Syntheses of Organic *N,N*-Dialkyldithiocarbamates or Organic Thiocyanates from Organozincs and Corresponding Thio-Anions via the Inversion of Electronic Reactivity of the Anions with NCS-Oxidation

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Novel displacement of metal ions from organometallic compounds with nucleophilic reagents was achieved in the reaction between organozinc compounds and *N,N*-dialkyldithiocarbamate ions (*N,N*-DAD$^-$) or thiocyanate ion by the assistance of NCS, whereby alkyl or aryl *N,N*-DAD or alkyl, alkenyl, alkynyl, aryl, or heteroaryl thiocyanates were obtained in moderate to excellent yields as the result of novel bond construction between carbon fragments from organozinc compounds and thio-anions.

Electrophilic substitution of carbon nucleophiles from organolithiums or Grignard reagents with polar reagents like SCl_2, RSCl, SO_2, RN_3, PCl_3, or $POCl_3$ is one of the most frequently employed synthetic methods of heteroatom (X)-substituted organic compounds (X = S, N, or P).[1] The heteroatoms (X) in these reagents are charged positively and, therefore, act as electrophiles toward such organometallic compounds. Meanwhile, heteroatoms (X) in more common reagents like R_2S, RSNa, R_3N, or R_3P are nucleophilic by nature and can not react rapidly with the organometallic compounds. However, in view of the fact that the latter reagents are rather conventional and easily handled compared to the former,[2] utilization of reagents of the latter type in the construction of C–X bonds from organometallic compounds would appear to be quite useful. Hitherto, this type of transformation has been accomplished in the reaction of organobismuth compounds (Bi^{3+}), organolead compounds (Pb^{4+}), or organothallium compounds (Tl^{3+}) with group VB or VIB nucleophiles in the presence or absence of transition metals.[3,4] Therein, metal ions acted as nucleofuges and decreased their formal oxidation states by 2 after the displacement: this type of reaction might be called "nucleophilic displacement of organometallic compounds with nucleophiles."

Here we consider another method to attain the same transformation. That is, we proposed the oxidation of nucleophiles (X) as a means of inverting their electronic reactivity from nucleophilic to electrophilic.[5] If the oxidation is carried out in the presence of organometallic compounds, the resulting species would be attacked by the nucleophilic centers in organometallic compounds to yield new C–X bonds. In this case, leaving groups (metal ions) keep their formal oxidation states throughout the reaction, and the total reaction may be formally called "electrophilic displacement of organometallic compounds with nucleophilic reagents." In this paper, we wish to demonstrate successful examples of this methodology, in which the replacement of Zn^{2+} from organozincs with such thio-nucleophiles as *N,N*-DAD$^-$ or SCN^- was accomplished with the assistance of NCS.[6]

Results and Discussion

The reaction of various phenylmetals with *N,N*-DAD$^-$ in THF was examined at first in the presence of NCS as an oxidizing agent.[7] As shown in Table 1, neither phenyllithium, tetraphenyllead, nor tetraphenyltin reacted with the sodium or zinc salt of *N,N*-DAD$^-$, but sodium tetraphenylborate reacted with either salt to afford phenyl *N,N*-DAD albeit in low yield. A phenylzinc compound, conveniently prepared in situ from phenyllithium and the zinc salt of *N,N*-diethyldithiocarbamate (*N,N*-DED$^-$), reacted with *N,N*-DED$^-$ to afford phenyl *N,N*-DED in a yield of 58%. Chlorobenzene was also formed in a yield of 26%. A similar run except for the absence of NCS did not yield phenyl *N,N*-DED at all. Unfortunately, efforts such as changing molar ratios of each component or using NBS or CAN in the place of

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[2] Sandler, S. R.; Karo, W. In *Organic Functional Group Preparation*, 2nd ed.; Academic Press: San Diego, 1986; Vol. 2, p 323; Vol. 3, p 171.

[3] Reviews: (a) Abramovitch, R. A.; Barton, D. H. R.; Finet, J.-P. *Tetrahedron* **1988**, *44*, 3039. (b) Meio, G. D.; Morgan, J.; Pinhey, J. T. *Tetrahedron* **1993**, *49*, 8129.

