The nutation experiments were carried out as described previously.[7,9] The ^{13}C magnetization (at 15 MHz) was generated by an ^1H–^{13}C cross-polarization sequence using a 40-kHz Hartmann–Hahn match,[12] and proton broadening was then removed during data acquisition by a strong (2.5 mT) 60-MHz decoupling field. The nutation excitation sequence was the same for both samples: an 8-μs carbon transmitter pulse (3.6-mT rotating component), followed by a 9.9-μs delay and a 7-μs receiver window. The carbon carrier frequency was kept close to the center of the spectrum in the laboratory frame. The temperature of the samples was 77 K.

The phenylacetylene (93% $^{13}C_0$, 4% $^{13}C_2$)[13] was polymerized by combining it in toluene either at –20 °C for 3 h with MoCl₅ plus $(C_6H_5)_4Sn$ (1/100 equiv of each, previously incubated for 10 min at room temperature)[14,15] or at 0 °C for 4.5 h with titanium tetrabutoxide and triethylaluminum (1/50 and 4/50 equiv, previously incubated for 20 min at room temperature).[16] The polymers were purified by repeatedly dissolving them in cold chloroform and precipitating them with methanol, and they were then dried at –35 °C for 12 h. The yields were 28% and 4%, respectively, and the ^1H NMR spectra were characteristic of 97% and 75% "cis" (E) materials.[17,18]

For the experiments to succeed with the catalysts containing molybdenum pentachloride, the poly(phenylacetylene) samples had to be prepared, purified, and maintained below 0 °C. When they were prepared at room temperature, the spectra exhibited prominent peaks characteristic of ^{13}C's separated both by single and by double bonds, implying that the positions of the double bonds, which remain fixed in the cold samples, move on warming.[7b,17,19] When WCl₆ was substituted for MoCl₅,[14] it was impossible, even with samples prepared at –20 °C,[20] to distinguish whether eq 1 or 2 applied, for the intensities of the two kinds of peaks were similar.

When the Casey metal–carbene [pentacarbonyl(diphenylmethylene)tungsten][6a,21] or the Fischer metal–carbyne [trans-bromotetracarbonyl(phenylmethylidyne)tungsten][18,22] was used

as the initiator, the experiments did distinguish the alternatives, but the results were unexpected and are at present unexplained. The composition of the polymers was essentially the same as when the titanium-containing mixture was the initiator.[23]

However, that the titanium- and molybdenum-initiated reactions seemingly follow different paths agrees with the observation that compounds of titanium, unlike those of molybdenum, are only marginally effective in bringing about olefin metatheses.[24] It might also account for another distinction, in selectivity, that the literature seems to reveal: that titanium-containing initiators are more effective than those containing molybdenum in polymerizing unsubstituted acetylene,[27] whereas the reverse is true for substituted acetylenes.[5b,28]

