

Scheme 2. Insertion of the platinum fragment into a P–C bond.

P–C bond of the four-membered ring to give a 1-platina-2-phosphaacenaphthene framework.

Experimental Section^[13]

3: PhPCl_2 (6.5 mL, 48 mmol) was added at -30°C to a suspension of **2** in hexane (60 mL) which was prepared from 1-bromonaphthalene (5 mL, 36 mmol).^[7b] After vigorous stirring at -30°C for 1 h and then at 0°C for 3 h, the products were collected by filtration. The products were suspended in hexane: CH_2Cl_2 and loaded onto an Al_2O_3 column and a yellow band was collected by using CH_2Cl_2 :hexane (1:1) as the eluent. After removal of the solvents, recrystallization from diethyl ether gave a white powder, 4.88 g (59% based on PhPCl_2). ^1H NMR (300.4 MHz, CDCl_3 , TMS): δ = 7.18 (m, 10H; Ph), 7.60 (m, 2H; 3,6-naph), 7.82 (m, 2H; 1,7-naph), 7.93 ppm (d, J = 8.1 Hz 2H; 4,5-naph); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3 , TMS): δ = 127.4, 128.0, 128.5, 132.1, 132.2, 133.6, 138.4, 141.8, 142.0 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.45 MHz, CDCl_3 , H_3PO_4): δ = -8.0 ppm.

4: A diethyl ether solution of **2**, prepared from 1,8-dibromonaphthalene (250 mg, 0.874 mmol),^[7a] was added to a solution of $i\text{Pr}_2\text{NPCl}_2$ (0.20 mL, 1.05 mmol) in diethyl ether (3 mL) at 0°C . The mixture was stirred overnight, then LiCl was removed by filtration. After evaporation of the solvents, the residue was loaded onto an Al_2O_3 column. A light yellow band was eluted with hexane, and collected. After removal of the solvents 169 mg of **4** (75%) was obtained as a white powder. ^1H NMR (300.4 MHz, CDCl_3 , TMS): δ = 1.18 (d, $^3J(\text{H,H})$ = 6.6 Hz, 12H; CHMe_2), 3.29 (m, 2H; CHMe_2), 7.42 (d, $^3J(\text{H,H})$ = 6.6 Hz, 2H; naph), 7.52 (m, 2H; naph), 7.70 ppm (d, $^3J(\text{H,H})$ = 8.2 Hz, 2H; naph); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3 , TMS): δ = 23.8, 47.6, 122.5, 123.8, 127.5, 129.4, 147.2 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.45 MHz, CDCl_3 , H_3PO_4): δ = -8.4 ppm.

6: **5** (764 mg, 1.31 mmol), which was prepared from the reaction of **4** and $[\text{W}(\text{CO})_5(\text{thf})]$, was treated with $[\text{Pt}(\text{PPh}_3)_4]$ (1635 mg, 1.31 mmol) in toluene (90 mL) at 45°C for 3 h, and the mixture was then purged with CO gas for 10 min. The resulting solution was heated at 90°C for 2 h, followed by removal of the toluene under reduced pressure. The residue was loaded onto an Al_2O_3 column, and a yellow band was collected by elution with CH_2Cl_2 :hexane (1:4). After removal of the solvents 1252 mg (89%) of **6** was obtained. ^1H NMR (300.4 MHz, CDCl_3 , TMS): δ = 1.20 (d, $^3J(\text{H,H})$ = 6.6 Hz, 6H; CHMe_2), 1.35 (d, $^3J(\text{H,H})$ = 6.8 Hz, 6H; CHMe_2), 4.25 (m, 2H; CHMe_2), 6.77 (m, 1H), 7.30–7.60 (m, 13H), 7.73 (m, 6H), 7.87 ppm (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.4 MHz, CDCl_3 , TMS): δ = 181.2 (PtCO), 198.3 (*cis* WCO), 201.7 ppm (*trans* WCO); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.45 MHz, CDCl_3 , H_3PO_4): δ = 22.3 (d, $^2J(\text{P,P})$ = 225 Hz, $^1J(\text{P,Pt})$ = 1736 Hz; PPh_3), 75.2 ppm (d, $^2J(\text{P,P})$ = 225 Hz, $^1J(\text{P,Pt})$ = 1706 Hz, $^1J(\text{P,W})$ = 227 Hz).

