verted to the same products in 77.3% overall yield, and the isolated yields of **2**, **3**, and **4** based on the consumed **1** were 63.6%, 13.0%, and 4.2%, respectively. The increased yield of **2** at the lower temperature is consistent with the mechanism. The higher conversion of **1** and the lower yield of **4** also support that **5** is more stable at the low temperature and less photodissociation occurs. In order to get a direct evidence for the existence of **5**, a CDCl$_3$ solution of **1** (0.18 M) and furan (4.2 M) at -60 °C was irradiated through a Pyrex filter for 3 hours, and ^{1}H-NMR spectra were taken at -50 °C for the reaction mixture and for the resulting solution after standing at 25 °C for 1 hour (Figure 2). The results indicated that **2** was not initially formed. The major product, supported by the ^{1}H NMR spectrum and the Cope rearrangement to **2** at 25 °C, was assigned to be **5**. The low-temperature NMR study confirms that the proposed mechanism is correct.

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Geminal Substituent Effects on Decyanation Reactions

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The geminal substitunet effects[1] refer to either stabilization or destabilization caused by the interaction between two functional groups centered at the same atom and this have beem a subject of research interests in organic reactions. If the central atom is substituted with two σ-and π-acceptors, the resultion interaction is destabilization, while substituted with σ-and π-donors, overall stabilization results.

Recently we have reported a reductive decyanation of α-cyano and α-alkoxycarbonyl substituted nitriles promoted by samarium(II) iodide.[2] The reaction involves a carbon-carbon bond cleavage (C-CN bond) and takes places under mild conditions, but the successful reactions require activation by geminal substituents such as another nitrile or alkoxycarbonyl group. Another characteristic of the reaction
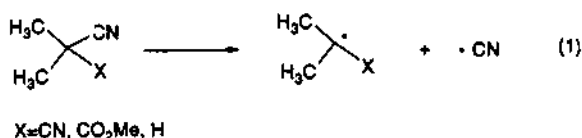
$$H_3C \diagdown \underset{H_3C}{\overset{}{\diagup}} \diagdown X \longrightarrow H_3C \diagdown \underset{H_3C}{\overset{\cdot}{\diagup}} \diagdown X + \cdot CN \qquad (1)$$

X=CN, CO₂Me, H

Table 1. C-CN bond dissociation energies (kcal/mol) of the model compounds by semiempirical and *ab initio* calculations

X	PM3	STO-3G/UHG	6-31G*/UHF*
CN	121.2	75.2(1.5034)	78.9(1.4824)
CO₂Me	120.7	79.5(1.5001)	85.6(1.4812)
H	129.0	99.1(1.4985)	126.5(1.4793)

*The values in parentheses are the C-CN bound distances of reactants in Angstrom.

is the temperature required for the reaction. Decyanations of geminal dinitriles and α-ethoxycarbonyl substituted nitriles undergoes at relatively low temperature, 0°C and room temperature, repectively. This makes a good contrast to the case when the central atom is substituted only with one nitrile group, *i.e.*, without any other additional activation. It has been well known that the C-CN bond could be reductively cleaved even in the case with no activation. The cleavage, however, needs rather vigorous reaction conditions, for example, potassium at reflux in toluene.[3]

The reactivity difference on geminal substituents prompts us to investigate the geminal substituent effect in the decyanation of α-cyano and α-alkoxycarbonyl substituted nitriles. In this theoretical study simple geminally-substituted compounds shown in Eq. (1) has been selected as model compounds. Initially geometries were minimized using the molecular mechanics method in Chim-X,[4] followed by the semiempirical PM3 calculations with MOPAC 6.0[5] and *ab initio* STO-3G and 6-31G* calculations at the Hartree-Fock level of theory with the Gaussian 94 using the Cray C-90 at SERI. Zero-point energy corrections are not considered in this study.

The C-CN bond dissociation energies obtained are summarized in Table 1. Lower energy values imply unfavorable geminal interactions for the reaction or the destabilization interactions between substituents X and CN leading to lengthening of the C-X and C-CN bonds. Favorable geminal interactions for the reaction or the stabilization interactions usually result in bond shortening and make bond dissociation difficult. In this vein, those molecules destabilized by unfavorable geminal interactions are somewhat more reactive than those stabilized favorable interactions.

Data in Table 1 imply that the semiempirical PM3 calculations do not provide a clear trend in energy differences (also, dissociation energy values are somewhat exaggerated). On the other hand, *ab initio* calculations give reasonable reactivity tendencies for the C-CN bond breaking of the model compounds, that is, more sizable reactivity differences between the C-CN bond dissionciation energies. Since the 6-31G* basis set is considerably larger that the STO-3G basis set, the 6-31G* basis set generally leads to more reliable results than the STO-3G basis set does. Although absolute energy differences values for homolytic cleavage by calculation, even in *ab initio* models, have to be taken carefully, at least the reaction trend shown in Table 1 has clearly demonstrated the utility of the cal-

culation methods. Therefore it is reasonable to conclude that the molecule having X=H will be decyanized with difficulty compared to the other two molecules having X=CN or X=CO₂Me. According to their geminal substituents (represented by X), we may assign the overall reactivity tendency among three compounds as the following order: CN>CO₂Me>>H.

