October, 1986] Bull. Chem. Soc. Jpn., 59, 3073—3077 (1986)

Metallation of Aliphatic Carbon Atoms. IV. Syntheses and Characterization of the Cyclopalladated Complexes of 2-*t*-Butylbenzothiazole

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(Received April 23, 1986)

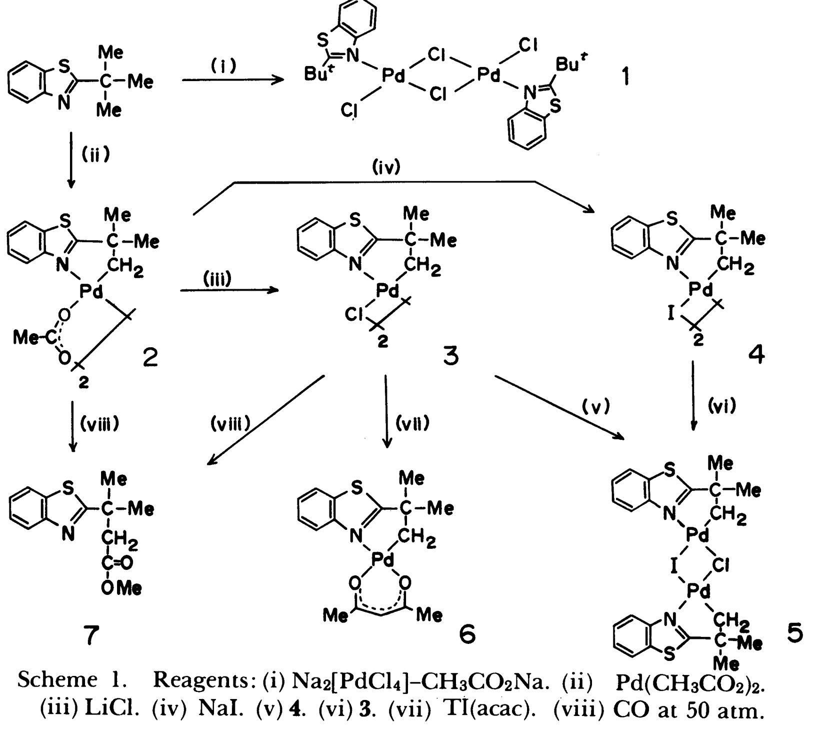
2-*t*-Butylbenzothiazole reacts with palladium(II) acetate in acetic acid to produce the cyclopalladated dimer [{Pd(CH_2CMe_2-C_7H_4NS)(μ-$MeCO_2$)}$_2$] (**2**) (C_7H_4NS=2-benzothiazolyl). Complex **2** shows temperature-dependent ^{1}H NMR spectra, which have been interpreted on the basis of the inversion motion of the acetato bridges. Metatheses of **2** with lithium chloride and sodium iodide result in the formation of the chloro- and iodo-bridged analogues, [{Pd(CH_2CMe_2-C_7H_4NS)(μ-Cl)}$_2$] (**3**) and [{Pd(CH_2CMe_2-C_7H_4NS)(μ-I)}$_2$] (**4**), respectively, each of which is found to be composed of cis and trans isomers. The ^{1}H NMR spectra of **3** and **4** depend on temperature and are ascribed to rapid exchange between the two isomers. Equimolar amounts of **3** and **4** afford a μ-chloro-μ-iodo binuclear complex, [(C_7H_4NS-CMe_2CH_2)Pd(μ-Cl)(μ-I)Pd(CH_2CMe_2-C_7H_4NS)]. The reaction of **3** with thallium(I) acetylacetonate [Tl(acac)] produces a mononuclear cyclopalladated complex [Pd(CH_2CMe_2-C_7H_4NS)(acac)]. Complexes **2** and **3** react with CO in methanol to give $MeO_2CCH_2CMe_2$-C_7H_4NS, the formation of which comfirms also the cyclopalladated structure of 2-*t*-butylbenzothiazole in **2** and **3**.

It has been demonstrated that the activation of C-H bonds in saturated organic compounds is one of the most intriguing goals of organometallic chemistry.[1,2] We have been challenging this theme through cyclometallation reactions. Up to date we have achieved the cyclopalladations of alkyl groups in 2-neopentylpyridine,[3] *N*,*N*-dimethylneopentylamine,[4] 1,3-di(2-pyridyl)propane,[5] and 2-(trimethylsilyl)pyridine[6] by using palladium(II) acetate as a metallating reagent. In this paper we wish to report the new C-H bond activation of *t*-butyl group in 2-*t*-butylbenzothiazole by palladium(II) acetate and the dynamic behavior of the resulting binuclear cyclopalladated complexes.