Received: June 24, 2002 [Z19593]

- [1] R. W. Hoffmann, W. Sieber, *Angew. Chem.* **1965**, 77, 810–811; *Angew. Chem. Int. Ed. Engl.* **1965**, 4, 786.
 [2] a) A. Hergel, H. Pritzkow, W. Siebert, *Angew. Chem.* **1994**, 106, 1342–1343; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1247–1248; b) J. D. Hoefelmeyer, F. P. Gabbaï, *Organometallics* **2002**, 21, 982–985.
 [3] A. Kumar, F. E. Friedli, L. Hsu, P. J. Card, N. Mathur, H. Shechter, *J. Org. Chem.* **1991**, 56, 1663–1666, and references therein; L. S. Yang, H. Shechter, *J. Chem. Soc. Chem. Commun.* **1976**, 775; J. Ohshita, K. Matsushige, A. Kunai, A. Adachi, K. Sakamaki, K. Okita, *Organometallics* **2000**, 19, 5582–5588; M. A. G. M. Tinga, G. J. H. Buisman, G. Schat, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets, A. L. Spek, *J. Organomet. Chem.* **1994**, 484, 137–145.

- [4] J. Meinwald, S. Knapp, *J. Am. Chem. Soc.* **1974**, 96, 6532–6534; J. Meinwald, S. Knapp, S. K. Obendorf, R. E. Hughes, *J. Am. Chem. Soc.* **1976**, 98, 6643–6649.
 [5] A triphosphazene-bridged naphthalene, insufficiently characterized, was reported; M. B. Sayed, *Thermochim. Acta* **1994**, 232, 249–260.
 [6] For a recent review, see A. Marinetti, D. Carmichael, *Chem. Rev.* **2002**, 102, 201–230.
 [7] a) R. L. Letsinger, J. A. Gilpin, W. J. Vullo, *J. Org. Chem.* **1962**, 27, 672–674; b) L. Brandsma, H. D. Verkruijsse, *Preparative Polar Organometallic Chemistry, Vol. 1*, Springer, Berlin, **1987**, pp. 195–197.
 [8] Crystal data for **3**:^[14] colorless crystal ($0.50 \times 0.15 \times 0.10$ mm), monoclinic, $P2_1/c$, $a = 15.8680(8)$, $b = 5.7220(1)$, $c = 19.631(1)$ Å, $\beta = 100.087(2)^\circ$, $V = 1754.1(1)$ Å³, $\rho_{\text{calcd}} = 1.296$ g cm⁻³, $2\theta_{\text{max}} = 55^\circ$, $\text{MoK}\alpha(\lambda = 0.71609$ Å), $T = 295$ K, 4217 reflections measured, 3824 independent reflections, 3642 ($I/\sigma(I) > 0.0$) reflections used, $\mu(\text{MoK}\alpha) = 2.47$ cm⁻¹, R/wR factors ($I/\sigma(I) > 2.0$) 0.0646/0.1324.
 [9] A. Karaçar, M. Freytag, H. Thönnessen, P. G. Jones, R. Bartsch, R. Schmutzler, *J. Organomet. Chem.* **2002**, 643–644, 68–80.
 [10] A ring-expansion mechanism for 1,2-dihydrophosphete was proposed by Mathey and co-workers.; N. Maigrot, N. Avarvari, C. Charrier, F. Mathey, *Angew. Chem.* **1995**, 107, 623; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 590–592.
 [11] Crystal data for **4**:^[14] colorless crystal ($0.75 \times 0.40 \times 0.25$ mm), monoclinic, $P2_1/c$, $a = 7.674(7)$, $b = 14.559(5)$, $c = 13.880(5)$ Å, $\beta = 101.15(6)^\circ$, $V = 1521(1)$ Å³, $\rho_{\text{calcd}} = 1.123$ g cm⁻³, $2\theta_{\text{max}} = 55^\circ$, $\text{MoK}\alpha(\lambda = 0.71609$ Å), ω - 2θ scan mode, $T = 295$ K, 3954 reflections measured, 3489 independent reflections, 1458 ($I/\sigma(I) > 0.0$) reflections used, $\mu(\text{MoK}\alpha) = 1.64$ cm⁻¹, max./min. transmission 0.998/0.746, R/wR factors ($I/\sigma(I) > 2.0$) 0.0933/0.1365.
 [12] H. Roohi, F. Deyhimi, A. Ebrahimi, *J. Mol. Struct. THEOCHEM* **2001**, 540, 287–294.
 [13] **2** prepared by method A is in a homogeneous diethyl ether/hexane solution,^[7a] whereas the product obtained by the method B is an adduct with N,N,N',N' -tetramethyl-1,2-ethanediamine (TMEDA) and is sparingly soluble in hexane.^[7b] Although both methods, A and B, were applied to preparation of **3** and **4**, the procedure giving a better yield is that described in the Experimental Section.
 [14] CCDC-188236 (**3**) and CCDC-188237 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Butane-2,3-diacetals of Glyceraldehyde: A Stable Alternative to Glyceraldehyde Acetonide**