(11) (a) all-trans-Retinal: Hamanaka, T.; Mitsui, T.; Ashida, T.; Kakudo, M. Acta Crystallogr., Sect. B: Struct. Sci. 1972, B28, 214. (b) 11-cis-Retinal: Gilardi, R. D.; Karle, I. L.; Karle, J. Acta Crystallogr., Sect. B: Struct. Sci. 1972, B28, 2605. (c) 1-trans,3-trans,5-trans-Hexatriene: Traetteberg, M. Acta Chem. Scand. 1968, 22, 628. (d) 1-cis,3-cis,5-cis-Hexatriene: Traetteberg, M. Acta Chem. Scand. 1968, 22, 2294. (e) trans-2-Methyl-1,3,5-hexatriene: Traetteberg, M.; Paulen, G. Acta Chem. Scand. Ser. A 1974, A28, 1150. (f) cis-2-Methyl-1,3,5-hexatriene: Traetteberg, M.; Paulen, G. Acta Chem. Scand., Ser. A 1974, A28, 1. (g) 2,3-Dimethylbutadiene: Aten, C. F.; Hedberg, L.; Hedberg, K. J. Am. Chem. Soc. 1968, 90, 2463. (h) 3,4-Dimethylhexa-2,4-diene (all isomers): Traetteberg, M. Acta Chem. Scand. 1970, 24, 2295.
(12) Yannoni, C. S. Acc. Chem. Res. 1982, 15, 201.
(13) Analyzed by electron impact mass spectrometry: 92.8% $^{13}C_0$, 3.2% $^{13}C_1$, and 4.0% $^{13}C_2$ for the sample used for the experiment in eq 1 and 93.9% $^{13}C_0$, 2.1% $^{13}C_1$, and 4.0% $^{13}C_2$ for the one in eq 2. The materials were prepared from $^{13}CH_3^{13}CO_2Na$ (90 atom % ^{13}C) according to the procedures described in: (a) Murray, A., III, Williams, D. L., Eds. "Organic Syntheses with Isotopes"; Interscience Publishers: New York, 1958; Part I, p 662. (b) Casanova, J., Jr.; Geisel, J. M.; Morris, R. N. Org. Prep. Proc. Int. 1969, 1, 81.
(14) Masuda, T.; Thieu, K.-Q.; Sasaki, N.; Higashimura, T. Macromolecules 1976, 9, 661.
(15) Hasegawa, K. Eur. Polym. J. 1977, 13, 315.
(16) Simionescu, C.; Dumitrescu, S. Makromol. Chem. 1970, 136, 47.
(17) (a) Simionescu, C. I.; Percec, V.; Dumitrescu, S. J. Polym. Sci., Polym. Chem. Ed. 1977, 15, 2497. (b) Simionescu, C. I.; Percec, V. J. Polym. Sci., Polym. Chem. Ed. 1980, 18, 147. (c) Simionescu, C. I.; Percec, V. J. Polym. Sci., Polym. Lett. Ed. 1979, 17, 421. (d) Percec, V. Polym. Bull. (Berlin) 1983, 10, 1. (e) Percec, V. Polym. Bull. (Berlin) 1983, 9, 548. (f) Sanford, T. J.; Allendoerfer, R. D.; Kang, E. T.; Ehrlich, P. J. Polym. Sci., Polym. Phys. Ed. 1980, 18, 2277. (g) Sanford, T. J.; Allendoerfer, R. D.; Kang, E. T.; Ehrlich, P.; Schaefer, J. J. Polym. Sci., Polym. Phys. Ed. 1981, 19, 1151.
(18) Katz, T. J.; Ho, T. H.; Shih, N. Y.; Ying, Y.-C.; Stuart, V. I. W. J. Am. Chem. Soc. 1984, 106, 2659.
(19) The scrambling was much less when the titanium initiator was used. A sample prepared (14% yield, 63% E) at room temperature during 9¹/₂ h (acetylene:Ti:Al = 140:1:4) had 13% of ^{13}C's separated by single bonds.
(20) 47% yield after 2 h, 39% E. The greater structural inhomogeneity of samples of poly(phenylacetylene) prepared with WCl₆ rather than MoCl₅ has been analyzed by Percec.[17d,e,18]
(21) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. J. Am. Chem. Soc. 1977, 99, 2127.

(22) Fischer, E. O.; Kreis, G. Chem. Ber. 1976, 109, 1673.
(23) In the polymer obtained in 33% yield (35% E) after 5 h in a vacuum at 30 °C with the carbene (acetylene:W = 53), 15% of the ^{13}C's were separated by single bonds. In the polymer obtained in 14% yield (74% E) after 75 h at 0 °C with the carbyne (acetylene:W = 100), ca. 8% of the ^{13}C's were separated by single bonds. This last figure rose to only 13% in a similar sample prepared at ca. 25 °C.
(24) Titanium catalysts do not metathesize common olefins appreciably.[1] Titanium tetrachloride plus triethylaluminum (or related materials) metathesizes strained olefins,[25] and the Tebbe reagent exchanges isotopically labeled terminal methylenes.[26]
(25) (a) Truett, W. L.; Johnson, D. R.; Robinson, I. M.; Montague, B. J. Am. Chem. Soc. 1960, 82, 2337. (b) Natta, G.; Dall'Asta, G.; Mazzanti, G.; Motroni, G. Makromol. Chem. 1963, 69, 163.
(26) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. J. Am. Chem. Soc. 1978, 100, 3611. (b) Lee, J. B.; Ott, K. C.; Grubbs, R. H. J. Am. Chem. Soc. 1982, 104, 7491.
(27) Aldissi, M.; Linaya, C.; Sledz, J.; Schue, F.; Giral, L.; Fabre, J. M.; Rolland, M. Polymer 1982, 23, 243.
(28) (a) Higashimura, T.; Deng, Y.-X.; Masuda, T. Macromolecules 1982, 15, 234. (b) Masuda, T.; Kuwane, Y.; Higashimura, T. Polym. J. 1981, 13, 301. (c) Masuda, T.; Okano, Y.; Kuwane, Y.; Higashimura, T. Polymer J. 1980, 12, 907. (d) Masuda, T.; Kawasaki, M.; Okano, Y.; Higashimura, T. Polym. J. 1982, 14, 371.

