methyldisilyl azide in THF and then treated in the same manner, the acid **8** resulted. This high stereoselectivity in the enolization step is responsible for the efficiency of the process and has been observed before in these laboratories.[4a]

Conversion of these acids[15] individually to their corresponding benzyl ethers **10** and **11** followed standard procedures and then protiodesilylation of these ethers **10** and **11** was efficiently accomplished in high yield by treatment with aqueous HBF_4 in hot CH_3CN. Other more standard conditions for desilylation (CsF, KF, I_2, and $ArSO_2H$)[16] either failed to react or destroyed the starting material. This is a useful new method for the non-oxygen-assisted desilylation of vinylsilanes.

These results demonstrate the utility of α-silylallylic alcohols as chiral primary alcohol equivalents, and the value of such a concept for the previous prostanoid synthesis[2] is under investigation. In addition to their use in the ester enolate Claisen rearrangement, chiral α-silylallylic alcohols hold great potential as chiral substrates for other synthetic processes (S_N2, Wittig rearrangements, olefin additions, etc.) and selected of these are currently under investigation. In essence, as a result of this work, the α-silyl group can be envisaged as a "chirality inducing grouping".

Supplementary Material Available: Analytical data (IR, NMR, R_f, rotation) on all compounds, elemental analysis on compounds **1–4** and **7–13**, and experimental procedures for compounds **8** and **9** (8 pages). Ordering information is given on any current masthead page.

---

[15] The fluorboric acid desilation was attempted on the acid **9**, and a 54% yield of the desired product was obtained. Subsequent experiments indicated the remainder of material consisted of the five-membered lactone with the *tert*-butyldimethylsilyl group still attached to the molecule. Under forcing conditions (HBF_4, CH_3CN, °C, 12 h), this lactone gave the desired product. In order to avoid such cyclizations and possible epimerization, the acid was reduced and the resultant alcohol protected as shown.

[16] (a) Utimoto, K.; Kitai, M.; Hitosi, N. *Tetrahedron Lett.* **1975**, *2825*–2828. (b) Buchi, G.; Wuest, H. *Ibid.* **1977**, 4305–4306 and references cited therein.

Novel Synthesis of Acetylenes and Polyenes via Desulfonylation Reaction

Tadakatsu Mandai, Terumi Yanagi, Kunio Araki,
Yoshihiro Morisaki, Mikio Kawada, and Junzo Otera*

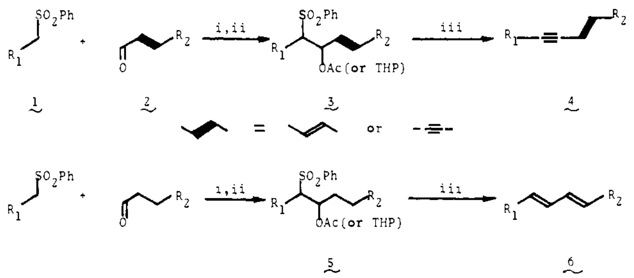
Okayama University of Science
Ridai-cho, Okayama 700, Japan

Received March 5, 1984

We wish to communicate a simple and novel synthetic method for a variety of enyne, diyne, and polyene derivatives.[1,2]

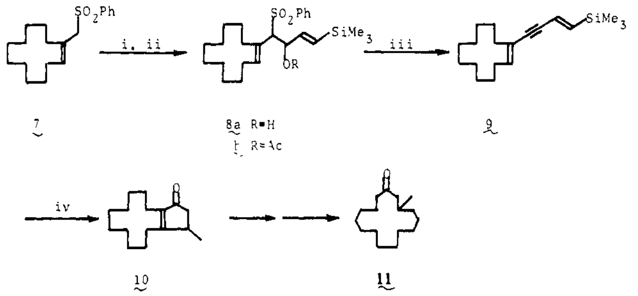
In the course of studies on the synthetic utilization of the desulfonylation reaction,[3] we have previously revealed that phenyl α-methoxyalkyl sulfones are converted into methyl alkenyl ethers on treatment with *t*-BuOK.[3e,4] Now we have found that presence of an acetoxy (OAc) or tetrahydropyranyloxy (OTHP) group at the β-position of the phenylsulfonyl group results in the unique acetylenic or polyenic bond formation, giving rise to a variety of enyne, diyne, and polyene compounds.