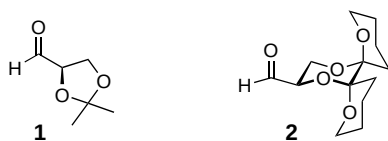
Patrick Michel and Steven V. Ley*

D-Glyceraldehyde acetonide **1** has been used extensively as a three-carbon building block for organic synthesis.^[1] However, it must always be freshly prepared owing to its propensity to polymerize, racemize, and form hydrates.^[2] This can result in severe problems, particularly on scale-up. Thus, a readily available, stable alternative that is accessible in both

[*] Prof. Dr. S. V. Ley, Dr. P. Michel
 Department of Chemistry
 University of Cambridge
 Lensfield Road, Cambridge CB2 1EW (UK)
 Fax: (+44) 1223-336-442
 E-mail: svl1000@cam.ac.uk

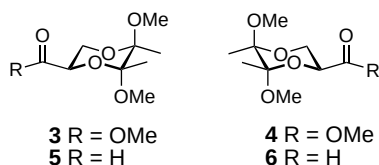
[**] We thank the BBSRC (to P.M.) and the Novartis Research Fellowship (to S.V.L.) for financial support.

enantiomeric series has the potential to be a powerful building block for synthesis. Here we describe a possible solution to this long-standing problem.

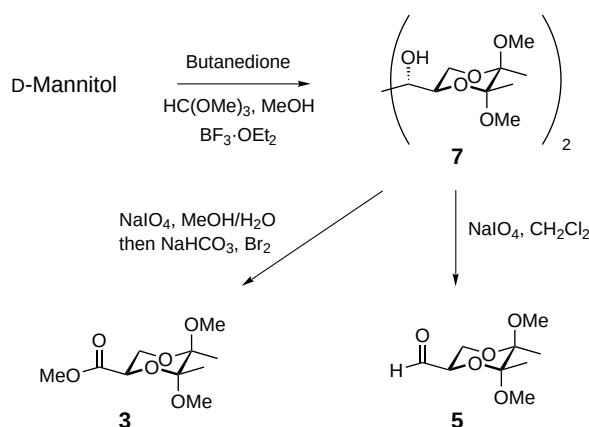


Some time ago we reported the preparation and utility of a dispiroketal-protected glyceraldehyde derivative **2**.^[3] This possessed considerable advantages over acetonide **1** in regard to both stability and reactivity, presumably due to the enhanced crystallinity of these dispiroketals and the favored placement of the aldehyde unit in a more stable equatorial environment. Although this was a step forward, the considerable increase in molecular weight and also difficulties in large-scale preparation meant that it failed to be adopted as a general replacement for **1**. We have continued to seek alternatives and have chosen to focus on the use of butane-2,3-diacetals^[4] as these are easily prepared from cheap starting materials, leading to a range of building blocks for synthesis.^[5]

Initially we investigated an approach that would produce both enantiomeric series of esters **3** and **4** and glyceraldehydes **5** and **6**.



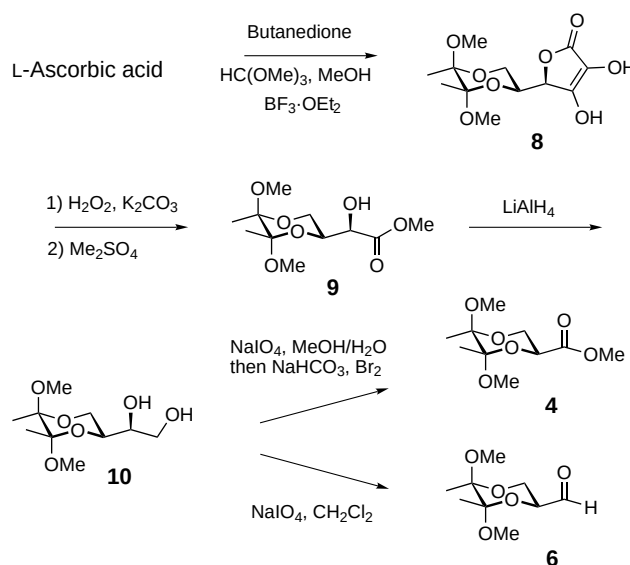
As planned, D-mannitol reacts with butane-2,3-dione in the presence of trimethyl orthoformate and boron trifluoride etherate^[4d] in methanol to give the diol **7** as the major product which could be isolated in a pure form by recrystallization from hexane (Scheme 1). Alternatively, oxidative cleavage of the crude diol **7** with sodium periodate in methanol, followed by bromine oxidation of the methyl hemiacetal^[6] gave the ester **3**^[7] as a colorless oil in 45 % yield over the two steps. The aldehyde **5** (white solid at -20°C) on the other hand, could be



