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Metallic Dysprosium Induced Silyl Radical Reactions: Intermolecular Cyclization and Reduction of Alkynes and Imines

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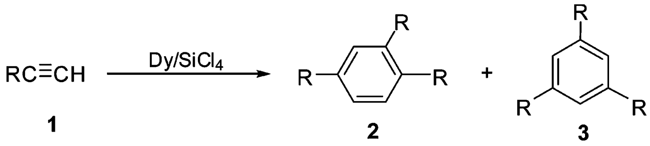
Summary: We have found that the combination of chlorosilane and metallic Dy can serve as an effective promoter for the radical cyclotrimerization of alkynes as well as the transformation of imines to imidazolidines and hydrazines. In addition, catalytic quantities of $SiCl_4$/Dy can also effectively promote the radical polymerization of methyl methacrylate.

Recently, Yang and Verkade[1] and we[2] discovered that silyl radical could effectively catalyze the cyclotrimerization of alkynes. However, these methodologies require the use of either expensive radical precursors such as Si_2Cl_6[1] or a not easily available initiator (DyI_2),[3] along with the need for a special workup procedure. Furthermore, it is found that the regioselectivity of these reactions was remarkably affected by the nature of the initiating system. To further perfect this rare silyl radical catalyzed reaction, we have been interested in the possibility of developing a simple alternative method to generate silyl radicals from common chlorosilanes using more readily available metal species as initiators.

Lanthanide metals are stable in air, are nontoxic and cheap, and have strong reducing power. Noticeably, although the use of lanthanide metals as versatile reductants has been shown in organic synthesis, all of these have been focused on stoichiometric reactions.[4] The finding that the Sm/SmI_2 system is more active than "SmI_2" prompts us to examine whether metallic Dy can be used instead of DyI_2 in initiating silyl radical reactions.[5] Moreover, we are also interested in incorporating the stoichiometric reaction with lanthanide metals in some catalytic context. Herein, we report a novel, highly efficient, and general method to initiate silyl radical reactions using metallic Dy and a successful application of this system in organic synthesis.

As shown in Table 1, a Dy/chlorosilane system proved to be effective in radical cyclotrimerization of terminal alkynes, indicating that Dy alone can be used instead of DyI_2 as an initiator during this reaction.[2] All acetylenes gave very high regioselectivity, except for alkylacetylenes. After we screened a variety of such silanes, $SiCl_4$ gave the best results (Table 2).

Table 1. Dy/$SiCl_4$-Catalyzed Cyclotrimerization of Alkynes[a]



entry	alkyne	R	isolated yield (%)	**2**/**3**
1	**1a**	C_6H_5	98	94/6
2[b]	**1a**	C_6H_5	74	94/6
3	**1b**	*p*-MeC_6H_5	78	99/1
4	**1c**	*p*-FC_6H_5	75	94/6
5	**1d**	*p*-F, *o*-MeC_6H_4	56	96/4
6	**1e**	1-cyclohexenyl	42	97/3
7	**1f**	3-thienyl	20	98/2
8	**1g**	*n*-hexyl	68	56/44
9	**1h**	*n*-butyl	64	55/45
9	**1i**	Me_3Si	43	93/7

[a] All reactions were carried out in THF at 70 °C for 3 days, except for entry 3, which was carried out in toluene. [b] alkynes/Dy = 10/1, while others are 3/1.

Table 2. Cyclotrimerization of Phenylacetylene in Different Systems[a]

entry	catalyst[b]	isolated yield (%)	**2a**/**3a**
1	Dy/Me_3SiCl	92	94/6
2	Dy/$Me_2PhSiCl$	70	95/5
3	Dy/$SiCl_4$	98	94/6
4	Sm/$SiCl_4$	81	98/2
5	Er/$SiCl_4$	30	91/9
6	Yb/$SiCl_4$	75	95/5
7	Dy		
8	$SiCl_4$		
9	Na/$SiCl_4$		
10	SmI_2/$SiCl_4$		

[a] All reactions were carried out in THF at 70 °C. [b] All ratios of metal to chlorosilane to substrate were 1:3:3.

Cyclotrimerization of alkynes represents an attractive strategy for the preparation of substituted benzenes, owing to its intrinsic atom economy.[6] Despite significant recent advances in this area,[7] most of them belong to transition-metal-based reactions. The major limitation of these processes is that the metallic catalysts or precursors employed are expensive and/or not easily available. To the best of our knowledge, examples of the radical-based intermolecular cyclotrimerization of alkynes are very rare. In comparison with the $Cl_3SiSiCl_3$-mediated identical reaction,[1] the present system not only provides a more convenient method for the formation of $SiCl_3$ radical under mild conditions from

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(1) (a) Yang, J. C.; Verkade, J. G. *J. Am. Chem. Soc.* **1998**, *120*, 6834. (b) Yang, J. C.; Verkade, J. G. *Organometallics* **2000**, *19*, 893.

(2) Zhu, Z. Y.; Wang, C. W.; Xiang, X.; Pi, C. F.; Zhou, X. G. *Chem. Commun.* **2006**, *19*, 2066.

