One-Pot Synthesis of *N*-Heterocyclic Compounds from Cyclopropenethione Derivatives

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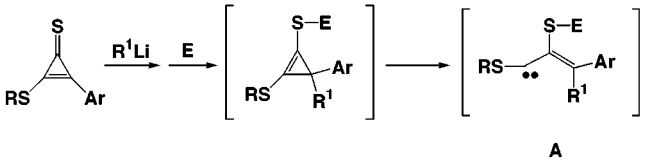
The one-pot reaction of 2-*tert*-butylthio-3-phenylcyclopropenethione (**1a**) and its 3-(2-thienyl) derivative (**1b**) with lithium pyrrolidinide at −70 °C, followed by methylation with methyl iodide, gives 6-methylthio-5-phenyl-2,3-dihydro-1*H*-pyrrolizine (**2a**) and its 5-(2-thienyl) derivative (**2b**), respectively. The reaction of 2-*tert*-butylthio-3-(pyrrolidin-1-yl)cyclopropenethione (**1c**) with phenyllithium gives also **2a** in a high yield under similar conditions, and the reactions of **1a** with *N*-lithium salts of 3-pyrroline, hexamethyleneimine, indoline, and carbazole, piperidine−potassium *tert*-butoxide mixture, and phenyllithium give 6-methylthio-5-phenyl-3*H*-pyrrolizine (**3**), 2-methylthio-3-phenyl-6,7,8,9-tetrahydro-5*H*-pyrrolo[1,2-*a*]azepine (**5**), 6-*tert*-butylthio-5-methylthio-4-phenyl-1,2-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinoline (**6**), 4-*tert*-butylthio-5-methylthio-6-phenyl-4*H*-pyrido[3,2,1-*jk*]carbazole (**7**), 2-methylthio-3-phenyl-5,6,7,8-tetrahydroindolizine (**4**), and 1-*tert*-butylthio-2-methylthio-3-phenylindene (**9**), respectively. The structures of **2a** and **3** were determined by X-ray analyses of their tricarbonylchromium complexes.

Introduction

Although cyclopropenethiones[1] are a reactive unsaturated small-ring system, the application of this ring system in organic synthesis remains undeveloped. Recently, we have reported that the reaction of 2-*tert*-butylthio-3-phenylcyclopropenethione (**1a**) with phenyllithium at room temperature, followed by treatment with methyl iodide, gives 1-*tert*-butylthio-1-methylthio-3,3-diphenylallene in a high yield.[2,3] This reaction proceeds via a regioselective addition of phenyl anion to the 3-position of **1a**, followed by a selective cleavage of the C_1-C_3 bond of the adduct anion. However, if the ring opening of the adduct anion is inhibited for any reaction, for example, by a stabilizing effect of a substituent on the cyclopropenethione ring, such an adduct anion could react with an electrophile that is present in the reaction system. This reaction would then lead to the formation of a cyclopropene derivative that undergoes ring opening to form a vinylcarbene intermediate (**A**).[4] Since vinylcarbene is a versatile reactive species, the conversion of cyclopropenethiones is expected to provide a new synthetic methodology. This paper describes an efficient one-pot method for the preparation of nitrogen-heterocyclic compounds and an indene derivative by use of 2-*tert*-butylthio-3-arylcyclopropenethiones and its pyrrolidin-1-yl derivatives.[5]



A

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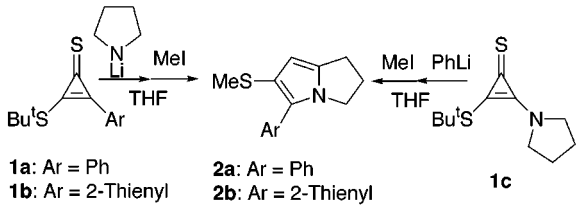
Scheme 1



Results and Discussion

One-Pot Preparation of 1*H*-Pyrrolizine Derivatives 2a,b from Cyclopropenethiones 1a−c. The reaction of lithium pyrrolidinide, which had been prepared from pyrrolidine and *n*-butyllithium, with **1a** under argon in THF at −70 °C, followed by treatment with methyl iodide, gave **2a** in a 90% yield. Similarly, **1b** was converted to **2b** in a 35% yield (Scheme 1). The reaction of **1c** with phenyllithium under similar conditions gave **2a** in an 81% yield (Scheme 1). However, when the

