of **1a** or **1b** followed by oxidative addition of Cl_2 and treatment with $Me_3SiNSNSiMe_3$.[11] The compounds (R = R′ = F; R = F, R′ = Ph) are obtained from the reaction of PF_5 (or $PhPF_4$) with $Me_3SiNSNSiMe_3$, but that approach cannot be extended to other derivatives.[24]

If **4a** produced by this new method is heated, without isolation in boiling toluene, then **1a** is obtained in an overall yield of ca. 90% (Scheme I). In principle, this route to **1** should be applicable to other derivatives, since a variety of reagents of the type $R_2P(NSiMe_3)[N(SiMe_3)_2]$ can be prepared from the reaction of $R_2PN(SiMe_3)_2$ with trimethylsilyl azide. We have used this new procedure for the synthesis of **1b**, but the attempted purification of the crude product by sublimation resulted in the known thermal decomposition of **1b**[7] to give 1,5-$(Me_2P)_2N_4S_2$ and S_4N_4 in overall yields of 53% and 41%, respectively, based on 70% conversion of **4b** into **1b** followed by decomposition according to eq 1.

$$2Me_2PN_3S_2 \rightarrow (Me_2P)_2N_4S_2 + S_4N_4 \tag{1}$$

Compound **1c** (R = Et) [$\delta(^{31}P) = +6.9$, *m/e* 195 (M^+)] was also prepared by this new procedure, but the thermal instability of this new derivative prevented its full characterization. It should be noted, however, that thermally unstable phosphadithiatriazines can be conveniently stored as norbornadiene adducts.[6b,11]

Synthesis of 1,5-$(R_2P)_2S_2N_4$ (R = Ph (2a), Me (2b)). The reaction of $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ with SCl_2 was investigated by using a variety of solvents and reaction conditions before the optimum procedure was established. This involves the dropwise addition of SCl_2 to a solution of the phosphorus reagent in methylene dichloride using a 3:2 molar ratio of the reagents.

$$2Ph_2P(NSiMe_3)[N(SiMe_3)_2] + 3SCl_2 \rightarrow (Ph_2P)_2N_4S_2 + 6Me_3SiCl + {}^1/_8S_8 \tag{2}$$

However, the detection of **1a**, $(Ph_2P)_2N_3SCl$,[22] and two unidentified phosphorus-containing products in the reaction mixture by ^{31}P NMR spectroscopy shows that the reaction is more complicated than indicated by eq 1. Nevertheless, pure **2a** can be isolated in 50% yield based on the amount of phosphorus reagent used by taking advantage of its low solubility, compared to that of the other products, in acetonitrile. This procedure represents a marked improvement over previous methods for the preparation of **2a**,[8] and it can also be used for the preparation of **2b** in ca. 50% yield. Similar reactions with other reagents of the type $RR'P[N(SiMe_3)_2(NSiMe_3)$[21] should lead to new derivatives of the heterocycle **2**, including those with different substituents on phosphorus.

Summary. Specific synthetic procedures have been developed for the preparation of the individual ring systems **1a**, **4a**, and **4b** in excellent yields from readily obtainable starting materials. A much improved synthesis of **2a** and **2b** that is potentially applicable to other derivatives of **2** has also been achieved. These new methods should facilitate investigations of the chemistry of these cyclophosphathiazenes.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support in the form of operating grants and a postgraduate scholarship (S.W.L.) and the STEP program of the Province of Alberta for a summer research assistantship (T.P.). We are grateful to Professor R. T. Oakley for communication of his results on the synthesis of **4a**.

Registry No. **1a**, 76958-87-7; **1b**, 80126-92-7; **2a**, 85028-71-3; **2b**, 80106-10-1; **4a**, 90498-60-5; **4b**, 90498-61-6; S_4N_4, 28950-34-7; $Ph_2P(NHSiMe_3)(NSiMe_3)$, 21955-74-8; $Ph_2P[N(SiMe_3)_2](NSiMe_3)$, 61500-31-0; $(NSCl)_3$, 5964-00-1; $Me_2P[N(SiMe_3)_2](NSiMe_3)$, 21385-93-3; SCl_2, 10545-99-0.