Scheme 1. Reaction of D-mannitol with butane-2,3-dione to give the ester **3** and the aldehyde **5**.

isolated in 40 % overall yield by oxidative cleavage with sodium periodate in dichloromethane. These reactions were all carried out on scales in excess of 50 g, in which the only purification is a single distillation under vacuum at the final stage.

For the other enantiomeric series, we started from L-ascorbic acid as the source of chirality (Scheme 2). Protection with butane-2,3-dione gave the corresponding butane-2,3-



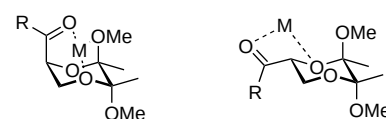
Scheme 2. Reaction of L-ascorbic acid with butane-2,3-dione to give the ester **4** and the aldehyde **6**.

diacetal **8** in 72 % yield, which was readily converted to the ester **9** by oxidative cleavage with hydrogen peroxide followed by methylation with dimethyl sulfate.^[8] Reduction to the diol **10** with LiAlH_4 followed by oxidation with periodate under the previously described conditions furnished either **4** or **6** in 52 % or 35 % overall yield, respectively, from **8**. Once again, the only purification is a single distillation at the final stage.

Although the esters **3** and **4** and the aldehydes **5** and **6** are stable and can be stored readily at -20°C for long periods of time (at least 6 months), the aldehydes decompose slowly at room temperature. Nevertheless they are considerably more stable than **1** and are significantly more convenient for use in synthesis programs.

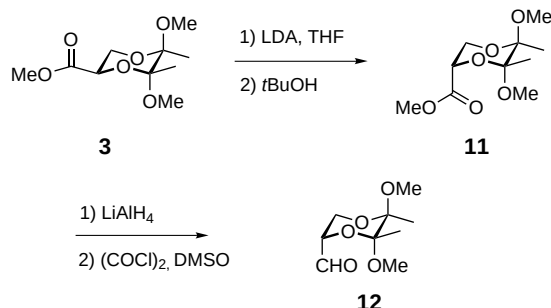
Preliminary studies concerned with the addition of organomagnesium reagents to aldehyde **5** indicated that the *syn/anti* selectivity of addition is similar to that observed with dispiroketalaldehyde **2**.^[3] It was reasoned that an aldehyde in an axial position could potentially give even higher selectivities by improved chelation control (Scheme 3).

Thus, we decided to investigate an inversion protocol to obtain an aldehyde in an axial position. Treatment of ester **3**



Scheme 3.

with lithium diisopropylamide (LDA) at -78°C followed by protic workup with $t\text{BuOH}$ at low temperature and subsequent quenching with aqueous ammonium chloride afforded mainly the inverted ester **11** (Scheme 4).^[7] Recrystallization from hexane gave only one product as a highly crystalline and stable material (53 % yield) whose structure was confirmed by X-ray crystallography.^[9] Reduction with LiAlH_4 in THF and

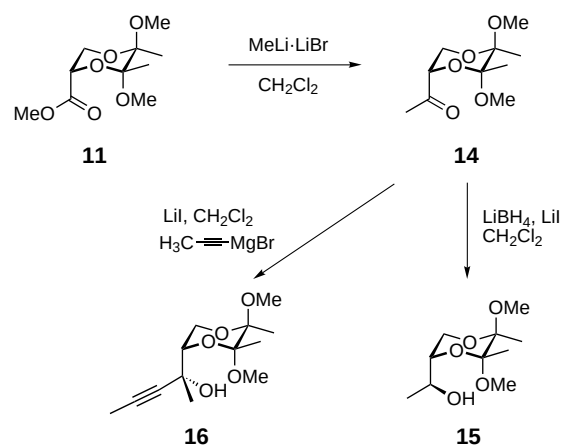


Scheme 4. Conversion of **3** to give the axial aldehyde **12**.

oxidation with oxalyl chloride and DMSO gave the axial aldehyde **12**^[7] (83 % overall yield on a 20 g scale) as a white crystalline solid whose structure was again confirmed by X-ray crystallography.^[9] This material is stable and storable for long periods of time (at least 3 months at room temperature or greater than 9 months at -20°C) and can be used without complications over several months.

