conformations (~80:20) also were found for the methoxymethyl side chain of the chiral auxiliary.

The molecular structure of the β-crystalline form (mp 127–128 °C) is shown in Figure 2. The most striking difference between the α- and β-form is the pronounced cant of the C(3′)–C(4′) bond of the butenyl group toward the C(5)–C(6) double bond of the cyclohexadienone ring in the β-crystal and the little deviation from a pseudosymmetric averaged positioning of the butenyl group in the α-crystal.

In contrast to the solution-state photochemistry of **1b**, irradiation (366 nm) of α- and β-crystals of **1b** provided remarkably high diastereoselectivities (Table I). At 60% conversion, the α-form gave **2b** and **3b** in a ratio of 1:10.[8] With higher conversions the crystalline structure of the sample visibly deteriorated, and at complete conversion the diastereoselectivity eroded to 1:2. Irradiation of the β-crystal gave a near complete reversal of the sense of diastereoselection for formation of **2b** and **3b** (>20:1) at very low conversions.[9]

It is often assumed that reactions in crystalline solids should take place with minimum atomic and molecular movement.[10] However, local stress generated by reaction in the crystal can cause reactive intermediates to follow indirect trajectories rather than least-motion paths.[11] Considering only the molecular structure of **1b** in the β-crystal (Figure 2), it is clear that a proximity argument cannot be used to explain the preferential formation of **2b**; in fact, to generate **2b**, the 4-(3′-butenyl) group must swing toward the C(2)–C(3) rather than the more proximate C(5)–C(6) double bond.

Computer-assisted modeling of the packing arrangement of the α- and β-forms of **1b** has provided a reasonable explanation for the observed diastereoselectivities (supplementary material). It is possible to see an available reaction volume for butenyl group movement in regions that correspond to the preferred paths for 2 + 2 photocycloadditions at low conversions of the α- and β-crystals.

Fortuitous crystallizations and the erosion of diastereoselectivities with increasing degrees of photoconversion limit the synthetic utility of the solid-state photochemistry exemplified here with **1b**. Rather, the importance of this study is the demonstration that relatively subtle crystal lattice restraints can result in dramatic changes in the course of unimolecular solid-state photoreactions. It should be clear that the type of orientational control described for **1b** is very different from the distance and geometric requirements uncovered during studies of the 2 + 2 photodimerizations of cinnamic acids in the solid state.[12] We expect that these observations can be incorporated into the design of potentially more stable crystalline matrices[13] for stereocontrolled unimolecular photoreactions.

Acknowledgment. This work was supported by the National Institute of General Medical Science (Grant GM 26568). We thank Dr. Adi Treasurywala for assistance with molecular modeling experiments and Sterling Winthrop for support of the Sterling Laboratory for Molecular Modeling. We thank the National Institutes of Health for funds to purchase the Evans and Sutherland computer system via the Biomedical Research Support Grant SO7RRO7104.

Supplementary Material Available: Experimental procedures for preparation of **1b**; tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates; packing diagrams for the α-form of **1b**, the β-form of **1b**, and the epoxy ketone **5b**; and computer-generated views of the nearest neighbor interactions (39 pages). Ordering information is given on any current masthead page.

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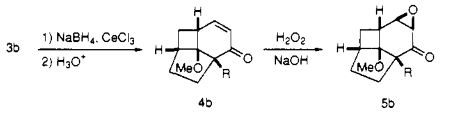
[8] Assignments of relative configuration to **2b** and **3b** could not be made directly but were deduced by an X-ray crystallographic analysis of epoxy ketone **5b**, prepared from **3b** by the sequence of reactions shown below.



[9] For rare examples of reactivity differences between two polymorphic modifications in a unimolecular photoreaction, see: (a) Evans, S. V.; Omkaram, N.; Scheffer, J. R.; Trotter, J. *Tetrahedron Lett.* **1986**, *27*, 1419. (b) Lewis, T. J.; Rettig, S. J.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1991**, *113*, 8180.

[10] Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386.

[11] McBride, J. M. *Acc. Chem. Res.* **1983**, *16*, 304.

[12] Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.

[13] For progress in the design of cocrystals and other aggregate structures, see: Etter, M. C.; Frankenbach, G. M. *Chemistry of Materials* **1989**, *1*, 10 and references cited therein.

