

## Fast Synthesis of Hydrazine and Azo Derivatives by Oxidation of Rare-Earth-Metal-Nitrogen Bonds

Lijun Zhang,\*<sup>,†</sup> Jing Xia,<sup>†</sup> Qinghai Li,<sup>†</sup> Xihong Li,<sup>†</sup> and Shaowu Wang<sup>\*,†,‡</sup>

<sup>†</sup>Laboratory of Functionalized Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, Institute of Organic Chemistry, School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, People's Republic of China, and <sup>‡</sup>State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, People's Republic of China

Received October 19, 2010

Summary: A novel N-N coupling reaction was developed through the oxidation of rare-earth-metal-nitrogen bonds produced by treatment of the easily available rare-earth-metal amides [ $(Me_3Si)_2N$ ]<sub>3</sub> $RE(\mu-Cl)Li(THF)_3$  with aromatic primary or secondary amines. The reaction provides the symmetrical or unsymmetrical azo compounds and hydrazine derivatives in good to high yields within a very short time under mild conditions.

Recently, various metal-initiated coupling reactions have emerged as promising synthetic reactions. Much progress has been made on the C–X (X = C, N, O, S) coupling reactions<sup>1</sup> initiated by such metals as palladium,<sup>2</sup> copper,<sup>3</sup> ruthenium,<sup>4</sup> silver,<sup>5</sup> and rare-earth-metal complexes.<sup>6,7</sup> However, N–N coupling reactions initiated by metal complexes still present a challenge.

The N–N coupling reaction provides a useful strategy for the preparation of hydrazine derivatives and azo compounds,

(1) de Meijere, A., Diederich, F., Eds. *Metal Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH: Chichester, U.K., 2004; Vols. *1* and *2*.

(2) For selected reviews on palladium-initiated coupling reactions, see: (a) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133. (b) Slagt, V. F.; de Vries, A. M.; de Vries, J. G.; Kellogg, R. M. *Org. Process Res. Dev.* **2010**, *14*, 30. (c) Yang, Y.; Cheng, K.; Zhang, Y. *Org. Lett.* **2009**, *11*, 5606. (d) Kogan, V.; Aizenshtat, Z.; Popovitz-Biro, R.; Neumann, R. *Org. Lett.* **2002**, *4*, 3529.

(3) For selected reviews on copper-initiated coupling reactions, see: (a) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054. (b) Tye, J. W.; Weng, Z.; Johns, A. M.; Incarvito, C. D.; Hartwig, J. F. J. Am. *Chem. Soc.* **2008**, *130*, 9971. (c) Hamada, T.; Ye, X.; Stahl, S. S. J. Am. *Chem. Soc.* **2008**, *130*, 833.

(4) For selected reviews on copper-initiated coupling reactions, see:
(a) Denichoux, A.; Fukuyama, T.; Doi, T.; Horiguchi, J.; Ryu, I. Org. Lett. 2010, 12, 1. (b) Yi, C. S.; Lee, D W. Organometallics 2010, 29, 1883.
(c) Gao, R.; Yi, C. S. J. Org. Chem. 2010, 75, 3144. (d) Yi, C. S.; Lee, D W. Organometallics 2009, 28, 4266.

(5) Weibel, J.-M.; Blanc, A.; Pale, P. Chem. Rev. 2008, 108, 3149.

