DOI: 10.1002/ejoc.200800258

Transformation of *gem*-Dicyanoethenes by Samarium: Direct Formation of Indenes or Direct Decyanation with in Situ Disilylation

Yongjun Liu,[a] Fuqiang Zhang,[a] Yan Qi,[a] Yongmin Zhang,[b] and Shusheng Zhang*[a]

Keywords: Samarium / Fused-ring systems / Dicyanoethenes / Cyanides / Disilylation

Intramolecular cyclization of 1,1-diaryl-2,2-dicyanoethenes promoted by samarium metal in DMF in the presence of TMSCl allowed direct construction of the indene core, whereas 1-alkyl-1-aryl-2,2-dicyanoethenes underwent intermolecular coupling cyclization and decyanation under the same conditions. Simultaneously, disilylation occurred at the amino moiety resulting from the reduction of the cyano group. However, only simple reduction of the C=C bonds is observed when a trace amount of water presented.

Introduction

As important synthetic intermediates, more and more indenes and their derivatives have been widely used in pharmaceutics, catalysis, metal complexes, polymer chemistry, and the synthesis of natural products.[1] To date, several synthetic methodologies towards indenes have been described.[2–5] Recently, Gridnev et al. and Yamamoto et al. reported Pd-catalyzed or Pt-catalyzed intramolecular carbalkoxylation reactions accompanied by an unprecedented 1,2-alkyl migration for the synthesis of functionalized indenes.[3] Additionally, Larock et al. reported a convenient method for the preparation of indenes by the palladium-catalyzed carboannulation of internal alkynes with functionally substituted aryl halides.[4] A very recent study reported a convenient approach for the synthesis of 2,3-disubstituted indenes from diethyl 2-[2-(1-alkynyl)phenyl]malonates and a wide variety of organic halides.[5] In most cases, however, the formation of the indene skeleton requires laborious operational procedures and relatively harsh reaction conditions.

In the last decade, samarium reagent promoted cyclizations have been developed as an alternative synthetic methodology for organic transformations, especially for the syntheses of natural products.[6] The direct use of metallic samarium as a reducing agent in organic syntheses has recently attracted the attention of a number of organic chemists.[7] By virtue of the potential transformations that samarium can induce in synthetic chemistry, various original means were adopted to try many organic reactions and many unprecedented reactions were developed in the course of these attempts.[8] The mild and selective nature of samarium has led to its widespread application in target synthesis, and an array of cyclization protocols have been employed successfully to assemble many different ring systems.[6,9] In some cases, an inducing reagent should be used to activate samarium metal, for example, TMSCl, which usually acts as an activator in reduction reactions promoted by metals such as titanium.[10] Commonly, THF is the preferred reaction medium in organic reactions containing samarium,[9] but we have explored some drastically interesting characteristics of metallic samarium as a reducing agent when *N*,*N*-dimethylformamide (DMF) is used as the solvent.[11] Herein we wish to report the interesting transformation of 1,1-dicyanoethenes when treated with samarium/TMSCl in DMF.

Results and Discussion

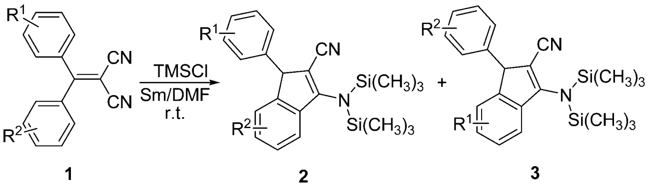
Intramolecular Cyclization and Disilylation of 1,1-Dicyano-2,2-diarylethenes Promoted by Samarium in DMF in the Presence of TMSCl: Construction of Indene Skeletons

As shown in Scheme 1, when 1,1-dicyano-2,2-diarylethenes (**1**) were treated with samarium metal in the presence of TMSCl in DMF, polysubstituted indenes **2** and **3** were obtained in moderate-to-excellent yields. The results of the influence of the substituents and regioselectivity are summarized in Table 1.

Though two kinds of indenes were afforded, the reaction was regioselective. With all the substrates tested, indenes with a relatively electron-rich aromatic ring were preferentially formed and, therefore, predominated in the products

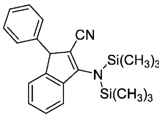
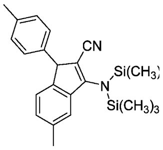
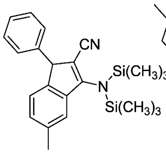
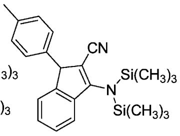
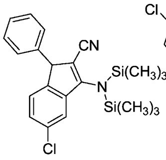
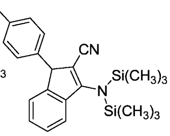
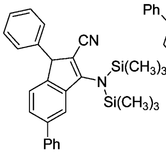
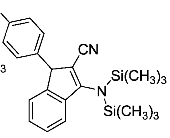
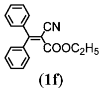
---

[a] Key Laboratory of Eco-chemical Engineering, Ministry of Education; College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology,
Qingdao 266042, P. R. China
Fax: +86-532-84023927
E-mail: shushzhang@126.com
[b] Department of Chemistry, Zhejiang University,
Hangzhou 310028, P. R. China



Scheme 1.

Table 1. Regioselective intramolecular cyclization and disilylation of 1,1-dicyano-2,2-diarylethenes promoted by samarium in DMF in the presence of TMSCl.

