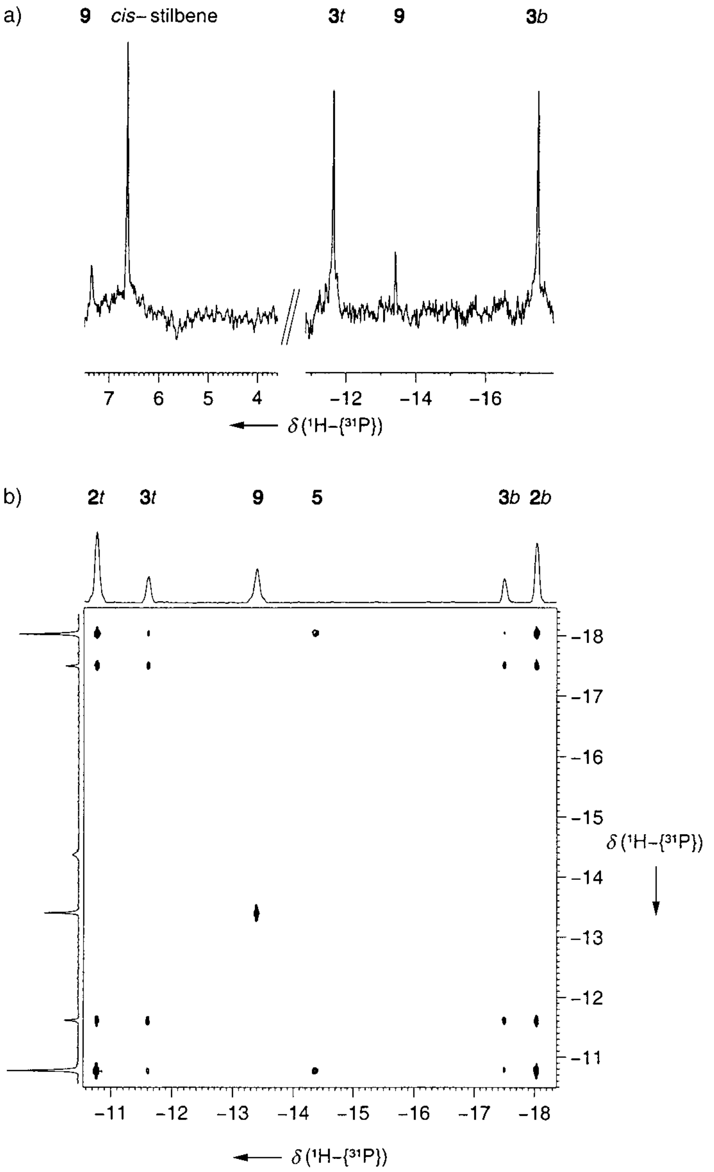


Figure 3. a) 1D ^{1}H-{^{31}P} EXSY NMR spectrum recorded in $CDCl_3$ at 301 K on a sample containing **1**, *p*-H_2, and a 100-fold excess of diphenylacetylene. The resonance for **3***t was* selectively excited and the results for a reaction time of 700 ms are displayed. Exchange into 3b, **9**, and *cis*-stilbene is indicated; b) 2D ^{1}H-{^{31}P} EXSY spectrum (positive contours) of an identical sample employing a mixing time of 400 ms. Off-diagonal peaks arise due to chemical exchange.

sum of the squares of the differences. The rate constants obtained in this way were multiplied by two.[14]

Received: May 21, 2001
Revised: July 10, 2001 [Z17141]

---

[1] For example see: *Catalysis by Di- and Polynuclear Metal Cluster Complexes* (Eds.: R. D. Adams, F. A. Cotton), Wiley, New York, **1998**.

