of families of metal complex-based oligomers which are able to act as molecular conduits for long-range electron and energy transfer.

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The First Deoxygenative Coupling of Amides by an Unprecedented Sm/SmI_2 System

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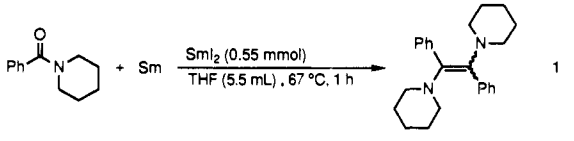
Herein we report the novel finding that a samarium/samarium diiodide mixed reagent (Sm/SmI_2) successfully effects the deoxygenative coupling of amides, which provides a powerful tool for preparing *vic*-diaminoalkenes.[1,2] In marked contrast to the deoxygenative coupling of aldehydes, ketones, and esters, which has constituted a general method for olefin formation,[3] the use of amides for this purpose has remained largely unexplored. We postulated that the requisite reagents for the desired coupling reaction of amides should possess both powerful reducing ability and good oxophilicity. A low-valent titanium reagent ($TiCl_4$/$LiAlH_4$)[4] or samarium diiodide[5] would appear to be suitable candidates but, in fact, these reagents did not work well. However, a reaction system combining SmI_2 with samarium metal accomplished deoxygenative coupling to provide *vic*-diaminoalkenes in excellent yields (e.g., eq 1).

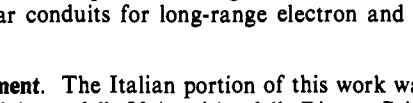


1a, 1 mmol 0.65 mmol **2a**, 74 (94) % [*E*/*Z* = 84/16]

As can be seen in the experiments varying the molar ratio of Sm/SmI_2 (Table I), the yield of coupling product **2a** was dependent on the amount of samarium metal (runs 1–3). The coupling reaction with Sm proceeded even in the presence of a catalytic amount of SmI_2 (run 4). More remarkable is the observation that magnesium metal ($Mg^{2+}/Mg = -2.37$ V), which has a reducing power similar to that of samarium metal ($Sm^{3+}/Sm = -2.41$ V), also effected the coupling of **1a** in the presence of SmI_2 (run 6). From these results and the fact that both Sm and SmI_2 are essential for this coupling reaction (runs 1 and 5), it is proposed that SmI_2 activates the surface of Sm metal. However, the deoxygenative coupling of **1a** using Sm metal "washed" with $LiAlH_4$ or SmI_2 (with removal of the SmI_2 prior to addition of amide) resulted in the recovery of the starting materials.[6] This result suggests that SmI_2 is also playing a direct role in the reaction.[7]

Table II lists examples of the reductive coupling of amides. Substrate **1f**, which includes two amide units, demonstrated in-

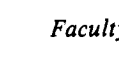
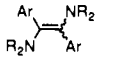
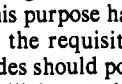
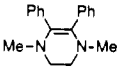
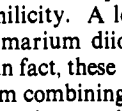
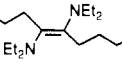
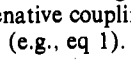
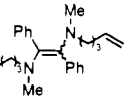
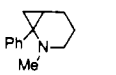
Table I. Deoxygenative Coupling of 1-Benzoylpiperidine



run	Sm (mmol)	SmI_2 (mmol)	additive	yield of **2a**[a] (%)	*E*/*Z*[b]
1	–	2.2		NR	
2[c]	0.34	2.2		43	85/15
3[c]	1	2.2		88	85/15
4[d]	2	0.1		61	84/16
5	2	–		NR	
6[c,e]	–	1.1	Mg (4.9 mmol)	72[f]	82/18

[a] NMR yield. [b] Determined by ^1H NMR. [c] 4 h. [d] THF (2 mL). [e] THF (11 mL). [f] Isolated yield.

