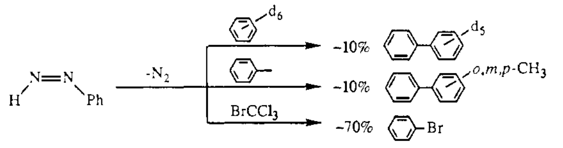
Phenyl radicals are thought to be involved in the aerobic reactions of *trans*-NH=NPh,[3] and we have strong evidence, from displacements of **2** from **1** in the presence of radical traps, that they are also important in the anaerobic reaction chemistry of **2**. For example, when **2** is generated and allowed to react in benzene-d_6, biphenyl-d_5 is produced in about 11% yield based on **1** (eq 6); similarly *o*-, *m*-, and *p*-tolylbenzene isomers are produced (10% total yield) when the displacement is effected in toluene (eq 7).[10] In the presence of excess $BrCCl_3$, **2** reacts to afford bromobenzene in a higher (70%) yield (eq 8).[11] The products in eq 6–8 are typical ones of cage-escaped phenyl radicals, and we feel that they are also involved in the reactions of **2** with alkynes (eq 4 and 5) because of the following reasons: (1) The regiochemistries of the products are consistent with a Kharasch-type addition of Ph• to the alkyne terminus to give a vinyl radical intermediate that subsequently abstracts H• to give the olefin.[12] The observation that 1-hexyne reacts with ND=NPh (**2-*d***, > 95% d_1) to give (*E*)-1-phenylhexene that is only partially deuterated (~50% d_1) supports such an H• abstraction mechanism (not simple H-transfer) for the reaction in eq 4 (similar label loss occurs in the reaction of **2-*d*** with PhC≡CH). (2) Isomerization of the stilbenyl radical is fast, and the observed ratio of *cis*:*trans*-stilbene formed in the reduction of phenylethyne by **2** (eq 5) is in accord with the known partition of *cis*- and *trans*-stilbene formed from stilbenyl radicals prepared by other means (eq 9).[13] (3) The overall yields of olefinic products in eq 4 and 5 are similar to the yields of Ph• trapped products in eq 6 and 7 (corresponding to ~10–15% radical cage escape).



(6)

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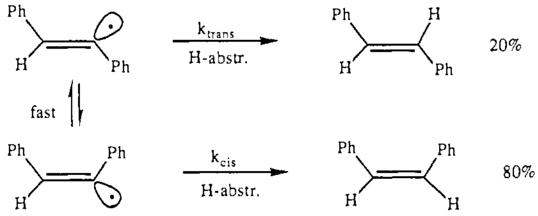

(9)

In summary, the results reported herein provide insight into the mode of reaction of *cis*-NH=NPh with terminal alkynes. In contrast to reductions of alkynes involving NH=NH, where reduction proceeds in a highly stereoselective (cis) fashion, the reactions of *cis*-NH=NPh with terminal alkynes appear to be radical processes involving Ph• transfer, and the stereoselectivities of the reductions are consequently sensitive to the nature of the substrate.

Acknowledgment. Financial support from the National Science Foundation (CHE-8818607) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (21031-AC3), is sincerely appreciated. G.L.H. acknowledges a fellowship from the Alfred P. Sloan Foundation (1989–1991). The NMR facilities were supported in part through the University of Chicago Cancer Center Grant (NIH-CA-14599).

Supplementary Material Available: Experimental details and spectral data (^1H, ^{13}C NMR, GC/MS) for phenylethyne-d_1 and *cis*-NH=NPh with phenylethyne, 1-hexyne, benzene and toluene, and bromotrichloromethane (3 pages). Ordering information is given on any current masthead page.