[2] For example see: a) G. Süss-Fink, G. Herrmann, *J. Chem. Soc. Chem. Commun.* **1985**, 735; b) T. Hayashi, Z. H. Gu, T. Sakakura, M. Tanaka, *J. Organomet. Chem.* **1988**, *352*, 373; c) J. A. Caeza, J. M. Ferandez-Colinas, A. Llamazares, V. Riera, *Organometallics* **1993**, *12*, 4141; d) F. Ragaini, A. Ghitti, S. Cenini, *Organometallics* **1999**, *18*, 4925; e) B. Fontal, M. Reyes, T. Suarez, F. Bellandi, N. Ruiz, *J. Mol. Catal. A* **1999**, *149*, 87; f) B. Fontal, M. Reyes, T. Suarez, F. Bellandi, J. C. Diaz, *J. Mol. Catal. A* **1999**, *149*, 75; g) G. Gervaiso, R. Giordano, D. Marabello, E. Sappa, *J. Organomet. Chem.* **1999**, *588*, 83.

[3] a) C. R. Bowers, D. H. Jones, N. D. Kurur, J. A. Labinger, M. G. Pravica, D. P. Weitekamp, *Adv. Magn. Reson.* **1990**, *14*, 269; b) J. Natterer, J. Bargon, *Prog. Nucl. Magn. Reson. Spectrosc.* **1997**, *31*, 293; c) S. B. Duckett, C. J. Sleigh, *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 71.

[4] C. J. Sleigh, S. B. Duckett, R. J. Mawby, J. P. Lowe, *Chem. Commun.* **1999**, 1223.

[5] S. Aime, W. Dastru, R. Gobetto, A. Russo, A. Viale, D. Canet, *J. Phys. Chem. A* **1999**, *103*, 9702.

[6] M. Haake, J. Barkemeyer, J. Bargon, *J. Phys. Chem.* **1995**, *99*, 17539.

[7] S. A. Colebrooke, S. B. Duckett, J. A. B. Lohman, *Chem. Commun.* **2000**, 685.

[8] A. J. Deeming, S. Hasso, M. Underhill, *J. Chem. Soc. Dalton Trans.* **1975**, 1614.

[9] B. A. Messerle, C. J. Sleigh, M. G. Partridge, S. B. Duckett, *J. Chem. Soc. Dalton Trans.* **1999**, 1429.

[10] Signals from **4** were not visible under these conditions.

[11] a) M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, H. R. Reiger, M. L. Williams, *J. Chem. Soc. Chem. Commun.* **1982**, 442; b) M. I. Bruce, J. G. Matisons, B. K. Nicholson, *J. Organomet. Chem.* **1983**, *247*, 321.

[12] S. B. Duckett, C. L. Newell, R. Eisenberg, *J. Am. Chem. Soc.* **1994**, *116*, 10548.

[13] W. D. Jones, G. P. Rosini, J. A. Maguire, *Organometallics* **1999**, *18*, 1754.

[14] M. L. H. Green, L. L. Wong, A. Sella, *Organometallics* **1992**, *11*, 2660.

Samarium-Catalyzed Tandem Semipinacol Rearrangement/Tishchenko Reaction of α-Hydroxy Epoxides: A Novel Approach to Highly Stereoselective Construction of 2-Quaternary 1,3-Diol Units[**]

Chun-An Fan, Bao-Min Wang, Yong-Qiang Tu,[*] and Zhen-Lei Song

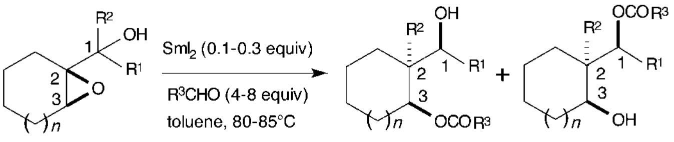
Diastereoselective constructions of 1,3-diol units have always been in high demand in synthetic organic chemistry, and preparation of 2-quaternary 1,3-diol units is of major importantance for the synthesis of many biologically significant molecules, such as the Furaquinocins,[1] and chiral ligands.[2] However, the quaternary carbon atom is generally difficult to construct with high diastereoselectivity, because a simple aldol reaction of carbonyl compounds is not efficient in this situation. Several procedures for construction of 2-quaternary 1,3-diol units have already been developed on the basis of the Lewis acid mediated semipinacol rearrangement of α-hydroxy epoxides. However, they generally need one equivalent or an excess of a promoter and produce only the β-