[4] (a) Matano, Y.; Azuma, N.; Suzuki, H. *Tetrahedron Lett.* **1993**, *34*, 8457. (b) Uemura, S.; Uchida, S.; Okano, T.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3254.

[5] Electronic reactivities of organometallic compounds could be inverted from nucleophilic to electrophilic using (*i*) transmetalation reaction (Godleski, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M. Ed.; Pergamon Press: Oxford, 1991; Vol. 4, p 606) or (ii) anodic or chemical oxidation: Yoshida, J.; Itoh, M.; Morita, Y.; Isoe, S. *J. Chem. Soc., Chem. Commun.* **1994**, *549* and references cited therein.

[6] Preliminary communication: Takagi, K.; Takachi, H.; Hayama, N. *Chem. Lett.* **1992**, 509.

[7] (a) Fieser, L. F.; Fieser, M. In *Reagents for Organic Synthesis*; John Wiley & Sons: New York, 1967; Vol. 1, p 139. For the utility of *N*-haloamides as positive-halogen equivalents, see: (b) Block, E.; Schwan, A. B. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 4; p 355. (c) Ende, D. V.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 279. (d) Jasserand, D.; Girard, J. P.; Ross, J. C.; Granger, R. *Tetrahedron Lett.* **1976**, 1581. (e) Wilbur, D. S.; Stone, W. E.; Anderson, K. W. *J. Org. Chem.* **1983**, *48*, 1542.

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Scheme 1. Reaction of Organometallic Compounds (MR) with Nucleophiles (Nu^-) To Form Bonds between R and Nu

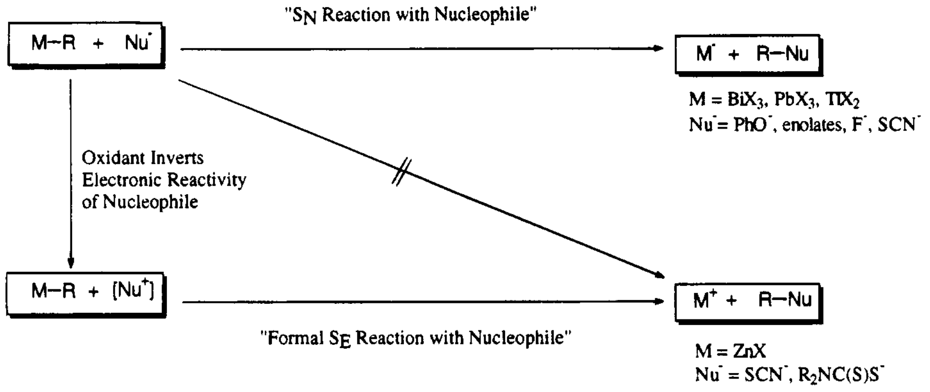

Table 1. Synthesis of Organic *N,N*-Dialkyldithiocarbamates

		$[R'_2NC(S)S]nM'$			molar ratio	yield[a] (%)	
entry	RM	R′	n	M′	$RM/[R'_2NC(S)S]nM'/NCS$	$R'_2NC(S)SR$	RCl
1	PhLi	Et	1	Na	1/1/1.2	0	
2	Ph_4Sn	Et	1	Na	1/1/1.2	<1	
3	Ph_4Sn	Et	2	Zn	1/1/1.2	<1	
4	Ph_4Pb	Et	2	Zn	1/1/1.2	2	
5	Ph_4B^-	Et	1	Na	1/2/1.2	6	
6	Ph_4B^-	Et	2	Zn	1/1/1.2	14	
7	PhLi	Et	2	Zn	1/1/1	58	26
8	PhLi	Et	2	Zn	1/1/0	0	
9	PhLi	Et	2	Zn	1/1.5/1	64 (51)	20
10	PhLi	Et	2	Zn	1/1/2	32	64
11	PhLi	Et	2	Zn	2/1/1	26	54
12	PhLi	Et	2	Zn	1/1.2/1.2	66	30
13	PhLi	Et	2	Zn	1/1.2/1.2 (NBS)	28	60[b]
14	PhLi	Et	2	Zn	1/1.2/1.2 (CAN)	<1	
15	PhLi	Bu	2	Zn	1/1.2/1.2	(63)	
16	BuLi	Et	2	Zn	1/1.2/1.2	(70)	

[a] Isolated Yields. The values in parentheses were determined by GLC. [b] Yield of bromobenzene.