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Effect of Pressure-Induced Freezing on the Energy of the Intervalence Electronic Absorption Band of a Binuclear Mixed-Valence Complex

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Received August 21, 1987

Intramolecular electron transfer (IET) is one of the most fundamental and important chemical processes.[3] Creutz and Taube[4] and Cowan and Kaufman[5] pioneered the use of binuclear transition-metal mixed-valence complexes[6] to study IET. A distinguishing characteristic of the electronic spectrum of many binuclear mixed-valence complexes is a low-energy band which cannot be attributed to either metal center alone, since it arises when electron transfer is photoinduced from one metal center to the other. This excitation is often referred to as an intervalence-transfer (or IT) band. In two previous papers we demonstrated that (1) the energy of the IT band maximum was very sensitive to concentration[7] and (2) a dielectric continuum model is not an adequate description of the energy of the IT band in solution.[8] In this paper we continue our study of the application of the dielectric continuum model to IET.

Some authors[9–11] have described the energy (λ) of the IT band as arising from two contributions: one (λ_{out}) from the reorganization of the outer-sphere coordination, i.e. the solvent structure, and the other (λ_{in}) from the reorganization of the inner sphere as indicated in eq 1. Usually a dielectric continuum model is

$$\lambda = \lambda_{out} + \lambda_{in} \tag{1}$$

used to describe the solvent reorganizational contribution

$$\lambda_{out} = k(\Delta e)^2(D_{op}^{-1} - D_s^{-1}) \tag{2}$$

where the proportionality factor k can be explicitly given in terms of the radii of the reactants in certain cases and in other cases can be treated with numerical techniques. In eq 2, Δe is the charge transferred, D_{op} is the optical dielectric constant (usually taken as the square of the refractive index n), and D_s is the low-frequency dielectric constant of the medium. It should be noted that eq 2 was developed by Marcus[12] for *inter*molecular electron transfer and others have applied it to interpret the energy of the IR band observed for mixed-valence complexes.[10,11] Specifically the application has been to localized mixed-valence compounds. There have been several calculations[13] carried out on the basis of eq 2.

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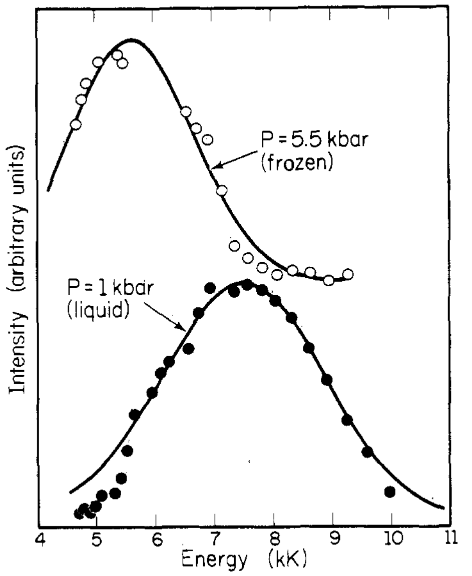


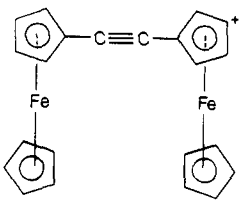
Figure 1. Near-IR electronic absorption spectrum of the I_3^- salt of diferrocenylacetylene in CD_3CN.