© 2011 American Chemical Society

which can be applied as drugs, pharmaceuticals, agrochemicals, and dyes in industries or precursors in organic synthesis.<sup>8</sup> However, until now only a very limited number of methods have been devised for the synthesis of hydrazine derivatives. Alkylation of hydrazines has become the most frequently used method.<sup>9</sup> Almost all these transformations originating from hydrazine demand several steps (protection and deprotection) for obtaining the required products.<sup>10</sup> On the other hand, some methodologies for azobenzenes were obtained: (i) oxidation of aromatic primary amines;<sup>11</sup> (ii) reduction of nitro-aromatic compounds;<sup>12</sup> (iii) coupling of primary arylamines with nitroso compounds (Mills reaction); (iv) electrophilic reactions of diazonium salts;<sup>13</sup> (v) oxidation of hydrazo derivatives; (vi) reduction of azoxybenzene derivatives.<sup>8c</sup> However, long reaction time (10 h to 3 days)<sup>14</sup> and generally low chemical selectivity with many byproducts leave some space for these methods to be improved. It was reported that aromatic azo compounds could be synthesized from anilines catalyzed by expensive gold nanoparticles using  $O_2$  (3–5 bar) as an oxidant at 100 °C.<sup>15</sup> Very recently Jiao and co-workers developed the inexpensive catalyst CuBr/pyridine to prepare symmetric and unsymmetric azo compounds.<sup>16</sup> Though new advances have been made, the long reaction time is still a challenge to be improved. Most important of all, until now, the direct synthesis of hydrazine derivatives starting from the easily available secondary

(12) (a) Biradar, A. V.; Kotbagi, T. V.; Dongare, M. K.; Umbarkar, S. B. *Tetrahedron Lett.* **2008**, *49*, 1828. (b) Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. *Tetrahedron Lett.* **2003**, *44*, 5835.

(13) (a) Přikryl, J.; Černý, M.; Bělohlavová, H.; Macháček, V.; Lyčka, A. *Dyes Pigm.* **2007**, *72*, 392. (b) Mijin, D. Z.; Baghbanzadeh, M. Reidlinger, C. Kappe, C. O. *Dyes Pigm.* **2010**, 85, 73

M.; Reidlinger, C.; Kappe, C. O. *Dyes Pigm.* **2010**, *85*, 73. (14) Reuter, R.; Hostettler, N.; Neuburger, M.; Wegner, H. A. *Eur. J. Org. Chem.* **2009**, 5647.

(15) Grirrane, A.; Corma, A.; García, H. Science 2008, 322, 1661.

(16) Zhang, C.; Jiao, N. Angew. Chem., Int. Ed. 2010, 49, 6174.

Published on Web 01/11/2011

<sup>\*</sup>To whom correspondence should be addressed. E-mail: zljun@mail. ahnu.edu.cn (L. Zhang); swwang@mail.ahnu.edu.cn (S. Wang).

 <sup>(6) (</sup>a) Müler, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M.
 *Chem. Rev.* 2008, 108, 3795–3892. (b) Amin, S. B.; Marks, T. J. Angew.
 *Chem., Int. Ed.* 2008, 47, 2006–2025. (c) Chen, E. Y.-X. Chem. Rev. 2009, 109, 5157 and references therein.

<sup>(7) (</sup>a) Komeyama, K.; Sasayama, D.; Kawabata, T.; Takehira, K.;
Takaki, K. J. Org. Chem. 2005, 70, 10679. (b) Hou, Z.; Fujita, A.; Zhang,
Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. J. Am. Chem. Soc. 1998, 120,
754. (c) Zhang, W. -X.; Nishiura, M.; Hou, Z. Angew. Chem., Int. Ed. 2008,
47, 9700. (d) Zhang, W.-X.; Nishiura, M.; Hou, Z. J. Am. Chem. Soc. 2005,
127, 16788. (e) Cornehl, H.; Hornung, G.; Schwarz, H. J. Am. Chem. Soc.

<sup>(8) (</sup>a) Bredihhin, A.; Groth, U. M.; Mäeorg, U. Org. Lett. **2007**, *9*, 1097. (b) Bredihhin, A.; Mäeorg, U. Tetrahedron **2008**, *64*, 6788. (c) Hamon, F.; Djedaini-Pilard, F.; Barbot, F.; Len, C. Tetrahedron **2009**, *65*, 10105. (d) Iranpoor, N.; Firouzabadi, H.; Khalili, D.; Motevalli, S. J. Org. Chem. **2008**, *73*, 4882. (e) But, T. Y. S.; Toy, P. H. J. Am. Chem. Soc. **2006**, *128*, 9636.