Scheme I[a]



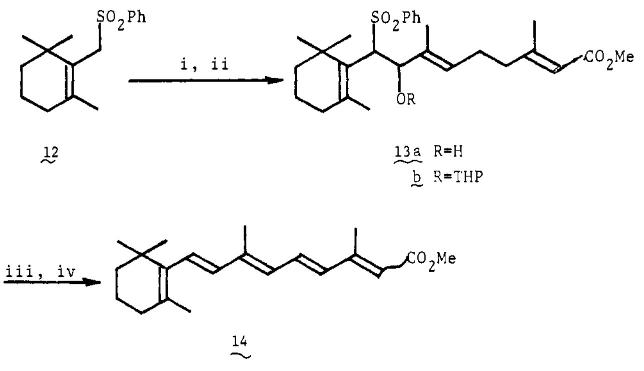
[a] (i) *n*-BuLi, THF, −78 °C. (ii) Ac_2O–Py or dihydropyran, *p*-TsOH. (iii) *t*-BuOK, THF or THF/*t*-BuOH, room temperature/reflux.

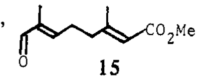
Scheme II[a]



[a] (i) *n*-BuLi, $Me_3SiCH{=}CHCHO$, −78 °C, THF. (ii) Ac_2O-Py. (iii) *t*-BuOK, THF, room temperature/reflux. (iv) $AcOH$-H_2SO_4.

Scheme III[a]



[a] (i) *n*-BuLi,  **15** THF, −78 °C. (ii) dihydropyran, *p*-TsOH, CH_2Cl_2. (iii) *t*-BuOK, *t*-BuOH. (iv) CH_2N_2, Et_2O.

As depicted in Scheme I, the procedure is quite simple. One equivalent of a β-acetoxy sulfone or the corresponding tetrahydropyranyl ether **3**, which can be easily prepared from the α-sulfonyl carbanion **1** and an α,β-enal or ynal **2**, and *t*-BuOK (2.5–10 equiv) were stirred in THF or THF/*t*-BuOH (1:1) under the conditions shown in Table I. Extraction of the reaction mixture with hexane–water and usual workup followed by column chromatography (silica gel) yielded the acetylenes **4**. Entries 1–6 in Table I illustrate the versatility of the present method for preparing difficult-to-obtain acetylenic compounds employing readily available starting materials. The broad scope and utility of these acetylenic compounds as synthetic intermediates are apparent from the successful formation of ene–yne, ene–yne–ene, yne–yne, and ene–yne–yne moieties with various functionalities. It should be noted, however, that no acetylenes are obtained from α,β-enals or -ynals with an allylic or proparglyic hydrogen in R_2. Formation of acetylenes is also suppressed when alkyl aldehydes are used, except in the case where aldehydes possess no α hydrogens. Polyenes **6** are produced in all of these cases as shown in entries 7–10 in Table I.

---

[1] For the most recent study of enyne compounds, see: Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1983**, *105*, 1383.

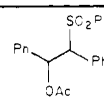
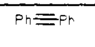
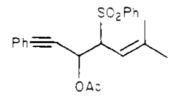
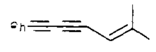
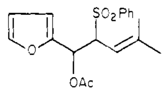
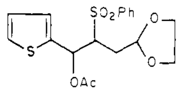
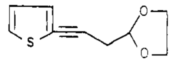
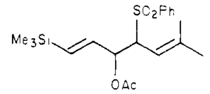
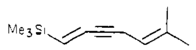
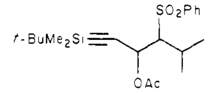
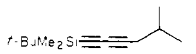
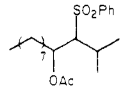
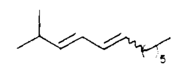
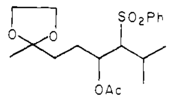
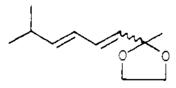
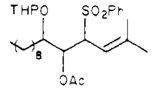
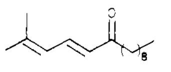
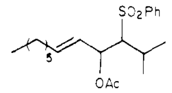
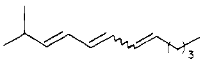
[2] For conjugated polyene synthesis, see: (a) Hayashi, T.; Hori, I.; Oishi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2909. (b) Fischetti, W.; Mak, K. T.; Stakem, F. G.; Kim, J.-I.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 948.