The potential of **12** as a new chiral building block is illustrated by the stereofacially selective addition of Grignard reagents via β -chelation control (Scheme 3). Addition of a 1.5M Grignard reagent in dichloromethane to a solution of **12** in toluene at -95°C gave the corresponding secondary alcohols in good yield and excellent diastereoselectivity (Table 1). The stereochemical outcome of addition was confirmed by X-ray crystallography of the 4-nitrobenzoyl ester derivatives^[9] (Table 1, entries 1, 2, and 3). It was observed that several of these derivatives adopted a boat conformation whilst maintaining both methoxy groups in pseudo-axial positions.

To access the other configuration of the newly formed stereogenic center in the Grignard addition reactions, we also prepared the methyl ketone derivative **14** (Scheme 5) by addition of MeLi at -78°C to the ester **11** in dichloromethane (79 % yield; this compound could also be obtained via a



Scheme 5. Synthesis of the methyl ketone derivative **14** and its conversion to **15** and **16**.

Weinreb amide). This ketone **14** reacted with lithium borohydride in dichloromethane containing some lithium iodide at -78°C to give **15** (80 % yield, > 15:1 stereoselectivity). If **14** was pretreated with lithium iodide in dichloromethane at -78°C and then propynyl magnesium bromide added, alcohol **16** was obtained in > 15:1 stereoselectivity. A single recrystallization from hexane afforded alcohol **16** as a single diastereoisomer (90 % yield), the structure of which was confirmed by X-ray crystallography^[9] (Scheme 5).

In summary, we have described the large-scale preparation of both enantiomers of new butanediactal-protected glycer-aldehyde and glyceric acid derivatives. These new building blocks should find application in a range of synthetic programs.

Received: June 3, 2002 [Z19457]

Table 1. Additions of Grignard reagent to **12**.

Entry	RMgX	Yield [%]	d.r.
1	CH_3MgCl	81	25:1
2	$\text{H}-\text{C}\equiv\text{C}-\text{MgBr}$	95	15:1
3	$\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{MgBr}$	93	15:1
4	$\text{CH}_3\text{CH}=\text{CH}-\text{MgBr}$	88	15:1
5	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}-\text{MgBr}$	80	15:1

- [1] J. Jurczak, S. Pikul, S. Bauer, *Tetrahedron* **1986**, 42, 447–488.
- [2] a) V. Jäger, V. Wehner, *Angew. Chem.* **1989**, 101, 512; *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 469–470; b) L. W. Hertel, C. S. Grossman, J. S. Kroin, *Synth. Commun.* **1991**, 21, 151–154; c) C. Hubschwerlen, J.-L. Specklin, J. Higelin, *Org. Synth.* **1995**, 72, 1–5; d) C. R. Schmid, J. D. Bryant, *Org. Synth.* **1995**, 72, 6–13.
- [3] a) S. V. Ley, M. Woods, A. Zanotti-Gerosa, *Synthesis* **1992**, 52–54; b) S. V. Ley, R. Downham, P. J. Edwards, J. E. Innes, M. Woods, *Contemp. Org. Synth.* **1995**, 2, 365–392.
- [4] a) U. Berens, D. Leckel, S. C. Oepen, *J. Org. Chem.* **1995**, 60, 8204–8208; b) J.-L. Montchamp, F. Tian, M. E. Hart, J. W. Frost, *J. Org. Chem.* **1996**, 61, 3897–3899; c) N. L. Douglas, S. V. Ley, H. M. I. Osborn, D. R. Owen, H. W. M. Priepe, S. L. Warriner, *Synlett* **1996**, 793–795; d) A. Hense, S. V. Ley, H. M. I. Osborn, D. R. Owen, J.-F. Poisson, S. L. Warriner, K. E. Wesson, *J. Chem. Soc. Perkin Trans. 1* **1997**, 2023–2031; e) S. V. Ley, P. Michel, *Synlett* **2001**, 1793–1795.
- [5] For a review see: a) S. V. Ley, D. K. Baeschlin, D. J. Dixon, A. C. Foster, S. J. Ince, H. W. M. Priepe, D. J. Reynolds, *Chem. Rev.* **2001**, 101, 53–80; for recent examples see: b) E. Diez, D. J. Dixon, S. V. Ley, *Angew. Chem.* **2001**, 113, 2990–2993; *Angew. Chem. Int. Ed.* **2001**, 40, 2906–2909; c) D. J. Dixon, S. V. Ley, A. Polara, T. Sheppard, *Org. Lett.* **2001**, 3, 3749–3752; d) D. J. Dixon, S. V. Ley, F. Rodriguez, *Org. Lett.* **2001**, 3, 3753–3755; e) D. J. Dixon, S. V. Ley, F. Rodriguez, *Angew. Chem.* **2001**, 113, 4899–4901; *Angew. Chem. Int. Ed.* **2001**, 40, 4763–4765.
- [6] F. W. Lichtenthaler, P. Jarglis, K. Lorenz, *Synthesis* **1988**, 790–792.
- [7] a) **3**: $[\alpha]_{\text{D}}^{25} = -158.8$ ($c = 1.22$ in CHCl_3); ^1H NMR (400 MHz, CDCl_3): $\delta = 4.53$ (dd, $J = 11.2, 7.6$ Hz, 1H; CH), 3.81 (dd, $J = 11.2, 11.2$ Hz, 1H; CHH), 3.72–3.68 (m, 4H; CHH, CO_2CH_3), 3.28 (s, 3H; OCH_3), 3.24 (s, 3H; OCH_3), 1.35 (s, 3H; CCH_3), 1.26 ppm (s, 3H; CCH_3); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 169.1, 99.7, 98.0, 67.1, 59.9, 52.1, 48.3, 48.0, 17.5$.