Table II. Sm/SmI_2-Induced Reductive Coupling of Amides[a]

run	amide	Ar =	R_2N =	product	yield (%)[b]	*E*/*Z*[c]
						
1	**1b**	Ph	Et_2N	**2b**	72 (86)	38/62
2[d]	**1c**			**2c**	50 (61)	84/16
3	**1d**			**2d**	67 (99)	47/53[e]
4	**1e**			**2e**	50[f] (99)	34/66
5	 **1f**			 **2f**	62 (83)	
6[g]	 **1g**			 **2g**	23	
7	 **1h**			 **2h**	12	47/53
				 **3h**	41 (54)	

[a] Unless otherwise noted, amide (1 mmol) was allowed to react with Sm (0.65–0.70 mmol) and SmI_2 (0.1 M in THF, 0.55 mmol) at 67 °C for 2–4 h. [b] Isolated (NMR) yield. [c] *E*/*Z* ratio was determined by ^1H NMR. [d] Sm (1.2 mmol) and SmI_2 (1.1 mmol) were used. [e] The *E*/*Z* ratio was changed to 87/13 during workup. [f] Only *Z* isomer was isolated. It was difficult to isolate *E* isomer in pure form. [g] Sm (1.0 mmol), SmI_2 (2.2 mmol), HMPA (0.5 mL), and toluene (5 mL), reflux, 26 h. See supplementary material.

(1) The reaction of *N*,*N*-diethylbenzamide with (triethylsilyl)lithium afforded 1,2-bis(diethylamino)stilbene (14%) as a byproduct, see: Bravo-Zhivotovskii, D. A.; Pigarev, S. D.; Kalikhman, I. D.; Vyazankina, O. A.; Vyazankin, N. S. *J. Organomet. Chem.* **1983**, *248*, 51.

(2) Recently we have developed the Cu(0)-induced deselenative coupling of selenoamides, see: Sekiguchi, M.; Ogawa, A.; Kambe, N.; Sonoda, N. *Chem. Lett.* **1991**, 315.

(3) For the deoxygenative coupling of aldehydes and ketones, see: (a) Kahn, B. E.; Rieke, R. D. *Chem. Rev.* **1988**, *88*, 733. (b) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513. (c) Lenoir, D. *Synthesis* **1989**, 883. For the acyloin condensation, see: (d) Bloomfield, J. J.; Owsley, D. C.; Nelke, J. M. *Org. React.* **1976**, *23*, 259.

(4) The reaction of 1-benzoylpiperidine **1a** with $TiCl_4/LiAlH_4$ (for preparation, see: Ishida, A.; Mukaiyama, T. *Chem. Lett.* **1976**, 1127) resulted in the formation of a complex mixture (67 °C, 46 h).

(5) For the formation of pinacols from aldehydes and ketones under the influence of SmI_2, see: (a) Namy, J. L.; Souppe, J.; Kagan, H. B. *Tetrahedron Lett.* **1983**, *24*, 765. (b) Souppe, J.; Danon, L.; Namy, J. L.; Kagan, H. B. *J. Organomet. Chem.* **1983**, *250*, 227.

(6) Activated Mg, such as Rieke's Mg,[3a] did not cause the deoxygenative coupling of amides.

(7) Two explanations are suggested: (1) disproportionation between Sm and SmI_2[8] generates samarium iodide (SmI),[9] which is the true reducing species; (2) highly oxophilic SmI_2 coordinates with the amide carbonyl, and samarium metal serves as the reducing agent. We can not specify at present which, if either, of these processes is operative.

(8) Several rare-earth monohalides were prepared by disproportionation between rare-earth metals and their trihalides (or dihalides), see: (a) Mattausch, H.; Hendricks, J. B.; Eger, R.; Corbett, J. D.; Simon, A. *Inorg. Chem.* **1980**, *19*, 2128. (b) Araujo, R. E.; Corbett, J. D. *Inorg. Chem.* **1981**, *20*, 3082 and references therein.

