DyI$_2$ initiated mild and highly selective silyl radical-catalyzed cyclotrimerization of terminal alkynes and polymerization of MMA†

Zhenyu Zhu,[a] Chuanfeng Wang,[a] Xu Xiang,[a] Chengfu Pi[a] and Xigeng Zhou*[ab]

An efficient method for the formation of SiCl$_3$ radicals by the reaction of abundant and cheaper chlorosilanes with DyI$_2$ has been established, not only demonstrating new distinctive reactivities of solvated DyI$_2$ but also suggesting that the presence of lanthanide ions can improve the selectivity of some silyl radical-catalyzed reactions.

Radical reactions have become an important tool in synthetic chemistry.[1] Surprisingly, the C–C bond-forming reactions promoted by silyl radicals have been poorly developed to date, even though this should be a fertile area, since they have proved to have a somewhat different reactivity compared to other radicals.[2,3] The reasons are probably the lack of convenient and clean sources of the free silyl radicals, and the difficulty in controlling the selectivity. Up to now, silyl radicals are most frequently produced by treating the corresponding hydrosilanes with other radicals. On the other hand, the presence of hydrosilanes should make controlling the C–C bond formation difficult in the free radical reaction due to the competing H-transfer from hydrosilanes to alkyl radicals.[2,4] In addition, organic initiators may participate in reactions.[2c] Therefore, to avoid such obstacles, it is highly desirable to develop efficient methods of forming silyl radicals from non-hydrosilane precursors. Recent pioneering work shows that the ˙SiCl$_3$ radical, produced by the thermal cleavage of the Si–Si bond of Si$_2$Cl$_6$, can catalyze the cyclotrimerization of alkynes.[3a] However, there are some problems associated with this methodology. For example, the regioselectivity is low and the Si$_2$Cl$_6$ precatalyst is expensive.

On the other hand, since the discovery of a new soluble divalent 4f element system by Bochkarev et al. in 1997,[5] the chemistry of molecular complexes of divalent thulium, dysprosium and neodymium have received considerable attention.[6] Despite great success in their stoichiometric reactions, so far there is no information about their catalytic reactions. Given that SmI$_2$ can be used as an initiator in radical reactions of halohydrocarbons,[7] we were interested in finding out whether solvated LnI$_2$ (Ln = Nd, Dy, Tm) are feasible as initiators for radical-catalyzed transformations that are highly valuable but incontrollable with other initiating systems. We report now on the first use of catalytic amounts of DyI$_2$ in organic synthesis and methyl methacrylate

(MMA) polymerization. The results not only highlight the unique reactivity of DyI$_2$, but also provide a new method for the production of silyl radicals from cheaper, unactivated chlorosilanes.

Initially, we examined the reaction of DyI$_2$ with an excess of terminal alkynes in THF to afford **2**, along with a small amount of **3**, in modest but significant yields between 10 and 24% (Scheme 1).‡ However, 1-phenyl-1-propyne did not form the benzene derivative under the same conditions. The results indicate that the dysprosium acetylides might be the active species in the catalytic cyclotrimerization (Scheme 2).[8] Consistent with this hypothesis, treatment of a THF suspension of DyCl$_3$ with PhC≡CK, followed by reacting with excess PhC≡CH, also gave a small amount of **2a**.

Metal-catalyzed alkyne cyclotrimerization represents a challenging but attractive strategy for the preparation of substituted benzenes.[9] Despite significant recent advances in this area, no organolanthanide has been found to catalyze this kind of reaction. Only linear dimers and/or oligomers were obtained in previously reported homogeneous lanthanide-mediated reactions of terminal alkynes.[10] The unusual catalytic activity of DyI$_2$ in the present reaction might be attributed to its high reductive activity and the fact that it is less sterically demanding compared to other organolanthanide complexes.[6,10]