(3) (a) Fagin, A. A.; Bochkarev, M. N. *Chem. Eur. J.* **1999**, *5*, 2990. (b) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11749. (c) Evans, W. J.; Allen, N. T.; Workman, P. S.; Meyer, J. C. *Inorg. Chem.* **2003**, *42*, 3097.

(4) (a) Banik, B. K. *Eur. J. Org. Chem.* **2002**, *15*, 2431. (b) Ogawa, A.; Nanke, T.; Takami, N.; Sumino, Y.; Ryu, I. *Chem. Lett.* **1994**, *2*, 379. (c) Nishino, T.; Watanabe, T.; Okada, M.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem.* **2002**, *67*, 966. (d) Hou, Z. M.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7843. (e) Hou, Z. M.; Yamazaki, H.; Fujiwara, Y.; Taniguchi, H. *Organometallics* **1992**, *11*, 2711.

(5) (a) Ogawa, A.; Takami, N.; Sekiguchi, M.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 8729. (b) Ogawa, A.; Takami, N.; Nanke, T.; Ohya, S.; Hirao, T.; Sonoda, N. *Tetrahedron* **1997**, *53*, 12895.

(6) (a) Trost, B. M. *Science* **1991**, *254*, 1471. (b) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695.

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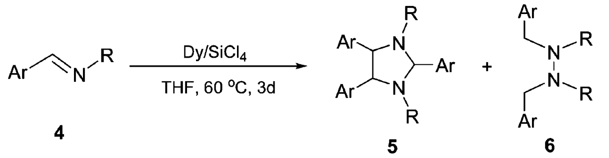
Table 3. Dy/SiCl$_4$-Promoted Reactions of Imines



imine	Ar	R	product	isolated yield (%)
4a	Ph	*n*-butyl	**5a**	75
4b	Ph	Me	**5b**	76
4c	Ph	Et	**5c**	72
4d	Ph	Ph	**5d, 6d**	15, 40
4e	*p*-MeC$_6$H$_4$	Ph	**5e, 6e**	10, 20
4f	*p*-FC$_6$H$_4$	Ph	**5f, 6f**	trace, 30

the abundant and cheap SiCl$_4$ that is ineffective as a precursor in terms of the thermolytic or photochemical production of silyl radical due to its exceedingly high first dissociation energy (ca. 111 kcal/mol) but also typically gave superior regioselectivity. However, in the sole Si$_2$Cl$_6$ catalytic system the cyclotrimerization of **1a** afforded **2a** and **3a** in an approximately 1:1 ratio.

To determine if other reducing reagents could be used in place of Dy in this method, the reaction was examined with Sm, SmI$_2$, Er, Yb, and Na, respectively. As revealed in Table 2, all cyclotrimerizations of **1a** promoted by the lanthanide metal/SiCl$_4$ systems led to the formation of **2a** as the main product, although the yields were generally lower than those achieved with Dy/SiCl$_4$. Surprisingly, this method is not applicable in the present reaction, although the reduction of a silyl bromide by sodium has been found to produce a persistent silyl radical.[8] More remarkable is the observation that metallic Sm was effective in the reaction with good yield and high selectivity but SmI$_2$ did not work well, indicating that lanthanide metals can be expected to provide more powerful reductants for reactions which are difficult to carry out in SmI$_2$ systems under certain conditions.

To extend our methodology, the Dy/SiCl$_4$-promoted reaction of imines was also studied, giving unexpected imidazolidines (**5**) and tetrasubstituted hydrazines (**6**) (Table 3), which have been unavailable in other silyl radical initiating systems[9] or in the reduction of imines with lanthanide metals.[10] Imidazolidines[11] and hydrazines[12] are important building blocks in biologically active compounds. Although transformations of imines have been studied extensively, very few examples of forming imidazolines are known and most of them involve cleavage of THF.[13] On the other hand, the N−N coupling reaction of imines was previously feebly observed only in the electrochemical reductive alkylation of **4d**.[14] Clearly, the Dy/SiCl$_4$ combination used here possesses some unique functions and can provide an alternative method for the synthesis of imidazolidines and hydrazines. The structure of **6f** has been determined by X-ray analysis (Figure 1).[15]

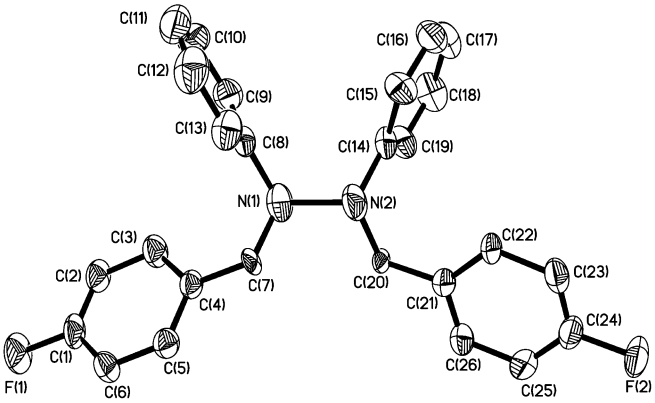


Figure 1. Molecular structure of **6f**.