Long-Range Energy Transfer in Oligomeric Metal Complex Assemblies

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Recently we demonstrated by transient infrared spectroscopy that $\mathrm{Re^{I}} \rightarrow$ phen metal-to-ligand charge-transfer (MLCT) excitation of $[\mathrm{(phen)(CO)_3Re^{I}(NC)Ru^{II}(bpy)_2(CN)}]^+$ (phen is 1,10-phenanthroline; bpy is 2,2′-bipyridine) in $\mathrm{CH_3CN}$ was followed by rapid (~10 ps), intramolecular energy transfer.[1] We

$$\begin{tikzcd}
{[\mathrm{(phen^{\bullet -})(CO)_3Re^{II}(NC)Ru^{II}(bpy)_2(CN)}]^{+*}} \arrow[dr, "k = 1 \times 10^{11}\ \mathrm{s^{-1}}"] & \\
 & {[\mathrm{(phen)(CO)_3Re^{I}(NC)Ru^{III}(bpy)(bpy^{\bullet -})(CN)}]^{+*}} \arrow[dl, "k = 1.2 \times 10^{6}\ \mathrm{s^{-1}}"] \\
{[\mathrm{(phen)(CO)_3Re^{I}(NC)Ru^{II}(bpy)_2(CN)}]^{+}} \arrow[uu, "h\nu"] &
\end{tikzcd}$$

have extended the cyano-bridging chemistry to the oligomers, $[\mathrm{(phen)(CO)_3Re(CN)[Ru(bpy)_2(CN)]_{\mathit{n}}Ru(bpy)_2(CN)}]^{(n+1)+}$ (n = 0–3), in which every $\mathrm{Ru^{II}}$ center is linked to two cyanides, one by binding to carbon and one to nitrogen, and report here that they can function as molecular conduits for long-range energy transfer.

The oligomers were prepared by warming solutions of a reactive solvento intermediate generated by the reaction[2]

$$\textit{cis}\text{-}[\mathrm{Ru(bpy)_2(NO)(CN)}]^{2+} + \mathrm{N_3^-} + \mathrm{CH_3OH} \rightarrow \textit{cis}\text{-}[\mathrm{Ru(bpy)_2(CH_3OH)(CN)}]^{+} + \mathrm{N_2} + \mathrm{N_2O}$$

The oligomers which formed were end-capped with $\mathrm{Re(phen)(CO)_3(CN)}$ in a second step and separated by chromatography.[3]

$$(n+2)\textit{cis}\text{-}[\mathrm{Ru(bpy)_2(CH_3OH)(CN)}]^{+} \rightarrow [\mathrm{(CH_3OH)Ru(bpy)_2(CN)[Ru(bpy)_2(CN)]_{\mathit{n}}Ru(bpy)_2(CN)}]^{n+} + (n+1)\mathrm{CH_3OH} \quad (n = 0\text{–}3)$$

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[1] Gordon, K. C.; Dyer, R. B.; Schoonover, J. R.; Meyer, T. J.; Bignozzi, C. A.; Argazzi, R. *J. Phys. Chem.*, in press.

[2] (a) Adeyemi, S. A.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1972**, *11*, 994. (b) Bignozzi, C. A.; Roffia, S.; Chiorboli, C.; Davila, J.; Indelli, M. T.; Scandola, F. *Inorg. Chem.* **1989**, *28*, 4350.

[3] To a 0.60-g sample of $[\mathrm{Ru(bpy)_2(NO)(CN)}](\mathrm{PF_6})_2$ (0.79 mmol)[2b] suspended in 60 mL of $\mathrm{CH_3OH}$ was added 0.051 g of $\mathrm{NaN_3}$ (0.79 mmol). The resulting purple-brown solution was heated at reflux for 2 h, and 0.7 g of $\mathrm{Re(phen)(CO)_3(CN)}$ (1.57 mmol)[4] was added. The mixture was heated at reflux for 9 h, and the solvent was removed by evaporation. The solid was redissolved in $\mathrm{CH_3CN}$ and filtered to remove $\mathrm{Re(phen)(CO)_3(CN)}$, and the $\mathrm{CH_3CN}$ solution was eluted on a 1.5 × 5 cm silica gel column with $\mathrm{CH_2Cl_2}$ to remove $\mathrm{Re(phen)(CO)_3(CN)}$, with methanol to collect the Re–Ru complex, and with a NaCl-saturated methanol solution containing 5–15% water to collect the Re–Ru–Ru oligomer followed by Re–Ru–Ru–Ru and Re–Ru–Ru–Ru–Ru. Higher oligomers were irreversibly retained on the column. The eluted bands were concentrated, NaCl was filtered off, $\mathrm{PF_6^-}$ salts were precipitated by the addition of $\mathrm{(NH_4)(PF_6)}$, and excess $\mathrm{Cl^-}$ was removed by reprecipitation with added $\mathrm{(NH_4)(PF_6)}$. The reprecipitation cycle was repeated three times.