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[11] The substantially higher yield of trapping product in the reaction of **2** with $BrCCl_3$ is consistent with the following facts: (i) The rate for bromine abstraction from $BrCCl_3$ by Ph• approaches the diffusion-controlled limit, while the rate of Ph• addition to benzene is much slower.[11a] (ii) The reaction of Ph• with $BrCCl_3$ yields PhBr and a chain *sustaining* Cl_3C•, while the reaction of Ph• with benzene (or toluene) requires an additional radical in a chain *terminating* H-atom abstraction from the following intermediate:[11b]

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Catalytic Formation of α-Keto Acids by Artificial CO_2 Fixation

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Artificial CO_2 fixation has been widely conducted in the viewpoints of the utilization of the ultimate oxidation product of organic molecules and mimicking biological carbon assimilation. Highly reduced species such as CH_4[1,2] and CH_3OH[3] have been obtained in some CO_2 reductions though most of the products in those reductions are CO and/or HCOOH.[4-17] On the other hand, four CO_2 molecules are fixed in one complete turn of the reductive carboxylic acid cycle in photosynthetic bacteria.[18-21] Two of them are incorporated at the carbonyl carbon of $CH_3C(O)SCoA$ and $HOOCCH_2CH_2C(O)SCoA$ (CoASH = coenzyme A) to form α-keto acids, pyruvate, and α-ketoglutarate (eq 1), where reduced

$$RC(O)SCoA + CO_2 + 2e^- \rightarrow RC(O)COO^- + CoAS^- \quad (R = CH_3, CH_2CH_2COOH) \qquad (1)$$

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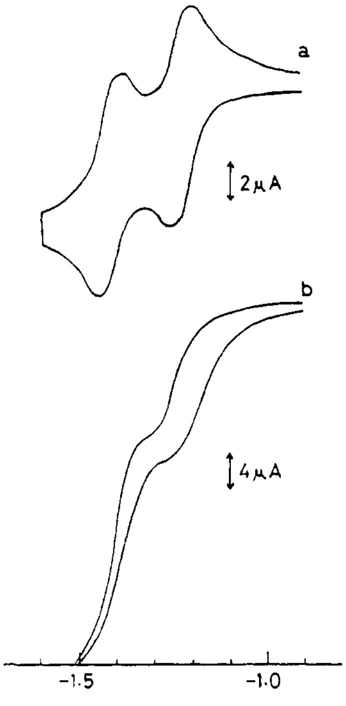

Figure 1. Cyclic voltammograms of $[(C_2H_5)_4N]_3[Fe_6Mo_2S_8(SC_2H_5)_9]$ in CH_3CN (a) and of the mixture of $[(C_2H_5)_4N]_3[Fe_6Mo_2S_8(SC_2H_5)_9]$ and $CH_3C(O)SC_2H_5$ in CO_2-saturated CH_3CN (b): sweep rate 5 mV/s.

ferredoxins function as electron donors. The other two CO_2 molecules are fixed at the carbons adjacent to the carbonyl group of pyruvate and α-ketoglutarate to form oxalacetate and isocitrate. We have recently succeeded in catalytic β-keto acids formation by artificial CO_2 fixation accompanied by cleavaging of a carbon–hydrogen bond of ketones.[22] With respect to nonenzymatic α-keto acid formation by CO_2 fixation, Tabushi et al. suggested the formation of $C_6H_5CH_2C(O)COO^-$ as a precursor of $C_6H_5CH_2CH(NH_2)COO^-$ (0.3% yield) formed in the reaction of $C_6H_5CH_2C(O)SC_8H_{17}$ with CO_2 in the presence of $(FeS_4C_4Ph_4)_2$, $Na_2S_2O_4$, and $NaHCO_3$, followed by treatment with pyridoxamine and zinc acetate.[23] Taking into account the fact that $C_6H_5CH_2C(O)COO^-$ is smoothly converted to $C_6H_5CH_2CH(NH_2)COO^-$ under the above reaction conditions,[24] the yield of $C_6H_5CH_2C(O)COO^-$ as the CO_2 fixation product is considered to be very low. A catalytic formation of α-keto acids by CO_2 fixation is, therefore, highly desired in the viewpoints not only of the useful precursors of amino acids synthesis but also of mimicking CO_2 assimilation as the key steps in the reductive carboxylic acid cycle.