(1) (a) Yoneda, S.; Hirai, H.; Yoshida, *Z. Chem. Lett.* **1976**, 1051. (b) Yoshida, Z.; Shibata, M.; Kida, S.; Miki, S.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.* **1984**, *25*, 345. (c) Yoneda, S.; Ozaki, K.; Inoue, T.; Sugimoto, A.; Yanagi, K.; Minobe, M. *J. Am. Chem. Soc.* **1985**, *107*, 5801. (d) Yoneda, S.; Ozaki, K.; Tsubouchi, A.; Kojima, H.; Yanagi, K. *J. Heterocycl. Chem.* **1988**, *25*, 559. (e) Sugimoto, T.; Nagatomi, T.; Ando, H.; Yoshida, Z. *Angew. Chem.* **1988**, *100*, 597. (f) Yoshida, H.; Shimizu, J.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2445. (g) Matsumoto, K.; Uchida, T.; Yagi, Y.; Tahara, H.; Acheson, R. M. *Heterocycles* **1985**, *23*, 2041. (h) Ikemi, Y. *J. Heterocycl. Chem.* **1990**, *27*, 1597. (i) Eicher, T.; Krause, D. *Synthesis* **1986**, 899. (j) Musicki, B. *J. Org. Chem.* **1991**, *56*, 110.

(2) Yagyu, Y.; Matsumura, N.; Tanaka, H.; Maeda, Z.; Inoue, H. *J. Chem. Res., Synop.* **1995**, 420.

(3) Yagyu, Y.; Matsumura, N.; Tanaka, H.; Inoue, H.; Yasui, M.; Iwasaki, F. *J. Chem. Res., Miniprint* **1996**, 1516; *J. Chem. Res., Synop.* **1996**, 272.

(4) (a) Yoshida, Z. *Top. Curr. Chem.* **1973**, *40*, 47. (b) Yoneda, S.; Hirai, H.; Yoshida, Z. *Chem. Lett.* **1976**, 1051.

(5) A part of this study has been reported in our preliminary paper. Yagyu, Y.; Ito, M.; Matsumura, N.; Inoue, H.; Mizuno, K.; Adachi, T. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1175.

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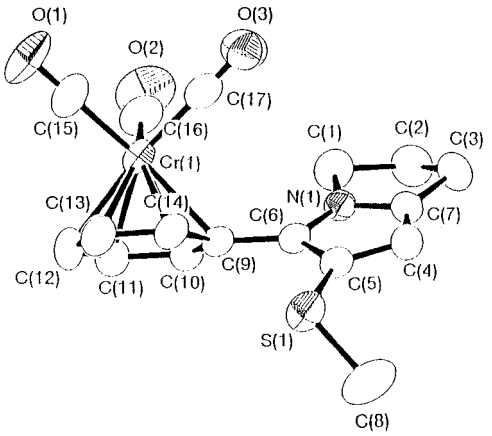
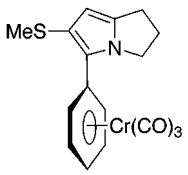


Figure 1. ORTEP drawing and atomic numbering of **2a′**. Selected structural parameters: Cr(1)−C(9) 2.244(1), Cr(1)−C(15) 1.835(2), S(1)−C(5) 1.756(1), O(1)−C(15) 1.1482(2), N(1)−C(1) 1.456(2), N(1)−C(6) 1.379(2), N(1)−C(7) 1.361(2), C(6)−C(9) 1.460(2) Å. C(9)−Cr(1)−C(10) 36.55(5)°, C(9)−Cr(1)−C(15) 89.14(6)°, C(5)−S(1)−C(8) 102.08(8)°, C(1)−N(1)−C(6) 136.4(1)°, C(1)−N(1)−C(7) 113.5(1)°, C(6)−N(1)−C(7) 110.1(1)°, S(1)−C(5)−C(6) 124.9(1)°, N(1)−C(6)−C(9) 123.5(1)°.

reaction of **1c** with phenyllithium was carried out at room temperature, a complex mixture of compounds was obtained. On the other hand, the reaction of **1c** with phenyllithium at −70 °C, followed by the addition of silica gel, gave **1a** in a 72% yield, indicating that the pyrrolidinyl group of **1c** was replaced by phenyl group.