[3] (a) Mandai, T.; Yamaguchi, H.; Nishikawa, K.; Kawada, M.; Otera, J. *Tetrahdron Lett.* **1981**, *22*, 763. (b) Mandai, T.; Nishikawa, K.; Yamaguchi, H.; Kawada, M.; Otera, J. *Chem. Lett.* **1981**, 473. (c) Mandai, T.; Iuchi, Y.; Suzuki, K.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1982**, *23*, 4721. (d) Otera, J.; Mandai, T.; Shiba, M.; Saito, T.; Shimohata, K.; Takemori, K.; Kawasaki, Y. *Organometallics* **1983**, *2*, 332. (e) Mandai, T.; Hara, K.; Nakajima, T.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1983**, *24*, 4993.

[4] A few studies of oxidative desulfonylation with *t*-BuOK to give olefinic compounds have been reported: (a) Colter, A. K.; Miller, R. E., Jr. *J. Org. Chem.* **1971**, *36*, 1898. (b) Fuchs, P. L.; Hamann, P. R. *Ibid.* **1983**, *48*, 914.

0002-7863/84/1506-3670$01.50/0

Table I. Conversion of β-Acetoxy Sulfones **3** and **5** into Acetylenes **4** and Polyenes **6**

entry	**3** or **5**	*t*-BuOK/ **3** or **5**[a]	reaction conditions	product **4** or **6**	compd	yield,[b] %
1		4.0	THF, reflux, 2 h		**4a**	86
2		2.5	THF, rt, 3 h		**4b**	81
3		3.0	THF, rt, 8 h		**4c**	73
4		2.2	THF, rt, 3 h		**4d**	95
5		2.4	THF, rt, 1 h		**4e**	52
6		10.0	THF/*t*-BuOH, rt, 4 h/50 °C, 5 h		**4f**	90
7		9.0	*t*-BuOH, rt, 3 h/reflux 4 h	 (*EZ*/*EE* = 81:19)	**6a**	77
8		8.0	*t*-BuOH, 60 °C, 12 h	 (*EZ*/*EE* = 62.38)	**6b**[c]	82
9		3.5	THF, rt, 5 h	 (*E* only)	**6c**	60
10		4.0	*t*-BuOH, reflux, 10 h		**6d**[d]	64

[a] Molar ratio. [b] Isolated yields after column chromatography. [c] Deketalization afforded (E,E)-$\alpha,\beta,\gamma,\delta$-dienone exclusively. [d] Stereochemistry is not determined.

The synthetic utility of the method is examplified by the synthesis of *d,l*-muscone (**11**) as shown in Scheme II. The carbanion of sulfone **7** (960 mg, 3 mmol), generated by *n*-BuLi (2.95 mmol), was treated with α-trimethylsilylacrolein (358 mg, 2.8 mmol) in THF (25 mL) at −78 °C to give **8a** (1.15 g, 92%) after column chromatography (silica gel, 10:1 hexane–ether). The corresponding acetate **8b** (422 mg, 0.86 mmol) and *t*-BuOK (1.93 g, 17.2 mmol) were stirred in *t*-BuOH (20 mL) for 3 h at room temperature and further heated under reflux for 36 h. Usual workup and column chromatography (silica gel, hexane) afforded ene–yne–ene compound **9** (161 mg, 65%). Then, **9** (145 mg, 0.5 mmol) was subjected to the Nazarov cyclization[5] (CH_3COOH (5 mL)/H_2SO_4 (1 mL), 50–60 °C, 10 min), yielding cyclopentenone **10** (75.3 mg, 64%) after column chromatography (silica gel, 10:1 hexane–ether). Conversion of **10** to *d,l*-muscone (**11**) has already been reported.[6]