<sup>(9) (</sup>a) Arterburn, J. B.; Rao, K. V.; Ramdas, R.; Dible, B. R. *Org. Lett.* **2001**, *3*, 1351. (b) Brown, M. J.; Clarkson, G. J.; Fox, D. J.; Inglis, G. G.; Shipman, M. *Tetrahedron Lett.* **2010**, *51*, 382. (c) Bredihhin, A.; Groth, U. M.; Mäeorg, U. *Org. Lett.* **2007**, *9*, 4975.

<sup>(10)</sup> Dey, S. K.; Lightner, D. A. J. Org. Chem. 2007, 72, 9395.

<sup>(11)</sup> For selected reviews on synthesis of azobenzene through oxidation of aromatic primary amines, see: (a) Corma, A.; Serna, P. Science 2006, 313, 332. (b) Li, S.-C.; Diebold, U. J. Am. Chem. Soc. 2010, 132, 64. (c) Goldstein, S. L.; McNelis, E. J. Org. Chem. 1973, 38, 183. (d) Huang, H.; Sommerfeld, D.; Dunn, B. C.; Lloyd, C. R.; Eyring, E. M. Dalton Trans. 2001, 1301. (e) Farhadi, S.; Zaringhadam, P.; Sahamieh, R. Z. Acta Chim. Slov. 2007, 54, 647. (f) Lu, W.; Xi, C. Tetrahedron Lett. 2008, 49, 4011. (g) Biradar, A. V.; Kotbagi, T. V.; Dongare, M. K.; Umbarkar, S. B. Tetrahedron Lett. 2008, 49, 3616. (h) Launay, J. P.; Tourrel-Paggis, M.; Lipskier, J. F.; Marvaud, V.; Joachim, C. Inorg. Chem. 1991, 30, 1033. (i) Lim, Y. K.; Lee, K. S.; Cho, C. G. Org. Lett. 2003, 5, 979.

## Table 1. Optimization Reactions Conditions for the Preparation of Azo Compounds

$Ph-NH_2 \xrightarrow{1. base} Ph-N=N-Ph$							
entry	base	ratio <sup>a</sup>	temp (°C)	$t1 + t2 (min)^{b}$	solvent	yield (%) <sup>c</sup>	
1	$YN_3^d$	1:1	room temp	30 + 30	THF	92	
2	YN <sub>3</sub>	1:1	room temp	15 + 30	THF	92	
3	YN <sub>3</sub>	1:1	room temp	10 + 30	THF	83	
4	YN <sub>3</sub>	1:1	room temp	5 + 30	THF	80	
5	$YN_3$	1:1	room temp	15 + 15	THF	86	
6	$YN_3$	1:1	room temp	15 + 20	THF	93	
7	YN <sub>3</sub>	1:1	room temp	15 + 35	THF	92	
8	$Y[N(SiMe_3)_2]_3$	1:1	room temp	15 + 20	THF	97	
9	$YN_3$	1:1	60	15 + 20	THF	95	
10	$LiN(SiMe_3)_2$	1:1	room temp	15 + 20	THF	79	
11	$NaN(SiMe_3)_2$	1:1	room temp	15 + 20	THF	35	
12	$KN(SiMe_3)_2$	1:1	room temp	15 + 20	THF	40	
13	Mg[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (THF) <sub>2</sub>	1:1	room temp	15 + 20	THF	no	
14	$Ca[N(SiMe_3)_2]_2(THF)_2$	1:1	room temp	15 + 20	THF	no	
15	<i>n</i> -BuLi	1:1	room temp	15 + 20	THF	73	
16	C <sub>2</sub> H <sub>5</sub> ONa	1:1	room temp	15 + 20	THF	25	
17	NaOH	1:1	room temp	15 + 20	THF	trace	
18	$YN_3$	1:0.5	room temp	15 + 20	THF	48	
19	YN <sub>3</sub>	1:0.8	room temp	15 + 20	THF	72	
20	YN <sub>3</sub>	1:1.5	room temp	15 + 20	THF	98	
21	YN <sub>3</sub>	1:1.3	room temp	15 + 20	THF	97	
22	YN <sub>3</sub>	1:1.3	room temp	15 + 20	toluene	60	
23	YN <sub>3</sub>	1:1.3	room temp	15 + 20	hexane	32	
24	YN <sub>3</sub>	1:1.3	room temp	15 + 20	$Et_2O$	76	
25	YN2	1.1.3	room temp	$15 \pm 20$	$C\tilde{H}_{2}Cl_{2}$	65	