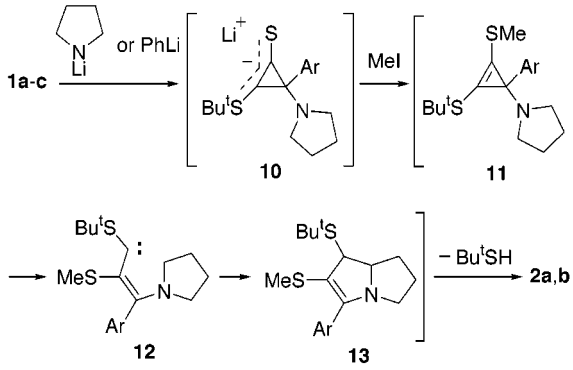
The structures of **2a,b** were determined from their IR and ^{1}H and ^{13}C NMR spectra and elemental analyses (see Experimental Section). To gain further information about the structures of the products, the X-ray crystallographic study of **2a** was attempted, but a single crystal of **2a** could not be obtained. Therefore, **2a** was converted into the chromium complex **2a′** by the reaction with $Cr(CO)_6$.[6]



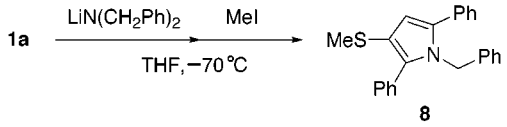
2a'

Recrystallization of the complex from CH_2Cl_2−hexane gave yellow, nicely shaped crystals. The ORTEP drawing of **2a′** is shown in Figure 1. From this drawing, it can be seen that the benzene ring of **2a** forms a chromium complex with $Cr(CO)_3$ species, and the phenyl and methylthio groups are attached to the 5- and 6-positions of the pyrrolizine ring, respectively. The ORTEP drawing also indicates that the plane of the benzene ring binds to the plane of the pyrrolizine ring with a lean of 40° and the $Cr(CO)_3$ group is situated at the *N*-atom side of the pyrroline ring. The IR spectrum of **2a′** showed absorptions due to three carbonyl groups at 1961, 1905, and 1883 cm^{-1}. The ^{1}H and ^{13}C NMR spectra of **2a′** indicated that the signals due to the phenyl group were shifted to a higher field compared to those of **2a**.

Scheme 2

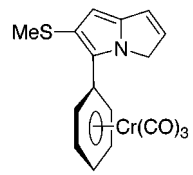


Scheme 3



A possible pathway for the formation of **2a,b** is shown in Scheme 2. The addition of pyrrolidinyl and phenyl anions to the cyclopropenethione ring occurs regioselectively at the 3-position, where the phenyl, 2-thienyl, and pyrrolidinyl groups are attached, giving the adduct **10**. The fact that **1c** is converted into **1a** by treatment with silica gel after the reaction with phenyllithium indicates that the ring opening of **10** does not occur under these conditions. Methylation of **10** with methyl iodide gives the cyclopropene **11**.[3] The ring opening of **11** leads to the formation of the vinylcarbene intermediate **12** in which the carbenic carbon is stabilized by the electron-donating *tert*-butylthio group. The carbenic carbon undergoes an intramolecular cyclization with the pyrrolidinyl group to give **13**, which is then converted into **2a,b** by elimination of *tert*-butanethiol. The reaction of **1a** with lithium dibenzylamide afforded 1-benzyl-2,5-diphenyl-3-methylthiopyrrole (**8**) in an 83% yield (Scheme 3). This reaction also proceeds via a pathway similar to that shown in Scheme 2.