Furthermore, we found that DyI$_2$ is an efficient initiator for the generation of silyl radicals from chlorosilanes, which can dramatically improve the regioselectivity of radical-catalyzed cyclotrimerization of terminal alkynes.[3a,b] After testing a variety of silanes, SiCl$_4$ was found to give the best results (Table 1). However, SmI$_2$, DyCl$_3$ and Na in presence of excess phenyl acetylene, with or without the addition of SiCl$_4$, did not afford any cyclotrimer under the same conditions. Additionally, we proved that SiCl$_4$ by itself is ineffective as a catalyst in the reaction. All the results indicate that DyI$_2$ is essential, and its strong reductive power may play a key role in initiating the silyl radical-catalyzed reaction. Furthermore, we found the reaction achieved the highest
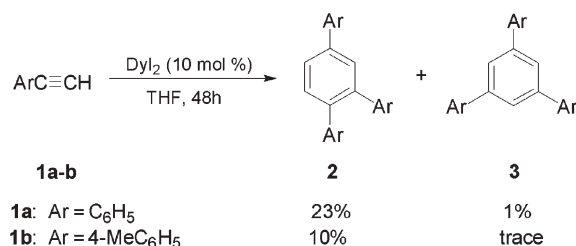
[a] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, People's Republic of China. E-mail: xgzhou@fudan.edu.cn; Fax: (+86) 21 65641740; Tel: (+86) 21 65643769
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China
† Electronic Supplementary Information (ESI) available: Full procedures and characterization data. See DOI: 10.1039/b602883g

1a-b		2		3
1a: Ar = C$_6$H$_5$		23%		1%
1b: Ar = 4-MeC$_6$H$_5$		10%		trace
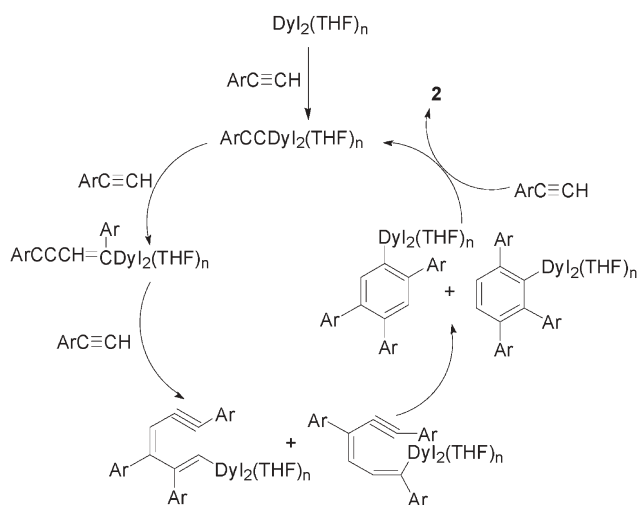
Scheme 1

Scheme 2 Proposed pathway for the formation of **2**.

Table 1 Comparison of the cyclotrimerization of phenylacetylene in different catalytic systems[a]

Entry	Catalyst	T/°C	Yield (%)[b]	2/3
1	DyI$_2$/Me$_3$SiCl	70	36	90/10
2	DyI$_2$/Me$_2^t$BuSiCl	70	20	91/9
3	DyI$_2$/SiCl$_4$	70	95	97/3
4	DyI$_2$/SiCl$_4$	70	90	94/6
5	DyI$_2$/SiCl$_4$	35	90	91/9
6	DyI$_2$/CCl$_4$	70	—	—
7	DyCl$_3$/SiCl$_4$	70	—	—
8	SmI$_2$/SiCl$_4$	70	—	—
9	Na/SiCl$_4$	70	—	—
10	SiCl$_4$	70	—	—
11	Si$_2$Cl$_6$[c]	200	100	50/50
12	Cl$_3$SiH/(PhCO$_2$)$_2$[d]	70	—	—

[a] All the reactions were carried out in THF, except entries 3 and 12, which were carried out in DME and cyclohexane, respectively. [b] Yields of isolated products. [c] Reported in ref. 3a and ref. 3b. [d] Reported in ref. 4a.

yield with excellent regioselectivity in DME, but led to complex mixtures in toluene.

