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Synthesis and Characterization of Bis(N,N-dimethyl-2-aminomethylthiophenium)Tetrahalocuprate(II)

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Bis(N,N-dimethyl-2-aminomethylthiophenium)tetrahalocuprate(II) salt, (dmamH)₂CuCl₄ and (dmamH)₂CuBr₄ were prepared and characterized by spectroscopic (IR, UV-Vis, EPR, XPS), electrochemical method, and magnetic susceptibility measurement. The experimental results reveal that the compounds have pseudotetrahedral symmetry around copper(II) site due to the steric hinderance of the bulky 2-(dimethylaminomethyl)thiophene in the complex. The N-H...Cl type hydrogen bonding is expected in (dmamH)₂CuCl₄ from the XPS and IR data. Magnetic susceptibility data show that both of the compounds follow Curie-Weiss law in the range of 77-300 K with negative Weiss constant exhibiting antiferromagnetic interaction between copper(II) ions in solid state.

Introduction

The 4-coordinated tetrahalocuprate(II) ions have been found to possess a variety of geometries from square planar to near-tetrahedral symmetry.¹⁻⁴ This stereochemistry of tetrahalocuprate(II) ions is strongly influenced by the nature of the counteranion. When the cation is relatively large, the square planar CuX₄²⁻ units are distorted to pseudotetrahedral symmetry due to the steric hinderance of the cation. The final structure is determined by a balance between the ligand field stabilization energy of the square planar geometry (so called the Jahn-Teller effect) and the destabilization effect of the ligand-ligand repulsions. It is interesting that spectroscopic and magnetic properties of tetrahalocuprate(II) ion with pseudotetrahedral structure are similar to those of type(I) Cu(II) ion involved in the blue copper protein. Therefore the pseudotetrahedral tetrahalocuprate(II) complexes have been suggested as simple model compounds of the copper protein,⁵ and physical and chemical studies about the coordination environment have been undertaken.⁶

Recently we reported that (dmamH)₂CuCl₂ compound has pseudotetrahedral symmetry around copper(II) site due to the steric hinderance of the bulky 2-(dimethylaminomethyl)thiophene.⁷ Moreover, the investigation of (dmamH)₂CoCl₄ indicates that a N-H...Cl type hydrogen bonding exists in (dmamH)₂CoCl₄ by the single crystal X-ray analysis.⁸

In this study, we prepared a series of tetrahedrally distorted copper complexes with the tetrachlorocuprate(II) and tetrabromocuprate(II) of protonated 2-(dimethylaminomethyl)thiophene (dmamH⁺). We examined whether the hydrogen

bonding is present in (dmamH)₂CuCl₄ as in (dmamH)₂CoCl₄ and the influence of hydrogen bonding on the geometry around Cu(II) site. The prepared complexes were characterized by spectroscopic (IR, UV-Vis., EPR, XPS), electrochemical method, and magnetic susceptibility measurement.

Experimental

All chemicals were of the best available reagent or spectroscopic grades. The (dmamH)₂CuCl₄ was prepared by reaction of stoichiometric quantities of 2-(dimethylaminomethyl)thiophene·HCl salt and anhydrous copper(II) chloride. 2-(Dimethylaminomethyl)thiophene·HCl salt was prepared by adding an excess of concentrated hydrochloric acid into 2-(dimethylaminomethyl)thiophene (6 mmol) in 20 mL mixture solvent of ethanol/triethylorthoformate (5 : 1). Copper(II) chloride (3 mmol) was dissolved in 10 mL of the same solvent. The solutions were mixed and heated with stirring for several hours and allowed to cool slowly in ice bath. The precipitates were isolated by filtration and rinsed with ethanol. The (dmamH)₂CuBr₄ was also prepared from the similar method using anhydrous copper(II) bromide.

Anal. Calcd. for (dmamH)₂CuCl₄, green, C₁₄H₂₄N₂S₂CuCl₄: C, 34.32; H, 4.93; N, 5.72. Found: C, 33.42; H, 4.81; N, 5.43. Anal. Calcd. for (dmamH)₂CuBr₄, black, C₁₄H₂₄N₂S₂CuBr₄: C, 25.18; H, 3.60; N, 4.20. Found: C, 24.93; H, 3.73; N, 4.40. The C, H, N analytical data were obtained for the prepared complexes by using a Carlo Erba Instruments E. A. 1108 Elemental Analyzer in the Korea Basic Science Center (Seoul Branch).