---

[*] Prof. Dr. Y.-Q. Tu, Dr. C.-A. Fan, B.-M. Wang, Z.-L. Song
Department of Chemistry and
National Laboratory of Applied Organic Chemistry
Lanzhou University, Lanzhou 730000 (China)
Fax: (+86) 931-8912582
E-mail: tuyq@lzu.edu.cn

[**] This work was supported by NSFC (No. 29972019, 29925205 and QT program), FUKTME of China, the Young Teachers' Fund of Ministry of Education and the Fund of Ministry of Education (No. 99209).

hydroxyketone.[3] Therefore, diastereoselective reduction of the ketone carbonyl group is additionally required.[4, 6e, 8l] We previously reported a one-step procedure based on the Al(iPrO)$_3$-promoted semipinacol/Meerwein–Ponndorf–Verley reduction of α-hydroxy epoxides,[5] but it still requires at least one equivalent of Lewis acid, and stereocontrol at C1 and C2 is not always perfect. Recently, we discovered that a catalytic amount of SmI$_2$ (0.1–0.3 equiv)[6] can promote a novel semipinacol rearrangement/Tishchenko reaction[6c, 7] of α-hydroxy epoxides to form efficiently 2-quaternary 1,3-diol monoesters with high diastereoselectivity (Scheme 1). This transformation is a new tandem reaction promoted by a catalytic amount of SmI$_2$, which is generally used as a single-electron reducing reagent in stoichiometric amounts or in excess.[8]



Scheme 1. Formation of 2-quaternary 1,3-diol monoesters.

The synthetically important features of this reaction are: 1) It constructs efficiently three contiguous stereocenters, one of which is quaternary, in one step; 2) mixed substrates **1** with two C1 epimers[3a, 5, 9] can form one diastereoisomer product **2** and/or **2′** (the acyl migration product[7b,e,g] of **2**), where **2** and **2′** were shown by NMR spectroscopy to have the same 2-quaternary 1,3-diol core on the products of their methanolysis with NaOH/MeOH;[10] 3) it is effective with catalytic amounts of SmI$_2$, instead of stoichiometric or excess quantities; and 4) the newly generated secondary C1−OH group has the β-configuration, as confirmed by 2D NMR spectroscopy on the acetonide of the 2-quaternary 1,3-diol obtained by methanolysis of **2** and/or **2′** with NaOH/MeOH,[10] which is not readily accessible by the previous procedure.[5] Consequently, this tandem reaction could be developed into a general procedure for diastereoselective construction of 2-quaternary 1,3-diol units with C1,C2 *anti* configuration.

The tertiary α-hydroxy epoxides we examined were prepared from the corresponding allylic alcohols through epoxidation with m-chloroperbenzoic acid (mCPBA) or tBuOOH/[VO(acac)$_2$] by literature procedures (Hacac = acetyl acetone).[3a, 5, 9] We invesigated substrates with five- or six-membered rings because of their wide occurrence in natural products. As shown in Scheme 1, a solution of **1** (1 equiv) in toluene, SmI$_2$ (0.1–0.3 equiv), and aldehyde (4–8 equiv) were heated at 80–85 °C until the substrate was completely consumed, as shown by TLC (4–8 h), and the 2-quaternary 1,3-diol monoester **2** and/or **2′** was obtained in a total yield of 70–96%. The experimental results (Table 1) show that the configuration at C1 of the 2-quaternary 1,3-diol monoester products is independent of that of the substrates. Particularly remarkable is the high degree of diastereocontrol of three contiguous carbon centers in all cases. We could not isolate C1,C2-*syn* diastereoisomers in our investigations (see below and Scheme 3). The reversed stereochemistry at C1 compared with that of the products of the Al(iPrO)$_3$-mediated reaction is noteworthy.[5]