<sup>*a*</sup>Ratio of aniline to base. <sup>*b*</sup>t1 = reaction time under an argon atmosphere; t2 = reaction time on exposure to the air. <sup>*c*</sup> Isolated yield based on the aniline. <sup>*d*</sup>YN<sub>3</sub> =  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub>.

amines has remained unexplored. Herein, we wish to report a novel N–N coupling reaction by oxidation of rare-earthmetal-nitrogen bonds for the generation of the symmetrical azo and hydrazine derivatives in good to high yields from easily available amines with only one step within a very short time (35 min) under mild conditions. The N–N coupling reaction mechanism was proposed on the basis of experimental evidence.

On exploration of the reactivity of the rare-earth-metal amides  $[(Me_3Si)_2N]_3RE(\mu$ -Cl)Li(THF)<sub>3</sub><sup>17</sup> with benzene-1,2diamine, the unexpected azo product 2,2'-(diazene-1,2-divl)dianiline, which was confirmed by X-ray analysis (see the Supporting Information), was isolated upon exposure of the reaction mixture to air after 10 min of reaction. When aniline was used to react with  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub>, a good yield of the azo product was also obtained. Therefore, optimization experiments for the reaction of aniline with the yttrium amide  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub> or other bases were performed (Table 1). It was found that the isolated yields for reactions initiated by other bases such as MN- $(SiMe_3)_2$  (M = Li, Na, K) (Table 1, entries 10-12), M[N- $(SiMe_3)_2]_2(THF)_2$  (M = Mg, Ca) (Table 1, entries 13 and 14), *n*-BuLi (Table 1, entry 15), and NaOR ( $R = H, C_2H_5$ ) (Table 1 entries 16 and 17) were lower than those initiated by yttrium amide under the given conditions. Reaction conditions such as the reaction ratio, temperature, reaction time, and solvents were examined. The optimized conditions were reaction of aniline with yttrium amide [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>- $Y(\mu$ -Cl)Li(THF)<sub>3</sub> (1:1.3 mol) for 15 min and then exposure to the air for 20 min (Table 1, entry 21) at room temperature. It is noteworthy that only the azo product was isolated and no other byproducts such as azoxy, anil, or hydroxylamine compounds were observed, indicating the advantage of our methods in comparison with others.<sup>11f,g</sup> In addition, the reaction was completed within a very short time.

Under the optimized conditions, various substituted aromatic primary amines were reacted with  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub>, providing azo compounds in moderate to quantitative yields (Table 2). The electronic nature of the substituents on the benzene ring of anilines affects the efficiency of the reaction greatly. The electron-rich anilines were almost quantitatively converted to the corresponding products (>92% yield) (Table 2, entries 2, 3, and 5). The reaction of 4-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (Table 2, entry 5) afforded the azo product in 99% yield within 10 min. 4-Isopropylaniline (entry 4) led to low yield, probably due to steric effects. A 54% yield of the azo product could be obtained with 4-BrC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (Table 2, entry 6). However, the electron-deficient aniline  $4-O_2NC_6$ -H<sub>4</sub>NH<sub>2</sub> did not undergo the coupling reaction under the optimized reaction conditions. Anilines with substituents at the 2- or 2,6-positions were also effective in spite of large or small substituent groups, but large substituents gave low yields of products due to steric effects (Table 2, comparison of the result of entry 9 with the results of entries 10 and 11). Again, in all the examined cases, only the azo products were isolated and no other byproducts such as azoxy, anil, or hydroxylamine compounds were observed, indicating the advantage of our methods in comparison with others.