Entry	R^1, R^2	Time [min]	Products		Yield [%][a]
			2	**3**	
1	H, H (**1a**)	40			87 (**2a**)
2	4-CH_3, 4-CH_3 (**1b**)	35			92 (**2b**)
3	4-CH_3, H (**1c**)	30			90 (**2c**/**3c**, 74:26)[b]
4	4-Cl, H(**1d**)	25			64 (**2d**/**3d**, 5:95)[b]
5	4-Ph, H (**1e**)	40			47 (**2e**/**3e**, 100:0)[c]
6	 (**1f**)	30			–[d]
7	4-CH_3, 4-CH_3 (**1b**)	40			–[d,e]

[a] Isolated yields based on substrates **1**. [b] The ratios were determined by ^{1}H NMR spectroscopy. [c] Isolated products. [d] A complex mixture was obtained. [e] DMSCl (dimethyldichlorosilane) was used instead of TMSCl.

(see Table 1 for ratios of **2**/**3**). Nevertheless, attempts to extend the intramolecular cyclization to 1,1-diphenyl-2-cyano-2-ethoxycarbonylethylene (Table 1, entry 6) were not successful and only a complex mixture was obtained.

It should be pointed out that the adoption of TMSCl is essential here, as the reaction did not proceed in the absence of TMSCl. When DMSCl (Table 1, entry 7) was used instead of TMSCl, the reaction failed. At the same time, the use of DMF is indispensable to this reaction. When THF was used as the solvent, the reaction failed to give the desired indenes but the C=C bonds of 1,1-dicyano-2,2-diarylethenes were reduced.

In addition to the NMR and IR spectroscopic and MS data of products **2**, a single-crystal X-ray diffraction structure of **2a** was obtained. It determined unambiguously that product **2** has an indene core and that the two trimethylsilyl groups are attached to the nitrogen atom (Figure 1). Furthermore, the fact that all products **2** share similar data suggests similar structures for these compounds.

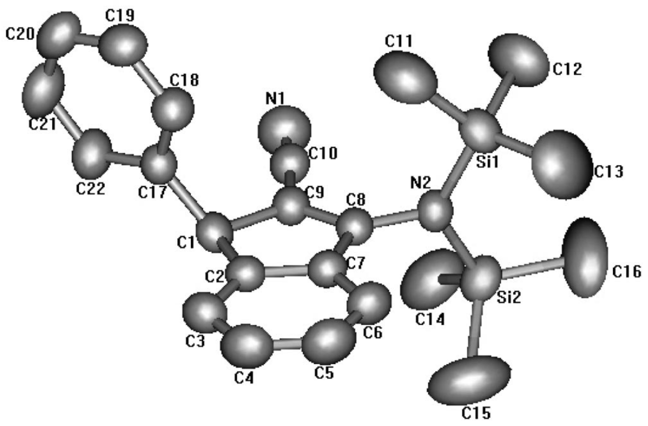
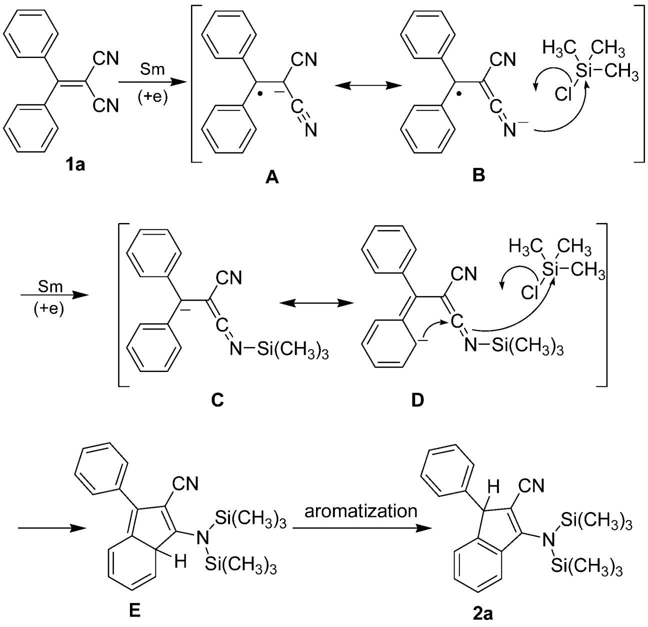


Figure 1. The crystal structure of **2a**.

1,1-Dicyano-2,2-diarylethylenes, like diaryl ketones, were reported to be able to form stable radical anions as a result of the similarity between the $C=C(CN)_2$ and C=O groups.[11] On the basis of this property, the reductive cross-coupling reaction of 1,1-diaryl-2,2-dicyanoethylenes or 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes with aromatic nitriles mediated by samarium diiodide were successfully realized to prepare polysubstituted 3*H*-pyrroles.[12] On the basis of the previous work and the results presented in this paper, the following tentative reaction pathway is proposed as a rational mechanism (Scheme 2). First, radical anion intermediate **A** is formed by electron transfer from samarium to substrate **1**.[11] Structure **A** would be in resonance with structure **B**, which reacts with the TMSCl electrophile and then accepts another electron from samarium to afford anion **C**. Anion **C** would be in resonance with **D**, the carbon atom of which attacks the C=C=N moiety, possibly in a Michael-type fashion. Silylation at the N atom forms **E**, which aromatizes (possibly by two 1,5-H shifts) to produce final product **2a**.

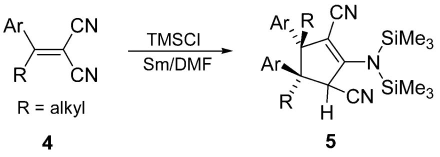
This is a rare example of an in situ silylation reaction with the use of TMSCl in the presence of samarium reagents, although TMSCl usually acts as an activator in some reductive reactions promoted by metal, for example, samarium and titanium,[7,9,13] and may constitute a potentially alternative protocol for the synthesis of organosilanes or for the protection of sensitive groups such as hydroxy, amino, etc.[14,15]



Scheme 2.

Intermolecular Cyclization, Decyanation and Disilylation of 1,1-Dicyano-2-aryl-2-alkylethylenes Promoted by Samarium in DMF in the Presence of TMSCl

In the interest to clarify the influence of the substituent on the dicyanoethylene, 1,1-dicyano-2-aryl-2-alkylethylenes **4** were used instead of **1** to expand the investigation. Instead of the formation of the anticipated indene product, an intermolecular coupling, cyclization, and unusual decyanation sequence occurred to produce cyclic products in high yields (Scheme 3).