NCS did not supress the side reactions. Other organic *N,N*-DAD-, like phenyl *N,N*-dibutyldithiocarbamate (*N,N*-DBD) or butyl *N,N*-DED, however, were obtained from the corresponding organolithiums and Zn^{2+} salts by the treatment with NCS.[8]

Next, the replacement of metal ions from organometallic compounds with SCN^- was examined. In a similar manner as above, a phenylzinc compound was generated in situ from phenyllithium and $Zn(SCN)_2$ in THF. Subsequent to the addition of NCS to the solution, the replacement of Zn^{2+} with SCN^- took place smoothly to yield PhSCN in an excellent yield. In marked contrast to the synthesis of organic *N,N*-DAD, chlorobenzene was formed in less than 1%, and other conceivable side-products such as phenyl isothiocyanate[9] or diphenyl sulfide[10] were not detected in the reaction mixture by a GLC analysis.

Encouraged by this result, we then attempted the thiocyanation of various organozinc compounds. Organozinc compounds were conveniently prepared in situ from $Zn(SCN)_2$ and the corresponding organolithiums. As shown in Table 2, by the assistance of NCS, organozinc compounds reacted smoothly with SCN^- under mild conditions to afford the corresponding organic thiocyanates (alkyl, alkenyl, alkynyl, aryl including carbamoyl- or oxazolinyl-substituted one, or heteroaryl thiocyanates) in good to excellent yields. At present, numerous synthetic methods of organic thiocyanates are available.[11] However, those suffer from the defects of low yields, troublesome procedures, and/or difficulties in obtaining starting materials (substrates or reagents). Therefore,

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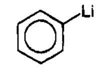
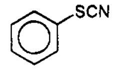
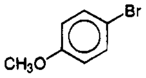
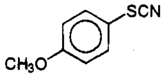
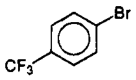
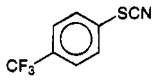
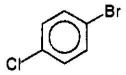
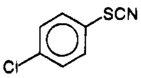
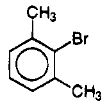
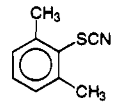
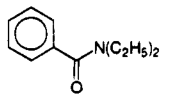
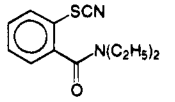
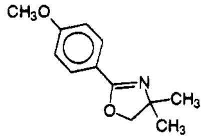
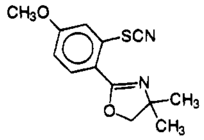
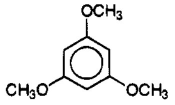
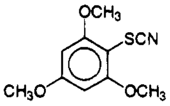
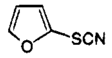
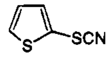
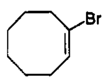
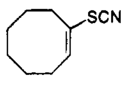
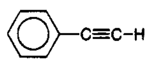
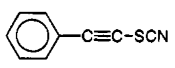
[8] For the synthesis of organic *N,N*-disubstituted dithiocarbamates, numerous methods are known. However, present reaction is still of great value to the synthesis, especially, of aryl *N,N*-DAD since troublesome chemicals such as thiophosgene or arenediazonium salts have been utilized for the synthesis: Walter, W.; Bode, K. D. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 281. Duus, F. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon Press: Oxford, 1979; Vol. 3, p 469.

[9] March, J. In *Advanced in Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; pp 411, 429, and 670.

[10] Wakefield, B. J. In *Organolithium Methods*; Academic Press: London, 1988; p 139.