Results and Discussion

Synthesis of the Cyclopalladated Complexes. 2-*t*-Butylbenzothiazole reacted with an equimolar amount of sodium tetrachloropalladate(II) in the presence of sodium acetate at 80—85 °C to afford a crystalline complex **1**. The ^{1}H NMR spectrum of **1** was not clear owing to its low solubility. On the basis of the elemental analysis and the similarity of the IR spectrum of **1** to that of 2-*t*-butylbenzothiazole, **1** was assigned to a dinuclear addition complex [{(Pd(μ-Cl)Cl(CMe_3-C_7H_4NS)}$_2$] (C_7H_4NS=2-benzothiazolyl group).

2-*t*-Butylbenzothiazole and palladium(II) acetate reacted in acetic acid at 80—85 °C to give yellow crystals, [{Pd(CH_2CMe_2-C_7H_4NS)(μ-CH_3CO_2)}$_2$] (**2**). Its IR spectrum showed characteristic bridged acetato bands at 1415 and 1580 cm^{-1}.[7] The ^{1}H NMR spectrum of **2** at −22 °C showed an AB type quartet at δ 2.20 (2H, $\Delta\delta$=0.26, $^2J_{HH}$=8 Hz) and a singlet at δ 2.49 (2H), ascribable to methylene group, which was formed by the cyclopalladation of one methyl group



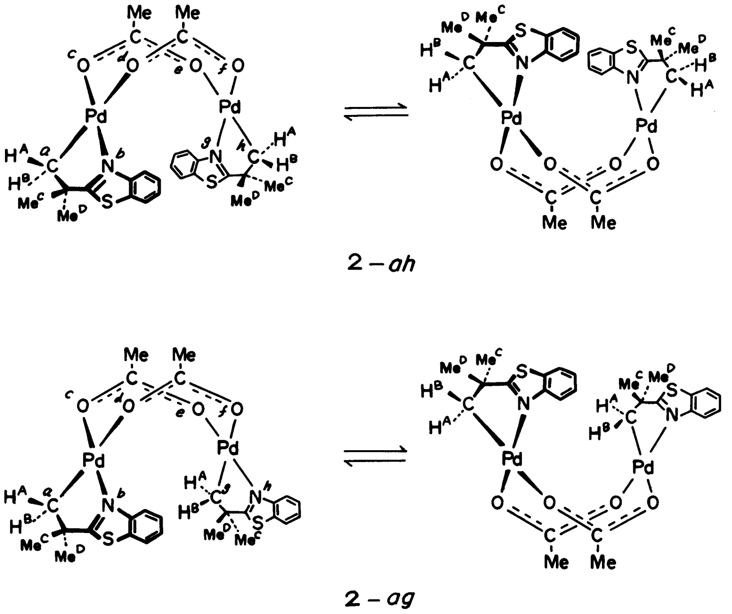
Scheme 1. Reagents: (i) $Na_2[PdCl_4]$-CH_3CO_2Na. (ii) $Pd(CH_3CO_2)_2$. (iii) LiCl. (iv) NaI. (v) **4**. (vi) **3**. (vii) Tl(acac). (viii) CO at 50 atm.

in 2-*t*-butylbenzothiazole. In addition, the spectrum exhibited three singlets due to the methyl protons of the bridging acetato ligands at δ 2.09 (1.5H), 2.15 (3.0H), and 2.21 (1.5H). The central singlet at δ 2.15 is assignable to a trans isomer with a C_2 symmetry, whereas the other two singlets at δ 2.09 and 2.21 are ascribable to a cis isomer with a C_s symmetry. On the basis of these results and the elemental analysis together with the characterization of derivatives from **2**, **2** was assigned to a 1:1 mixture of trans and cis isomers of novel binuclear cyclopalladated complex, di-μ-acetato-bis[2-(2-benzothiazolyl)-2-methylpropyl-C^1, *N*]dipalladium(II) [$\{Pd(CH_2CMe_2\text{-}C_7H_4NS)(\mu\text{-}CH_3CO_2)\}_2$]. The trans isomer was palladated at *a*- and *h*-positions (**2-*ah***), as shown in Fig. 1, whereas the cis isomer was done at *a*- and *g*-positions (**2-*ag***). The formation of the two kinds of isomers has been observed in other several acetato-bridged cyclopalladated complexes.[3,4,6,8)]