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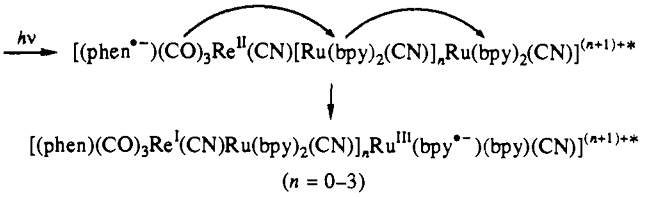
Table I. Photophysical Properties and $E_{1/2}$(Ru$^{III/II}$ or Re$^{II/I}$) Values in CH_3CN for the Oligomers $[(phen)(CO)_3Re(CN)[Ru(bpy)_2(CN)]_nRu(CN)(bpy)_2]^{(n+1)+}$ (n = 0–3)

complex	$E_{1/2}$ (V)^a	$\lambda_{max}{}^b$ abs (nm)	$\lambda_{max}{}^b$ em (nm)	$\Phi_{em}{}^c$	τ (ns)
Re(phen)$(CO)_3$(CN)	1.58^d	334	582		920
$n = 0$	0.94, 1.78^d	482	667	2.0×10^{-2}	422
$n = 1$	0.76, 1.37, 1.74^d	480	694	4.7×10^{-3}	133
$n = 2$	0.75, 1.10, 1.63,^{d} 1.77^d	479	694	4.5×10^{-3}	149
$n = 3$	0.73, 1.08, 1.34, 1.60,^{d} 1.77^d	477	694	3.9×10^{-3}	127

^{a}In CH_3CN with 0.1 M tetramethylammonium tetrafluoroborate versus SCE by cyclic voltammetry. ^{b}±2 nm; for absorption λ_{max} is the wavelength of maximum absorption in the MLCT manifold. ^{c}Relative to $[Ru(bpy)_3]^{2+}$, $\Phi_{em} = 6.2 \times 10^{-2}$ in CH_3CN: Calvert, J. M.; Casper, J. V.; Binstead, R. A.; Westmoreland, T. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *106*, 6620. ^{d}Irreversible wave, anodic peak potential, scan rate 200 mV/s.

They were isolated as PF_6^- salts and characterized by elemental analysis and FAB mass spectrometry (n = 0, 1, 2) and the Re/Ru ratios by X-ray fluorescence and infrared spectroscopy. In the infrared experiments, the ratio of intensities of the ν(CO) band at 2086 cm^{-1} and the band for the ν(bpy) out-of-plane bending mode at 764 cm^{-1} were measured in KBr. The results of the two experiments gave the same Re/Ru ratios and were in agreement with calculated ratios by ±10%.

In Table I are listed Ru$^{III/II}$,Re$^{II/I}$ reduction potentials and photophysical properties. From the properties of these and related complexes,[2b,5] the order of MLCT excited-state energies in the oligomers is predicted to be Re^{II}(phen$^{\bullet-}$) > Ru^{III}(bpy$^{\bullet-}$)(adj) > Ru^{III}(bpy$^{\bullet-}$)(bridge) > Ru^{III}(bpy$^{\bullet-}$)(term), where the abbreviations refer to Ru sites adjacent (adj) to Re^I, in the bridge (bridge), or at the terminus (term).[6] This ordering creates a basis for long-range energy transfer by an energy-transfer cascade:



$$\xrightarrow{h\nu} [(phen^{\bullet-})(CO)_3Re^{II}(CN)[Ru(bpy)_2(CN)]_nRu(bpy)_2(CN)]^{(n+1)+*}$$