UV-visible spectra were recorded from 1100 to 200 nm on a Shimadzu 1601-PC Spectrophotometer in CH₃CN solution. The EPR spectral measurements were made on CH₂Cl₂/DMF (1:1) solutions at 77 K with a Bruker Instruments ESP-300S EPR spectrometer at X-band frequency. The field modulation frequency was 100 kHz. The magnetic susceptibility data were collected from 77 K to room temperature by using Faraday method with Cahn 2000 electrobalance operating at a field strength of 3.05 ± 0.02 kG. Temperatures were measured using copper-constantan thermocouple with a digital voltmeter (USA Fluke 2100A). The magnetometer was calibrated with HgCo(SCN)₄. The data were collected for temperature independent paramagnetism of the copper(II) ion and the diamagnetism corrections for all of the constituents were made using Pascal's constants.⁹ Cyclic voltammograms were recorded on a Bio Analytical Systems 50-W Cyclic Voltammography with a Hewlett Packard recorder. Cyclic voltammetric measurements were made with a three electrode system. The reference electrode was Ag/Ag⁺ (0.01 M AgNO₃/0.1 M TEAP CH₃CN solution) electrode. The working electrode was a platinum disc electrode, and the auxiliary electrode was a small piece of a platinum wire. The X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer Physical Electrons model 5400 X-ray photoelectron spectrometer equipped with a magnesium anode X-ray source and a hemispherical analyzer. The residual gas pressure was 5×10^{-9} torr. The binding energies were calibrated using the Au 4f_{7/2} peak at 84.9 eV and the Cu 2p_{3/2} peak at 932.4 eV. The adventitious C 1s line at 284.6 eV was used from charge referencing. The solid IR spectra (400-4,000 cm⁻¹) were obtained by using potassium bromide (KBr) pellets with a Polari's FT-IR spectrometer.

Results and Discussion

The electronic spectral data were obtained in CH₃CN solution. The *d-d* transition band maxima (λ_{max}) were observed at 915 nm ($\epsilon=138$) and at 907 nm ($\epsilon=77$) for (dmamH)₂CuCl₄ and (dmamH)₂CuBr₄, respectively. Based on the crystal field theory, the *d-d* transition energies decrease and intensity increases upon going from planar CuCl₄²⁻ to tetrahedral CuCl₄²⁻. For example, the single crystal polarized spectra of Cs₂CuCl₄ exhibited four transitions below 1,000 nm,¹⁰ whereas the absorption has shifted to 800-590 nm in the planar [CuCl₄]²⁻ ion.¹¹ The *d-d* transition energy of band maximum below 900 nm in the electronic spectra of (dmamH)₂CuCl₄ and (dmamH)₂CuBr₄ indicates that they contain a pseudotetrahedral CuX₄²⁻ ions. The ligand-to-metal charge transfer bands were also examined at 459 nm ($\epsilon=715$) for (dmamH)₂CuCl₄ and at 635 nm ($\epsilon=916$), 430 nm ($\epsilon=1240$) for (dmamH)₂CuBr₄.¹² X-band EPR spectra were obtained for frozen glass samples (DMF/CH₂Cl₂=50/50) at 77 K. It exhibits four hyperfine lines resulting from the coupling of the unpaired electron with the nuclear spin of copper(II) ion. The typical EPR spectra of (dmamH)₂CuCl₄ complex is shown in Figure 1. The data are listed in Table 1. The EPR spectra of (dmamH)₂CuX₄ complexes exhibited relatively small *A*_{||} value in the range of $129-136 \times 10^{-4}$ cm⁻¹. It is well known that the parallel hyperfine coupling *A*_{||} for CuCl₄²⁻ decreases upon distortion from square planar to dis-

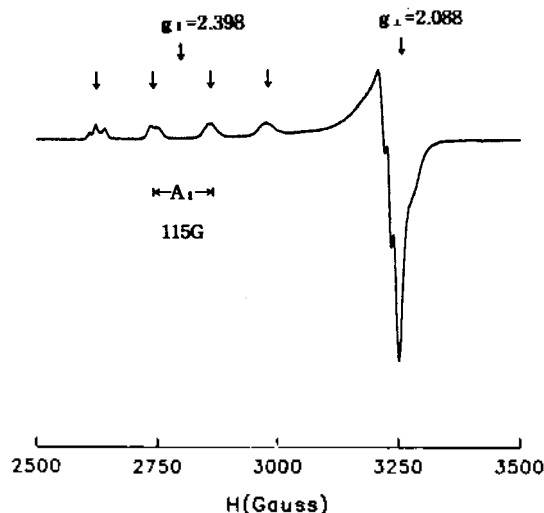


Figure 1. X-band EPR spectra of (dmamH)₂CuCl₄ in CH₂Cl₂/DMF (1:1) at 77 K.