The acetato-bridged complex **2** was converted into the corresponding chloro-bridged analogue [$\{Pd(CH_2CMe_2\text{-}C_7H_4NS)(\mu\text{-}Cl)\}_2$] (**3**) and iodo-bridged one [$\{Pd(CH_2CMe_2\text{-}C_7H_4NS)(\mu\text{-}I)\}_2$] (**4**) by the metathetical reactions of **2** with lithium chloride and sodium iodide, respectively, in THF. The equimolar mixture of these two complexes afforded an interesting mixed halogeno-bridged binuclear complex, [$(C_7H_4NS\text{-}CMe_2\text{-}CH_2)Pd(\mu\text{-}Cl)(\mu\text{-}I)Pd(CH_2CMe_2\text{-}C_7H_4NS)$] (**5**) in a high yield. Furthermore, mononuclear cyclopalladated complex **6**, [$Pd(CH_2CMe_2\text{-}C_7H_4NS)(acac)$] (acac=acetylacetonato) was obtained by treating **3** with Tl(acac) in dichloromethane. Characteristic *O,O'*-chelating acac bands were observed at 1510 and 1580 cm^{-1} in the IR spectrum of **6**.

All the complexes (**2**—**6**) synthesized in this study are fairly stable in air. Their elemental analyses, yields, and ^{1}H NMR data are summarized in Tables 1 and 2.

Dynamic Behavior of the Acetato-Bridged Dimer 2. Complex **2** showed temperature-dependent ^{1}H NMR spectra (Fig. 2). At −22 °C, the methylene protons of **2-*ah*** showed the AB type quartet and the protons of the two remaining methyl groups were nonequivalent, resonating as two singlets at δ 0.70 and 1.14. The methyl protons of **2-*ag*** appeared also as two singlets at δ 1.45 and 1.54. These facts indicate unambiguously that the both isomers of **2** have a folded structure,



2-*ah*

2-*ag*

Fig. 1. Inversion motions of the isomers of 2.

Table 1. Yield and Elemental Analyses

Compound	Yield	Mp$^{a)}$	Found (Calcd) (%)		
	%	θ_m/°C	C	H	N
1	45	185—190	36.02(35.84)	3.69(3.55)	3.53(3.80)
2	51	199—202	43.75(43.89)	4.21(4.25)	4.00(3.94)
3	88	250—252	38.91(39.78)	3.66(3.64)	4.12(4.22)
4	61	225—227	30.82(31.19)	2.99(2.86)	3.17(3.31)
5	72	205—207	35.22(34.96)	3.23(3.20)	3.60(3.71)
6	75	116—118	48.09(48.55)	4.99(4.84)	3.57(3.54)
7	96$^{b)}$	—$^{c)}$	62.51(62.63)	6.12(6.06)	5.57(5.62)

a) With decomposition. b) From 3. c) Oil.

Table 2. ^{1}H NMR Data[a]

Compd	Temp[b]	$C\underline{H}_2$	$C\underline{H}_3$	2-Benzothiazolyl group[c]				Others[d]
	°C			4-$\underline{H}$	5- and	6-$\underline{H}$'s	7-$\underline{H}$	
2-*ah*	−22	2.20q[e]	0.70s 1.14s	8.15d	7.15t	7.42t	7.86d	2.15s($C\underline{H}_3CO_2$)
2-*ag*	−22	2.49s	1.45s 1.54s	7.75d	6.62t	7.38t	7.60d	2.09s($C\underline{H}_3CO_2$) 2.21s($C\underline{H}_3CO_2$)
2-*ah*	43	2.21s	1.05brs	8.33d	7.17t	7.43t	8.01d	2.10s($C\underline{H}_3CO_2$)
2-*ag*	43	2.51s	1.36brs	7.76d	6.72t	7.41t	7.60d	2.04s($C\underline{H}_3CO_2$) 2.16s($C\underline{H}_3CO_2$)
3	−32	2.50s 2.59s[f]	1.63s	8.60d 8.85d[f]	7.46t	7.61t	7.89d	—
	54	2.56s	1.60s	8.80d	7.44t	7.60t	7.86d	—
4	−35	2.42s 2.54s	1.66s	8.63d 8.87d	7.46t	7.54t	7.83d	—
	50	2.48s	1.66s	8.85d	7.45t	7.52t	7.81d	—
3+4[g]	50	2.45s	1.59s	8.84brd	7.45t	7.52t	7.79d	—
5	−35	2.33s	1.62s	8.77d	7.39t	7.54t	7.82d	—
	50	2.40s	1.60s	8.87d	7.38t	7.52t	7.79d	—
6	24	2.38s	1.58s	8.93d	7.38t	7.52t	7.78d	1.96s, 2.06s(acac-$C\underline{H}_3$) 5.33s(acac-$C\underline{H}$)
7	24	2.84s	1.58s	7.86d	7.21t	7.35t	7.77d	3.54s($C\underline{H}_3O$)