A series of aryl-substituted acetylenes were subjected to the above optimal reaction conditions (Table 2). All reactions gave **2** as major products. The reactivity of alkynes is controlled by the steric and electronic properties of the substituents. Electron-neutral aromatic acetylenes, such as phenylacetylene and *para*-tolylacetylene, trimerize most readily to the corresponding 1,2,4-trisubstituted benzenes in high yield and with excellent regioselectivity,

Table 2 DyI$_2$/SiCl$_4$ catalyzed cyclotrimerization of alkynes[a]

| Entry	Ar	[Sub]/[Cat]	Yield (%)[b]	2/3
1	C$_6$H$_5$	3 : 1	95	97/3
2	C$_6$H$_5$	10 : 1	73	91/9
3	p-MeC$_6$H$_5$	3 : 1	87	97/3
4	p-MeC$_6$H$_5$	10 : 1	70	91/9
5	p-BrC$_6$H$_5$	3 : 1	60	95/5
6	p-FC$_6$H$_5$	3 : 1	67	97/3
7	o-MeC$_6$H$_5$	3 : 1	50	87/13
8	p-MeOC$_6$H$_5$	3 : 1	25	>99/1

[a] All reactions were carried out in DME at 70 °C or refluxing temperature for 3 d, except entry 8, which was carried out in THF. [b] Yields of isolated products.

whereas electron-withdrawing groups, like bromide and fluoride in the *para*-position, seem to negatively affect the yield of the reaction. However, the percentage distribution of isomers remains essentially constant. Noticeable for *p*-MeOC$_6$H$_4$C≡CH, the apparent intramolecular trapping of the resulting alkenyl radical by a methoxy group led to a remarkable decrease in the yield. In addition, the steric effect of the substituent in the *ortho*-position also lowers the reaction yield and selectivity.

The reaction pathway shown in Scheme 3 is proposed to account for the DyI$_2$/SiCl$_4$ co-catalyzed cyclotrimerization of alkynes. Namely, ˙SiCl$_3$ radicals, produced by the single electron reduction of SiCl$_4$ by DyI$_2$, mediate the alkyne cyclotrimerization *via* a tandem radical addition/cyclization/elimination pathway. The radical mechanism was substantiated by the lack of detectable products when 1,4-benzoquinone or hydroquinone were added to the reaction mixture as a radical trap. Additional evidence for the presence of ˙SiCl$_3$ radicals was obtained from the formation of small amounts of authentic disilane derivatives such as hexachlorodisilane. Apparently, the function of the metal species in the present reaction can be distinguished from that in Me$_3$SiCl–Pd/C-cocatalyzed reactions of alkynes, where the resulting Pd complex might be the actual catalyst.[11] Furthermore, it is evident that Pd/C and PdCl$_2$ act as radical traps at 140 °C.[3a] In addition, the present chemoselectivity is in sharp contrast to that in the Me$_3$SiCl–Pd/C catalytic system, where internal alkynes gave cyclotrimers in excellent yield but phenylacetylene did not afford any cyclotrimer product.[11] This different behavior could be of great importance in a synthetic strategy, as the two reagents could complement each other.

The present results not only provide a convenient method for the formation of silyl radicals from cheaper chlorosilanes such as SiCl$_4$ and Me$_3$SiCl, which are ineffective as precursors in terms of
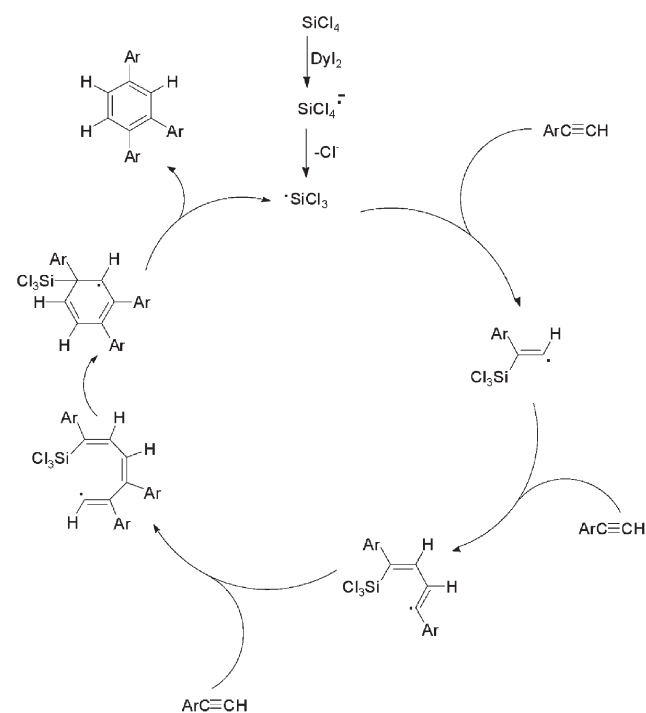
Scheme 3 Proposed mechanism for the silyl radical-catalyzed cyclotrimerization of alkynes.

the thermolytic or photochemical production of silyl radicals due to their exceedingly high first dissociation energies (*e.g.* for $SiCl_4$ *ca.* 111 kcal mol^{-1}), but also achieve success in both controlling the regioselectivity and reducing reaction conditions.