Reaction of 1a with *N*-Lithium and Potassium Amides of Cyclic Amines. The reactions of **1a** with *N*-lithium salts of 3-pyrroline, hexamethyleneimine, indoline, and carbazole, and with piperidine−potassium *tert*-butoxide mixture were carried out under conditions similar to those described above. The results are summarized in Table 1. The structures of **3**−**7** were assigned from their IR, ^{1}H and ^{13}C NMR spectra, and elemental analyses. Compound **3** was converted into complex **3′** by

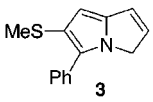
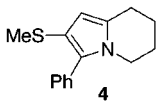
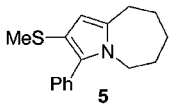
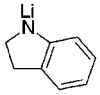
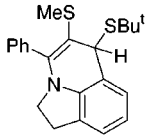
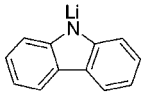
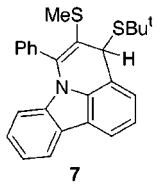


3'

the reaction with $Cr(CO)_6$, and the X-ray crystallographic analysis of the complex was successfully made. The ORTEP drawing of **3′** is shown in Figure 2. The results

(6) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 921. (b) Pearson, A. J. *Metallo-Organic Chemistry*; John Wiley and Sons: New York, 1985; p 348. (c) Uemura, M. Tricarbonyl(arene)chromium Complexes in Organic Synthesis. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, 1991; Vol. 2, p 195.

Table 1. Preparation of *N*-Heterocyclic Compounds from 1a

Cyclopropenethione	Nucleophile	Product	Yield, %[a]
1a		 **3**	57
1a		 **4**	51
1a		 **5**	25
1a		 **6**	52
1a		 **7**	46

[a] Isolated yield based on **1a**.

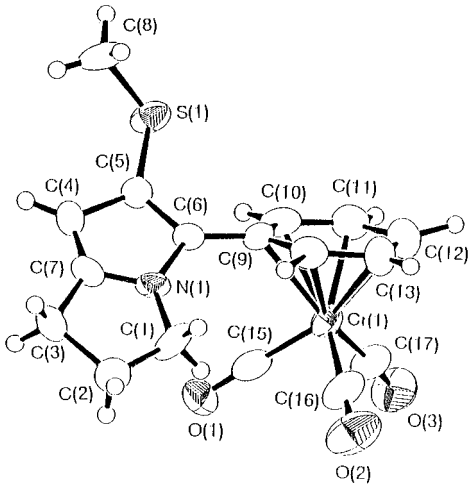


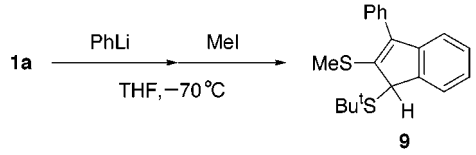
Figure 2. ORTEP drawing and atomic numbering of **3′**.

of Table 1 indicate that the reaction of **1a** with *N*-anions of cyclic amines also proceeds via the processes shown in Scheme 2. It should be noted that the carbenic carbons of vinylcarbene intermediates derived from the reaction of **1a** with *N*-anions of indoline and carbazole undergo cyclization with the benzene ring of indoline and carbazole moieties.

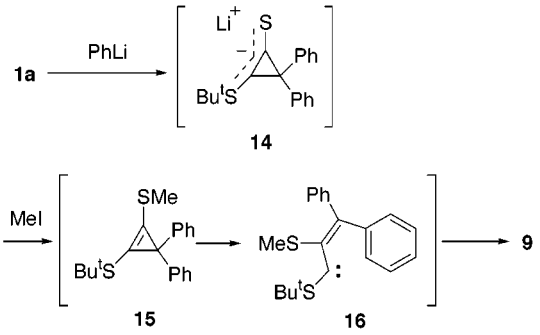
Reaction of 1a with Phenyllithium. The reaction of **1a** with phenyllithium at −70 °C followed by treatment with methyl iodide at the same temperature gave **9** in a 70% yield (Scheme 4). The structure of **9** was determined by its IR, ^{1}H and ^{13}C NMR spectra, and elemental analysis (see Experimental Section).

In a previous paper, we have reported that the reaction of **1a** with phenyllithium at room temperature gave 1-*tert*-butylthio-1-methylthio-3,3-diphenylallene by a direct ring opening.[3] However, the formation of **9** at −70 °C indicates that a ring opening of the adduct anion **14** is depressed at −70 °C, and the adduct anion can be converted into the cyclopropene derivative **15** by treatment with methyl iodide. The cyclopropene thus produced undergoes a ring opening to form the vinylcarbene **16**, which ultimately gives **9** via an intramolecular cyclization (Scheme 5).

Scheme 4



Scheme 5



Experimental Section

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 270 MHz for solutions in $CDCl_3$with TMS as an internal standard. Column chromatography was performed on silica gel.