(9) (a) Struck, C. W.; Baglio, J. A. *High Temp. Sci.* **1990**, *30*, 113. (b) Ganiel, U. *Z. Phys.* **1967**, *200*, 419.

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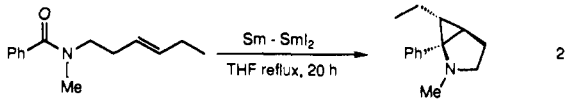
tramolecular coupling (run 5). Likewise, aliphatic amide **1g** underwent deoxygenative coupling with Sm/SmI_2 in the presence of HMPA[10] upon heating at 110 °C (run 6).

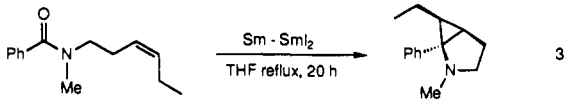
Two mechanistic pathways can be proposed for this coupling reaction, each beginning with a one-electron reduction of the amide to afford anion radical **4a**.[11] The first postulates dimerization of **4a** followed by deoxygenation to provide *vic*-diaminoalkene. The second hypothesis suggests that the initially formed anion radical **4a** undergoes further reduction to give α-aminocarbene intermediate **5a**. To explore the mechanism of this reaction, amide

4a **5a**

1h having an olefinic unit at an appropriate position was prepared and, upon subjection to the coupling conditions, yielded bicyclic product **3h** (41%) together with the coupling product **2h** (12%) (run 7). The formation of a three-membered ring is intriguing,[12] deserving additional inquiry into the stereochemistry of cyclopropanation.[13] As represented in eqs 2 and 3, the reaction of *trans*- and *cis*-3-hexenyl-substituted amides (*trans*- and *cis*-**1i**) gave rise to exo and endo products **3i**, respectively, with high stereoselectivity.[14] The stereospecificity observed in the cyclopropanation suggests the intermediacy of an α-aminocarbene.[15,17]



trans-1i *exo*-3i



cis-1i *endo*-3i

In summary, this work describes the first example of efficient deoxygenative coupling of amides, which has been achieved by the novel combination of Sm with SmI_2, and thus provides a straightforward access to *vic*-diaminoalkenes. Further studies on the scope and the precise mechanism of this coupling reaction are underway.

Acknowledgment. This research was supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining mass spectra with a JEOL JMS-DX303 instrument.

Supplementary Material Available: Listings of analytical data for the compounds prepared (IR, ^1H NMR, ^{13}C NMR, and mass spectra; elemental analyses) (5 pages). Ordering information is given on any current masthead page.

(10) Inanaga, J.; Ishikawa, M.; Yamaguchi, M. *Chem. Lett.* **1987**, 1485.
(11) When the reaction of **1a** with Sm/SmI_2 was carried out at room temperature, benzil (7%) was formed in addition to **2a** (59%), probably via the dimerization of anion radical **4a** followed by hydrolysis.
(12) For the samarium-promoted cyclopropanation of allylic alcohols and ethers, see: (a) Sasaki, M.; Collin, J.; Kagan, H. B. *Tetrahedron Lett.* **1988**, *29*, 6105. (b) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1987**, *52*, 3942. (c) Molander, G. A.; Harring, L. S. *J. Org. Chem.* **1989**, *54*, 3525. (d) Imamoto, T.; Kamiya, Y.; Hatajima, T.; Takahashi, H. *Tetrahedron Lett.* **1989**, *30*, 5149.
(13) Shono, T.; Masuda, H.; Murase, H.; Shimomura, M.; Kashimura, S. *J. Org. Chem.* **1992**, *57*, 1061.
(14) The exo/endo selectivity of this cyclopropanation is as follows: exo/endo = 9/1 (starting from *trans*-**1i**), 1/8 (from *cis*-**1i**).
(15) The reaction of *N*-benzylbenzamide with Sm/SmI_2 provided dibenzylamine (43%),[16] probably via an imine intermediate ($PhCH{=}NCH_2Ph$).[2] The formation of the imine may be explained by N-H insertion of the α-aminocarbene. For the N-H insertion of carbenes, see: (a) Husinec, S.; Juranic, I.; Llobera, A.; Porter, A. E. A. *Synthesis* **1988**, 721. (b) Singh, S. B.; Mehrotra, K. N. *Can. J. Chem.* **1981**, *59*, 2475. (c) Mehrotra, K. N.; Prasad, G. *Tetrahedron Lett.* **1978**, *43*, 4179.
(16) Kamochi, Y.; Kudo, T. *Tetrahedron Lett.* **1991**, *32*, 3511.
(17) For reports concerning α-aminocarbenes, see: (a) Schöllkopf, U.; Hauptreif, M.; Dippel, J.; Nieger, M.; Egert, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 192. (b) Gambaryan, N. P.; Kaitmazova, G. S.; Kagramanova, E. M.; Simonyan, L. A.; Safronova, Z. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1102. (c) Moreno, M.; Lluch, J. M.; Oliva, A.; Bertran, J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 183.