a) δ Value from TMS. Recorded in $CDCl_3$ on a JEOL JNM-MH 100 spectrometer. b) Measured temperature. c) Coupling constants between the adjacent protons in this ring ($^3J_{HH}$) are ca. 7 Hz. d) Assignment is given in the parentheses. e) $\Delta\delta=0.26$, $^2J_{HH}=8$ Hz. f) Corresponding to the major isomer. g) **3**+**4** in a 2:1 molar ratio. See the text.

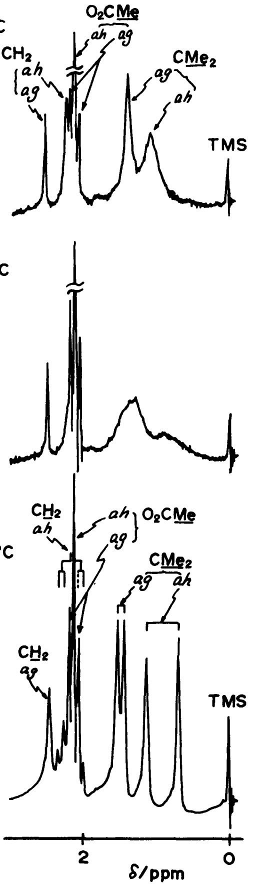


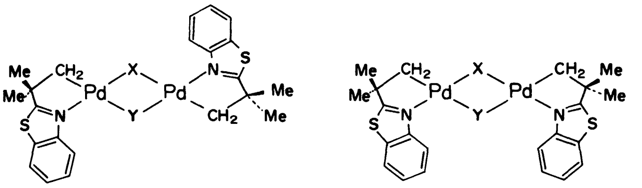
Fig. 2. The temperature-dependent ^{1}H NMR spectra of **2**.

as other acetato-bridged binuclear palladium(II) complexes have.[9–11] As for **2-*ah***, the protons of the both methyl groups resonated at higher fields in comparison with the corresponding methyl protons in **2-*ag***. This seems to be associated with the anisotropic shielding by the facing benzothiazolyl group.[10] Furthermore, the anisotropic shielding acts on one of the methylene protons situated at the innerside of the folded structure in **2-*ah***, shifting the resonance to the higher field (at δ 2.07). However, the methylene protons of **2-*ag*** do not undergo such anisotropic shielding owing to the mirror image relationship of the structure, resonating at δ 2.49 as a singlet.

On raising the measured temperature, the two methyl resonances in each of **2-*ah*** and **2-*ag*** coalesced at 28 °C, and then became broad singlets at δ 1.05 and 1.36, respectively, at 43 °C. However, these two singlets did not coalesce at 60 °C, indicating that the exchange between **2-*ah*** and **2-*ag*** did not occur even at this temperature. The temperature-dependency of the ^{1}H NMR spectra of **2** is attributable to such the typical inversion motion of the acetato bridges (Fig. 1) as the other acetato-bridged complexes exhibit.[4,6,10,11]

Dynamic Behavior of the Halogeno-Bridged Binuclear Complexes. The chloro-bridged dimer **3** also exhibited the temperature-dependent ^{1}H NMR spectra. At −32 °C palladium-bonded methylene protons resonated as two singlets at δ 2.50 (1.4H) and 2.59 (2.6H), whereas 4-H of the 2-benzothiazolyl moiety appeared as two doublets at δ 8.60 (0.7H) and 8.85 (1.3H). These data indicate that **3** consists of two isomers, trans type with (*a*-C, *b*-N; *e*-N, *f*-C) chelations and cis one with (*a*-C, *b*-N; *e*-C, *f*-N) chelations as seen in Fig. 3.