[11] (a) Hogg, D. R. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon Press: Oxford, 1979; Vol. 3, p 302. (b) Harusawa, S.; Shioiri, T. *J. Synth. Org. Chem. Jpn.* **1981**, *39*, 741. For recent examples of the synthesis of organic thiocyanates, see: (c) Kitamura, T.; Furuki, R.; Zheng, L.; Fujimoto, T.; Taniguchi, H. *Chem. Lett.* **1992**, 2241. (d) Grudutt, K. N.; Rao, S.; Srinivas, P. *Indian J. Chem., Sect. B* **1991**, *30*, 343. (e) Kimura, T.; Fujita, M.; Ando, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1213. (f) Meda, H.; Kawaguchi, T.; Masui, M.; Ohmori, H. *Chem. Pharm. Bull.* **1990**, *38*, 1389. (g) Clark, J. H.; Jones, C. W.; Duke, C. V. A.; Miller, J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 81. (h) Saito, K.; Harada, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2562. (i) Kagabu, S.; Maehara, M.; Sawahara, K.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1485. (j) Ando, T.; Clark, J. H.; Cork, D. G.; Fujita, M.; Kimura, T. *J. Org. Chem.* **1987**, *52*, 681. (k) Barluenga, J.; Martinez-Gallo, J. M.; Najera, C.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1017. (l) Akelah, A.; Galil, A.; Fathy, M. *Phosphorus Sulfur* **1987**, *30*, 91. (m) Nishiyama, K.; Oba, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2692. (n) Schneider, H.-J.; Busch, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 911. (o) Trifonov, A.; Nikiforov, T. *J. Mol. Catal.* **1984**, *24*, 15. (p) Landini, D.; Maria, A.; Montanari, F. *J. Am. Chem. Soc.* **1984**, *106*, 2917. (q) Testaferri, L.; Tiecco, M.; Chianelli, D.; Montanucci, M. *Phosphorus Sulfur* **1983**, *15*, 263. (r) Molina, P.; Alajarin, M.; Ferao, A.; Lidon, M. J.; Fresneda, P. M.; Vilaplana, M. J. *Synthesis* **1982**, 472.

Table 2. Synthesis of Organic Thiocyanates

entry	starting material	lithiation condition	RSCN	yield[a](%)
17				89 (94)
18		n-BuLi, -78 °C		87
19		n-BuLi, -78 °C		89
20		n-BuLi, -78 °C		90
21		n-BuLi, -78 °C		81
22		s-BuLi, TMEDA, -78 °C		81
23		n-BuLi, 0 °C		85
24		n-BuLi, 0 °C		91
25		n-BuLi, 0 °C		90
26		n-BuLi, 0 °C		91
27		2eq t-BuLi, -78 °C		72
28	n-C_4H_9—C≡C—H	n-BuLi, -78 °C	n-C_4H_9—C≡C—SCN	83
29		n-BuLi, -78 °C		79
30	n-C_4H_9Li		n-C_4H_9SCN	90
31	t-C_4H_9Li		t-C_4H_9SCN	60

[a] Isolated yields. The value in parentheses was determined by GLC.

our new reaction provides an efficient and general method for the syntheses of a wide variety of organic thiocyanates.[12]

Finally, in order to know about the NCS-induced displacement of organozinc compounds with SCN^- in detail, control experiments were run using a substitute for each component. The results were summarized in Table 3.

(1) Metal species: No phenylmetal compounds generated in situ from $Hg(SCN)_2$ + PhLi, $Pb(SCN)_2$ + PhLi, or KSCN + PhLi allowed a yield of PhSCN even after the addition of NCS to each mixture. Thus, Zn^{2+} is the best leaving group among the metal ions examined for the NCS-induced displacement of organometallic com-

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(12) For application of organic thiocyanates to organic syntheses, see, for example: (a) Kochetkov, N. K.; Malysheva, N. N.; Klimov, E. M.; Demchenko, A. V. *Tetrahedron Lett.* **1992**, *33*, 381. (b) Nikifovov, T. T.; Connolly, B. A. *Tetrahedron Lett.* **1991**, *32*, 3851. (c) Davis, R. C.; Grinter, T. J.; Leaver, D.; O'Neil, R. M.; Gordon, A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2881. (d) Al-Rawi, J. M. A.; David, R. Y.; Elvidge, J. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2499. (e) de Jong, R. L. P.; Meijer, J.; Sukhai, R. S.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 310.

