium chloride and magnesium chloride–potassium chloride melts.[2,3] The second equilibrium, which occurs in pure zinc chloride and neighboring compositions as solvents, is almost certainly associated with the tendency of molten zinc chloride to form chloride-bridged polymers in which zinc is tetrahedrally coordinated.[4] We propose that the tetrahedral nickel(II) species in pure zinc chloride consists of a nickel ion occupying a zinc site within a polymer unit, while the octahedral species is a nickel ion at interpolymer positions. Addition of CsCl to molten $ZnCl_2$ breaks chloride bridges and destroys the polymer structure,[5] thereby increasing the density of interpolymer positions and, hence, the concentration of octahedrally coordinated nickel(II).

The effect of temperature was studied from 300 to 600°. For melts containing 50–62 mole % $ZnCl_2$, with increasing temperature the equilibrium shifts in favor of four-coordinate nickel just as it does when LiCl–KCl and $MgCl_2$–KCl are the solvents. For melts containing higher zinc chloride concentrations, the behavior is more intricate than this, but it appears that with increasing temperature the fraction of nickel ions at zinc sites in 100% $ZnCl_2$ decreases as expected because of the breakup of the polymer network.

The results reported here are taken from an extensive study of nickel(II) ions in solvents ranging in composition from pure CsCl to pure $ZnCl_2$. This research will be reported in detail in subsequent publications.

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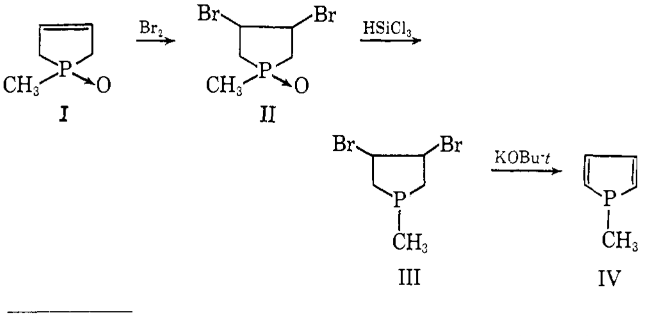
1-Methylphosphole[1]

Sir:

The extent of delocalization of the phosphorus electron pair in phospholes into an aromatic system has not yet been defined[2] even though the ring system has been known since 1959.[3] Molecular orbital calculations suggest a considerable degree of conjugation energy (1.49 β; *cf.* to 1.37 β for pyrrole) for the parent compound.[4] The phospholes characterized to date all bear several substituents, one[5] or more[3,6] of which are phenyl groups. A phenyl substituent, with conjugative effects of its own, is undesirable when attempting to define the electronic character of the parent ring system. We have accomplished a synthesis of a phosphole (IV) bearing but a single methyl substituent; the existence of "aromatic character" for the phosphole system can be expected to be reliably manifested in the properties of this type of simple derivative.

Phospholene derivatives (dihydrophospholes) are now readily available[7] and are potential starting materials for phosphole syntheses.



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(1) Supported by Research Grant CA-05507, National Cancer Institute, U. S. Public Health Service.

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