The former two singlets at δ 2.50 and 2.59 coalesced at 3 °C and changed to one sharp singlet at



3 - *trans* X=Y=Cl
4 - *trans* X=Y=I
5 - *trans* X=Cl, Y=I

3 - *cis* X=Y=Cl
4 - *cis* X=Y=I
5 - *cis* A X=Cl, Y=I
B X=I, Y=Cl

Fig. 3. Isomers of the halogeno-bridged binuclear complexes.

δ 2.56 at 54°C. Similarly, the latter two doublets at δ 8.60 and 8.85 were turned into one doublet at δ 8.80 at the same temperature. This temperature-dependent ^{1}H NMR spectra did not change at all by adding 10-fold excess of acetone or water to the NMR sample solution of **3** in $CDCl_3$. Such temperature dependence is attributed to an exchange between the cis and trans isomers rather than that between **3** and a mononuclear species $[Pd(CH_2CMe_2-C_7H_4NS)ClL]$ $(L=Me_2CO$ or $H_2O)$. This is also supported by easy formation and isolation of the chloro-iodo-mixed bridged binuclear complex as stated later. The iodo-bridged dimer **4** also exhibited similar temperature-dependent ^{1}H NMR spectra in the range of −35—+50 °C (Table 2), indicating that **4** consisted of cis and trans isomers (Fig. 3) and a rapid exchange between the two isomers took place above −10°C. Galli et al.[12] reported recently the analogous exchange between the cis-trans isomers of halogeno-bridged cyclopalladated dimers of *t*-butyl methyl ketone *N*-methyl-*N*-phenylhydrazone $[\{Pd[CH_2CMe_2C(=N\text{-}NMePh)Me]X\}_2]$ (X=Cl, Br, and I).

When the ^{1}H NMR spectra of the equimolar mixture of **3** and **4** were measured in $CDCl_3$, only one set of signals, corresponding neither to **3** nor **4**, was obtained. Moreover, this species also showed temperature-dependent ^{1}H NMR spectra. At 50°C, the palladium-bonded methylene protons and 4-H of the 2-benzothiazolyl moiety resonated as one singlet at δ 2.40 and one doublet at δ 8.87, respectively. On lowering the temperature, these signals broadened at 18°C, and then changed again to one sharp singlet at δ 2.33 and one resolved doublet at δ 8.77 at −35°C. This species could be isolated as a chloro-iodo-bridged binuclear complex $[(C_7H_4NS\text{-}CMe_2CH_2)Pd(\mu\text{-}Cl)(\mu\text{-}I)Pd(CH_2CMe_2\text{-}C_7H_4NS)]$ (**5**). Of course, **5** showed the same temperature-depending ^{1}H NNR spectra as the above-mentioned mixture of **3** and **4**. It is interesting that **5** showed only one set of ^{1}H NMR signals, though there are three possible isomers, trans, cis-A, and cis-B, as shown in Fig. 3.

When the mixture of **3** and **4** in a molar ratio of 2:1 was run in a ^{1}H NMR tube, there appeared three sets of signals; one corresponded to **5** and the other two did to two sets observed for **3** at −35°C. On increasing the temperature all the three sets coalesced at 25°C, and then appeared as one single set of signals at 60°C. These results clearly indicate that the chloro-bridged dimer **3** as well as the iodo-bridged dimer **4** experiences exchange between cis- and trans-isomers. In other words at high temperature (ca. 50°C) the exchange between the two species is rapid, giving averaged single set of signals, and at low temperature (ca. −35°C) the exchange is actually quenched to result in affording two sets of signals corresponding to cis and trans isomers.

Carbonylation of the Cyclopalladated Complexes, 2 and 3. The acetato-bridged dimer **2** as well as the chloro-bridged one **3** reacted with carbon monoxide in methanol in an autoclave to give methyl 3-(2-benzothiazolyl)-3-methylbutyrate (**7**) in almost quantitative yields. This fact unambiguously indicates that metallation occurs on the methyl carbon of the 2-*t*-butylbenzothiazole, and that methoxycarbonyl group can be introduced quantitatively and regiospecifically onto one of the methyl groups via cyclopalladated complex.