Preparation of Cyclopropenethiones 1a−c. Compounds **1a−c** were prepared according to the method described previously.[2]

Reactions of 1a,b with Lithium Pyrrolidinide. To pyrrolidine (1.1 mmol) in THF (10 mL) at −70 °C under argon was added *n*-butyllithium (*n*-BuLi, 1.1 mmol in hexane), and then the mixture was stirred at the same temperature for 30 min. The mixture was added to a solution of **1a** or **1b** (1 mmol) in THF (10 mL) cooled at −70 °C, and the resulting mixture was stirred at the same temperature for 1 h. Methyl iodide (2 mmol) was added, and the mixture was then further stirred at −70 °C for 30 min. After saturated aqueous NH_4Cl solution was added, the mixture was extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2−hexane (1:9 v/v). The yields of **2a** and **2b** were 90% and 35%, respectively.

6-Methylthio-5-phenyl-2,3-dihydro-1*H*-pyrrolizine (2a): colorless crystals; mp 75−76 °C (CH_2Cl_2−hexane); ^{1}H NMR δ 2.27 (s, 3 H, SMe), 2.38−2.49 (m, 2 H, CH_2), 2.85−2.91 (m, 2 H, CH_2), 3.93−3.98 (m, 2 H, CH_2), 6.02 (s, 1H, 7-position-H), 7.23−7.50 (m, 5 H, phenyl); ^{13}C NMR δ 20.6, 24.6, 27.3, 46.8, 103.8, 115.7, 126.6, 127.7, 128.2 (2C), 128.6 (2C), 132.3, 137.1; IR (KBr) 3061, 2974, 2950, 2914, 2897, 1601 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NS$: C, 73.32; H, 6.59; N, 6.11. Found: C, 73.29; H, 6.79; N, 5.96.

6-Methylthio-5-(2-thienyl)-2,3-dihydro-1*H*-pyrrolizine (2b): pale red viscous liquid; ^{1}H NMR δ 2.32 (s, 3 H, SMe), 2.48 (m, 2 H, CH_2), 2.88 (m, 2 H, CH_2), 4.09 (m, 2 H, CH_2), 5.99 (s, 1 H, 7-CH═), 7.05−7.08 (m, 1H, thienyl), 7.20−7.24 (m, 2 H, thienyl); ^{13}C NMR δ 20.4, 24.4, 27.0, 47.1, 104.4, 110.9, 123.8, 124.1, 124.9, 126.8, 133.8, 137.3; IR (neat) 2926, 1561 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.24; H, 5.57; N, 5.95. Found: C, 61.02; H, 5.79; N, 6.16.

Reaction of 1c with Phenyllithium. A solution of phenyllithium (1.1 mmol) in ether−cyclohexane (1.07 mL) was added under argon to a solution of **1c** (1 mmol) in THF (20 mL) at −70 °C. The mixture was stirred at the same temperature for **1h** and then worked up in a similar manner as described above. The yield of **2a** was 81%.

Reactions of 1a with the *N*-Lithium Salts of Amines. A solution of *n*-BuLi (1.1 mmol) in hexane was added under argon to a solution of an amine (3-pyrroline, hexamethyleneimine, indoline, carbazole, or dibenzylamine) (1.1 mmol) in THF (10 mL) at −70 °C, and the mixture was stirred for 30 min. The lithium amide solution was added under argon to a solution of **1a** (1 mmol) in THF (10 mL) cooled at −70 °C, and the mixture was stirred at the same temperature for 1.5 h. Methyl iodide (2 mmol) was added and further stirred for 30 min. After saturated NH_4Cl solution was added, the resulting mixture was extracted with ether. The ethereal layer was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2−hexane (1:9−4:6 v/v). The yields of **3** and **5**−**8** were 57%, 25%, 52%, 46%, and 83%, respectively.

6-Methylthio-5-phenyl-3*H*-pyrrolizine (3): pale yellow viscous liquid; ^{1}H NMR δ 2.27 (s, 3 H, SMe), 4.54 (m, 2 H, 3-CH_2), 6.12 (s, 1 H, 7-CH═), 6.29 (m, 1 H, 2-CH═), 6.61 (m, 1 H, 1-CH═), 7.30−7.65 (m, 5 H, phenyl); ^{13}C NMR δ 19.9, 53.3, 102.5, 116.3, 122.8, 127.4, 127.9 (2C), 128.6, 128.8 (2C), 129.0, 132.5, 141.6; IR (neat) 2918, 1600 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NS$: C, 73.97; H, 5.76; N, 6.16. Found: C, 73.69; H, 5.93; N, 6.30.