Synthesis of Three-Dimensional Nanoscaffolding†

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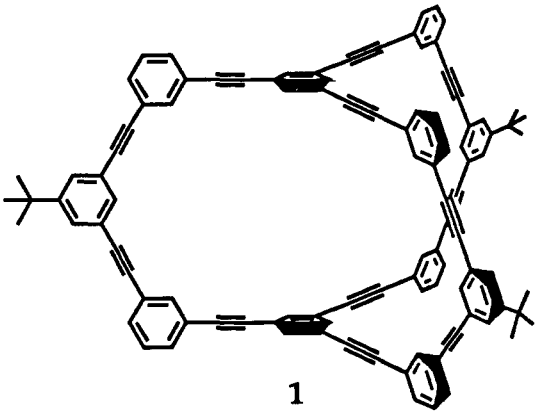
Recently there has been growing interest in the development of efficient synthetic methods that can function as "nanosize construction tools" for the assembly of geometrically well-defined objects on the molecular level.[1] Interest in these nanoarchitectures is driven by a diverse array of emerging ideas: the fabrication of multienzyme arrangements that provide unique catalytic possibilities,[2] the modular construction of large, discrete, and ordered molecular assemblies from prefabricated molecular components,[3] the achievement of mechanical control on the nanometer scale,[3] the assembly of devices that store and process information on the molecular level,[4] the fabrication of molecular monolayers of defined structure on the nanometer scale,[5] and the formation of perforated monolayers based on rationally designed molecular pores.[6] We have previously described an efficient method for synthesizing linear, phenylacetylene sequences[7] and showed how these could be cyclized into large planar macrocycles.[8]



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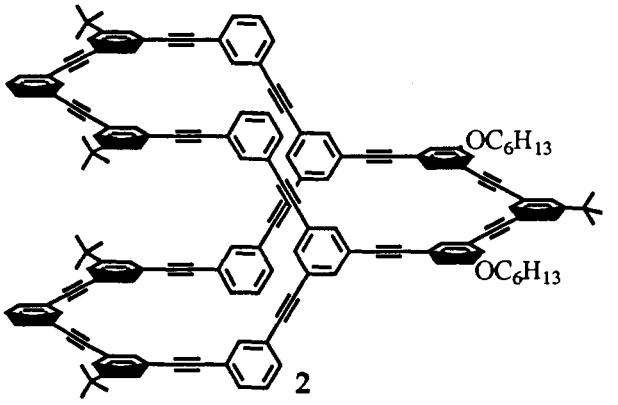

2

† Nanoarchitectures. 4. For part 3, see: Zhang, J.; Moore, J. S. Aggregation of Hexa(phenylacetylene) Macrocycles in Solution: A Model System for Studying π–π Interactions. Submitted for publication.
‡ National Science Foundation Young Investigator, 1992–1997.

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