A further application is shown by the novel synthesis of methyl retinoate (**14**) given in Scheme III. To a THF solution of the anion of **12**[7] (1.05 g, 5.5 mmol), generated by *n*-BuLi (5.5 mmol), was added aldehyde **15**[8] (447 mg, 2.29 mmol) at −78 °C. After being stirred for 1.5 h at this temperature, the reaction mixture was quenched with water followed by extraction with benzene. Usual workup and column chromatography (silica gel, 15:1 hexane–ethyl acetate) yielded **13a** (937 mg, 87%). The *t*-BuOH solution (10 mL) of the corresponding tetrahydropyranyl ether **13b** (212 mg, 0.38 mmol) and *t*-BuOK (341 mg, 3.04 mmol) was stirred for 3 h at room temperature followed by heating under reflux for 4 h. The reaction mixture was extracted with benzene–ice-cooled 1 N HCl. The benzene layer was washed with water, dried ($MgSO_4$), and evaporated to yield a mixture of **14** and retionic acid. The mixture was treated with excess CH_2N_2 to give pure **14** (88 mg, 74%) containing the **13**-*cis* and -*trans* isomers in a 1:1 ratio.[3c] This process seems to offer a simple and promising route for vitamin A derivatives since the retinoic acid skeleton is assembled through only one carbon–carbon bond formation employing readily available starting materials.

Registry No. **1** (R_1 = Ph), 3112-88-7; **1** (R_1 = $CH{=}C(CH_3)_2$), 15874-80-3; **1** (R_1 = $CH_2\overline{CHOCH_2CH_2O}$), 56161-51-4; **1** ($R_1$ = $CH(CH_3)_2$), 34009-07-9; **3a**, 90083-21-9; **3b**, 90083-22-0; **3c**, 90083-23-1; **3d**, 90083-24-2; **3e**, 90083-25-3; **3f**, 90083-26-4; **4a**, 501-65-5; **4b**, 90083-31-1; **4c**, 90083-32-2; **4d**, 90083-33-3; **4e**, 90083-34-4; **4f**, 90083-35-5; **5a**, 90083-27-5; **5b**, 90083-28-6; **5c**, 90083-29-7; **5d**, 90083-30-0; (*E,Z*)-**6a**, 90083-36-6; (*E,E*)-**6a**, 90083-37-7; (*E,Z*)-**6b**, 90083-38-8; (*E,E*)-**6b**, 90083-39-9; **6c**, 90083-40-2; **6d**, 90083-41-3; **7**, 90083-42-4; **8a**, 90083-43-5; **8b**, 90083-44-6; **9**, 90083-45-7; **10**, 90083-46-8; **11**, 956-82-1; **12**, 56691-74-8; **13a**, 90105-85-4; **13b**, 90083-47-9; *cis*-**14**, 16760-45-5; *trans*-**14**, 339-16-2; **15**, 90083-48-0; PhCHO, 100-52-7; $PhC{\equiv}CCHO$, 2579-22-8; $\overline{OCH{=}CHCH{=}}CCHO$, 98-01-1; $\overline{SCH{=}CHCH{=}}CCHO$, 98-03-3; $Me_3SiCH{=}CHCHO$, 58107-34-9; *t*-$BuMe_2SiC{\equiv}CCHO$, 90083-19-5; $CH_3(CH_2)_7CHO$, 124-19-6; $\overline{OCH_2CH_2O}C(CH_3)CH_2CH_2CHO$, 24108-29-0; $CH_3(CH_2)_8CH(OTHP)CH$-

---

(5) Santelli-Rouvier, C.; Santelli, Mm. *Synthesis* **1983**, 429.

(6) Eschenmoser, A.; Felix, D.; Ohloff, G. *Helv. Chim. Acta* **1967**, *50*, 708.

(7) Torii, S.; Uneyama, K.; Ishihara, M. *Chem. Lett.* **1975**, 479.