Using less than 0.1–0.3 equiv of SmI$_2$ leads to partial formation of β-hydroxyketone, which can not be converted completely to **2** and/or **2′**, even by prolonging the reaction time. The reaction is dependent, to some extent, on the electronic effect and quantity of the aldehyde employed. The reactions of entries 1–8 proceeded well with benzaldehyde, but others did not. For example, performing the reaction of entry 9 with benzaldehyde gave only 30% of **2**/**2′**, and those of entries 10 and 11 did not give any monoester products with benzaldehyde, but only the β-hydroxyketones. This has not been found in the previously reported Tishchenko reactions,[7] but is important because it implies that we can expand the scope of the reaction by screening aldehydes. Generally, employment of only one equivalent of aldehyde makes this reaction slow, so we used 4–8 equiv. In addition, we found that the solvent also has an effect on the reaction. It proceeds readily in benzene, toluene, or 1,2-dichloroethane, but is very slow in THF, and can not even be initiated in protic solvents such as in MeOH or EtOH. Note, however, that we have successfully conducted only one reaction with alkyl group migration (entry 11), which would be the only limitation of the present reaction.

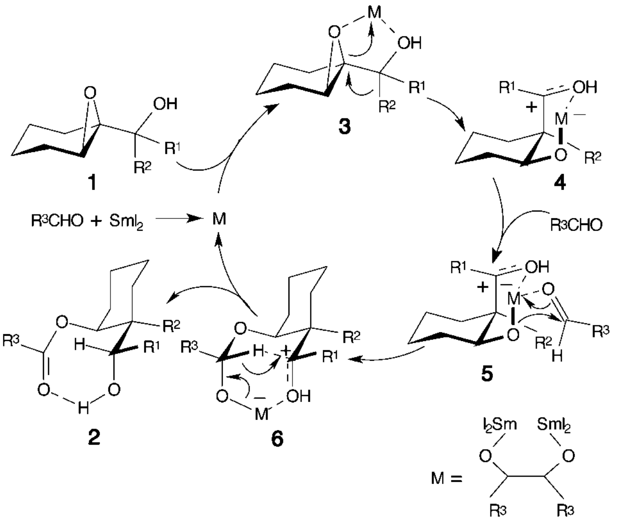
To assign a possible reaction mechanism, we conducted supporting experiments. First, Sm pinacol complex (0.1 equiv) was prepared in situ from benzaldehyde and SmI$_2$[11] then added as catalyst to a solution of **1** in toluene (entry 1, 1 equiv)

Table 1. Samarium-catalyzed tandem semipinacol rearrangement/Tishchenko reaction of α-hydroxy epoxides **1**.

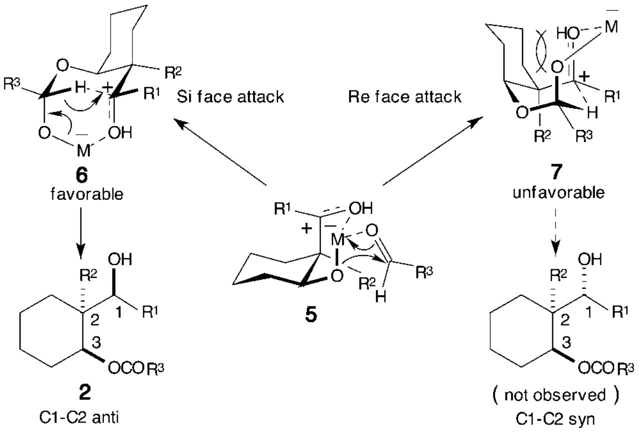
Entry	n	*syn*:*anti*[a]	R^1	R^2	R^3	SmI$_2$ [equiv]	Yield [%][b]	**2**:**2′**	t [h]
1	1		Ph	Ph	Ph	0.1	95	100:0	4
2	1	70:30	Me	Ph	Ph	0.15	96	100:0	4
3	1	61:39	Et	Ph	Ph	0.15	92	100:0	4
4	1	87:13	iPr	Ph	Ph	0.2	92	100:0	6
5	1	56:44	Allyl	Ph	Ph	0.3	70	100:0	8
6	1	100:0	Bn	Ph	Ph	0.3	95	0:100	2
7	1	79:21	nBu	Ph	Ph	0.3	78	100:0	6
8	0	70:30	Bn	Ph	Ph	0.3	88	44:56	6
9	0	80:20	Me	Ph	p-C$_6$H$_4$Cl	0.3	85	74:26	7
10	1	60:40	Me	2-thiophenyl	p-C$_6$H$_4$Cl	0.25	83	0:100	4
11	1	91:9	Me	cyclopropyl	p-C$_6$H$_4$Cl	0.3	78	93:7	4