Moreover, we found $DyI_2/SiCl_4$ could effectively initiate the polymerization of MMA. However, in related reactions initiated by Cl_3SiH/organic peroxide systems, only telomers are obtained due to H-abstraction from Cl_3SiH competing with the formation of the adduct radicals.[2c] Addition of 1,4-benzoquinone inhibited the polymerization completely, indicating that the reaction took place in a radical fashion. Both the average molecular weight ($M_n > 178\ 000$) and the syndiotactic content (rr triad, 71%) are higher than those usually reported for poly(methyl methacrylate) (PMMA) initiated by other conventional free radicals, while the molecular weight (M_w) distribution ($M_w/M_n = 1.74$) is smaller.[3c,12] These values probably provide unique information about the influence of the resulting Dy^{3+} ion on the silyl radical-catalyzed reaction. The fact which supports the assumption is that the presence of $DyCl_3$ could narrow significantly the molecular weight distribution of PMMA promoted by AIBN.

In summary, we have developed an efficient method for the production of silyl radicals under mild conditions from cheaper unactivated chlorosilanes *via* the reduction of DyI_2. Significant versatility and excellent control of the selectivity presented here illustrates that this should be an attractive strategy for the development of the silyl radical-catalyzed C–C bond-forming reactions due to the avoidance of hydrosilylation and the probable cooperative action of trivalent lanthanide ions. On the other hand, the results further highlight the distinctive reactivity of DyI_2, beyond that possible with the traditional divalent lanthanide halide reagents of Sm, Eu and Yb, and exemplify for the first time the potential of the "new" divalent lanthanide diiodides as catalytic and initiating reagents in organic synthesis.

Notes and references

‡ All manipulations involving air- and moisture-sensitive compounds were carried out under purified argon. Full procedures and characterization data are given in the ESI.†
General Procedures
1. DyI_2-catalyzed cyclotrimerization of terminal alkynes.
In general, the reactions were performed in THF at ambient or refluxing temperature with a molar ratio of substrate/DyI_2 = 3 : 1 or 10 : 1. The yield of the products and their isomeric distribution were determined by GC–MS, chromatography on silica gel columns or by fractional crystallization.
2. $DyI_2/SiCl_4$-catalyzed cyclotrimerization of terminal alkynes.
To a dark green solution of DyI_2 (0.5 mmol) in DME was added $SiCl_4$ (0.5 mmol). The solution changed immediately into a pale grey suspension, to which was added alkyne (1.5 mmol). After stirring at 70 °C or refluxing for 3 d, the reaction mixture was quenched with saturated sodium

bicarbonate. The mixture was extracted with ether, the organic layer separated and dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography to afford desired substituted benzenes.
3. Polymerization.
To a dark green solution of DyI_2 (0.210 g, 0.5 mmol) in THF was added $SiCl_4$ (0.06 ml, 0.5 mmol). Then the MMA monomer (5 ml) was injected into the suspension. The reaction mixture was allowed to stir at 0 °C for 10 h and was filtered, the filtrate quenched, and washed three times with methanol.

1 (*a*) C. Ollivier and P. Renaud, *Chem. Rev.*, 2001, **101**, 3415; (*b*) J. Iqbal, B. Bhatia and N. K. Nayyar, *Chem. Rev.*, 1994, **94**, 519; (*c*) B. P. Roberts, *Chem. Soc. Rev.*, 1999, **28**, 25; (*d*) *Radicals in Organic Synthesis*, ed. P. Renaud and M. P. Sibi, Wiley-VCH, Weinheim, 2001.

2 (*a*) C. Chatgilialoglu, *Chem. Rev.*, 1995, **95**, 1229; (*b*) C. Chatgilialoglu, *Acc. Chem. Res.*, 1992, **25**, 188; (*c*) H. Sakurai, in *Free Radicals*, ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, ch. 25.