The scope of the reaction was further examined by treatment of secondary amines such as N-substituted anilines with rareearth-metal amides, as the N-N coupling reactions of secondary amines remained unexplored. It was found that hydrazine derivatives as the only N-N coupling products

<sup>(17) (</sup>a) Zhang, L.; Wang, S.; Zhou, S.; Yang, G.; Sheng, E. J. Org. Chem. **2006**, *71*, 3149. (b) Li, Q.; Wang, S.; Zhou, S.; Yang, G.; Zhu, X.; Liu, Y. J. Org. Chem. **2007**, *72*, 6763. (c) Zhang, L.; Wang, S.; Sheng, E.; Zhou, S. Green Chem. **2005**, *7*, 683.

Table 2. Products of Reactions of Primary Amines with YttriumAmide $^{a}$ 

	R-NH <sub>2</sub>	YN <sub>3</sub> THF (15 m	in) 20 min F	R−N=N−R 1	
entry	R	product	t1 + t2 (min)	yield $(\%)^b$	trans:cis <sup>c</sup>
1	$C_6H_5$	1a	15 + 20	97	87:13
2	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1b	15 + 20	92	84:16
3	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1c	15 + 20	98	89:11
4	$4 - i PrC_6 H_4$	1d	15 + 20	45	84:16
$5^d$	$4-NH_2C_6H_4$	1e	5 + 5	96	100:0
6	$4-BrC_6H_4$	1f	15 + 20	54	90:10
7	$2 - CH_3C_6H_4$	1g	15 + 20	93	78:22
$8^d$	$2-NH_2C_6H_4$	1ĥ	5 + 5	99	100:0
9	$2,6-Me_2C_6H_3$	1i	15 + 20	90	66:34
10	$2,6-Et_2C_6H_3$	1j	15 + 20	47	67:33
11	$2.6^{-i} Pr_2 C_6 H_3$	1k	15 + 20	45	81:19
12	C <sub>10</sub> H <sub>7</sub>	11	15 + 20	60	100:0

<sup>*a*</sup> Reaction conditions: reaction of aniline with  $YN_3$  (1:1.3 mol) at room temperature for 15 min and then exposure to the air for 20 min. <sup>*b*</sup> Isolated yield, based on the amine. <sup>*c*</sup> Determined by <sup>1</sup>H NMR. <sup>*d*</sup> Conditions: reaction of amine (1 mmol) with  $YN_3$  (1.3 mmol) in THF at room temperature for 5 min in a Schlenk line and then exposure to the air for 5 min.

Table 3. Products of Coupling Reactions of the Secondary



<sup>*a*</sup> Conditions: reaction of the amine (1 mmol) with  $[(Me_3Si)_2N]_3Y(\mu-Cl)Li(THF)_3$  (1.3 mmol) in THF at room temperature for 15 min in a Schlenk line and then exposure to the air for 20 min.

were generated (Table 3) in moderate to good yields by treatment of the corresponding secondary amines with the yttrium amide  $[(Me_3Si)_2N]_3Y(\mu-Cl)Li(THF)_3$ . Reaction of the electron-rich *N*-methyl-4-methylbenzenamide gave a yield of the product higher than that of the electron-deficient *N*-methylbenzenamide (Table 3; **2b**,**c**). The results were consistent with the reactions of aromatic primary amines with yttrium amide. The *N*-ethylbenzenamide reacted with yttrium amide, resulting in only a 52% yield of the product, indicating steric effects on the reaction. This process is also compatible with heterocycles such as indole (**2h**,**i**).