[a] The ratio of two C1 epimers in substrate **1**; see refs. [3a, 5, 9]. [b] Total yield of isolated product **2** and/or **2′**.

and benzaldehyde (4 equiv). The reaction mixture was stirred for 4 h at 80 °C and the product **2** (entry 1) was obtained in 95 % yield. This result is similar to the one-pot reaction shown in Table 1. To further confirm this, the Sm pinacol complex (0.1 equiv) was prepared separately by treating dilithium 1,2-diphenylethanediolate[12] with SmI$_3$[13] in dry THF under Ar at room temperature for 1 h and then used for the reaction of **1** (entry 1, 1 equiv) with benzaldehyde (4 equiv) at 80 °C for 4 h. The result obtained was still similar to the above. In the general procedure, when SmI$_2$ in THF was added to the solution of **1** and aldehyde in toluene, the deep blue of SmI$_2$ in THF disappeared immediately. This suggests that SmI$_2$ is not the actual catalyst, but only a catalyst precursor.[6e, g] We further found that SmI$_3$ alone is less efficient as a catalyst.[6e, 7g] These results indicate that the catalytically active species in the present reaction may be the Sm pinacol complex (a bidentate Lewis acid catalyst,[14]represented by M in Scheme 2). In addition, benzaldehyde and *p*-chlorobenzaldehyde were used in a cross-experiment for clarifying the origin of hydride[6e] and the acyl group in this reaction. Benzaldehyde was treated with SmI$_2$ to afford the Sm pinacol complex (0.1 equiv),[11] which was used for the reaction of **1** (entry 1, 1 equiv) with *p*-chlorobenzaldehyde (4 equiv) for 0.5 h at 80 °C to give the 2-quaternary 1-hydroxy-3-*p*-chlorobenzoate in 97 % yield without any detectable presence of **2** (entry 1, 2-quaternary 1-hydroxy-3-benzoate). Similarly, when the Sm pinacol complex (0.1 equiv) prepared in situ from *p*-chlorobenzaldehyde and SmI$_2$ was used for the reaction of **1** (entry 1, 1 equiv) with benzaldehyde (4 equiv) for 0.5 h at 80 °C the product **2** (entry 1, 2-quaternary 1-hydroxy-3-benzoate) was obtained in 95 % yield without formation of 2-quaternary 1-hydroxy-3-*p*-chlorobenzoate. Hence, hydride and the acyl group do not originate from the aldehyde that forms the Sm pinacol complex, but from the other aldehyde. On the basis of the above results and literature reports,[5, 6e,g, 7, 11, 14] semipinacol rearrangement/Tishchenko reaction with catalysis by a Sm pinacol complex is proposed (Scheme 2). In particular, the high diastereoselectivity of this reaction is explained (Scheme 3). When the *Si* face of the aldehyde carbonyl plane is attacked, a favorable transition state **6** is formed, which leads to the formation of **2** with C1,C2-*anti* configuration. In contrast, attack at the *Re* face results in transition state **7**, which is unfavorable because of steric hindrance between the cyclohexane ring and the 1,3-dioxo heterocycle. Consequently, we could not isolate the C1,C2-*syn* diastereoisomers.[5]



Scheme 2. Proposed catalytic cycle.



Scheme 3. Proposed mechanism for diastereoselectivity.

Experimental Section

General procedure (Table 1, entry 1): A solution of SmI$_2$ (0.1 M in THF, 0.4 mL) was added dropwise to a solution of **1** (entry 1, 112.0 mg, 0.4 mmol) and freshly distilled benzaldehyde (1.6 mmol) in dry toluene (4 mL) at room temperature under an argon atmosphere. The reaction mixture was stirred for 4 h at 80 – 85 °C, after which TLC analysis showed the substrate **1** (entry 1) had disappeared completely. Then a saturated solution (3 mL) of sodium hydrogencarbonate was added. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined extracts were dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent and column chromatography of the crude product on silica gel (petroleum/ethyl acetate 30/1 → 15/1) afforded **2** (entry 1, 147.0 mg, 0.38 mmol, 95 %).