Table 3. Effect of Reaction Components on Thiocyanation of Phenylmetals

entry	phenylmetals	SCN^- source	oxidant	yield[a] (%)
17	PhLi	$Zn(SCN)_2$	NCS	94
32	PhLi	$Hg(SCN)_2$	NCS	0
33	PhLi	$Pb(SCN)_2$	NCS	0
34	PhLi	KSCN	NCS	0
35	PhLi (2 equiv)	$Zn(SCN)_2$	NCS	85
36	PhZnCl	KSCN	NCS	15
37	PhZnCl	Bu_4NSCN	NCS	55
38	PhZnCl	ClSCN		48
39	PhZnCl	$(SCN)_2$		59
40	PhZn(OTf)	$(SCN)_2$		53
41	PhLi	$Zn(SCN)_2$	NBS	70 (PhBr 14)
42	PhLi	$Zn(SCN)_2$	NIS	<1 (PhI 57)
43	PhLi	$Zn(SCN)_2$	Cl_2	14

[a] Yields were determined by GLC.

pounds not only with *N,N*-DAD^- (Table 1) but also with SCN^-. The polarity of the C−Zn bond ("slightly polar")[13] and/or Lewis acidity of Zn^{2+} species[13] might account for predominant reactivity of zinc over other metals.[14]

(2) Oxidizing reagent: NBS promoted the thiocyanation of phenylzinc(II) compound to afford PhSCN in a yield of 70%. In this run, bromobenzene was also formed in a yield of 14%. In contrast to NCS and NBS, NIS induced iodination reaction only.

(3) SCN^- species: A combination of $ZnCl_2$ with some SCN^- source including insoluble KSCN and soluble Bu_4NSCN is less effective for the thiocyanation. Thiocyanogen halides are plausible intermediates resulting from the reaction of NCS or NBS with SCN^- and well-known reactive electrophile.[15] In fact, formation of PhSCN was observed in the reaction of PhZnCl with ClSCN which was prepared by the reaction of $(SCN)_2$ with Cl_2,[15] but the yield was only in 50%. Thus, $Zn(SCN)_2$ was the best SCN^- source for the thiocyanate synthesis.

The exact nature of reaction mechanism is not clear at present. The results summarized in Tables 2 and 3 indicate that a combination of organolithium compounds, $Zn(SCN)_2$, and NCS is essential for the high yield synthesis of organic thiocyanates. Substitution of one of these components gave a lower yield or resulted in no reaction. The reaction of organolithium compounds with Zn(II) salts has been widely used for the preparation of organozinc compounds.[16] In fact, the ^{13}C NMR spectrum of the mixture of phenyllithium with $Zn(SCN)_2$ in THF was very similar to that prepared with $ZnCl_2$ (see supporting information) and thus indicated formation of organozinc compound(s) in the reaction mixture. As a plausible intermediate, organozinc thiocyanates such as RZn(SCN) and $[RZn(SCN)_2]Li$ would be proposed. The importance of innersphere SCN^- was evidenced by the control experiments using outer SCN^- and independently prepared ClSCN or $(SCN)_2$ as described above. Oxidative decomposition of organotransition metal complexes generally proceed by the oxidation of the metal center following reductive elimination.[17] However, formation of high valent organozinc compounds, i.e., organozinc(III) species, would be rather rare[18] and is not evidenced in the case of these reactions. Thus, NCS acts as an oxidant for the coordinated SCN^- or carbanion center[19] rather than Zn^{2+}, and the products would be derived by the coupling of the organic group with SCN^- on the zinc metal.

In conclusion, a new methodology for the construction of bonds between carbon fragments from organozinc compounds and some thio-nucleophiles was advanced, which not only, practically, afforded an effective synthetic method for organic *N,N*-DAD or organic thiocyanates but also made us recognize the importance of organozinc compounds as synthetic reagents, again.

Experimental Section

General. 1-Bromocyclooctene,[20] 2-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline,[21] thiocyanogen,[22] and thiocyanogen chloride[15] were prepared according to the standard methods described in the literature. All other chemicals were commercial products and were used without further purification. ^1H NMR and ^{13}C NMR spectra were determined in $CDCl_3$ at 200 and 50 MHz, respectively.