$$\downarrow$$

$$[(phen)(CO)_3Re^{I}(CN)Ru(bpy)_2(CN)]_nRu^{III}(bpy^{\bullet-})(bpy)(CN)]^{(n+1)+*}$$

$$(n = 0\text{–}3)$$

The existence of long-range energy transfer is suggested by the near constancy in Φ_{em} and τ for n = 1–3 (Table I), the exponential emission decays, and the overlap between corrected excitation and absorption spectra. These results are consistent with intramolecular energy transfer to the terminal site following Re^I → phen, Ru^{II} → bpy(adj), or Ru^{II} → bpy(bridge) excitation. Energy transfer occurs on a time scale shorter than the resolution of the transient emission device used in the experiments (~30 ns).[2b]

Evidence that the excitation energy reaches the terminus comes from the solvent dependence of the emission energy, E_{em}. In solvents ranging from acetone to methanol, E_{em} varies linearly with the acceptor number of the solvent (AN) with a slope of $(2.0 \pm 0.2) \times 10^{-2}$ cm^{-1}/AN unit.[7] The same dependence (1.9×10^{-2}) is found for $[Ru(bpy)_2(py)(CN)]^+$ (py is pyridine), and it is ca. one-half that for $Ru(bpy)_2(CN)_2$ (3.8×10^{-2}).[7d] In the absence of terminal cyano groups, e.g., for $[Ru(bpy)_3]^{2+}$, variations with solvent do not correlate with acceptor number and are less by a factor of >10.[7d]

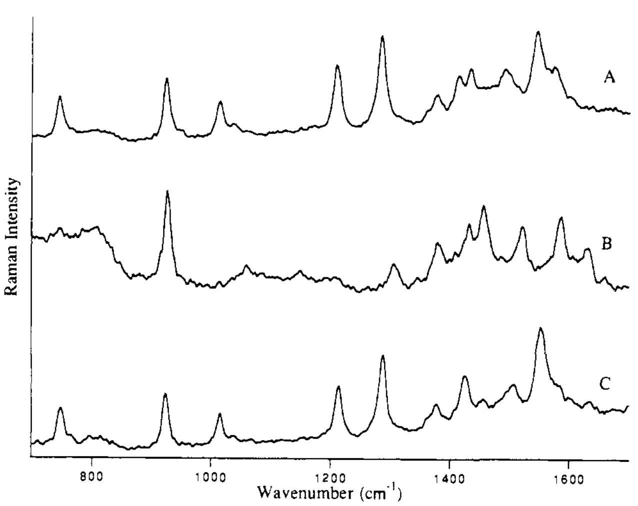


Figure 1. Time-resolved resonance Raman spectra of (A) $[(phen)(CO)_3Re(NC)Ru(bpy)_2(CN)]^+$, (B) $[(phen)(CO)_3Re(NC)Ru(phen)_2(CN)]^+$, and (C) $[(phen)(CO)_3Re(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)]^{2+}$ in CH_3CN. The third harmonic (354.7 nm) of a Quanta-Ray DCR-2A Nd:YAG laser was utilized to both create and probe the excited state. The scattered radiation was collected in a 135° back-scattering geometry into a SPEX 1877D triple spectrometer. The Raman scattering was detected by a Princeton Instruments IRY-700 optical multichannel analyzer and ST-110 controller. Timing was controlled by a Princeton Instruments FG100 pulse generator, and data processing and storage were controlled by an IBM AT. Each spectrum is a result of 16 min of total integration time.

Direct evidence has been obtained by excited-state resonance Raman measurements. In Figure 1 are illustrated excited-state spectra for $[(phen)(CO)_3Re(NC)Ru(bpy)_2(CN)]^+$, $[(phen)(CO)_3Re(NC)Ru(phen)_2(CN)]^+$, and $[(phen)(CO)_3Re(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)]^{2+}$ in CH_3CN. For $[(phen)(CO)_3Re(NC)Ru(bpy)_2(CN)]^+$, Re^I → phen and Ru^{II} → bpy excitation results in characteristic bands for (bpy$^{\bullet-}$) appearing at 1214, 1288, 1366, 1426, 1497, 1507, and 1550 cm^{-1}.[8] Under identical experimental conditions, excitation of $[(phen)(CO)_3Re(NC)Ru(phen)_2(CN)]^+$ results in bands characteristic of (phen$^{\bullet-}$) at 1149, 1305, 1432, 1455, 1522, and 1586 cm^{-1}.[9] For $[(phen)(CO)_3Re(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)]^{2+}$, only bands for (bpy$^{\bullet-}$) appear consistent with complete energy transfer to the terminus within the laser pulse, ~7 ns for this experiment. It is, as yet, unclear as to whether energy transfer occurs by site-to-site hopping or by long-range energy transfer in a single step. Transient Raman and infrared measurements with picosecond time resolution may allow us to discriminate between the two. In either case, our results point toward the designed synthesis