Received: May 21, 2001 [Z17154]

---

[1] T. Saito, T. Suzuki, M. Morimoto, C. Akiyama, T. Ochiai, K. Takeuchi, T. Matsumoto, K. Suzuki, *J. Am. Chem. Soc.* **1998**, *120*, 11633.

[2] W. Hoeve, H. Wynberg, *J. Org. Chem.* **1985**, *50*, 4508.

[3] a) C. M. Marson, A. J. Walker, J. Picking, A. D. Hobson, R. Wrigglesworth, J. Campbell, *J. Org. Chem.* **1993**, *58*, 5944; b) K. Suzuki, M. Miyazama, G. Tsuchihaski, *Tetrahedron Lett.* **1987**, *28*, 3515; c) C. M. Marson, S. Harper, A. J. Walker, J. Picking, J. Campbell, *Tetrahedron* **1993**, *49*, 10339; d) B. Rickborn in *Comprehensive Organic Synthesis, Vol. 3* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 733 – 755; e) D. J. Morgans, K. B. Sharpless, *J. Am. Chem. Soc.* **1981**, *103*, 462; f) K. Maruoka, M. Hasegawa, H. Yamamoto, K. Suzuki, M. Shimazaki, G.-I. Tsuchihashi, *J. Am. Chem. Soc.* **1986**, *108*, 3827; g) K. Maruoka, J. Sato, H. Yamamoto, *J. Am. Chem. Soc.* **1991**, *113*, 5449; h) Y. Q. Tu, C. A. Fan, S. K. Ren, A. S. C. Chan, *J. Chem. Soc. Perkin Trans. 1* **2000**, 3791.

[4] a) W. J. Gensler, F. Johnson, A. D. B. Sloan, *J. Am. Chem. Soc.* **1960**, *82*, 6074; b) T. Nakata, Y. Tani, M. Hatozaki, T. Oishi, *Chem. Pharm. Bull.* **1984**, *32*, 1411; c) C. R. Sarko, S. E. Collibee, A. L. Knorr, M. Dimare, *J. Org. Chem.* **1996**, *61*, 868; d) K.-M. Chen, K. G. Gunderson, G. E. Hardtmann, K. Praasad, O. Repic, M. Shapiro, *Chem. Lett.* **1987**, 1923; e) I. Paterson, J. A. Channon, *Tetrahedron Lett.* **1992**, *33*, 797;

f) D. A. Evans, K. T. Chapman, E. M. Carreira, *J. Am. Chem. Soc.* **1988**, *110*, 3560.

[5] Y. Q. Tu, L. D. Sun, P. Z. Wang, *J. Org. Chem.* **1999**, *64*, 629.

[6] To the best of our knowledge, only a few SmI_2-promoted reactions are catalytically effective. See a) J. L. Namy, J. Souppe, J. Collin, H. B. Kagan, *J. Org. Chem.* **1984**, *49*, 2045; b) J. Prandi, J. L. Namy, G. Menoret, H. B. Kagan, *J. Organomet. Chem.* **1985**, *285*, 449; c) J. Collin, J. L. Namy, H. B. Kagan, *New J. Chem.* **1986**, *10*, 229; d) X. Lu, S. Ma, J. Zhu, *Tetrahedron Lett.* **1988**, *29*, 5129; e) D. A. Evans, A. H. Hoveyda, *J. Am. Chem. Soc.* **1990**, *112*, 6447; f) D. A. Evans, D. L. Rieger, T. K. Jones, S. W. Kaldor, *J. Org. Chem.* **1990**, *55*, 6260; g) P. V. Weghe, J. Collin, *Tetrahedron Lett.* **1993**, *34*, 3881; h) N. Takayuki, S. Hiroyuki, S. Satoshi, I. Yasutaka, *Tetrahedron Lett.* **2000**, *41*, 3389.