2-Methylthio-3-phenyl-6,7,8,9-tetrahydro-5*H*-pyrrolo[1,2-*a*]azepine (5): colorless solids; mp 109−111 °C (CH_2Cl_2−hexane); ^{1}H NMR δ 1.59−1.76 (m, 6 H, 3 × CH_2), 2.14 (s, 3 H, SMe), 2.72 (m, 2 H, CH_2), 3.78 (m, 2 H, NCH_2), 5.97 (s, 1 H, 1-position-H), 7.23−7.45 (m, 5 H, phenyl); ^{13}C NMR δ 18.8, 27.3, 27.6, 28.8, 30.0, 46.0, 108.5, 110.4, 126.7, 127.6 (2C), 130.2 (2C), 131.8, 133.4, 135.9; IR (KBr) 2924, 2845, 1514 cm^{-1}; UV ($CHCl_3$) λ_{max} (nm) (log ϵ) 225 (3.96). Anal. Calcd for $C_{16}H_{19}NS$: C, 74.64; H, 7.43; N, 5.46. Found: C, 74.96; H, 7.45; N, 5.46.

6-*tert*-Butylthio-5-methylthio-4-phenyl-1,2-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinoline (6): colorless solids; mp 170−172 °C (hexane); ^{1}H NMR δ 1.41 (s, 9 H, SBu^t), 2.25 (s, 3 H, SMe), 2.75−3.09 (m, 3 H, CH_2), 3.32−4.05 (m, 1 H, CH_2), 5.54 (s, 1H, 6-position-H), 6.74−7.43 (m, 8 H, aromatic); ^{13}C NMR δ 15.0, 28.1, 32.3 (3C), 46.9, 50.6, 64.4, 107.5, 118.4, 119.7, 123.3, 124.5, 124.9 (2C), 127.4 (2C), 128.3, 130.5, 140.2, 146.1, 155.7; IR (KBr) 2919, 1602 cm^{-1}; UV ($CHCl_3$) λ_{max} (nm) (log ϵ) 303 (4.11). Anal. Calcd for $C_{22}H_{25}NS_2$: C, 71.87; H, 6.85; N, 3.82. Found: C, 71.89; H, 6.91; N, 4.12.

4-*tert*-Butylthio-5-methylthio-6-phenyl-4*H*-pyrido[3,2,1-*jk*]carbazole (7): colorless solids; mp 178.5−180.5 °C (hexane); ^{1}H NMR δ 1.56 (s, 3 H, SMe), 1.59 (s, 9 H, SBu^t), 4.68 (s, 1 H, 4-position-H), 6.67−6.69 (d, 1 H, aromatic), 7.10 (t, 1 H, aromatic), 7.19−7.31 (m, 5 H, aromatic), 7.33−7.44 (m, 2 H, aromatic), 7.62−7.65 (d, 1 H, aromatic), 8.13−8.16 (d, 2 H, aromatic); ^{13}C NMR δ 14.7, 32.0 (3C), 44.7, 52.2, 110.7, 110.8, 118.2, 120.0, 120.1, 120.2, 120.2, 122.9, 123.3, 124.2, 125.6, 125.9, 126.1, 127.2, 131.9, 139.5, 140.0, 140.5, 143.1, 144.9; IR (KBr) 2967, 1592 cm^{-1}; UV ($CHCl_3$) λ_{max} (nm) (log ϵ) 292 (4.05). Anal. Calcd for $C_{26}H_{25}NS_2$: C, 75.12; H, 6.06; N, 3.38. Found: C, 75.36; H, 6.15; N, 3.08.