Novel Photoinduced Carbon–Carbon Bond Formation in Purines[1]

Vasu Nair* and Stanley D. Chamberlain

Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

Received November 6, 1984

Recently much attention has been focused on C-alkylated purines.[2–8] The reported antitumor activity of these compounds and the limited synthetic methodology available to attain them prompted us to consider alternate synthetic approaches to this class of compounds. This paper reports on the successful development of a new synthetically useful method of carbon–carbon bond formation in purines through a photochemical $S_{RN}1$ reaction

(1) Presented at the 188th National Meeting of the American Chemical Society, Philadelphia, PA, Aug 1984.
(2) Yamane, A.; Matsuda, A.; Ueda, T. Chem. Pharm. Bull. 1980, 28, 150.
(3) Bergstrom, D. E.; Reddy, P. A. Tetrahedron Lett. 1982, 23, 4191.
(4) Leonard, N. J.; Bryant, J. D. J. Org. Chem. 1979, 44, 4612.
(5) Taylor, E. C.; Martin, S. F. J. Am. Chem. Soc. 1974, 96, 8095.
(6) Yamane, A.; Inoue, H.; Ueda, T. Chem. Pharm. Bull. 1980, 28, 157.
(7) McGarrity, G. J.; Carson, D. A. Exp. Cell Res. 1982, 139, 199.
(8) Nair, V.; Richardson, S. G.; Coffman, R. E. J. Org. Chem. 1982, 47, 4520.

**Table I.** Products and Yields for the $S_{RN}1$ Reaction of Halopurines[13]

reactn of **1** with	prod(s)	% purified yield	keto:enol (%) in CDCl$_3$ (25 °C)	mp, °C
acetone	**3**, R = —CH$_2$-C(=O)CH$_3$ $\rightleftharpoons$ —CH=C(OH)CH$_3$	70	20:80	148–149
acetone and DNB (quenching expt)	**3**	6		
cyclopentanone	**4**, R ·	65	20:80	162–164
cyclohexanone	**5**, R ·	50	25:75	132–134
2-methylcyclohexanone	**6a**, R ·	30	100:0	76–78
	6b, R ·	7	~50:50	
α-tetralone	**7**, R ·	80	15:85	191–193
acetophenone	**8**, R = —CH$_2$C(=O)Ph $\rightleftharpoons$ —CH=C(OH)Ph	70	5:95	153–154
2-acetylfuran	**9**, R · —CH$_2$C $\rightleftharpoons$ —CH=C	67	15:85	146–148

(substitution, radical, nucleophilic, unimolecular).[9,10] The synthetic approach discussed has wide applicability. In addition, the products of these photoinduced reactions have remarkable versatility in terms of conversion to other biologically interesting purine systems.

When the potassium enolate of acetone **2** was photolyzed in a Rayonet photochemical reactor (3500 Å) in the presence of 6-iodo-9-ethylpurine (**1**)[11] in anhydrous liquid ammonia for $^1/_2$ h, 6-acetonyl-9-ethylpurine (**3**), mp 148–149 °C, was isolated in 70% yield after separation on preparative silica gel plates (Scheme I). The product was identified by its mass spectrum (m/z, 204, M$^+$), by its UV data in ethanol [λ_{max} 362 (ϵ 23 300), 345 (ϵ 18 450), 330 sh (ϵ 13 650), 266 nm (ϵ 3600)], by its high-field 360-MHz ^{1}H (Scheme I) and 90.6 MHz ^{13}C (ref 12) NMR data in CDCl$_3$, and by its FTIR data. The data were also consistent with a keto–enol equilibrium (in CDCl$_3$) with preponderance of the enol isomer probably because of added stabilization due to increased conjugation and hydrogen bonding (Table I). The keto and enol forms could be discerned, not only by the marked difference in the chemical shifts of H$_a$ but also from the downfield shift of H$_2$ observed in each case for the keto form (Scheme I). Further support for the existence of these two forms comes from the expected direction of shift in the keto–enol equilibrium observed with variation in solvent and temperature. At 25 °C, the keto:enol ratio in CDCl$_3$ for **3** is 20:80 but in D$_2$O this ratio is