torted tetrahedral due to the easier mixing of 4s and 4p orbitals in the ground state in low symmetry complexes.¹³ The EPR feature of these low-symmetry, nonplanar copper (II) complexes unusually shows small *A*_{||} values less than 150×10^{-4} cm⁻¹.

The *g*-values are also strongly dependent on the degree of distortion from tetrahedral symmetry. It was reported¹⁴ that (Et₂NH₂)₂CuCl₄ contains discrete CuCl₄²⁻ ions which are square coplanar, or nearly so. The *g*-values for (Et₂NH₂)₂CuCl₄ are lower than those found in less flattened CuCl₄²⁻ tetrahedral. The *g*-values of (dmamH)₂CuX₄ complex are somewhat higher than that of (Et₂NH₂)₂CuCl₄ complex and are comparable to that of Cs₂CuCl₄. This relatively small *A*_{||} values and large *g*-values in (dmamH)₂CuX₄ indicate that each CuX₄²⁻ ion in two compounds has pseudotetrahedral geometry.

Hyperfine parameters are related to the electronic structure of the complex, and perturbation theory is used to evaluate α^2 values by the equation, $A_{||} = -\kappa P \alpha^2 [2.0023 - g_{||} + 4/7\alpha^2 + \text{smaller terms}]$ where α^2 is represents the spin density in the half-occupied *d*_{x₂-y₂ orbital, $P = 380 \times 10^{-4}$ cm⁻¹ and $\kappa = 0.43$. The last two values were obtained from Hartree-Fock calculations on copper atoms.¹⁵ The calculated α^2 values of (dmamH)₂CuCl₄ and (dmamH)₂CuBr₄ complexes are 0.734 and 0.752 respectively. The smaller α^2 value reflects the greater delocalization of unpaired electron in *d*_{x₂-y₂ orbital in the ligand MO's. The delocalization for (dmamH)₂CuCl₄ is greater than that for (dmamH)₂CuBr₄, reflecting low *A*_{||} value and strong covalency in Cu-Cl bonding.}}

Magnetic susceptibility data were collected using Faraday method. The temperature variations of the magnetic susceptibility data of two complexes follow the Curie-Weiss law¹⁶

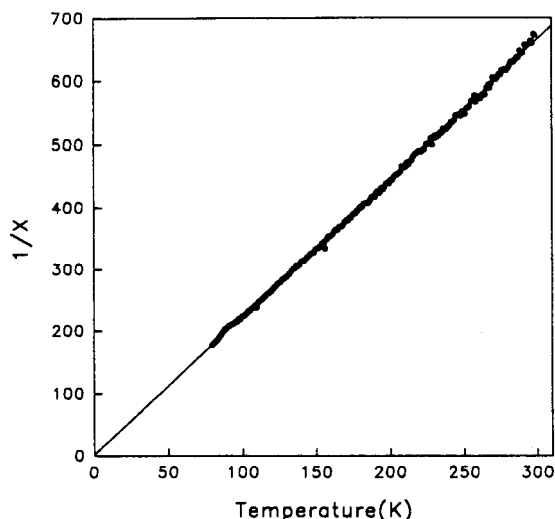
$$\chi = \frac{C}{T - \Theta} = \frac{Ng^2\beta^2S(S+1)}{3k(T - \Theta)}$$

where the symbols have their usual meanings, for temperatures above 77 K. Data were fit to the Curie-Weiss law using standard linear least-squares methods. The Curie-Weiss behavior of (dmamH)₂CuCl₄ is shown in Figure 2. The best

Table 1. Spin hamiltonian parameters for (dmamth)₂CuX₄ complexes in DMF/CH₂Cl₂ (1 : 1) at 77 K