1-Benzyl-3-methylthio-2,5-diphenylpyrrole (8): pale red viscous liquid; ^{1}H NMR δ 2.26 (s, 3 H, SMe), 5.09 (s, 2 H, CH_2), 6.41(s, 1 H, −CH═), 6.55−6.58 (m, 2 H, aromatic), 7.06−7.08 (m, 3 H, aromatic), 7.25−7.33 (m, 10 H, aromatic); ^{13}C NMR δ 19.7, 48.9, 112.2, 114.3, 125.8, 126.7, 127.1, 127.6, 128.0 (2C), 128.0 (2C), 128.3 (2C), 128.9 (2C),130.5 (2C), 131.7, 132.9, 135.7, 136.2, 138.5; IR (neat) 3030, 2917, 1601 cm^{-1}; UV ($CHCl_3$) λ_{max} (nm) (log ϵ) 297 (4.09), 226 (4.10). Anal. Calcd for $C_{24}H_{21}NS$: C, 81.07; H, 5.95; N, 3.95. Found: C, 80.68; H, 6.03; N, 3.93.

Reaction of 1a with Piperidine−Potassium *tert*-Butoxide Mixture. Potassium *tert*-butoxide (0.9 mmol) was added under argon to a solution of piperidine (0.3 mmol) in DMF (3 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. The mixture was added to a solution of **1a** (0.3 mmol) in DMF (6 mL) at −50 °C and stirred for 1 h. Methyl iodide (0.6 mmol) was then added and stirred at the same temperature for 30 min. After saturated aqueous NH_4Cl solution was added, the resulting mixture was extracted with CH_2Cl_2. The extract was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2−hexane (1:9 v/v) to give **4** in a 51% yield.

2-Methylthio-3-phenyl-5,6,7,8-tetrahydroindolizine (4): pale red viscous liquid; ^{1}H NMR δ 1.88−1.95 (m, 4 H, CH_2), 2.77 (m, 2 H, CH_2), 3.48 (s, 3 H, SMe), 3.71 (m, 2 H, 5-CH_2), 5.94 (s, 1 H, 1-CH═), 7.31−7.44 (m, 5 H, phenyl); ^{13}C NMR δ 20.0, 20.9, 23.3, 23.6, 44.7, 107.8, 112.7, 126.9, 127.1, 127.9 (2C), 130.4 (2C), 131.6, 132.4; IR (neat) 2924, 1557 cm^{-1}. Anal. Calcd for $C_{15}H_{17}NS$: C, 74.03; H, 7.04; N, 5.76. Found: C, 73.78; H, 7.31; N, 5.88.

Reaction of 1a with Phenyllithium. A solution of phenyllithium (1.1 mmol) in ether−cyclohexane solution (1.07 mL) was added under argon at −70 °C to a solution of **1a** (1 mmol) in THF (10 mL), and the mixture was stirred for 1 h. Methyl iodide (2 mmol) was then added and stirred at −70 °C for 30 min. After saturated NH_4Cl solution was added, the resulting mixture was extracted with ether. The ethereal layer was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with ether−hexane (5:95 v/v) to give **9** in a 70% yield.

1-*tert*-Butylthio-2-methylthio-3-phenylindene (9): pale orange viscous liquid; ^{1}H NMR δ 1.34 (s, 9 H, SBu^t), 2.23 (s, 3 H, SMe), 4.55 (s, 1 H, 1-position-H), 7.19−7.24 (m, 3 H, aromatic), 7.38−7.44 (m, 1 H, aromatic), 7.47−7.49 (m, 4 H, aromatic), 7.62−7.65 (m, 1 H, aromatic); ^{13}C NMR δ 17.1, 32.3 (3C), 45.7, 54.3, 119.6, 124.5, 125.2, 127.2, 127.3, 127.8, 128.4 (2C), 129.0 (2C), 134.5, 141.6, 143.5, 146.0; IR (neat) 3061, 3024, 2959, 2921, 2894, 2859, 1599 cm^{-1}; UV ($CHCl_3$) λ_{max} (nm) (log ϵ) 241 (4.42). Anal. Calcd for $C_{20}H_{22}S_2$: C, 73.57; H, 6.79. Found: C, 73.84; H, 7.04.

Preparation of Tricarbonylchromium Complex. Hexacarbonylchromium (2.6 mmol) was added to a solution of **2a** (2 mmol) in di-*n*-butyl ether (100 mL)−THF (10 mL), and the mixture was refluxed under argon with stirring at 140 °C for 16 h. The solvent was evaporated under reduced pressure, and ether (100 mL) was added to the residue. The ethereal layer was filtered with Celite, and the filtrate was evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2−hexane (1:1 v/v). The yield of **2a′** was an 85%. In a similar manner, the complex **3′** was obtained from **3**.