Scheme I
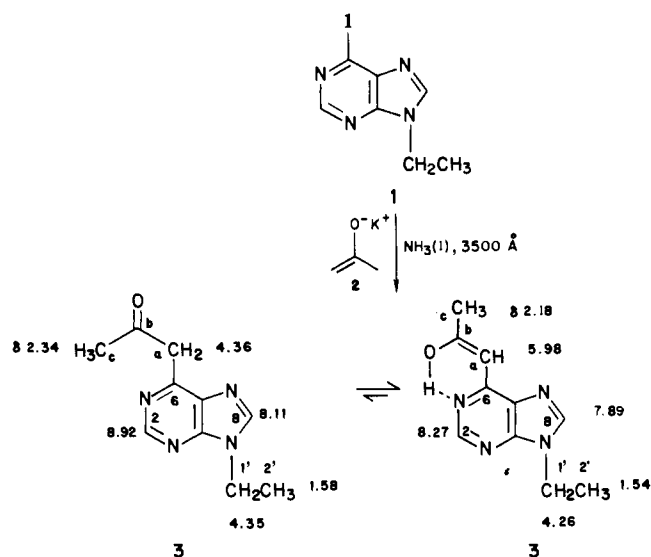
close to 50:50. Variable-temperature ^{1}H NMR data of **3** in Me$_2$SO-d_6 show an increase in the keto form from 18% at 15 °C to 46% at 100 °C.

Support for the $S_{RN}1$ mechanism came from several observations. The short reaction time and the mild reaction conditions are not consistent with a simple displacement reaction of a 6-halopurine. Also, when the photolysis was carried out in the presence of a known radical anion inhibitor (e.g., *p*-dinitrobenzene),[14] the yield of the reaction dropped to about 6%. In

(9) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463, 7464.

(10) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413 and references therein.

(11) Nair, V.; Richardson, S. G. *J. Org. Chem.* **1980** *45*, 3969.

(12) ^{13}C NMR (CDCl$_3$, K = keto, E = enol) δ 15.3 (C$_{2'}$, K), 15.6 (C$_{2'}$, E), 26.3 (C$_c$, E), 30.4 (C$_c$, K), 38.9 (C$_{1'}$, E), 39.0 (C$_{1'}$, K), 48.1 (C$_a$, K), 88.6 (C$_a$, E), 124.8 (C$_5$, E), 133.4 (C$_5$, K), 140.7, 144.1, 145.5, 146.5, 151.3, 152.3 (C$_2$, C$_4$, C$_8$), 151.0 (C$_6$, K), 154.8 (C$_6$, E), 185.9 (C$_b$, E), 203.2 (C$_b$, K).

(13) Reaction conditions: KO-*t*-Bu, NH$_3$(l), *hν* (3500 Å), $^1/_2$ h, –33 °C. Reaction rates and yields for 6-halogenated purines were in the order 6-I > 6-Br > 6-Cl.

(14) Hoffman, A. K.; Feldman, A. M.; Gelblum, E.; Hodgson, W. G. *J. Am. Chem. Soc.* **1964**, *86*, 639.

addition, the iodopurine is capable of a slow, dark substitution reaction[15] of low yield (22%) which apparently is of the $S_{RN}1$ type as evidenced by radical anion inhibition.