The cyclic voltammogram of $[(C_2H_5)_4N]_3[Fe_6Mo_2S_8(SC_2H_5)_9]$[25] (19.2 μmol) using a glassy carbon disk electrode shows the (3–/4–) and (4–/5–) redox couple at $E_{1/2} = -1.27$ and -1.46 V vs SCE, respectively, in CH_3CN (8.0 cm^3) as shown in Figure 1a, which was essentially unchanged by addition of $CH_3C(O)SC_2H_5$ (4.7 mmol) to the solution. A strong irreversible cathodic current, however, flows when CO_2 was bubbled into the CH_3CN solution containing $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ and $CH_3C(O)SC_2H_5$ (Figure 1b). The agreement of the threshold potentials of the strong cathodic current in Figure 1b and of the cathodic process of the $[Fe_6Mo_2S_8(SC_2H_5)_9]^{4-/5-}$ redox couple (Figure 1a) suggests that $[Fe_6Mo_2S_8(SC_2H_5)_9]^{5-}$ catalyzes the reduction of CO_2 in the presence of $CH_3C(O)SC_2H_5$. In accordance with this, the controlled potential electrolysis at -1.55 V (vs SCE)[26] of CO_2-saturated dry CH_3CN (19 cm^3) containing $[(C_2H_5)_4N]_3[Fe_6Mo_2S_8(SC_2H_5)_9]$ (38.0 μmol), $CH_3C(O)SC_2H_5$ (9.4 mmol), $(C_4H_9)_4NBF_4$ (1.9 mmol) and 3A molecular sieves (0.5 g) as a desiccant[27] catalytically produces not only $HCOO^-$ but also $CH_3C(O)COO^-$[28] with the current efficiency 11 and 27%, respectively, as depicted in Figure 2. On the other hand, the similar electrolysis using an Et_4N salt of $HCOO^-$ (1.9 mmol) in place of CO_2 under otherwise the same reaction conditions did not produce $CH_3C(O)COO^-$ at all.[29] Thus $CH_3C(O)COO^-$ (Figure 1) is formed by the reaction of $CH_3(O)SC_2H_5$ with CO_2, and the proton of $HCOO^-$ may result from the electrolyte $(C_4H_9)_4N^+$ since electrochemical reduction of CO_2 by $[Fe_4S_4(SCH_2C_6H_5)_4]^{2-}$ at potentials more negative than -2.0 V (vs SCE) in DMF produces $HCOO^-$ in the presence of $(C_4H_9)_4N^+$.[30] The electrochemical reoxidation at -1.0 V of the final solution obtained after the CO_2 fixation regenerated the same electronic absorption spectrum of the original $[Fe_6Mo_2S_8(SC_2H_5)_9]^{3-}$ with the optical density of 90%, suggesting that the FeMoS cluster retains the double cubane core during electrolysis. In addition, neither $CH_3C(O)COO^-$ nor $HCOO^-$ was formed in the controlled experiments conducted in the absence of $[Fe_6Mo_2S_8(SC_2H_5)_9]^{3-}$. Thus, the FeMoS cluster catalyzes the reaction of eq 2.

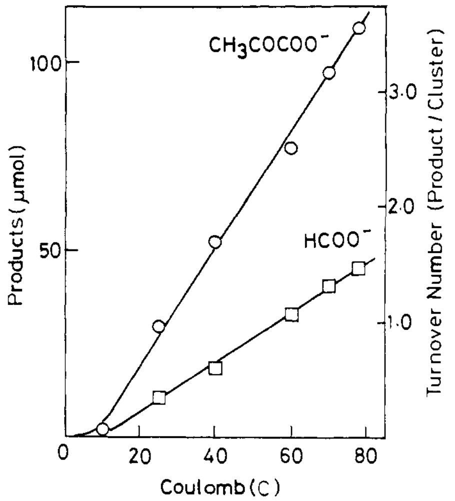

Figure 2. Electrochemical reduction of CO_2 under the controlled potential electrolysis at -1.55 V vs SCE in CO_2-saturated CH_3CN (19 cm^3) containing $[(C_2H_5)_4N]_3[Fe_6Mo_2S_8(SC_2H_5)_9]$ (38.0 μmol), $CH_3C(O)SC_2H_5$ (9.4 mmol), $(C_4H_9)_4NBF_4$ (1.9 mmol), and 3A molecular sieves.

$$CH_3C(O)SC_2H_5 + CO_2 + 2e^- \rightarrow CH_3C(O)COO^- + C_2H_5S^- \quad (2)$$