Scheme 3.

As shown in Scheme 3, when alkylethylenes **4** were used, another interesting phenomenon came forth, which was that one of the cyano groups was eliminated during the reaction process. The removal of the cyano group is extraordinarily considered to be a particular protocol not only for synthetic chemistry in which reductive decyanation reactions are usually difficult and only a few examples are available under reductive conditions,[16] but also for the exploration and application of samarium reagents that rarely exhibited the ability so far to reductively cleave a carbon–carbon single bond in previously known reports.

To investigate the scope and generality of this disilylation reaction, a number of 1,1-dicyano-2-aryl-2-alkylethylenes were used in this reaction and the results are summed up in Table 2. Although 1,1-dicyano-2-methyl-2-(2,4-dichlorophenyl)ethylene (**4g**) reacted smoothly with good yields to afford product **5g** (Table 2, entry 7), the desired disilylation products were not formed when the *ortho* positions of the phenyl rings of substrates **4** were occupied by a methyl group or a bromine atom, probably due to the bigger size of the methyl group or bromine atom than that of the chlorine atom (Table 2, entries 11 and 12), which may bring enough steric hindrance to make the coupling cyclization difficult. The rate of reduction of the nitro groups was faster than that of the alkene–nitrile system, thereby leading to a complex mixture of products when **4j** was used (Table 2, entry 10). The results also show that substrates attached to electron-withdrawing groups (chlorine, bromine) require longer reaction times and thus afford the corresponding products in lower yields.

Table 2. Samarium-promoted intermolecular cyclization–decyanation and disilylation of 1,1-dicyano-2-aryl-2-alkylethenes in the presence of TMSCl.

Entry	Ar, R in **4**	Time [min]	Product	Yield [%][a]
1	Ph, CH_3 (**4a**)	30	**5a**	92
2	4-$CH_3C_6H_4$, CH_3 (**4b**)	35	**5b**	87
3	4-PhC_6H_4, CH_3 (**4c**)	30	**5c**	90
4	4-ClC_6H_4, CH_3 (**4d**)	45	**5d**	71
5	4-BrC_6H_4, CH_3 (**4e**)	45	**5e**	65
6	4-$CH_3OC_6H_4$, CH_3 (**4f**)	30	**5f**	91
7	2,4-$Cl_2C_6H_3$, CH_3 (**4g**)	45	**5g**	77
8	Ph, C_2H_5 (**4h**)	35	**5h**	85
9	4-$CH_3C_6H_4$, C_2H_5 (**4i**)	30	**5i**	92
10	4-$NO_2C_6H_4$, CH_3 (**4j**)	45		–[b]
11	2-BrC_6H_4, CH_3 (**4k**)	45		–[b]
12	2-$CH_3C_6H_4$, CH_3 (**4l**)	45		–[b]

[a] Isolated yields based on substrates **4**. [b] A complex mixture was obtained.

The decyanation was confirmed by single-crystal X-ray diffraction analysis of **5f** (Figure 2), which unambiguously shows the presence of only two cyano groups in the molecule. In the HMQC spectrum (Figure 3), the only hydrogen atom (δ = 4.48 ppm in ^{1}H NMR) located in the five-member ring is correlated with the carbon atom (δ = 48.9 ppm in ^{13}C NMR). The series of compounds **5** share similar spectroscopic data, which suggests that the structures of these compounds are similar.

The characteristic process of disilylation is also smoothly realized here by following a pathway similar to that in Scheme 2. However, with only one aryl group, intermediate **F** (Scheme 4) is much less stable than **A** in Scheme 2; therefore, the radical dimerization reaction occurs rapidly as soon as **F** is produced. Intermediate **G** undergoes disilylation in the presence of TMSCl and compound **5a′** is thus formed. One of the cyano groups of **5a′** is removed in situ by samarium, possibly in a β-elimination manner by two single-electron transfer steps to the acrylonitrile fragment of **5a′**, which has been proven to be unstable in some cases in the presence of SmI_2.[16b,17] After acidification during the workup procedure, final product **5a** is afforded.

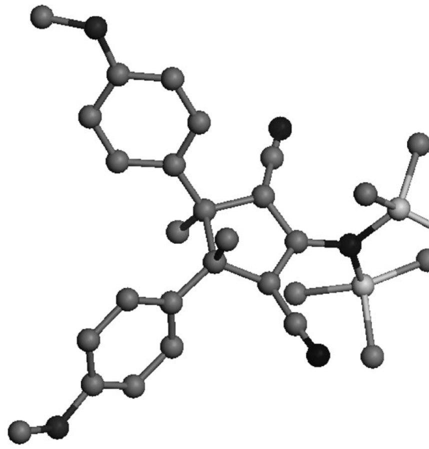


Figure 2. The crystal structure of **5f**.