We have extended these investigations to a variety of other ketone enolates (Table I). For example, cyclopentanone enolate reacts with **1** to give crystalline 6-(2-cyclopentanoyl)-9-ethylpurine (**4**) (65% yield) which exists largely (80%) in the enolic form. Cyclohexanone behaves similarly. When 2-methylcyclohexanone was treated with **1** under the same conditions, both the thermodynamic (major) and kinetic (minor) products **6a** and **6b** were formed. The thermodynamic product **6a** exists exclusively in the keto form as evidenced by ^{1}H and ^{13}C NMR and FTIR data. The lower yield of the products in this case results apparently from a significant (30%) competing side reaction, i.e., formation of 9-ethylpurine through hydrogen abstraction. Photolysis of the enolate of α-tetralone with **1** gave an excellent yield of the aralicylic substituted product **7**. The aralkyl ketone acetophenone also underwent a smooth photochemical $S_{RN}1$ reaction with the iodopurine **1**. The conversion product **8** exists almost exclusively in the enol form. We have discovered that purines can be modified at the 6-position with acylated heteroaromatic systems. Of particular interest to us was the furan derivative **9** because of the close structural resemblance to plant growth regulators called cytokinins.[16] We are currently extending this methodology to the synthesis of some biologically active highly functionalized nucleosides.

Supplementary Material Available: NMR (^{1}H and ^{13}C), UV, and mass spectral data for all adducts (8 pages). Ordering information is given on any current masthead page.

(15) Bunnett, J. F.; Scamehorn, R. G. *J. Org. Chem.* **1977**, *42*, 1449.
(16) Miller, C. O. *Annu. Rev. Plant Physiol.* **1961**, *12*, 395.

Extraordinary Micellar Enantioselectivity Coupled to Altered Aggregate Structure

Ryuichi Ueoka,*[1a] Robert A. Moss,*[1b] Shanti Swarup,[1b] Yoko Matsumoto,[1a] George Strauss,[1b] and Yukito Murakami[2]

Department of Industrial Chemistry
Faculty of Engineering
Kumamoto Institute of Technology
Ikeda, Kumamoto 860, Japan
Department of Chemistry
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08903

Received January 7, 1985

The diastereoselectivity exhibited in the thiolysis of (e.g) L,L- and D,L-(Z)-Trp-Pro p-nitrophenyl esters by long-chain thiocholine surfactants not only requires micellar surfactant, but a "second form" of the micellar aggregate is actually the stereoselective agent. These latter micelles are characterized by an apparent critical concentration about 5 times above the nominal cmc, and considerably larger hydrodynamic diameters as determined by dynamic light scattering (dls).[3] Now we report that the extraordinary enantioselectivity observed[4] in the cleavage of L or D-N-dodecanoylphenylalanine p-nitrophenyl esters (**1**) by the tripeptide histidine catalyst (Z)-L-Phe-L-His-L-Leu (**2**) in *coaggregates* of the single-chain surfactant cetyltrimethylammonium bromide
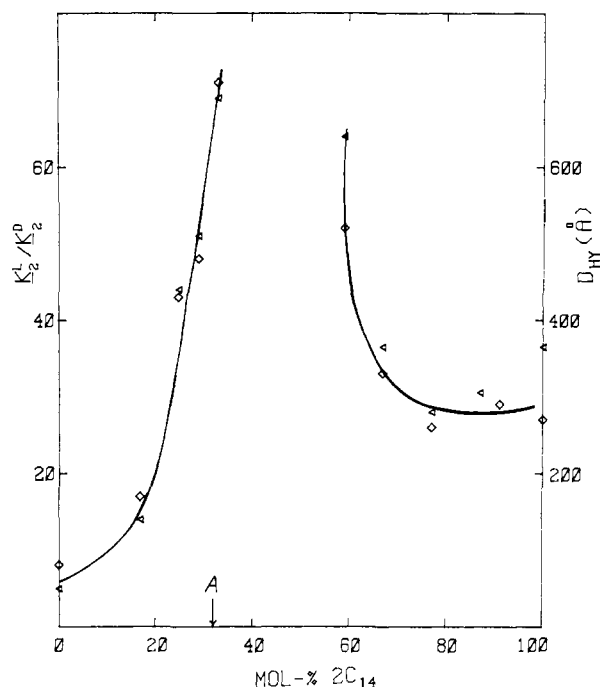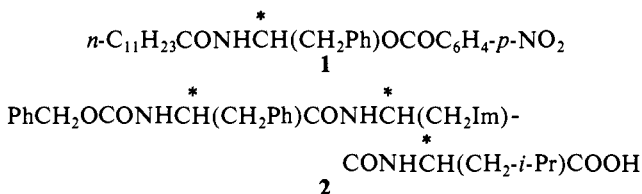
(1) (a) Kumamoto Institute of Technology. (b) Rutgers University.
(2) Department of Organic Synthesis, Kyushu University, Fukuoka 812, Japan.
(3) Moss, R. A.; Chiang, Y.-C. P.; Hui, Y. *J. Am. Chem. Soc.* **1984**, *106*, 7506.