[7] For Tishchenko reactions, see: a) K. Yokoo, N. Mine, H. Taniguchi, Y. Fujiwara, *J. Organomet. Chem.* **1985**, *279*, C19; b) E. R. Burkhardt, R. G. Bergman, C. H. Heathcock, *Organometallics* **1990**, *9*, 30; c) S.-Y. Onozawa, T. Sakakura, M. Tanaka, M. Shiro, *Tetrahedron* **1996**, *52*, 4291; d) T.-H. Chuang, J.-M. Fang, W.-T. Jiaang, Y.-M. Tsai, *J. Org. Chem.* **1996**, *61*, 1794; e) R. Mahrwald, B. Costisella, *Synthesis* **1996**, 1087; f) Y. Umekawa, S. Sakaguchi, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* **1997**, *62*, 3409; g) L. Lu, H.-Y. Chang, J.-M. Fang, *J. Org. Chem.* **1999**, *64*, 843; h) M. Adinolfi, G. Barone, F. De Lorenzo, A. Iadonisi, *Synlett* **1999**, 336; i) T. Ooi, T. Miura, K. Takaya, K. Maruoka, *Tetrahedron Lett.* **1999**, *40*, 7695; j) C. Delas, O. Blacque, C. Moïsoe, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2265; k) C. M. Mascarenhas, S. P. Miller, P. S. White, J. P. Morken, *Angew. Chem.* **2001**, *113*, 621; *Angew. Chem. Int. Ed.* **2001**, *40*, 601.

[8] a) P. Girard, L. Namy, H. B. Kagan, *J. Am. Chem. Soc.* **1980**, *102*, 2693; b) H. B. Kagan, M. Sasaki, J. Collin, *Pure Appl. Chem.* **1988**, *60*, 1725; c) H. B. Kagan, *New J. Chem.* **1990**, *14*, 453; d) G. A. Molander, *Chem. Rev.* **1992**, *92*, 29; e) G. A. Molander, C. R. Harris, *Chem. Rev.* **1996**, *96*, 307; f) M. Kawatsura, E. Kishi, M. Kito, T. Sakai, H. Shirahama, F. Matsuda, *Synlett* **1997**, 497; g) A. Krief, A.-M. Laval, *Chem. Rev.* **1999**, *99*, 745; h) C. U. Dinesh, H.-U. Reissig, *Angew. Chem.* **1999**, *111*, 874; *Angew. Chem. Int. Ed.* **1999**, *38*, 789; i) N. Taniguchi, T. Hata, M. Uemura, *Angew. Chem.* **1999**, *111*, 1311; *Angew. Chem. Int. Ed.* **1999**, *38*, 1232; j) K. Ohmori, M. Kitamura, K. Suzuki, *Angew. Chem.* **1999**, *111*, 1304; *Angew. Chem. Int. Ed.* **1999**, *38*, 1226; k) J. Concellón, P. L. Bernad, J. A. Pérez-Andrés, *Angew. Chem.* **1999**, *111*, 2528; *Angew. Chem. Int. Ed.* **1999**, *38*, 2384; l) G. E. Keck, C. A. Wager, T. Sell, T. T. Wager, *J. Org. Chem.* **1999**, *64*, 2172; m) J. M. Aurrecoechea, R. Fañanás, M. Arrate, J. M. Gorgojo, N. Aurrekoetxea, *J. Org. Chem.* **1999**, *64*, 1893; n) T. Kikukawa, T. Hanamoto, J. Inanaga, *Tetrahedron Lett.* **1999**, *40*, 7497; o) L. Yet, *Chem. Rev.* **2000**, *100*, 2963; p) T. Kan, S. Nara, T. Ozawa, H. Shirahama, F. Matsuda, *Angew. Chem.* **2000**, *112*, 363; *Angew. Chem. Int. Ed.* **2000**, *39*, 355; q) S. M. Kim, I. S. Byun, Y. H. Kim, *Angew. Chem.* **2000**, *112*, 744; *Angew. Chem. Int. Ed.* **2000**, *39*, 728; r) X. Jiang, C. Wang, Y. Hu, H. Hu, *J. Org. Chem.* **2000**, *65*, 3555; s) A. Caracoti, R. A. Flowers, *Tetrahedron Lett.* **2000**, *41*, 3039.