We also found that the Dy/SiCl$_4$ system could effectively promote the radical polymerization of methyl methacrylate.[16] In all the cases, the radical mechanism was substantiated by the lack of detectable products when 1,4-benzoquinone or hydroquinone was added to the reaction mixture as a radical trap. Furthermore, all of these reactions did not occur in the absence of Dy or SiCl$_4$ under the conditions involved.

In summary, a simple and general method for initiating silyl radical reactions under mild conditions using metallic Dy has been developed. In comparison with other methods of forming silyl radicals, the advantages of the present methodology are easy access to the reagents and simple operation. More important is the observation that the reactivity and catalytic behavior of silyl radicals could be modulated by lanthanide ions, thus affecting the outcome of a given reaction. One can readily accomplish the highly regioselective cyclotrimerization of terminal alkynes and the N−N reductive coupling of imines, which have been previously unavailable or relatively uncontrollable by other radical reactions. Furthermore, this work represents the first use of a catalytic amount of lanthanide metals in organic synthesis and sheds new light on the potential of lanthanide metals beyond that possible with other metals in organic synthesis. Further development in this methodology is currently under way in our laboratory.

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Supporting Information Available: Text, tables, and a figure giving experimental details and characterization data for all isolated compounds and a CIF file giving X-ray data for **6f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) (a) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901. (b) Tanaka, K.; Nishida, G.; Wada, A.; Noguchi, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 6510. (c) Sugihara, T.; Wabayashi, A.; Nagai, Y.; Takao, H.; Imagawa, H.; Nishaizawa, M. *Chem. Commum.* **2002**, *6*, 576. (d) O'Connor, J. M.; Friese, S. J.; Rodgers, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 16342. (e) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Organometallics* **2000**, *19*, 4289. (f) Cadierno, V.; Garcia-Garrido, S. E.; Gimeno, J. *J. Am. Chem. Soc.* **2006**, *128*, 15094. (g) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307. (h) Young, D. D.; Senaiar, R. S.; Deiters, A. *Chem. Eur. J.* **2006**, *12*, 5563. (i) Kakeya, M.; Fujihara, T.; Kasaya, T.; Nagasawa, A. *Organometallics* **2006**, *25*, 4131.

(8) Kira, M.; Obata, T.; Kon, I.; Hashimoto, H.; Ichinohe, M.; Sakurai, H.; Kyushin, S.; Matsumoto, H. *Chem. Lett.* **1998**, *11*, 1097.

(9) Chatgilialoglu, C. In *Organosilanes in Radical Chemistry*; Wiley: Chichester, U.K., 2004; Chapter 5.

(10) (a) Jin, W. S.; Makioka, Y.; Taniguchi, Y.; Kitamura, T.; Fujiwara, Y. *Chem. Commun.* **1998**, *10*, 1101. (b) Tsubaki, Y.; Tanaka, S.; Beppu, F.; Fujiwara, Y. *Chem. Lett.* **1990**, *2*, 203. (c) Banik, B. K. *Eur. J. Org. Chem.* **2002**, 2431.

(11) Katritzky, R.; Suzuki, K.; He, H. Y. *J. Org. Chem.* **2002**, *67*, 3109 and references therein.

(12) Wing, K. D. *Science* **1988**, *241*, 467.

(13) (a) Periasamy, M.; Reddy, M. R.; Kanth, J. V. B. *Tetrahedron Lett.* **1996**, *37*, 4767. (b) Periasamy, M.; Srinivas, G.; Karunakar, G. V.; Bharahi, P. *Tetrahedron Lett.* **1999**, *40*, 7577.

(14) Hess, U.; Lieberenz, C.; Feuerherd, B. *J. Prakt. Chem.* **1986**, *328*, 7.

(15) Crystal data for **6f**: C$_{26}$H$_{20}$F$_2$N$_2$, triclinic, $P\bar{1}$, $a = 8.307(6)$ Å, $b = 13.991(9)$ Å, $c = 20.044(13)$ Å, $\alpha = 110.425(7)°$, $\beta = 95.667(9)°$, $\gamma = 90.000(9)°$, $V = 2171(2)$ Å^3, $Z = 4$, $D_c = 1.219$ g cm^{-3}; 8891 reflections ($\theta_{max} = 50.00°$) measured, of which 7428 were unique ($R_{int} = 0.0578$). R1 = 0.1340 ($I > 2\sigma(I)$), wR2 = 0.3184.

(16) To a mixture of SiCl$_4$ (0.14 mL, 1.2 mmol) and Dy (0.065 g, 0.40 mmol) in THF was added MMA monomer (5 mL, 46.7 mmol) at 0 °C. After it was stirred at 0 °C for 10 h, the mixture was filtered. The filtrate was quenched, washed with methanol, and dried to give PMMA as a white powder. $M_n = 1.33 \times 10^5$, $M_w/M_n = 2.20$. ^{1}H NMR: CH$_3$ *mr*, δ 1.02 (30%); CH$_3$ *rr*, δ 0.85 (70%).