General Procedure for the Reaction with *N,N*-DAD^-. $Zn(DAD)_2$ (2.4 mmol) was dried by air-gun heating for 5 min under vacuum (1 mmHg). To the solid, THF (4 mL), RLi-solution (2.0 mmol), and NCS (320 mg, 2.4 mmol) were added successively at 0 °C under nitrogen, and the whole solution was allowed to slowly warm to room temperature with stirring. After 20 h, the resulting mixture was quenched by addition of aqueous NaOH. Workup by extraction with ether, washing with water, drying with $MgSO_4$, and evaporation of the solvent afforded a crude product which was chromatographed on silica gel with hexane as eluent. The yield is given in Table 1.

Phenyl *N,N*-dibutyldithiocarbamate:[23] colorless oil: IR (neat) 1070 cm^{-1}; ^1H NMR δ 1.0 (6H, q, $J = 6.3$ Hz), 1.4 (4H, m), 1.7 (4H, m), 3.8 (2H, t, $J = 7.2$ Hz), 4.0 (2H, t, $J = 7.2$ Hz), 7.4 (5H, s); ^{13}C NMR δ 9.7, 16.2, 25.5, 49.1, 51.2, 124.9, 125.7, 128.0, 133.1, 192.4. Anal. Calcd for $C_{15}H_{23}NS_2$: C, 64.0; H, 8.2; N, 5.0. Found: C, 64.13; H, 8.32; N, 5.11.

General Procedure for the Reaction with SCN^-. $Zn(SCN)_2$ (364 mg, 2.0 mmol) was dried by air-gun heating for 5 min under vacuum (1 mmHg). To the solid were successively added THF (4 mL) and RLi solution (2.0 mmol) at −78 °C under nitrogen, and the resulting mixture was allowed to stir for 1 h at 0 °C. Then NCS (267 mg, 2.0 mmol) in CH_2Cl_2 (4.4 mL) was added dropwise to the solution at 0 °C, and the whole solution was allowed to stir for 10 min at the temperature. The resulting mixture was quenched by addition of aqueous NaOH. Workup by extraction with ether, washing with water, drying with $MgSO_4$, and evaporation of the solvent afforded an almost pure product which was chromatographed on silica gel with hexane, hexane/ethyl acetate, or hexane/CH_2Cl_2 as eluent (method A) or was distilled by means of a Kugelrohr distillation apparatus (method B). The yield is given in Table 2.

4-(Trifluoromethyl)phenyl Thiocyanate. Method A: mp 30−30.5 °C; ^1H NMR δ 7.6 (s); ^{13}C NMR δ 108.7, 123.3 (q, $J = 272.1$ Hz), 126.9 (q, $J = 3.8$ Hz), 129.0, 131.4 (q, $J = 33.3$ Hz). Anal. Calcd for $C_8H_4F_3NS$: C, 47.3; H, 2.0; N, 6.9. Found: C, 47.26; H, 2.15; N, 6.75.

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2,6-Dimethylphenyl Thiocyanate.[24] Method A: mp 62–62.5 °C; IR ($CDCl_3$) 2160 cm^{-1}; ^{1}H NMR δ 2.6 (6H, s), 7.1–7.3 (3H, m); ^{13}C NMR δ 21.8, 110.1, 122.7, 129.1, 130.9, 142.8. Anal. Calcd for C_9H_9SN: C, 66.2; H, 5.6; N, 8.6. Found: C, 66.22; H, 5.56; N, 8.58.

2-(*N,N*-Diethylcarbamoyl)phenyl Thiocyanate.[25] Method A: pale yellow oil; IR (neat) 2190, 1630 cm^{-1}; ^{1}H NMR δ 1.1–1.5 (6H, m), 3.1–3.8 (4H, m), 7.2–7.6 (3H, m), 7.8 (1H, m); ^{13}C NMR δ 12.4, 13.8, 39.2, 43.1, 110.6, 123.2, 126.9, 128.9, 130.5, 131.1, 137.5, 167.3; HRMS calcd for $C_{12}H_{14}N_2OS$ *m/z* 234.0828, found *m/z* 234.0844.