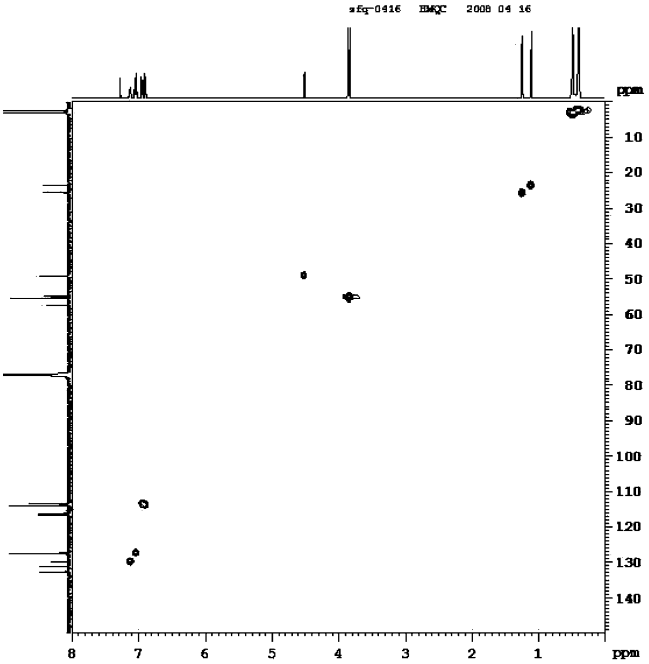
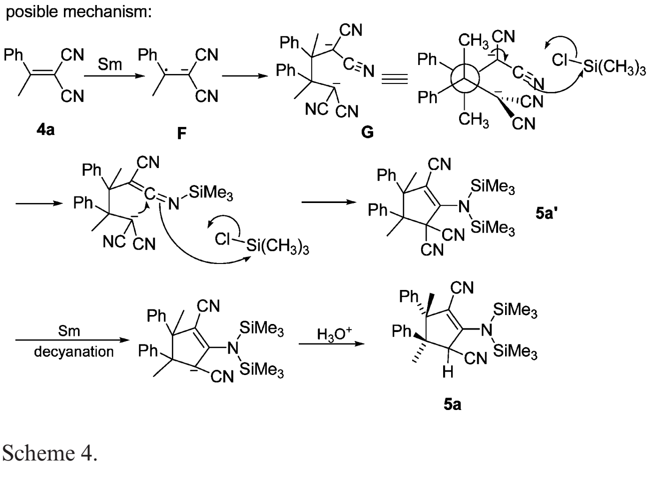
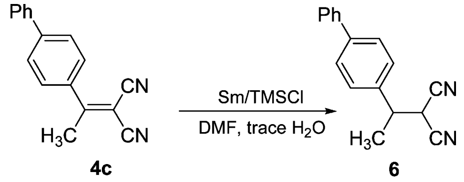


Figure 3. HMQC of **5f**.



Scheme 4.

Our experimental results also show that the cyclization–silylation of dicyanoethylenes is strongly sensitive to water, which may react with TMSCl to form HCl to promote the reductive ability of samarium, but on the other hand, it may also counteract the formation of the carbon anion. As an example (Scheme 5), when a trace amount of water was present in the reaction mixture of **4c** under the established conditions, both the cyclization and the disilylation failed to proceed, but the reduction of the C=C bond occurred to afford simple reduction products **6** in low yields, whereas only a complicated mixture was obtained when alcohol was used instead of water.



Scheme 5.

Conclusions

In the presence of TMSCl in DMF, metallic samarium exhibits the ability to realize the intramolecular cyclization of 1,1-diaryl-2,2-dicyanoethenes to afford indenes or to promote the intermolecular cyclization–decyanation of 1,1-dicyano-2-aryl-2-alkylethylenes to afford cyclopentamines, followed by an in situ disilylation of the amino groups. Under mild reaction conditions, short reaction times, easy operational procedures, and high product yields, not only does this reaction proceed regioselectively, but it also provides a promising protocol for either the construction of the indene core or the silylation of an amino group. As a reasonable result, the disilylation process is sensitive to proton sources such as water, which make the reaction complicated, and only the products resulting from reduction of the C=C bond are obtained in low yields.

Experimental Section

General: All NMR spectra were measured in $CDCl_3$ or $[D_6]DMSO$ and recorded with a Bruker AV 500 spectrometer (500 and 125 MHz for ^1H and ^{13}C, respectively) with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz. IR spectra were recorded with a Nicolet FTIR Magna-750 spectrometer. MS (EI) were determined with a HP5989B mass spectrometer. Elemental analyses were performed with a Vario-ELIII equipment. Single-crystal X-ray diffraction analyses were performed with a NONIUS-CAD4. Melting points are uncorrected. All the reactions in this paper were performed under a nitrogen atmosphere. DMF was redistilled from calcium hydride before use.

Typical Procedure for the Synthesis of Indenes: To a mixture of samarium powder (0.3 g, 2 mmol) and 1,1-diphenyl-2,2-dicyanoethylene (0.46 g, 2 mmol) in freshly distilled DMF (10 mL) was added TMSCl (0.6 mL, 5 mmol, freshly distilled) at 30 °C with magnetic stirring under a nitrogen atmosphere. The resulting solution turned dark brown within 5 min and an exothermic reaction was observed. After completion of the reaction (about 40 min), dilute hydrochloric acid (1 M, 5 mL) was added, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was separated by column chromatography over silica gel (ethyl acetate/hexane, 1:5) to obtain **2a** (0.65 g, 87%).

Typical Procedure for the Synthesis of Compounds 5: To a mixture of samarium powder (0.3 g, 2 mmol) and 1-methyl-1-phenyl-2,2-dicyanoethylene (0.33 g, 2 mmol) in freshly distilled DMF (10 mL) was added TMSCl (0.6 mL, 5 mmol, freshly distilled) at 40 °C with magnetic stirring under a nitrogen atmosphere. The resulting solution turned dark brown within 5 min and an exothermic reaction was observed. After completion of the reaction (about 40 min), dilute hydrochloric acid (1 M, 5 mL) was added, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was separated by column chromatography over silica gel (ethyl acetate/hexane, 1:5) to obtain **5a** (0.42 g, 92%).

Procedure for the Reduction of Compound 4c: To a mixture of samarium powder (0.15 g, 1 mmol), and **4c** (0.24 g, 1 mmol) in freshly distilled DMF (5 mL) was added TMSCl (0.25 mL, 2 mmol, freshly distilled) and distilled water (0.004 mL, 0.2 mmol) at room temperature with magnetic stirring under a nitrogen atmosphere. The resulting solution turned yellow within 5 min and an exothermic reaction was observed. After completion of the reaction (about 40 min), dilute hydrochloric acid (1 M, 3 mL) was added, and the resulting mixture extracted with ethyl acetate (3 × 5 mL). The combined organic layer was washed with brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was separated by column chromatography over silica gel (ethyl acetate/hexane, 1:5) to obtain **6** (0.14 g, 58%).