Experimental

2-*t*-Butylbenzothiazole[13] and thallium(I) acetylacetonate[14] were synthesized as published. General procedures were as described previously.[8]

Reaction of 2-*t*-Butylbenzothiazole with $Na_2[PdCl_4]$. 2-*t*-Butylbenzothiazole (215 mg), sodium acetate (92 mg), and $Na_2[PdCl_4]$ (300 mg) were mixed in 20 cm^3 of acetic acid, and then the mixture was heated at 80—85°C for 6 h. The resulting precipitates were collected, and washed with water and diethyl ether. Recrystallization from benzene and hexane gave 170 mg of $[\{Pd(\mu\text{-}Cl)Cl(CMe_3\text{-}C_7H_4NS)\}_2]$ (**1**) as beige crystals.

Reaction of 2-*t*-Butylbenzothiazole with $Pd(CH_3CO_2)_2$. The mixture of 2-*t*-butylbenzothiazole (940 mg) and $Pd(CH_3CO_2)_2$ (1000 mg) in 15 cm^3 of acetic acid was heated at 80—85°C for 2.5 h. The solvent was evaporated and the residue was chromatographed on a silica-gel column (200 mesh, 1.2×12 cm). A pale yellow-brown fraction eluted by THF/CH_2Cl_2 (1/1) was collected and evaporated to dryness. Recrystallization from dichloromethane and hexane afforded 800 mg of $[\{Pd(CH_2CMe_2\text{-}C_7H_4NS)(\mu\text{-}CH_3CO_2)\}_2]$ (**2**) as yellow crystals.

Metathesis of 2 with Lithium Chloride. Lithium chloride (107 mg) was added to a THF suspension (10 cm^3) of **2** (360 mg). The suspension became clear and was stirred for 1 d at room temperature. The solvent was removed and the residue was dissolved in 10 cm^3 of benzene. Pale beige crystals were precipitated after a few minutes, and were collected and washed with water, methanol, and then diethyl ether to give 295 mg of $[\{Pd(CH_2CMe_2\text{-}C_7H_4NS)(\mu\text{-}Cl)\}_2]$ (**3**).

Metathesis of 2 with Sodium Iodide. A clear THF solution (20 cm^3) of sodium iodide (421 mg) and **2** (400 mg) was left overnight and evaporated to dryness. The residue was extracted with dichloromethane. Hexane was added to the extract and 290 mg of $[\{Pd(CH_2CMe_2\text{-}C_7H_4NS)(\mu\text{-}I)\}_2]$ (**4**) was obtained as brown crystals.

Reaction of 3 with 4. Complex **3** (55 mg) was added to a dichloromethane solution (15 cm^3) of **4** (70 mg), and the resulting mixture was stirred at room temperature for 12 h. After the mixture was evaporated to dryness, the residue was recrystallized from benzene and hexane to give 100 mg of $[(C_7H_4NS\text{-}CMe_2CH_2)Pd(\mu\text{-}Cl)(\mu\text{-}I)Pd(CH_2CMe_2\text{-}C_7H_4NS)]$ (**5**) as yellow crystals.

Reaction of 3 with Thallium(I) Acetylacetonate. Thallium(I) acetylacetonate (286 mg) was added to a stirred solution of **3** (204 mg) in 10 cm^3 of dichloromethane. After 17 h, the resulting milk-white suspension was centrifugalized. The supernatant solution was purified through a short silica-gel column and evaporated at reduced pressure to 4 cm^3. Addition of hexane afforded 181 mg of $[Pd(CH_2CMe_2\text{-}C_7H_4NS)(acac)]$ (**6**) as pale yellow crystals.

Reaction of 2 or 3 with CO in MeOH. In 20 cm^3 of methanol, **2** (500 mg) was carbonylated at 80 °C under a carbon monoxide pressure of 50 atm for 20 h under stirring. The mixture was filtered to remove palladium black, and then evaporated to dryness. The product, methyl 3-(2-benzothiazolyl)-3-methylbutyrate (**7**), was isolated by extracting the resulting oil with pentane and evaporating and drying up in vacuo. Yield 268 mg (83%), colorless oil.

The compound **7** was also obtained from **3** by the similar way as described above. Yield, 200 mg (96%) from 300 mg of **3**.

Analytical and ^{1}H NMR data of **7** are also given in Tables 1 and 2, respectively.

We wish to thank Mr. Eiji Ueda of Shikamachi Technical High School for preparing the complex **1**. The present work was partially suported by a Grant-in-Aid for Scientific Research No. 58550572 from the Ministry of Education, Science and Culture.

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