Figure 1. Enantioselectivity ($k_2{}^L/k_2{}^D$) for the coaggregate catalyzed cleavage of L- or D-N-dodecanoylphenyalanine p-nitrophenyl ester by (Z)-L-Phe-L-His-L-Leu (◊) left-hand ordinate) and apparent hydrodynamic diameters of the coaggregates (Δ, d_{hy}, Å, right-hand ordinate) versus coaggregate composition (mol-% $2C_{14}$ in mixtures of $2C_{14}$ and CTAB, abscissa). Point A designates a composition of 33% $2C_{14}$ and 67% CTAB, where maxima are found for $k_2{}^L/k_2{}^D$ and d_{hy}.

(CTAB) and the double-chain surfactant ditetradecyldimethylammonium bromide ($2C_{14}$) appears to be coupled to a systematic variation of coaggregate structure that can be monitored by dls.

$$n\text{-}C_{11}H_{23}CONH\overset{*}{C}H(CH_2Ph)OCOC_6H_4\text{-}p\text{-}NO_2$$
$$\mathbf{1}$$

$$PhCH_2OCONH\overset{*}{C}H(CH_2Ph)CONH\overset{*}{C}H(CH_2Im)\text{-}$$
$$CONH\overset{*}{C}H(CH_2\text{-}i\text{-}Pr)COOH$$
$$\mathbf{2}$$

L- or D-**1** were cleaved by His peptide **2** in pure CTAB micelles, pure $2C_{14}$ vesicles, or coaggregates formed by cosonication of CTAB and $2C_{14}$.[5] Second-order cleavage rate constants (k_2, M^{-1} s^{-1}) ranged from 1700 (L-**1**) or 63 (D-**1**) in vesicular $2C_{14}$ to 270 (L-**1**) or 34 (D-**1**) in micellar CTAB. In Figure 1, we plot the enantioselectivity of the cleavage ($k_2{}^L/k_2{}^D$) on the left-hand ordinate vs. the coaggregate composition ($[2C_{14}]/([2C_{14}] + [CTAB])$) on the abscissa. These experiments were carried out at 25 °C, where maximum enantioselectivity is observed.[6] In response to the admixture of $2C_{14}$, the enantioselectivity rises sharply from ~8.0 in CTAB micelles to ~71 in coaggregates containing 67 mol % CTAB and 33 mol % $2C_{14}$ ("composition A"). Further addition of $2C_{14}$ leads to patent inhomogeneity until ~41% CTAB/59% $2C_{14}$, whereupon clear coaggregate solutions are again obtained. Here, the enantioselectivity is ~52, and it decreases with further addition of $2C_{14}$ before leveling off at ~30. Enantioselectivity is ~27 in unadulterated $2C_{14}$ vesicles.

On the right-hand ordinate of Figure 1, we plot the *apparent* mean hydrodynamic diameter (d_{hy}, Å) of the various aggregates as determined by dls.[7] The remarkable similarity in the de-

(4) Ueoka, R.; Matsumoto, Y.; Ihara, Y. *Chem. Lett.* **1984**, 1807.
(5) Conditions: 0.083 M aqueous Tris buffer, 0.083 M added KCl, pH 7.6, 3 vol % CH$_3$CN, 25 °C; [**1**] = 1.0 × 10^{-5} M, [**2**] = 5 × 10^{-5} M, [$2C_{14}$] = 1.0 × 10^{-3} M. The concentration of CTAB was varied as required to obtain the mole percent compositions shown in Figure 1. Sonication was carried out with a Bransonic 12 unit at 80 W, 50 °C, 1 h.
(6) Ueoka, R.; Matsumoto, Y.; Nagamatsu, T.; Hirohata, S. *Chem. Lett.* **1984**, 583.