3-[Bis(trimethylsilyl)amino]-1-phenyl-1*H*-indene-2-carbonitrile (2a): Colorless prism, m.p. 129–130 °C. IR (KBr): $\tilde{\nu}$ = 3065, 2956, 2207, 1587, 1557, 1498 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.29–7.49 (m, 6 H), 7.21–7.23 (m, 1 H), 7.12–7.13 (m, 2 H), 5.13 (s, 1 H), 0.22 (s, 9 H), 0.19 (s, 9 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 164.2, 147.3, 143.0, 137.1, 129.2, 129.1, 128.1, 127.8, 127.7, 124.6, 121.6, 117.4, 113.4, 54.5, 2.5, 2.3 ppm. MS (EI): *m*/*z* (%) = 377 (5.09) [M + 1]$^+$, 376 (13.69) [M]$^+$, 361 (31.27), 303 (3.33), 288 (2.38), 287 (4.19), 77 (2.55), 73 (100). $C_{22}H_{28}N_2Si_2$ (376.64): calcd. C 70.16, H 7.49, N 7.44; found C 70.34, H 7.50, N 7.42.

3-[Bis(trimethylsilyl)amino]-5-methyl-1-*p*-tolyl-1*H*-indene-2-carbonitrile (2b): Colorless prism, m.p. 142–143 °C. IR (KBr): $\tilde{\nu}$ = 3064, 2955, 2205, 1557, 1513 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.20–7.21 (m, 2 H), 7.14–7.16 (m, 2 H), 7.07–7.09 (m, 1 H), 6.97–6.99 (m, 2 H), 4.99 (s, 1 H), 2.40 (s, 3 H), 2.28 (s, 3 H), 0.21 (s, 9 H), 0.19 (s, 9 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 164.0, 144.8, 143.2, 137.5, 137.3, 134.2, 130.0, 129.8, 127.9, 124.3, 122.0, 117.6, 113.8, 53.8, 21.9, 21.2, 2.6, 2.4 ppm. MS (EI): *m*/*z* (%) = 405 (6.66) [M + 1]$^+$, 404 (17.85) [M]$^+$, 389 (42.59), 331 (12.58), 316 (2.10), 301 (8.98), 91 (1.69), 73 (100) ppm. $C_{24}H_{32}N_2Si_2$ (404.70): calcd. C 71.23, H 7.97, N 6.92; found C 71.31, H 7.94, N 6.95.

3-[Bis(trimethylsilyl)amino]-5-methyl-1-phenyl-1*H*-indene-2-carbonitrile (2c): Obtained as an inseparable mixture with **3c** (see Table 1). White solid. IR (KBr): $\tilde{\nu}$ = 3065, 2955, 2206, 1557, 1513 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 6.99–7.42 (m, 8 H), 4.75 (s, 1 H), 2.35 (s, 3 H), 0.26 (s, 9 H), 0.24 (s, 9 H) ppm. MS (EI): *m*/*z* (%) = 391 (9.73) [M + 1]$^+$, 390 (26.78) [M]$^+$, 375 (53.36), 317 (9.04), 301 (4.74), 287 (10.57), 77 (1.05), 73 (100). $C_{23}H_{30}N_2Si_2$ (390.67): calcd. C 70.71, H 7.74, N 7.17; found C 70.59, H 7.88, N 7.13.

3-[Bis(trimethylsilyl)amino]-1-*p*-tolyl-1*H*-indene-2-carbonitrile (3c): Obtained as an inseparable mixture with **2c** (see Table 1). White solid. IR (KBr): $\tilde{\nu}$ = 3065, 2955, 2206, 1557, 1513 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 6.99–7.42 (m, 8 H), 4.74 (s, 1 H), 2.45 (s, 3 H), 0.27 (s, 9 H), 0.25 (s, 9 H) ppm. MS (EI): *m*/*z* (%) = 391 (9.73) [M + 1]$^+$, 390 (26.78) [M]$^+$, 375 (53.36), 317 (9.04), 301 (4.74), 287 (10.57), 91 (1.44), 73 (100). $C_{23}H_{30}N_2Si_2$ (390.67): calcd. C 70.71, H 7.74, N 7.17; found C 70.59, H 7.88, N 7.13.

3-[Bis(trimethylsilyl)amino]-5-chloro-1-phenyl-1*H*-indene-2-carbonitrile (2d): Obtained as an inseparable mixture with **3d** (see Table 1). White solid. IR (KBr): $\tilde{\nu}$ = 3060, 2956, 2208, 1600, 1556, 1493, 1454 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.04–7.44 (m, 8 H), 4.78 (s, 1 H), 0.27 (s, 9 H), 0.24 (s, 9 H) ppm. MS (EI): *m*/*z* (%) = 411 (2.85) [M + 1]$^+$, 410 (7.44) [M]$^+$, 397 (12.15), 395 (27.30), 337 (1.84), 73 (100). $C_{22}H_{27}ClN_2Si_2$ (411.09): calcd. C 64.28, H 6.62, N 6.81; found C 64.33, H 6.67, N 6.91.