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(4) Leasure, R. M.; Sacksteder, L. A.; Nesselrodt, D.; Reitz, G. A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1991**, *30*, 3722.

(5) (a) Bignozzi, C. A.; Argazzi, R.; Schoonover, J. R.; Gordon, K. C.; Dyer, R. B.; Scandola, F. *Inorg. Chem.*, in press. (b) Bignozzi, C. A.; Scandola, F. *Inorg. Chem.* **1984**, *23*, 1540. (c) Bignozzi, C. A.; Paradisi, C.; Roffia, S.; Scandola, F. *Inorg. Chem.* **1988**, *27*, 408.

(6) A detailed discussion of this point will be given in a forthcoming manuscript.

(7) (a) The acceptor number (AN) is defined as the magnitude of the chemical shift of the ^{31}P resonance of Et_3PO in a solvent relative to hexane. The chemical shift of Et_3PO in hexane is arbitrarily assigned AN = 0, and the chemical shift of the $Et_3PO{:}SbCl_5$ adduct in 1,2-dichloroethane is assigned AN = 100. The acceptor number is a dimensionless quantity which is taken as a qualitative measure of the relative Lewis acidity of the solvent. (b) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum: New York, 1980. (c) Guttmann, V.; Resch, G.; Linert, W. *Coord. Chem. Rev.* **1982**, *43*, 133. (d) Bignozzi, C. A.; Timpson, C. J.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. Manuscript in preparation.

(8) (a) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391. (b) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441. (c) Strommen, D. P.; Mallick, P. K.; Danzer, G. D.; Lumpkin, R. S.; Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 1357.

(9) (a) Kumar, C. V.; Barton, J. K.; Turro, N. J.; Gould, I. R. *Inorg. Chem.* **1987**, *26*, 1455. (b) Kumar, C. V.; Barton, J. K.; Gould, I. R.; Turro, N. J.; Houton, J. V. *Inorg. Chem.* **1988**, *27*, 648. (c) Chang, Y. J.; Xiaobing, X.; Yabe, T.; Yu, S.-C.; Anderson, D. R.; Orman, L. K.; Hopkins, J. B. *J. Phys. Chem.* **1990**, *94*, 729.

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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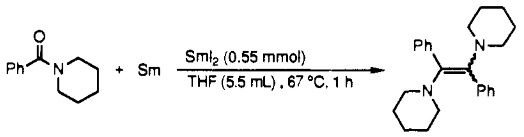
Herein we report the novel finding that a samarium/samarium diiodide mixed reagent (Sm/SmI_2) successfully effects the deoxygenative coupling of amides, which provides a powerful tool for preparing *vic*-diaminoalkenes.[1,2] In marked contrast to the deoxygenative coupling of aldehydes, ketones, and 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).



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]

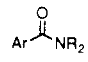
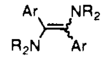
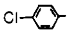
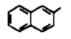
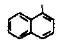
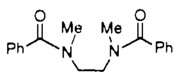
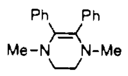
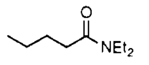
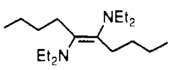
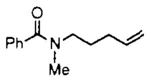
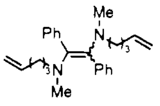
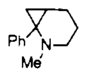
Table I. Deoxygenative Coupling of 1-Benzoylpiperidine

$$\underset{(1\ \text{mmol})}{\mathbf{1a}} \xrightarrow[\text{THF (22 mL)},\ 67\ °\text{C},\ 2\ \text{h}]{\text{Sm/SmI}_2} \mathbf{2a}$$

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.

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

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(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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