As shown in Table 4, almost all the rare-earth-metal amides exhibited good to high reactivities. It was observed that rareearth elements have some effect on the reaction activity. The

 
 Table 4. Effects of the Rare-Earth Metals on the Coupling Reaction<sup>a</sup>

	RE							
	Y	Pr	Nd	Sm	Eu	Но	Yb	
yield (%)	97	82	89	67	64	60	55	

<sup>*a*</sup> Conditions: reaction of aniline (1 mmol) with  $[(Me_3Si)_2N]_3RE$ ( $\mu$ -Cl)Li(THF)<sub>3</sub> (1.3 mmol) at room temperature for 15 min in THF in a Schlenk line and then exposure to the air for 20 min.

Scheme 1. Preparation of Unsymmetrical Azo Compounds<sup>a</sup>



 $^{a}$ Reaction ratio substituted amine:2-amineaniline:YN<sub>3</sub> 5:1:2; isolated yield based on the 2-amineaniline.

results were in contrast to the Lewis acidity of the  $RE^{3+}$  cations but were consistent with the oxophilicity of the  $RE^{3+}$  cations.<sup>18</sup>

Examination of the cross-coupling of different amines for the syntheses of unsymmetrical azo compounds was conducted. Treatment of benzene-1,2-diamine and aniline with  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub> in a 1:1:2 ratio resulted in a mixture with detectable cross-coupling products that were difficult to isolate. When the ratio of the reactants benzene-1,2-diamine and aniline with  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub> was changed to 5:1:2 and the reaction was run for 1 h, the unsymmetrical azo product 2-(phenyldiazenyl)aniline was isolated in 53% yield (Scheme 1). Other reactions of 2-amineaniline with substituted anilines such as 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, and 2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> in the presence of 2 equiv of yttrium amide were also examined, and the corresponding unsymmetrical azo compounds were obtained.

To investigate the mechanism of the N-N coupling reaction, the complex [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Yb(NPh<sub>2</sub>)(THF) (complex 4) was isolated by treatment of Ph<sub>2</sub>NH with  $[(Me_3Si)_2N]_3Yb(\mu$ -Cl)Li(THF)<sub>3</sub> (1:1) in THF and its structure was determined (Figure 1). Redissolution of [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Yb(NPh<sub>2</sub>)(THF) (complex 4) in THF and then exposure of the solution to the air for 20 min afforded the N-N coupling product Ph<sub>2</sub>N-NPh<sub>2</sub> in 80% yield (Scheme 2). This result suggested that the above reactions involve the formation of new rare-earthmetal amido complexes; oxidation of the rare-earth-metalnitrogen bonds leads to N-N coupling reactions affording the azo or hydrazine derivatives. Additional evidence was that exposure of the THF solution of Yb(NHC<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr<sub>2</sub>- $2,6)_3$ (THF)<sub>2</sub> (complex 5)<sup>19</sup> to the air for 20 min generated the corresponding azo products in 45% yield, further indicating that oxidation of the rare-earth-metal-nitrogen bonds leads to the N-N coupling reaction (Scheme 3).

The reaction of  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub> with the primary amine 4-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> (see Figure 1, line 1, signal **a** in the Supporting Information) was monitored by NMR techniques (see Figure 1 in the Supporting Information). Under an argon atmosphere, reaction of the amine 4-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>

<sup>(18)</sup> Mikami, K.; Terada, M.; Matsuzawa, H. Angew. Chem., Int. Ed. 2002, 41, 3554.

<sup>(19)</sup> Evans, W. J.; Ansari, M. A.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1996**, *35*, 5435.



Figure 1. Crystal structure of complex 4.