Compound	$\langle g \rangle^a$	g_{\parallel}	g_{\perp}	$\frac{ A_{\parallel} }{\langle G \rangle}$ $\times 10^{-4} \text{ cm}^{-1}$	$\frac{A_{\perp}}{\langle G \rangle}$	α^{2b}	Ref.
Cs ₂ CuCl ₄	2.191	2.384	2.083 2.105	—	—	—	(14)
(Et ₂ NH) ₂ CuCl ₄	2.118	2.253	2.050	—	—	—	(14)
(dmamth) ₂ CuCl ₄	2.191	2.398	2.088	115	129	0.734	this work
(dmamth) ₂ CuBr ₄	2.186	2.397	2.081	122	136	0.752	this work

^a $\langle g \rangle$ values were obtained from the expression $\langle g \rangle = 1/3(g_{\parallel} + 2g_{\perp})$. ^bThe calculation of α^2 was reported in the literature.¹⁵

**Figure 2.** Inverse magnetic susceptibility vs. temperature for (dmamth)₂CuCl₄. The solid line represents the best fit to the Curie-Weiss equation.

fit calculated values are $\Theta = -1.06$ K with $g = 2.20$. The values of $\Theta = -6.21$ K and $g = 2.22$ were also found in (dmamth)₂CuBr₄. The effective magnetic moment was calculated by using the equation $\mu_{\text{eff}} = 2.828[\chi \cdot T]^{1/2}$, and found to be 1.88 and 1.89 B.M. in (dmamth)₂CuCl₄ and (dmamth)₂CuBr₄, respectively, at room temperature. These values are higher than spin only value of 1.73 B.M. Lamotte-Brasseur¹⁷ demonstrated that a correlation between μ_{eff} and the flattening angle θ of the CuCl₄²⁻ ion exists. This is not surprising since the g -values are expected to decrease with flattening. Most tetrahalocuprate(II) containing discrete CuCl₄²⁻ ions have μ_{eff} values of 1.9–2.0 B.M. Figgis and Harris¹⁸ predicted that a regularly tetrahedral CuCl₄²⁻ ion should have an effective magnetic moment of about 2.2 B.M. Therefore the observed magnetic moment of (dmamth)₂CuCl₄ and (dmamth)₂CuBr₄ also support that they have pseudotetrahedral structure. The negative Weiss constant exhibits the antiferromagnetic interaction between copper(II) ions in solid state.

Cyclic voltammograms were recorded in CH₃CN/0.10 M TEAP from -0.2 to $+1.0$ V versus a Ag/Ag⁺ electrode. The results are summarized in Table 2. The mid-peak potentials ($E_{1/2}$) were estimated by averaging the anodic and cathodic peak potentials, and assigned by comparison to the observed CuX₂ data. The $E_{1/2}$ potential of (dmamth)₂CuCl₄ is somewhat less than that of (dmamth)₂CuBr₄ as shown in Table 2. This

Table 2. The peak potential values (E_p) for (dmamth)₂CuX₄ (X = Cl, Br) complexes versus Ag/Ag⁺ in CH₃CN solution

Compound	E_{pc} (V)	$E_{1/2}$ (V)	E_{pa} (V)	Process
CuCl ₂	0.45	0.50	0.55	Cu ²⁺ /Cu ⁺
	0.09	0.16	0.23	Cu ⁺ /Cu
CuBr ₂	0.59	0.66	0.73	Cu ²⁺ /Cu ⁺
	0.21	0.25	0.28	Cu ⁺ /Cu
(dmamth) ₂ CuCl ₄	0.47	0.53	0.58	Cu ²⁺ /Cu ⁺
	0.11	0.18	0.25	Cu ⁺ /Cu
(dmamth) ₂ CuBr ₄	0.57	0.63	0.68	Cu ²⁺ /Cu ⁺
	0.19	0.21	0.23	Cu ⁺ /Cu

is responsible for the reduction potential of halides (Cl₂/Cl⁻; 1.358 V, Br₂/Br⁻; 1.066 V).¹⁹ The reduction of Cu(II) center is mainly affected by the reducing power of coordinated ligands and is not greatly affected by the distortion of planarity of Cu(II) chromophore in this work. Similar result was reported that the $E_{1/2}$ potential of 4-coordinate distorted copper(II) sparteine complexes versus Ag/AgCl reference electrode (sp-CuCl₂; -0.15 V, sp-CuBr₂; $+0.02$ V).²⁰

The binding energy (B.E.) of core electrons was investigated by X-ray photoelectron spectroscopy (XPS). The XPS data are given in Table 3. In (dmamth)₂CuCl₄, the Cu 2p_{3/2} core electron peak is observed at a binding energy of 933.3 eV. This results are less than Cu(II) binding energies, 935.2–935.4 eV for Cu(II) 2p_{3/2}.²¹ The Cu 2p_{1/2} peak is located at an energy about 20.0 eV higher than that of the corresponding 2p_{3/2} peak. However, the XPS spectra of (dmamth)₂CuCl₄ exhibit shake-up satellites about 10 eV higher than that of the corresponding 2p peaks. This implies that the copper atoms of the compounds are in the paramagnetic Cu(II) states. Similar B.E.'s were examined in (dmamth)₂CuBr₄.