The reaction of eq 2 apparently involves a nucleophilic attack of CO_2 to $CH_3C(O)SC_2H_5$, and the similar CO_2 fixation by using $C_2H_5C(O)SC_2H_5$ and $C_6H_5C(O)SC_2H_5$ in place of $CH_3C(O)SC_2H_5$ also took place catalytically to afford $C_2H_5C(O)COO^-$ and $C_6H_5C(O)COO^-$[28] with current efficiency of 50 and 13% under otherwise the same electrolysis conditions. It should be mentioned that alkyl thiolate[31] as a leaving group may have a special meaning

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[27] In the case of an insufficient dehydration of the solvent, the current efficiency of $CH_3C(O)COO^-$ was dropped to less than 1% and not only was H_2 evolution catalyzed by the reduced form of the FeMoS cluster but also hydrolysis of $CH_3C(O)SC_2H_5$ affording CH_3COO^- and $C_2H_5S^-$ took place preferentially in the electrolysis.

[28] The CO_2 fixation products were analyzed not only by HPLC with columns packed with Shodex Ionpack KC-811 and ODS but also by a Shimazu isotachophoretic analyzer IP-2A. In addition, α-keto acids formed in CO_2 fixation were converted to the corresponding methyl esters by treatment with CH_2N_2, and those esters were identified by gas chromatography.

[29] No $CH_3C(O)COO^-$ was formed in a reaction of $CH_3C(O)SC_2H_5$ with $(Et_4N)HCOO$ in the presence of $(Et_4N)_3[Fe_6Mo_2S_8(SC_2H_5)_9]$ in dry CH_3CN for 24 h at ambient temperature.

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in the acylation of CO_2 since various acylating agents $CH_3C(O)X$ ($X = Cl, OC_2H_5, SC(O)CH_3, OC(O)CH_3$) did not give $CH_3C(O)COO^-$ under the similar electrolysis conditions. The present CO_2 fixation, which is essentially identical with that of pyruvate synthase, may therefore give a clue to elucidate the reaction mechanism of eq 1 as the key steps in the reductive carboxylic acid cycle.

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(31) Pyruvate was also produced catalytically when $CH_3C(O)SC_3H_5$ was used in place of $CH_3C(O)SC_2H_5$.

Polychalcogenide Synthesis in Molten Salts. Novel One-Dimensional Compounds in the K/Cu/S System Containing Exclusively S_4^{2-} Ligands

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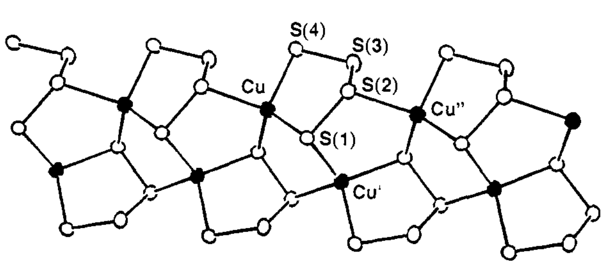
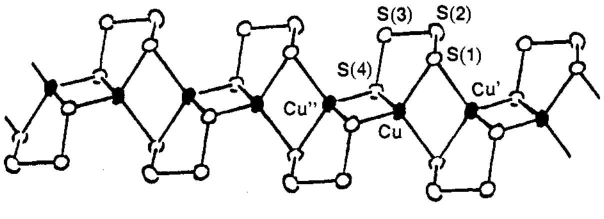
Thus far, the great majority of synthetic metal/chalcogenide chemistry has been carried out either in solution[1] at (or near) room temperature or in the solid state at high (>350 °C) temperatures.[2] The compounds obtained at low temperatures are soluble, discrete molecular species containing a diverse repertoire of Q_x^{2-} ($Q =$ S, Se, Te) ligands with x ranging from 1 (e.g., $[Na_2Fe_{18}S_{30}]^{8-}$ [3]) to 9 (e.g., $[Au(S_9)]^{1-}$ [4]). By far, among the discrete polychalcogenides, the Q_4^{2-} ligands are the most frequently occurring. The high-temperature compounds tend to be extended, three-dimensional, solid-state structures containing either Q^{2-} or Q_2^{2-} ligands. The higher Q_x^{2-} ligands are too thermally sensitive to be stabilized in solid-state compounds from high temperatures.[5] They dissociate to lower polychalcogenides and sulfur. In general, the low-temperature compounds can be viewed as metastable and thus capable of transforming to their high-temperature solid-state counterparts via interesting and perhaps isolable low-dimensional intermediates. These could occur in the intermediate temperature range (ca. 150–350 °C). Increasing interest in metastable low-dimensional polychalcogenides derives not only from the catalytic[6] and electronic properties of these materials[7] but also because they offer a bridge between molecular and solid-state chemistry. To date, a very limited effort has been invested in the systematic synthesis of inorganic and particularly chalcogen-rich compounds at intermediate temperatures. This is primarily because of the lack of suitable solvents.[8] A sensible approach would be to employ molten salt systems as solvents. Despite the considerable knowledge accumulated about molten salts and eutectics,[9] little chalcogenide synthesis has been reported. Alkali metal polychalcogenide systems are appropriate and have been previously used, at high temperatures, to prepare and/or recrystallize simple mostly binary metal sulfides.[10] Ibers and co-workers were successful in applying such synthetic approach at 340–375 °C to isolate the very interesting $K_4Ti_3S_{14}$ and $Na_2Ti_2Se_8$ which possess unusual one-dimensional structures featuring Q_2^{2-} ligands.[11] Recently we reported[12] on the new, metastable, one-dimensional $[Ag(Se_4)]_n^{n-}$, containing Se_4^{2-} ligands, and we have been investigating other coinage metals for similar behavior. It should be noted that the only other solid-state compound containing a Q_4^{2-} ligand is the $(NH_4)CuS_4$[13] which was prepared at room temperature. In this report we wish to contribute two novel one-dimensional compounds, in the K/Cu/S system, containing only S_4^{2-} ligands and prepared in molten alkali metal polysulfide solvents, at 215–250 °C.