3-[Bis(trimethylsilyl)amino]-1-(4-chlorophenyl)-1*H*-indene-2-carbonitrile (3d): Obtained as an inseparable mixture with **2d** (see Table 1). White solid. IR (KBr): $\tilde{\nu}$ = 3060, 2956, 2208, 1600, 1556, 1493, 1454 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.04–7.44 (m, 8 H), 4.76 (s, 1 H), 0.28 (s, 9 H), 0.26 (s, 9 H) ppm. MS (EI): *m*/*z* (%) = 411 (2.85) [M + 1]$^+$, 410 (7.44) [M]$^+$, 397 (12.15), 395 (27.30), 337 (1.84), 77 (1.90), 73 (100). $C_{22}H_{27}ClN_2Si_2$ (411.09): calcd. C 64.28, H 6.62, N 6.81; found C 64.33, H 6.67, N 6.91.

3-[Bis(trimethylsilyl)amino]-1,5-diphenyl-1*H*-indene-2-carbonitrile (2e): White solid, m.p. 145–146 °C. IR (KBr): $\tilde{\nu}$ = 3030, 2924, 2208, 1600, 1558, 1494, 1452 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.16–7.62 (m, 13 H), 4.84 (s, 1 H), 0.30 (s, 9 H), 0.28 (s, 9 H) ppm. MS (EI): *m*/*z* (%) = 453 (9.84) [M + 1]$^+$, 452 (16.57) [M]$^+$, 437 (25.82), 379 (3.99), 73 (100). $C_{28}H_{32}N_2Si_2$ (452.74): calcd. C 71.23, H 7.97, N 6.92; found C 71.37, H 7.93, N 6.99.

2-[Bis(trimethylsilyl)amino]-4,5-dimethyl-4,5-diphenylcyclopent-1-ene-1,3-dicarbonitrile (5a): Colorless crystals, m.p. 180–181 °C. IR (KBr): $\tilde{\nu}$ = 3430, 2969, 2218, 1616, 1498, 1256 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.35–7.46 (m, 6 H), 7.23–7.24 (m, 2 H), 7.13–7.15 (m, 2 H), 4.60 (s, 1 H), 1.29 (s, 3 H), 1.16 (s, 3 H), 0.51 (s, 9 H), 0.42 (s, 9 H) ppm. MS (EI): *m*/*z* (%) = 458 (3.87) [M + 1]$^+$, 457 (9.54) [M]$^+$, 442 (11.74), 384 (0.74), 73 (100). $C_{27}H_{35}N_3Si_2$ (457.76): calcd. C 70.84, H 7.71, N 9.18; found C 70.71, H 7.72, N 9.20.

2-[Bis(trimethylsilyl)amino]-4,5-dimethyl-4,5-di-*p*-tolylcyclopent-1-ene-1,3-dicarbonitrile (5b): Colorless crystals, m.p. 171–173 °C. IR (KBr): $\tilde{\nu}$ = 3032, 2956, 2214, 1617, 1516, 1454 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.01–7.20 (m, 8 H), 4.56 (s, 1 H), 2.40 (s, 3 H), 2.38 (s, 3 H), 1.26 (s, 3 H), 1.13 (s, 3 H), 0.51 (s, 9 H), 0.41 (s, 9 H) ppm. $C_{29}H_{39}N_3Si_2$ (485.81): calcd. C 71.70, H 8.09, N 8.65; found C 71.56, H 8.14, N 8.60.

2-[Bis(trimethylsilyl)amino]-4,5-dimethyl-4,5-bis(4-biphenyl)cyclopent-1-ene-1,3-dicarbo-nitrile (5c): Colorless crystals, m.p. 225–226 °C. IR (KBr): $\tilde{\nu}$ = 3032, 2959, 2216, 1631, 1448 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.09–7.69 (m, 18 H), 4.68 (s, 1 H), 1.27 (s, 3 H), 1.21 (s, 3 H), 0.55 (s, 9 H), 0.36 (s, 9 H) ppm. $C_{39}H_{43}N_3Si_2$ (609.95): calcd. C 76.80, H 7.11, N 6.89; found C 76.52, H 7.18, N 6.81.

2-[Bis(trimethylsilyl)amino]-4,5-bis(4-chlorophenyl)-4,5-dimethylcyclopent-1-ene-1,3-dicarbonitrile (5d): Colorless crystals, m.p. 236–237 °C. IR (KBr): $\tilde{\nu}$ = 2957, 2214, 1618, 1497, 1457 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.20–7.34 (m, 3 H), 6.98–7.14 (m, 3 H), 6.61–6.89 (m, 2 H), 4.52 (s, 1 H), 1.28 (s, 3 H), 1.15 (s, 3 H), 0.49 (s, 9 H), 0.34

(s, 9 H) ppm. $C_{27}H_{33}Cl_2N_3Si_2$ (526.65): calcd. C 61.58, H 6.32, N 7.98; found C 61.68, H 6.40, N 7.93.

2-[Bis(trimethylsilyl)amino]-4,5-bis(4-bromophenyl)-4,5-dimethylcyclopent-1-ene-1,3-dicarbonitrile (5e): Light-yellow crystals, m.p. 172–173 °C. IR (KBr): $\tilde{\nu}$ = 2956, 2213, 1618, 1494, 1452 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 6.66–7.30 (m, 8 H), 4.42 (s, 1 H), 1.28 (s, 3 H), 1.15 (s, 3 H), 0.50 (s, 9 H), 0.31 (s, 9 H) ppm. $C_{27}H_{33}Br_2N_3Si_2$ (615.55): calcd. C 52.68, H 5.40, N 6.83; found C 52.36, H 5.48, N 6.80.