2-(4-Methoxy-2-thiocyanophenyl)-4,4-dimethyl-2-oxazoline. Method A: mp 118–119 °C; IR (Nujol) 2190 cm^{-1}; ^{1}H NMR δ 1.40 (6H, s), 3.90 (3H, s), 4.06 (2H, s), 6.88 (1H, dd, J = 9 Hz, 2.4 Hz), 7.41 (1H, d, J = 2.4 Hz), 7.80 (1H, d, J = 9 Hz); ^{13}C NMR δ 28.4, 55.6, 68.6, 78.8, 112.3, 112.9, 113.1, 117.3, 130.6, 131.3, 159.6, 161.9. Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.5; H, 5.4; N, 10.7. Found: C, 59.66; H, 5.55; N, 10.24.

2,4,6-Trimethoxyphenyl Thiocyanate. Method A: mp 160–161 °C; IR (Nujol) 2145 cm^{-1}; ^{1}H NMR δ 3.8 (3H, s), 3.9 (6H, s), 6.2 (2H, s); ^{13}C NMR δ 55.5, 56.3, 90.1, 91.6, 111.6, 161.4, 164.3. Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.3; H, 4.9; N, 6.2. Found: C, 53.04; H, 4.90; N, 6.09.

2-Furyl Thiocyanate.[26] Method A: pale yellow oil; IR (neat) 3150, 2190 cm^{-1}; ^{1}H NMR δ 6.54 (1H, dd, J = 3.4 Hz, 2.2 Hz), 6.92 (1H, d, J = 3.4 Hz), 7.68 (1H, d, J = 2.2 Hz). Anal. Calcd for C_5H_3NOS: C, 48.0; H, 2.4; N, 11.2. Found: C, 47.98; H, 2.62; N, 11.07.

1-Cyclooctenyl Thiocyanate. Method A: pale yellow oil; IR (neat) 2200 cm^{-1}; ^{1}H NMR δ 1.4–1.6 (8H, m), 2.25 (2H, m), 2.55 (2H, m), 6.15 (1H, t, J = 10 Hz); ^{13}C NMR δ 25.5, 26.1, 27.9, 29.3, 30.6, 111.0, 125.3, 136.5; HRMS calcd for $C_9H_{13}NS$ *m/z* 167.0770, found *m/z* 167.0758.

1-Hexynyl Thiocyanate.[27] Method B: colorless oil; IR (neat) 2200, 2160 cm^{-1}; ^{1}H NMR δ 0.9 (3H, t, J = 6.4 Hz), 1.2–1.7 (4H, m), 2.4 (2H, t, J = 6.4 Hz); ^{13}C NMR δ 13.3, 19.7, 21.8, 29.8, 52.4, 102.4, 107.1; HRMS calcd for C_7H_9NS *m/z* 139.0457, found *m/z* 139.0464.

***tert*-Butyl Thiocyanate.**[28] Method B: pale yellow oil; IR (neat) 2150 cm^{-1}; ^{1}H NMR δ 1.5 (s); ^{13}C NMR δ 30.8, 52.0, 111.9; HRMS calcd for C_5H_9NS *m/z* 115.0457, found *m/z* 115.0459.

Reaction of Phenylzinc Chloride with Thiocyanogen Chloride. Thiocyanogen chloride solution was prepared by mixing quantitative amounts of thiocyanogen (0.5 M in CH_2Cl_2)[22] and chlorine (1 M in CH_2Cl_2) and used immediately. At 0 °C, 4 mmol of thiocyanogen chloride (0.66 M in CH_2Cl_2) was added to the solution, which was prepared from $ZnCl_2$ (1.5 mmol), phenyllithium (1.7 mmol, 1.8 M in cyclohexane–ether), and THF (5 mL) separately at −70 °C, and the resulting mixture was stirred for 30 min. The mixture was then treated by aqueous NaOH and extracted by ether. Gas chromatographic analysis of the extract (PEG 20M, 3 m, 160 °C) showed formation of 48% yield of phenyl thiocyanate.

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Supporting Information Available: ^{13}C-NMR spectra of phenylzinc compounds prepared by the reactions of PhLi with zinc(II) salts in THF/THF-d_8, ^{1}H- and ^{13}C-NMR spectra of 2-(4-methoxy-2-thiocyanophenyl)-4,4-dimethyl-2-oxazoline, and 1-cyclooctenyl thiocyanate (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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