Scheme 2. Reaction of Complex 4



Scheme 3. Reaction of Complex 5



with  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub> immediately generated a new yttrium amido complex (see Figure 1, lines 2–4, signal **b** in the Supporting Information). After exposure to the air, the intermediate of the hydrazine compound CH<sub>3</sub>PhNH– NHPhCH<sub>3</sub> could be observed in 5–10 min (see Figure 1, lines 6 and 7, signal **c** in the Supporting Information); the intermediate CH<sub>3</sub>PhNH–NHPhCH<sub>3</sub> was finally oxidized to CH<sub>3</sub>PhN=NPhCH<sub>3</sub> (trans + cis) upon further exposure of the reaction solution to air (see Figure 1, line 8, signals **d**, **d'** in the Supporting Information).

To further confirm the radical mechanism,<sup>20</sup> ESR techniques were used to probe the signal of the amino radical with phenyl *tert*-butyl nitrone (PBN) as the trapping agent. A PBN-amino radical signal,<sup>21</sup> which was generated from the combination of the amino radical with PBN, was observed during exposure of the YN<sub>3</sub>/PhNH<sub>2</sub>/PBN/THF mixture to air (see Figure 2, panel 3 in the the Supporting Information) ( $\alpha_{\rm H} = 3.44 \times 10^{-4}$  T,  $\alpha_{\rm N} = 13.68 \times 10^{-4}$  T). A typical ESR

Scheme 4. Propsed Mechanism for the N-N Coupling Reaction



signal for the PBN-amino radical was also observed by exposure of the yttrium amido complex  $Y(NHC_6H_3^{i}Pr_2-2,6)_3(THF)_2/PBN/THF$  to air (see Figure 2, panel 4 in the Supporting Information). This evidence clearly suggested that the reaction goes through the amino radical process.

In combination with the above experimental results, a plausible mechanism for the N–N coupling reaction is proposed (Scheme 4). Reaction of amine with the rare-earth-metal amides  $[(Me_3Si)_2N]_3RE(\mu$ -Cl)Li(THF)<sub>3</sub> generated the new rare-earth metal amido complex **A** (as evidenced by isolation of complex 4), which was oxidized to produce the radical **B** (ESR evidence) upon exposure to the air; coupling of the radical **B** formed the N–N coupling hydrazine product **C** (<sup>1</sup>H NMR evidence). When primary amines were used, further oxidation of **C** gave the azo products **D**.

In summary, a novel N-N coupling reaction for the generation of symmetrical or unsymmetrical azo compounds and hydrazine derivatives was developed with the participation of rare-earth-metal amides. The experimental evidence supported that the amino radical produced by oxidation of rare-earth-metal-nitrogen (RE-N) bonds is responsible for the N-N coupling reaction on the basis of isolation of the amido complex 4 and NMR and ESR probes of the intermediates. The results indicated that electron-rich amines are more effective for the coupling reaction. In comparison with previous approaches, the key advantages of this method are that both azo products and hydrazine products could be obtained within a very short time in good to excellent yields with a wide generality for the substrates.

Acknowledgment. The work was supported by the National Natural Science Foundation of China (Nos. 20702001, 21072004, 20832001) and grants from the Ministry of Education (No. 20103424110001) and the Anhui Education Department (Nos. TD200707, KJ2007A011).

Supporting Information Available: Text and figures giving experimental details for the characterization of all compounds, spectral data for the compounds 1a–1, 2a–i, and 3a–d, and <sup>1</sup>H NMR and ESR spectra for the probe of the intermediates (<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, HRMS) and CIF files giving crystal-lographic data for compound 1h and complex 4. This material is available free of charge via the Internet at http://pubs. acs.org.

<sup>(20)</sup> The nitrogen radical can be seen: Li, G.; Nelsen, S. F.; Jalilov, A. S.; Guzei, I. A. *J. Org. Chem.* **2010**, *75*, 2445.

<sup>(21)</sup> Teshima, W.; Nomura, Y.; Tanaka, N.; Urabe, H.; Okazaki, M.; Nahara, Y. *Biomaterials* **2003**, *24*, 2097.