2-[Bis(trimethylsilyl)amino]-4,5-bis(4-methoxyphenyl)-4,5-dimethylcyclopent-1-ene-1,3-dicarbonitrile (5f): Colorless crystals, m.p. 202–203 °C. IR (KBr): $\tilde{\nu}$ = 2962, 2217, 1615, 1516, 1461 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.09–7.12 (m, 2 H), 7.00–7.03 (m, 2 H), 6.90–6.92 (m, 2 H), 6.86–6.90 (m, 2 H), 4.48 (s, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 1.21 (s, 3 H), 1.08 (s, 3 H), 0.48 (s, 9 H), 0.39 (s, 9 H) ppm. ^{13}C NMR: δ = (CDCl$_3$): 158.8, 158.7, 158.6, 132.4, 130.9, 129.5, 127.1, 116.4, 116.2, 115.8, 113.6, 113.2, 57.1, 55.0, 54.7, 48.9, 25.4, 23.4, 3.0, 2.2 ppm. MS (EI): m/z (%) = 518.3 (100) [M + 1]$^+$. DEPT 135 (CDCl$_3$): 129.8, 127.4, 113.9, 113.5, 55.3, 49.1, 25.7, 23.6, 3.3, 2.4 ppm. $C_{29}H_{39}N_3O_2Si_2$ (517.81): calcd. C 67.27, H 7.59, N 8.11; found C 67.36, H 7.62, N 8.05.

2-[Bis(trimethylsilyl)amino]-4,5-bis(2,4-dichlorophenyl)-4,5-dimethylcyclopent-1-ene-1,3-dicarbonitrile (5g): Light-purple crystals, m.p. 176–177 °C. IR (KBr): $\tilde{\nu}$ = 3072, 2955, 2217, 1620, 1587, 1542, 1472 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.54–7.56 (m, 1 H), 7.43–7.45 (m, 1 H), 7.15–7.19 (m, 2 H), 7.04–7.06 (m, 2 H), 5.64 (s, 1 H), 1.97 (s, 3 H), 1.93 (s, 3 H), 0.45 (s, 9 H), 0.37 (s, 9 H) ppm. $C_{27}H_{31}Cl_4N_3Si_2$ (595.54): calcd. C 54.45, H 5.25, N 7.06; found C 54.28, H 5.17, N 6.99.

2-[Bis(trimethylsilyl)amino]-4,5-diethyl-4,5-diphenylcyclopent-1-ene-1,3-dicarbonitrile (5h): Colorless crystals, m.p. 177–178 °C. IR (KBr): $\tilde{\nu}$ = 3060, 2954, 2216, 1619, 1498, 1446 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.35–7.41 (m, 8 H), 7.01–7.08 (m, 2 H), 4.60 (s, 1 H), 1.91–2.08 (m, 1 H), 1.50–1.61 (m, 1 H), 1.30–1.43 (m, 1 H), 1.20–1.29 (m, 1 H), 0.83 (t, 3 H), 0.63 (t, 3 H), 0.54 (s, 9 H), 0.42 (s, 9 H) ppm. $C_{29}H_{39}N_3Si_2$ (485.81): calcd. C 71.70, H 8.09, N 8.65; found C 71.46, H 8.07, N 8.64.

2-[Bis(trimethylsilyl)amino]-4,5-diethyl-4,5-di-*p*-tolylcyclopent-1-ene-1,3-dicarbonitrile (5i): Colorless crystals, m.p. 215–216 °C. IR (KBr): $\tilde{\nu}$ = 3031, 2953, 2213, 1622, 1515, 1454 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.17–7.29 (m, 5 H), 6.93–7.00 (m, 3 H), 4.54 (s, 1 H), 2.38 (s, 3 H), 2.32 (s, 3 H), 1.94–1.98 (m, 1 H), 1.52–1.58 (m, 1 H), 1.29–1.39 (m, 1 H), 1.21–1.27 (m, 1 H), 0.80 (t, 3 H), 0.62 (t, 3 H), 0.52 (s, 9 H), 0.44 (s, 9 H) ppm. $C_{31}H_{43}N_3Si_2$ (513.86): calcd. C 72.46, H 8.43, N 8.18; found C 72.36, H 8.40, N 8.14.

2-[1-(4-Biphenyl)ethyl]malononitrile (6): Colorless crystals, m.p. 113–114 °C. IR (KBr): $\tilde{\nu}$ = 3074, 2975, 2214, 1633, 1486, 1409 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.64–7.66 (m, 2 H), 7.60–7.62 (m, 2 H), 7.39–7.50 (m, 5 H), 3.92 (d, J = 6 Hz, 1 H), 3.54 (m, 1 H), 1.72 (d, J = 7 Hz, 3 H) ppm. $C_{17}H_{14}N_2$ (246.31): calcd. C 82.90, H 5.73, N 11.37; found C 83.01, H 5.70, N 11.35.

CCDC-234282 (for **2a**) and -671772 (for **5f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Natural Science Foundation of Shandong Province (No. Z2006B01), the Project of Science and Technology of Shandong Province (No. 2006GG2203024), and the Foundation of Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (O4B0021400). The authors are grateful to Professor Gert J. Kruger (Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park, Johannesburg 2006, South Africa) for his help in determining the disordered model for structure **5f**.

---

[1] a) W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E. F. Paulus, *Organometallics* **1994**, *13*, 954–963; b) N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sirom, M. Moret, *Organometallics* **1990**, *9*, 3098–3105; c) R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965–994; d) J. Yang, M. V. Lakshmikantham, M. P. Cava, *J. Org. Chem.* **2000**, *65*, 6739–6742; e) D. F. Biggs, A. F. Casy, I. Chu, R. T. Coutts, *J. Med. Chem.* **1976**, *19*, 472–475.

[2] a) J. Holtsclaw, M. Koreeda, *Org. Lett.* **2004**, *6*, 3719–3722; b) M. J. Marsella, K. Yoon, S. Estassi, F. S. Tham, D. B. Borchardt, B. H. Bui, P. R. Schreiner, *J. Org. Chem.* **2005**, *70*, 1881–1884.

[3] a) I. Nakamura, G. B. Bajracharya, H. Wu, K. Oishi, Y. Mizushima, I. D. Gridnev, Y. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 15423–15430; b) I. Nakamura, G. B. Bajracharya, Y. Mizushima, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2002**, *41*, 4328–4331.