Tricarbonylchromium complex (2a′): yellow crystals; mp 97−99 °C (CH_2Cl_2−hexane); ^{1}H NMR δ 2.32 (s, 3 H, SMe), 2.48−2.56 (m, 2 H, CH_2), 2.83−2.88 (m, 2 H, CH_2), 4.10−4.15 (m, 2 H, CH_2), 5.31−5.33 (m, 1 H, phenyl), 5.43−5.48 (m, 2 H, phenyl), 5.68−5.70 (m, 2 H, phenyl), 5.97 (s, 1H, 7-position-H); ^{13}C NMR δ 20.3, 24.4, 27.5, 47.6, 91.2, 92.5 (2C), 92.9 (2C), 103.2, 104.4, 119.8, 122.4, 139.6, 233.3 (3 × C═O); IR (KBr) 3080, 2983, 2917, 1961 (C═O), 1905 (C═O), 1883 (C═O) cm^{-1}. Anal. Calcd for $C_{17}H_{15}CrNO_3S$: C, 55.88; H, 4.14; N, 3.83. Found: C, 55.75; H, 4.39; N, 3.61.

Tricarbonylchromium complex (3′): yellow crystals; mp 134−136 °C (CH_2Cl_2−hexane); ^{1}H NMR δ 2.34 (s, 3 H, SMe), 4.65 (m, 2 H, 3-CH_2), 5.57−5.58 (m, 1 H, phenyl), 5.65−5.70 (m, 2 H, phenyl), 5.98−6.01 (m, 2 H, phenyl), 6.17 (s, 1 H, −CH═), 6.48−6.52 (m, 1 H, −CH═), 6.64−6.67 (m, 1 H, −CH═); ^{13}C NMR δ 20.3, 53.5, 91.9 (2C), 92.0 (2C), 92.2, 101.6, 103.1, 119.5, 119.6, 122.5, 129.2, 142.5, 233.0 (3 × C═O); IR (KBr) 2957, 1950 (C═O), 1856 (2 × C═O) cm^{-1}. Anal. Calcd for $C_{17}H_{13}CrNO_3S$: C, 56.19; H, 3.61; N, 3.86. Found: C, 56.49; H, 3.52; N, 3.85.

X-ray Crystallography. Crystallographic data of **2a′** and **3′** were collected on a Rigaku AFC-5R four-circle diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069

Å). The structure was solved by a direct method and refined on F by full matrix least-squares using TEXSAN.[7]

Crystal data for 2a′: $C_{17}H_{15}CrNO_3S$, fw = 365.37, prismatic, space group $P1$ (#2), a = 9.371(1), b = 11.044(2), c = 8.918(1) Å, α = 101.29(1)°, β = 111.877(9)°, γ = 76.75(1)°, V = 827.5(2) Å^3, F_{000} = 398.00, Z = 2, D = 1.559 g/cm^3, μ (Mo Kα) = 8.36 cm^{-1}. A colorless crystal with dimensions of 1.10 × 0.50 × 0.40 mm^3 was used for data collection; 4058 unique reflections were obtained up to 2θ of 55.1°, and 3444 observed reflections ($|F_o| > 3.00\ \sigma(F)$) were used for refinement. R = 0.032 and R_w = 0.049.

Crystal data for 3′: $C_{17}H_{13}CrNO_3S$, fw = 363.37, prismatic, space group $P2_1/n$ (#14), a = 10.935(2), b = 13.019(3), c = 11.167(2) Å; β = 94.80(1)°, V = 1584.3(5) Å^3, F_{000} = 724.00, Z = 4, D = 1.477 g/cm^3, μ (Mo Kα) = 8.64 cm^{-1}. A yellow crystal with dimensions of 0.40 × 0.10 × 0.10 mm^3 was used for data collection; 2647 unique reflections were obtained up to 2θ of 50.1°, and 1902 observed reflections ($|F_o| > 2.50\sigma(F)$) were used for refinement. R = 0.034 and R_w = 0.039.

(7) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corporation: Kent, 1985 and 1992.

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