α-$[Cu(S_4)]_n^{n-}$



β-$[Cu(S_4)]_n^{n-}$

Figure 1. Top: View of the α-$[Cu(S_4)]_n^{n-}$ infinite chain (four unit cells) with labeling scheme. Selected distances are as follows: Cu–S(1) 2.299 (3), Cu–S(4) 2.298 (4), Cu′–S(1) 2.324 (3), Cu″–S(2) 2.432 (4), S(1)–S(2) 2.089 (5), S(2)–S(3) 2.093 (4), S(3)–S(4) 2.056 (6) Å. Selected angles are as follows: Cu–S(1)–Cu′ 102.0 (1), S(1)–Cu–S(4), 103.3 (1)°. Cu′ and Cu″ are crystallographically equivalent to Cu. Bottom: View of the β-$[Cu(S_4)]_n^{n-}$ infinite chain (four unit cells) with labeling scheme. Selected distances are as follows: Cu–S(1) 2.368 (2), Cu–S(4) 2.360 (2), Cu′–S(1) 2.372 (2), Cu″–S(4) 2.378 (2), S(1)–S(2) 2.078 (2), S(2)–S(3) 2.060 (3), S(3)–S(4) 2.079 (3) Å. Selected angles are as follows: S(1)–Cu–S(4) 110.33 (8), Cu–S(1)–Cu′ 66.7 (7), Cu–S(4)–Cu″ 68.4 (6), S(1)–Cu–S(1)′ 113.3 (1), S(4)–Cu–S(4)′ 111.6 (1), Cu″–Cu–Cu′ 173.5°. Cu, Cu′, and Cu″ atoms are crystallographically equivalent.

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(5) There are only two examples of higher polychalcogenides, S_3^{2-} and Se_5^{n-}, which occur in the compounds $P_2Nb_4S_{21}$ and Nb_2Se_9, respectively. These compounds are prepared at high temperatures (ca. 600 °C). The assignment of charge in the Se species however is ambiguous, and the trisulfide is not bonded to a metal center. (a) $P_2Nb_4S_{21}$: Brec, R.; Evain, M.; Grenouilleau, P.; Rouxel, J. *Rev. Chim. Miner.* **1983**, *20*, 283–294. (b) Nb_2Se_9: Meerschaut, A.; Guemas, L.; Berger, R.; Rouxel, J. *Acta Crystallogr.* **1979**, *B35*, 1747–1750.

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