A linear plot of E_{op} ($=\lambda$) versus ($n^{-2} - D_s^{-1}$) extrapolated to ($n^{-2} - D_s^{-1}$) = 0 is used to obtain the inner-sphere reorganizational energy E_{in} ($=\lambda_{in}$) of the mixed-valence complex.[10,11] In previous papers we demonstrated that expression 2 is *not* applicable to localized mixed-valence complexes.[7,8] One method we used was pressure-induced freezing. This technique is described more fully in ref 8. Briefly, pressure is used to freeze the solvent at ambient temperature. As the pressure on a liquid is increased, its freezing point rises.[14] Acetonitrile-d_3 (the solvent used in this study) at 25 °C freezes at a pressure of 4.5 kbar (1 bar = 0.9869 atm). It is well-known that upon freezing the static dielectric constant of a liquid decreases by a factor of 2–10 depending on its polarity. For CD_3CN, D_s = 43.3 at 1.0 kbar (liquid) and D_s = 3.9 at 5.5 kbar (frozen).[8] This is because the orientational polarizability, which is a major factor in D_s for polar liquids, is quenched when the liquid freezes. The effects of pressure and of freezing on D_{op} and D_s are discussed in detail in ref 8.

If eq 2 applies, there should be a large shift (1500–5000 cm^{-1}) of the IT band to lower energy for a frozen solution as compared to that for the liquid. For biferrocenium triiodide, biferrocenium hexafluorophosphate, and $[(bpy)_2ClRu]_2(pyz)(PF_6)_2$ (bpy is bipyridine and pyz is pyrazine) in several polar solvents at several concentrations, we observed very small shifts (never over 600 cm^{-1} and usually much less) when shifts of 1500–2500 cm^{-1} would be predicted by eq 2.[8]

The other method we used to demonstrate the limitations of eq 2 for localized mixed-valence complexes simply involved changing the concentration of mixed-valence complexes in the commonly used solvents.[7] It was found that the peak location, shape (half-width), and oscillator strength of the IT band for a given mixed-valence complex are strong functions of concentration for solvents such as nitrobenzene and dichloromethane. Electrical conductivity data for these same solutions conclusively showed that the observed concentration dependencies of the IT band are due to variations in the degree of ion aggregation as the concentration of the mixed-valence complex is varied. Thus, it is not possible to measure the energy of the IT band for a given mixed-valence complex in a series of solvents and expect that some variant of eq 2 can be used to evaluate E_{in}. Only if E_{op} could be determined at *very low concentrations* in low-dielectric solvents, could such data be employed to check or utilize eq 2.

Previous work[11b] on the mixed-valence diferrocenylacetylene cation in CD_3CN gave a value of 4700 cm^{-1} for E_{in} by employing eq 2 together with E_{op} values measured in a series of solvents. Thus, it seemed useful to measure the spectrum of this cation in CD_3CN at 25 °C below and above the freezing point (4.5 kbar).



I

In this paper we report the results of a study of the effect of pressure-induced freezing on the energy of the IT band of the I_3^- salt of the mixed-valence diferrocenylacetylene cation (I). Diferrocenylacetylene was prepared as described in ref 15. A CD_3CN solution of mixed-valence cation I was prepared by adding a CD_3CN solution of I_2 to a CD_3CN solution of diferrocenylacetylene. The concentration of diferrocenylacetylene used was 2.3 mM. Spectra taken at pressures below and above the freezing point are shown in Figure 1. The peak shifts significantly to lower energy (~1800 cm^{-1}) but by less than 40% of the value predicted by eq 2.

We conclude that a plot of E_{op} vs ($n^{-2} - D_s^{-1}$) for a series of solvents is not a satisfactory way of determining λ_{in}. As indicated in our previous paper,[8] a possible explanation is that for intramolecular electron transfer within a large metal complex with π electrons the field supplied by the ligands, in addition to that of the electrons in the metal–ligand bond plus that of a relatively rigid solvation shell, dilutes the effect of the dielectric continuum. This work, in conjunction with our earlier work on the dielectric continuum model[8] and the concentration dependence[7] of IT bands, reveals that there is still much to be learned about the nature of the IT band of mixed-valence complexes in solution.

Acknowledgment. This work was supported in part by the Materials Science Division, Department of Energy, under Contract DE-AC02-76ER01198 and in part by NIH Grant HL13652.

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