The reactivity trend may be attributable to the inherent electonic properties of geminal substituents considered in this study. It is generally accepted that geminal interactions become disfavorable by pairing of σ-or π-acceptors. Combination of either a σ-donor with a π-donor or a σ-acceptor with a π-donor is usually favorable for the reaction and does not cause lengthening of the bond. The cyano group (-CN) is a strong σ-acceptor as well as a π-acceptor while methoxycarbonyl group is usually considered as a σ-acceptor (but not a good π-acceptor). The hydrogen is considered as a neutral one, *i.e.*, neither a donor nor an acceptor. Based upon this classification, the compound having X=CN could be less stabilized and consequently exhibit higher reactivity than that having X=CO₂Me. The compound having no substituent (*i.e.*, X=H) is, in turn, most highly stabilized and shows the lowest reactivity. These results are also completely consistent with the experimental observations. Samarium (II) iodide-promoted decyanation of geminal dinitriles took place at 0 °C and the same reaction of α-ethoxycarbonyl substituted nitriles occurred at room temperature. For simple nitriles (without any substituent) the removal of the nitrile could not be observed under the conditions employing samarium (II) iodide, but requires much higher temperature in the presence of potassium.

Encouraged by the results obtaines by the STO-3G calculations, we have extended the study to a somewhat bigger system employed actually in the above mentioned samarum (II) iodide-promoted decyanations shown in Eq. (2). Due to the high cost of computation *ab initio* calculations employing 6-31G* basis sets were attempted. The results are listed in Table 2. Reactivity trend is comparable to those obtained for the model compounds in Table 1 and coincide well with the experimental observations. In this case also, data indicate that the absolute energy values by *ab initio* calculations for homolytic cleavage should be taken with caution. The C-CN bond dissociation energies in Table 2 are smaller than those shown in Table 1. This could be rationalized by the electronic effect contributed by the benzyl group, which is more electron-donating than the methyl
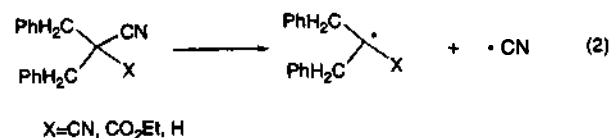
$$PhH_2C \diagdown \underset{PhH_2C}{\overset{}{\diagup}} \diagdown CN \longrightarrow PhH_2C \diagdown \underset{PhH_2C}{\overset{\cdot}{\diagup}} \diagdown X + \cdot CN \qquad (2)$$

X=CN, CO₂Et, H

Table 2. C-CN bond dissociation energies (kcal/mol) for the decyanation reactions of α-substituted α,α-dibenzylacetonitrile

X	STO-3G/UHF*
CN	43.8 (1.5045)
CO₂Et	45.2 (1.4992)

*The values in parentheses are the C-CN bond distances of reactants in Angstrom.

group and stabilizes the resultig radicals. From this line of reasoning, the degree of destabilization inherent to the geminal effect is supposed to be somewhat higher, and also the removal of nitrile occurs more readily in the reactions of Eq. (2) than those of Eq. (1).

In summary, theoretical results of the geminal effects qualitatively explain the esperimental observations on the decyanation of substituted nitriles.

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Potential Precursor for Heteropolynuclear Metal Complexes. Synthesis and Crystal Structure of cis-Co(NCS)₂(bpym)₂ (bpym=2,2'-bipyrimidine)

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Ligands that can serve as molecular bridges between metal centers and that also contain a delocalized π system have received considerable attention in recent years as potential electron "propagating" components for inner-sphere electron transfer reactions between metals,[1] magnetically coupled polynuclear systems,[2,3] models for binuclear rearrangements occuring in metalloenzymes,[4,5] and low-dimensional conducting coordination polymers.[6,7] Among various ligands for such goals, the bridging ability of 2,2'-bipyrimidine (bpym) towards first row transition metal has yielded a remarkable class of materials containing diverse architectures and functions.[8-18] In this context, the reaction of Co(NCS)₂ with bpym in a mole ratio of 2:3 in a mixtrue solvent of water and ethanol has been found to afford the dinuclear complex, [Co₂(bpym)₃(NCS)₄].[19] In particular, the design of compounds that exhibit desired properties has been continued. In the present contribution, 2,2'-bipyrimidine as a simple bidentate ligand such as 2,2'-bipyridine or 1,10-phenanthroline was clearly demonstrated by the change of reaction conditions. We report the synthesis and structural properties of the title complex along with potential applicability as a precursor for heteropolynuclear metal complexes.

bpym
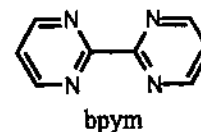
Experimental

Materials and Instrumentation. Co(NCS)₂ and 2,2'-bipyrimidine were purchased from Aldrich and Alfa, respectively, and used without purification. Elemental analysis (C, H, N) was carried out at the Chemical Analysis Center in KIST. Infrared spectrum was obtained in 4000-400 cm⁻¹ range on a Perkin Elmer 16F PC FTIR spectrometer with sample prepared as KBr pellet.

Preparation of cis-Co(NCS)₂(bpym)₂. A chloroform