Cleng *et al.*²² reported an XPS study of MgH₂EDTA, where the N 1s spectrum of MgH₂EDTA showed two equally strong peaks with binding energies of 399.0 and 402.2 eV. This result has led to conclude that the one nitrogen atom was unprotonated and the other protonated. Similar types of studies have been made on tetraphenylporphine and derived metalloporphyrins.²³ In case of (dmamth)₂CuX₄ (X = Cl, Br) complexes, the N 1s spectrum shows one peak arising from the protonated nitrogen atom at 402.7 and 403.0 eV respectively, supporting that nitrogen atoms in (dmamth)₂²⁺ are protonated, but sulfur atoms are unprotonated. XPS has also been useful in distinguishing between bridging and terminal

Table 3. Binding energies (eV) of (dmamth)₂CuX₄ (X=Cl, Br) complexes

Compound	Cu		Halides	C(1s)	S(2p)	N(1s)
	2p _{1/2}	2p _{3/2}				
(dmamth) ₂ CuCl ₄	953.3	933.3	198.7(Cl 2p _{3/2}) 200.4(Cl 2p _{3/2})	285.6	164.9	402.7
(dmamth) ₂ CuBr ₄	953.2	933.2	70.0(Br 3d _{5/2})	285.6	165.1	403.0
				287.3		

atoms. The Cl 2p_{3/2} binding energies in some rhenium metal complex halides were reported²⁴ that the chlorine binding energies of Re₃Cl₁₁²⁻ decrease in the sequence of M-Cl_b > M-Cl_t > Cl_i > Cl⁻ (where Cl_b=bridging chlorine, Cl_t=chlorine in plane terminal, Cl_i=chlorine in out-of-plane terminal, and Cl⁻=chlorine ion). In (dmamth)₂CuCl₄ complex the Cl 2p_{3/2} spectrum shows two peaks, one arising from the terminal chlorine atoms at 198.7 eV and the other from the bridged chlorine atoms at 200.4 eV. The bridged chlorine atoms were also observed in the corresponding Co(II) complex, (dmamth)₂CoCl₄.⁸ From the structure determination of (dmamth)₂CoCl₄, two different type of Co-Cl bond lengths were found, and two chlorine atoms in longer bond lengths were participated in the hydrogen bonding with dmamth⁺ unit. Therefore, from the two Cl 2p_{3/2} peaks, we propose that the bridged Cl atoms by the N⁺-H...Cl type hydrogen bonding exists in (dmamth)₂CuCl₄ as in (dmamth)₂CoCl₄. The Br 3d_{5/2} spectrum of (dmamth)₂CuBr₄ complex shows only one peak arising from the terminal bromine atoms at 70.0 eV. The C 1s spectrum of (dmamth)₂CuCl₄ complex shows two peaks, one arising from the aromatic carbon atoms at 285.6 eV and the other from the aliphatic carbon atoms binded nitrogen at 286.7 eV.²⁵

The hydrogen bonding in (dmamth)₂CuCl₄ is also confirmed by the ν_{N-H} stretching vibrational data. The values of ν_{N-H} were observed at 3371 cm⁻¹ and 3421 cm⁻¹ for (dmamth)₂CuCl₄ and (dmamth)₂CuBr₄, respectively. The uncomplexed amine hydrochloride which is considered to be the situation of maximum hydrogen bonding shifted its ν_{N-H} absorption to lower frequencies because N⁺-H...Cl interaction draws the electron density into the Cu-Cl bond, thus lengthening the N-H bond.

Conclusion

The experimental results reveal that the CuX₄²⁻ ions have pseudotetrahedral site symmetry around copper(II) ion both in (dmamth)₂CuCl₄ and (dmamth)₂CuBr₄ complexes.