[9] E. D. Mihelich, *Tetrahedron Lett.* **1979**, *20*, 4729.

[10] K. Mashimo, Y. Sato, *Tetrahedron* **1970**, *26*, 803.

[11] a) J. Souppe, L. Danon, J. L. Namy, H. B. Kagan, *J. Organomet. Chem.* **1983**, *250*, 227; b) J. Souppe, J. L. Namy, H. B. Kagan, *Tetrahedron Lett.* **1983**, *24*, 765.

[12] *n*BuLi (1 M, 2 equiv) was added to a solution of 1,2-diphenyl-1,2-ethanediol (1 equiv) in dry THF under Ar at 0 °C, and the reaction mixture stirred for 0.5 h. The reaction mixture (dilithium 1,2-diphenylethanediolate) was then added to a suspension of SmI_3 (2 equiv) in dry THF by syringe and stirred for 1 h at RT under Ar. The product thus formed (see Scheme 2) was used in the reaction as catalyst, and the result was similar to that obtained in the general procedure. For a similar experimental procedure, see: D. A. Evans, S. G. Nelson, M. R. Gagné, A. R. Muci, *J. Am. Chem. Soc.* **1993**, *115*, 9800.

[13] T. Imamoto, M. Ono, *Chem. Lett.* **1987**, 501.

[14] J. D. Wuest, *Acc. Chem. Res.* **1999**, *32*, 81.

Grafted Metal Oxide/Polymer/Carbon Nanostructures Exhibiting Fast Transport Properties[**]

Huan Huang and Linda F. Nazar[*]

Rechargeable lithium batteries are a superior alternative energy source for a variety of applications that demand advanced energy-storage systems.[1] However, accessing high charge/discharge rates without losing capacity is one of the biggest challenges, due to the often sluggish kinetics of Li^+ ion transport in solid electrodes.[2] Many otherwise suitable intercalation materials do not meet the criterion of fast ion and/or electron transport. In contrast to attempting to tailor a single material, nanocomposites can provide an optimum way of crafting desired characteristics for a target application.[3] Here, we describe a new class of materials which were prepared by the grafting of polymer electrolyte chains and metal oxide layers onto the surface of electronically conductive "graphite-like" carbon spheres. They exhibit an enhanced electrochemical response at remarkably high rates and improved electrochemical stability owing to their unique nanostructure.

A "nanostructure" containing two or more materials mixed on a nanometer scale, ideally is a composite in which the sum of the parts is greater than the whole. This concept, of fundamental interest for many years, is widely applicable.[4] Electrochemical applications include those involving V_2O_5, a widely studied cathode material that has kinetic limitations both for ionic and electronic transport.[5] Layered polymer/metal oxide nanocomposites of xerogel–V_2O_5[6] have shown tenfold enhancement of the Li^+ diffusion coefficient, owing to polymer "propping" of the host layers.[7] Layered nanocomposites of clays and polyethylene oxide produce highly ionically conductive materials potentially suitable for solid electrolyte applications.[8] Another approach has been to shorten the diffusion path. High surface area aerogel forms of V_2O_5 display a high capacity under pseudo-equilibrium conditions in thin films.[9] V_2O_5 prepared by electrodeposition in the presence of surfactants displays a porous thin-wall structure, also resulting in good behavior with a capacity of $220\,mA\,h\,g^{-1}$ at a fast rate.[10, 11] Nonetheless, a potential drawback with high surface area materials is poor volumetric capacity, and the attendant increase in catalytically active surface sites if the sites are not blocked, ultimately resulting in electrolyte degradation. However, none of the above approaches gives rise to a readily prepared, nor stable electrochemical system, nor takes advantage of a chemically nanostructured design.

---

[*] Prof. L. F. Nazar, H. Huang
Department of Chemistry
and the Waterloo Centre for Materials Research
University of Waterloo
Waterloo, ON, N2L 3G1 (Canada)
Fax: (+1) 519-746-0435
E-mail: lfnazar@uwaterloo.ca

[**] This work was supported by the National Sciences and Engineering Council of Canada through a Research Grant to L.F.N. H.H. thanks the Link Foundation (USA) for a scholarship in 2001.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.