(8) Aldehyde **15** was prepared by the Sharpless oxidation (*t*-BuOOH–SeO_2) of methyl geranate.

O, 90083-20-8; $CH_3(CH_2)_5CH{=}CHCHO$, 2463-53-8; *t*-BuOK, 865-47-4.

Supplementary Material Available: ^1H and ^{13}C NMR data for compounds **4a–f** and **6a–d** (1 page). Ordering information is given on any current masthead page.

Metal-Induced Transformations of Carbon Dioxide. Carbon–Carbon Bond Forming Processes Involving Anionic Group 6B Metal Derivatives and the X-ray Structure of [PNP][*cis*-$CH_3W(CO)_4P(CH_3)_3$]

Donald J. Darensbourg* and Rebecca Kudaroski

Department of Chemistry
Texas A&M University
College Station, Texas 77843

Received March 9, 1984

The reaction of carbon dioxide with metal alkyls represents a fundamental step in the eventual exploitation of carbon dioxide in the catalytic synthesis of organic substances derived from this most abundant C_1 feedstock. Although much effort has been expended in organometallic chemistry in characterizing migratory CO insertion processes,[1] systematic investigations of the corresponding processes involving CO_2 are lacking.[2] One aspect of our program in carbon dioxide chemistry is centered around gaining a more definitive knowledge of what factors affect CO_2 insertion reactions into M–H and M–C bonds.[3] Specifically we have shown that alkyl and aryl derivatives, $M(CO)_5R^-$ (M = Cr, W; R = CH_3 or Ph), smoothly undergo insertion reactions wtih carbon dioxide to provide the corresponding carboxylates (eq 1).

$$M(CO)_5R^- + CO_2 \rightarrow M(CO)_5OC(O)R^- \qquad (1)$$

We report herein mechanistically on these reaction processes, along with the effects on these reactions of modification of the electron affinity at the metal center as mediated by the ancillary ligands.

Observations on the intimate details of carbon dioxide insertion into $CH_3W(CO)_5^-$ to generate $CH_3CO_2W(CO)_5^-$ are consistent with a concerted (I_a) mechanism. The reaction was found to be first order in both metal substrate and carbon dioxide. A plot of the pseudo-first-order rate constant (k_{obsd}) for CO_2 insertion at ambient temperature (23 °C) as a function of CO_2 pressure[4] was linear up to a total CO_2 pressure of ca. 200 psi, beyond which Henry's law does not apply.[5]

A significant acceleration of CO_2 insertion was noted in the presence of alkali metal counterions which serve to neutralize the buildup of negative charge on the incipient carboxylate ligand. For example, reactions that occur only slowly (days) at high pressures of CO_2 in the absence of these alkali metal ions take place in hours and at low CO_2 pressures in the presence of a slight excess of lithium ions. Unfortunately, reactions subsequent to the CO_2 insertion process, i.e., alkali metal assisted displacement of the carboxylate ligand by other nucleophiles (e.g., eq 2), result in removal of the carboxylate ligand from the metal center.[6]