The XPS data indicate that (dmamth)₂CuCl₄ complex has the bridged Cl atoms by the N⁺-H...Cl type hydrogen bonding. The ν_{N-H} of (dmamth)₂CuCl₄ in vibrational spectra is lower than that of (dmamth)₂CuBr₄, which shows large possibility of N⁺-H...Cl type hydrogen bonding in (dmamth)₂CuCl₄. Usually, the N⁺-H...Cl interaction reduce the fractional charge on the Cl atom, leading to elongate the Cu-Cl bond and to reduce the ligand-ligand interaction, thereby flattening the Cu-Cl angle. However, even in spite of this hydrogen bonding effect on fattening the Cu-Cl angle, the

pseudotetrahedral symmetry around the copper(II) ions in (dmamth)₂CuCl₄ suggests that crystal packing effect due to the steric hinderance of the bulky cation units must be important in determining the relative Cl-Cu-Cl angle, in this case any rate.

In case of (dmamth)₂CuCl₄, green crystals of high quality were obtained by slow evaporation in ethanol solvent. From the single crystal analysis, the more correct structure will be identified.

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Ab initio Studies on the Hetero Diels-Alder Cycloaddition

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Hetero Diels-Alder reactions containing phosphorus atom at various positions of diene and dienophile as well as standard Diels-Alder reaction between ethylene and *cis*-1,3-butadiene have been studied using ab initio method. Activation energy showed a good linear relationship with the FMO energy gap between diene and dienophile, which can be normally used to explain Diels-Alder reactivity. Since π -bond cleavage and σ -bonds formation occur concertedly at the TS, geometrical distortion of diene and dienophile from the reactant to the transition state is the source of barrier. Based on the linear correlations between activation barrier and deformation energy, and between deformation energy and π -bond order change, it was concluded that the activation barrier arises mainly from the breakage of π -bonds in diene and dienophile. Stabilization due to favorable orbital interaction is relatively small. The geometrical distortions raise MO levels of the TS, which is the origin of the activation energy. The lower barrier for the reactions of phosphorus containing dienophile (reactions C, D, and E) can be explained by the electronegativity effect of the phosphorus atom.

Introduction

Diels-Alder (DA) reaction is one of the widely used chemical reactions in organic synthesis to form a six membered cyclic compound by the reaction of a diene and a dienophile. DA reaction is believed to proceed through a concerted [4+2] mechanism¹ or two step mechanism² involving diradical intermediate. It is generally accepted that the reaction proceeds through a concerted but not synchronous transition state.³

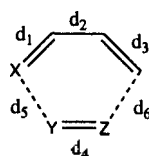
Reactivity of the DA reactions has been interpreted from the orbital interaction⁴ between frontier molecular orbitals (FMO) of reacting molecules. The primary interaction is the one between HOMO (or LUMO) of a diene and LUMO (or HOMO) of a dienophile. The regioselectivity of the DA reaction is well understood from the variation of the FMO energy level caused by the change in the reaction system, such as hetero atom substitution and/or attachment of substituents and, *inter alia*, secondary orbital interaction⁵ is the most important factor.

Hetero DA reaction is an important tool in synthesizing hetero cyclic compounds. After discovery of the existence of substituted phosphoethylene,⁶ experimental and theoretical works using this molecule as a dienophile have been actively studied.⁷ In an early study, the reactivity of the hetero DA reaction was explained based on the FMO levels,⁸ and thus information on the transition structures was not available

from the literature. In this work, we wish to study the reactivity and regioselectivity of DA reactions by the substitution of phosphorus atom at various positions of a diene and a dienophile shown in Scheme 1.

Calculation

Structures of reactants, transition states (TS), and products were minimized by the *ab initio* method using Gaussian 92 program.⁹ The 3-21G* basis set¹⁰ was used in the reaction of phosphorus containing compounds and 3-21G basis set¹¹ was used in the reaction between ethylene and *cis*-1,3-butadiene and this reaction is referred to a standard DA reaction. In all cases, *s-cis* conformer of a diene was used as a starting structure. Two isomers were possible in the case of *cis*-1,3-phosphabutadiene depending on the location of H atom attached to the phosphorus atom. Only the trans structure was used in the calculations.¹² Approximate TS's were located



A: X, Y, Z = CH₂

B: X = PH; Y, Z = CH₂

C: X, Z = CH₂; Y = PH

D: X, Y = PH; Z = CH₂

E: X, Z = PH; Y = CH₂

Scheme 1.

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