[4] D. Zhang, E. K. Yum, Z. Liu, R. C. Larock, *Org. Lett.* **2005**, *7*, 4963–4966.

[5] L.-N. Guo, X.-H. Duan, H.-P. Bi, X.-Y. Liu, Y.-M. Liang, *J. Org. Chem.* **2006**, *71*, 3325–3327.

[6] D. J. Edmonds, D. Johnston, D. J. Procter, *Chem. Rev.* **2004**, *104*, 3371–3404.

[7] a) S. Talukdar, J.-M. Fang, *J. Org. Chem.* **2001**, *66*, 330–333; b) Z. Li, K. Iida, Y. Tomisaka, A. Yoshimura, T. Hirao, A. Nomoto, A. Ogawa, *Organometallics* **2007**, *26*, 1212–1216; c) D. R. Williams, M. A. Berliner, B. W. Stroup, P. P. Nag, M. P. Clark, *Org. Lett.* **2005**, *7*, 4099–4102; d) Review: B. K. Banik, *Eur. J. Org. Chem.* **2002**, 2431–2444.

[8] a) M. Hojo, H. Aihara, A. Hosomi, *J. Am. Chem. Soc.* **1996**, *118*, 3533–3534; b) J. M. Concellon, H. Rodriguez-Solla, R. Llavona, *J. Org. Chem.* **2003**, *68*, 1132–1133.

[9] a) P. Girard, J. L. Namy, H. B. Kagan, *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698; b) A. Krief, A. M. Laval, *Chem. Rev.* **1999**, *99*, 745–777; c) G. A. Molander, *Acc. Chem. Res.* **1998**, *31*, 603–609; d) G. A. Molander, C. R. Harris, *Tetrahedron* **1998**, *54*, 3321–3354; e) G. A. Molander, C. R. Harris, *Chem. Rev.* **1996**, *96*, 307–338; f) G. A. Molander, *Chem. Rev.* **1992**, *92*, 29–68.

[10] a) Y. Liu, Q. Zhao, Y. Zhang, *Tetrahedron Lett.* **2004**, *45*, 4571–4575; b) Y. Liu, X. Liu, Y. Zhang, *Tetrahedron Lett.* **2003**, *44*, 1667–1670; c) Y. Liu, Y. Zhang, *Tetrahedron Lett.* **2003**, *44*, 4291–4294; d) Y. Liu, X. Xu, Y. Zhang, *Synlett* **2004**, 445–448; e) Y. Liu, Y. Zhang, *Tetrahedron Lett.* **2004**, *45*, 1295–1298; f) Y. Liu, Y. Zhang, *Tetrahedron* **2003**, *59*, 8429–8437; g) Y. Liu, X. Xu, Y. Zhang, *Tetrahedron* **2004**, *60*, 4867–4873.

[11] a) A. Yacovan, S. Hoz, *J. Org. Chem.* **1997**, *62*, 771–772; b) A. Yacovan, S. Hoz, I. Bilkis, *J. Am. Chem. Soc.* **1996**, *118*, 261–262; c) J. L. Namy, J. Souppe, H. B. Kagan, *Tetrahedron Lett.* **1983**, *24*, 765–766.

[12] a) L. Zhou, Y. Zhang, *J. Chem. Soc. Perkin Trans. 1* **1998**, 2399–2402; b) X. Xu, Y. Zhang, *J. Chem. Soc. Perkin Trans. 1* **2001**, 2836–2839.

[13] a) A. Furstner, A. Hupperts, *J. Am. Chem. Soc.* **1995**, *117*, 4468–4475; b) A. Gansäuer, H. Bluhm, *Chem. Rev.* **2000**, *100*, 2771–2788; c) A. Fürstner, *Pure Appl. Chem.* **1998**, *70*, 1071–1076.

[14] a) I. Ojima, Z. Li, J. Zhu in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), John Wiley & Sons, New York, **1998**, vol. 2, part 2, pp. 1687–1792; b) I. Ojima in *The Chemistry of Organic Silicon Compounds* (Eds.: Z. Li, J.

Zhu), John Wiley & Sons, New York, **1989**, vol. 1, part 2, pp. 1479–1526.

[15] a) E. Vedejs, F. G. West, *Chem. Rev.* **1986**, *86*, 941–955; b) M. Suginome, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221–3256; c) L. A. Paquette, *Chem. Rev.* **1986**, *86*, 733–750; d) H. Yamashita, M. Tanaka, M. Goto, *Organometallics* **1997**, *16*, 4696–4704; e) S. Z. Li, J. K. Whitehead, R. P. Hammer, *J. Org. Chem.* **2007**, *72*, 3116–3118.

[16] a) E. E. Van Tamelen, H. Rudler, C. Bjorklund, *J. Am. Chem. Soc.* **1971**, *93*, 7113–7114; b) H.-Y. Kang, W. S. Hong, Y. S. Cho, H. Y. Koh, *Tetrahedron Lett.* **1995**, *36*, 7661–7664; c) J.-M. Mattalia, N. Bodineau, J.-C. Négrel, M. Chanon, *J. Phys. Org. Chem.* **2000**, *13*, 233–236; d) S. D. Rychnovsky, S. S. Swenson, *J. Org. Chem.* **1997**, *62*, 1333–1340; e) D. P. Curran, C. M. Seong, *J. Am. Chem. Soc.* **1990**, *112*, 9401–9403.

[17] a) C. M. Jensen, K. B. Lindsay, R. H. Taaning, J. Karaffa, A. M. Hansen, T. Skrydstrup, *J. Am. Chem. Soc.* **2005**, *127*, 6544–6545; b) A. M. Hansen, K. B. Lindsay, P. K. S. Antharjanam, J. Karaffa, K. Daasbjerg, R. A. Flowers II, T. Skrydstrup, *J. Am. Chem. Soc.* **2006**, *128*, 9616–9617.

Received: March 8, 2008