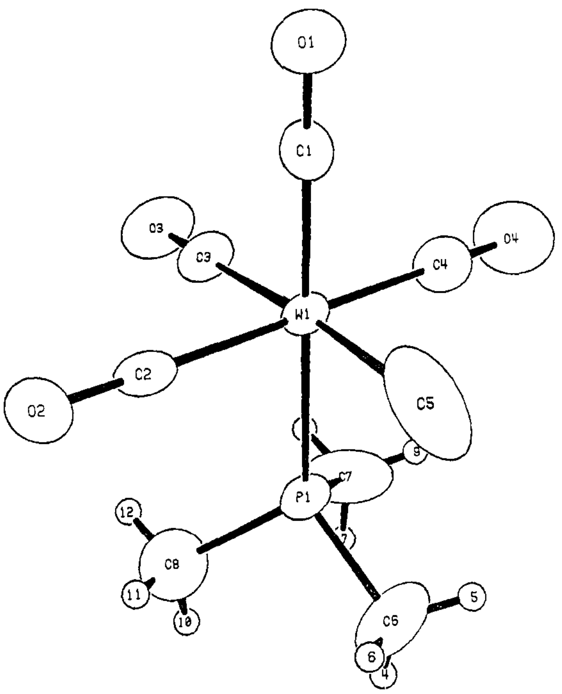


Figure 1. ORTEP drawing of the *cis*-$CH_3W(CO)_4PMe_3^-$ anion. Some bond lengths are as follows: W–C(CH_3), 2.18 (3) Å; W–P, 2.532 (3) Å; W–C_1, 1.941 (13) Å; W–C_2, 2.005 (13) Å; W–C_3, 2.09 (2) Å; W–C_4, 2.008 (15) Å.

$$CH_3CO_2M(CO)_5^- + LiCl \rightarrow ClM(CO)_5^- + CH_3CO_2^-Li^+ \qquad (2)$$

This enhanced rate of carbon dioxide insertion into M–C bonds in the presence of alkali metal ions has allowed us to investigate the effects of added carbon monoxide on the rate of the CO_2 insertion process. This is of importance since in the absence of alkali promoters, CO insertion into the M–C bond to afford acyls derivatives is much faster than CO_2 insertion to yield carboxylates. When reaction 1 where M = W and R = CH_3 was carried out in a mixture of carbon dioxide/carbon monoxide (100 psi/400 psi) in the presence of excess LiCl, no retardation of the reaction rate was noted when compared to the same reaction conditions in the absence of 400 psi of carbon monoxide.

In further compliance with an I_a reaction pathway the rate of carbon dioxide insertion into the M–C bond as described in eq 1 is Cr < W and CH_3 > Ph. This latter dependence on the nature of the R group has been noted by Casey and Polichnowski[7] for carbon monoxide insertion reactions of $RW(CO)_5^-$, and is seen as well for analogous processes involving the neutral $RMn(CO)_5$ derivatives.[8]

Since the interaction of carbon dioxide with metal centers is anticipated to intensify at electron-rich metal centers, we have synthesized alkyltungsten carbonyl derivatives with phosphorus donor ligand substituents. These derivatives were synthesized by alkylation of $Na_2W(CO)_4PR_3$ (derived from sodium naphthalenide reduction of *cis*-$W(CO)_4[PR_3]NC_5H_{11}$[9,10]) by methyl tosylate, followed by addition of [PNP][tosylate] to precipitate the [PNP][*cis*-$CH_3W(CO)_4PR_3$] salt. One of the derivatives was fully characterized by X-ray crystallography at −99 ± 1 °C in order to accurately define the W–C(CH_3) bond distance.[11] Figure 1

---

[1] Alexander, J. In "Chemistry of the Metal–Carbon Bond Stage 2"; Patai, S., Hartley, F. R., Eds.; Wiley: New York, 1983.

[2] (a) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. (b) Sneeden, R. P. A. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, p 225. (c) Darensbourg, D. J.; Kudaroski, R. *Adv. Organomet. Chem.* **1983**, *22*, 129.

[3] (a) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223. (b) Darensbourg, D. J.; Rokicki, A. *Ibid.* **1982**, *104*, 349. (c) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685.

[4] Carbon dioxide insertion reactions requiring pressure greater than atmospheric were carried out in a 300-mL Parr reactor fitted with a glass linear and a dip tube to allow sampling of the solution during the reaction. Temperatures were maintained by immersing the reactor in a constant temperature bath. The reactions were monitored by infrared spectroscopy in the ν(CO) region.

[5] (a) Buell, D. S.; Eldridge, J. W. *J. Chem. Eng. Data* **1962**, *7*, 187. (b) Vonderheiden, F. H.; Eldridge, J. W. *Ibid.* **1963**, *8*, 20.

[6] Related processes are seen for metal hydrides and chlorides. See, e.g.: Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics*, in press.

[7] Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565.

[8] Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

[9] (a) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1982**, *1*, 215. (b) Slater, S. G.; Lusk, R.; Schumann, B. F.; Darensbourg, M. Y. *Ibid.* **1982**, *1*, 1662.

[10] Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

0002-7863/84/1506-3672$01.50/0