3 (*a*) J. C. Yang and J. G. Vekade, *J. Am. Chem. Soc.*, 1998, **120**, 6834; (*b*) J. C. Yang and J. G. Vekade, *Organometallics*, 2000, **19**, 893; (*c*) A. Matsumoto and Y. Ito, *J. Org. Chem.*, 2000, **65**, 5707.

4 (*a*) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, 1958, **80**, 5298; (*b*) Y. Liu, S. Yamazaki and S. Yamabe, *J. Org. Chem.*, 2005, **70**, 556.

5 M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, T. V. Petrovskaya, J. W. Ziller, R. N. R. Broomhall-Dillard and W. J. Evans, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 133.

6 (*a*) W. J. Evans and N. T. Allen, *J. Am. Chem. Soc.*, 2000, **122**, 2118; (*b*) M. N. Bochkarev, *Coord. Chem. Rev.*, 2004, **248**, 835; (*c*) W. J. Evans, N. T. Allen and J. W. Ziller, *Angew. Chem., Int. Ed.*, 2002, **41**, 359; (*d*) M. N. Bochkarev, G. V. Khoroshenkov, H. Schumann and S. Dechert, *J. Am. Chem. Soc.*, 2003, **125**, 2894; (*e*) K. Izod, *Angew. Chem., Int. Ed.*, 2002, **41**, 743; (*f*) W. J. Evans, G. Zucchi and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 10; (*g*) W. J. Evans, N. T. Allen and J. W. Ziller, *J. Am. Chem. Soc.*, 2001, **123**, 7927; (*h*) W. J. Evans, P. S. Workman and N. T. Allen, *Org. Lett.*, 2003, **5**, 2041; (*i*) W. J. Evans, N. T. Allen and J. W. Ziller, *J. Am. Chem. Soc.*, 2000, **122**, 11749; (*j*) M. N. Bochkarev, I. L. Fedushkin, S. Dechert, A. A. Fagin and H. Schumann, *Angew. Chem., Int. Ed.*, 2001, **40**, 3176; (*k*) K. Izod, *Angew. Chem., Int. Ed.*, 2002, **41**, 743.

7 S. M. Ma and X. Y. Lu, *Tetrahedron*, 1990, **46**, 357.

8 W. J. Evans, R. A. Keyer and J. W. Ziller, *Organometallics*, 1993, **12**, 2618.

9 (*a*) S. Saito and Y. Yamamoto, *Chem. Rev.*, 2000, **100**, 2901; (*b*) K. Tanaka, G. Nishida, A. Wada and K. Noguchi, *Angew. Chem., Int. Ed.*, 2004, **43**, 6510; (*c*) T. Sugihara, A. Wabayashi, Y. Nagai, H. Takao, H. Imagawa and M. Nishaizawa, *Chem. Commun.*, 2002, **6**, 576; (*d*) J. M. O'Connor, S. J. Friese and B. L. Rodgers, *J. Am. Chem. Soc.*, 2005, **127**, 16342; (*e*) M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Organometallics*, 2000, **19**, 4289.

10 (*a*) H. J. Heeres and J. H. Teuben, *Organometallics*, 1991, **10**, 1980; (*b*) M. Nishiura, Z. M. Hou, Y. Wakatsuki, T. Yamaki and T. Miyamoto, *J. Am. Chem. Soc.*, 2003, **125**, 1184; (*c*) C. J. Schaverien, *Organometallics*, 1994, **13**, 69; (*d*) K. H. den Haan, Y. Wielstra and J. H. Teuben, *Organometallics*, 1987, **6**, 2053; (*e*) R. Duchateau, C. T. van Wee, A. Meetsma and J. H. Teuben, *J. Am. Chem. Soc.*, 1993, **115**, 4934; (*f*) M. Nishiura and Z. M. Hou, *J. Mol. Catal. A: Chem.*, 2004, **213**, 101; (*g*) X. G. Zhou and M. Zhu, *J. Organomet. Chem.*, 2002, **647**, 28.

11 A. K. Jhingan and W. F. Maier, *J. Org. Chem.*, 1987, **52**, 1161.

12 Q. Shao, H. M. Sun, X. G. Pang and Q. Shen, *Eur. Polym. J.*, 2004, **40**, 97.