17.4 ppm; b) **11**: m.p. 77 °C; $[\alpha]_{25}^D = -157.6$ ($c = 1.02$ in CHCl_3); ^1H NMR (400 MHz, CDCl_3): $\delta = 4.12\text{--}4.08$ (m, 2 H; CH, CHH), 3.94 (dd, $J = 12.0$, 5.0 Hz, 1 H; CHH), 3.76 (s, 3 H; CO_2CH_3), 3.28 (s, 3 H; OCH_3), 3.26 (s, 3 H; OCH_3), 1.32 (s, 3 H; CCH_3), 1.27 ppm (s, 3 H; CCH_3); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.0$, 99.6, 98.7, 68.1, 57.7, 51.9, 50.0, 48.2, 17.9, 17.7 ppm; c) **12**: m.p. 77 °C; $[\alpha]_{25}^D = -266.5$ ($c = 1.6$ in CHCl_3); ^1H NMR (400 MHz, CDCl_3): $\delta = 9.73$ (s, 1 H; CHO), 4.07 (d, $J = 11.6$ Hz, 1 H; CHH), 3.91–3.86 (m, 1 H; CHH), 3.77 (d, $J = 4.4$ Hz, 1 H; CH), 3.38 (s, 3 H; OCH_3), 3.28 (s, 3 H; OCH_3), 1.37 (s, 3 H; CCH_3), 1.24 ppm (s, 3 H; $\text{C(CH}_3)_3$); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 201.2$, 99.4, 98.5, 74.6, 55.6, 50.3, 48.2, 17.8, 17.7 ppm.

[8] a) H. S. Isbell, H. L. Frush, *Carbohydr. Res.* **1979**, 72, 301–304; b) C. C. Wei, S. De Bernardo, J. P. Teng, J. Borgese, M. Weigle, *J. Org. Chem.* **1985**, 50, 3462–3467; c) E. Abushanab, P. Vemishetti, R. W. leiby, H. K. Singh, A. B. Mikilineni, D. C.-J. Wu, R. Saibaba, R. P. Panzica, *J. Org. Chem.* **1988**, 53, 2598–2602.

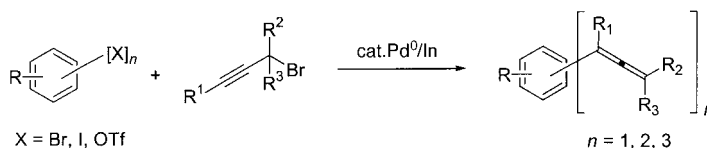
[9] CCDC-186381 to CCDC-186386 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Highly Efficient Catalytic Synthesis of Substituted Allenes Using Indium**

Kooyeon Lee, Dong Seomoon, and Phil Ho Lee*

Since allenes are versatile building blocks both for organic synthesis^[1] and in transition-metal-promoted carbon–carbon bond-forming reactions,^[2] development of practical methods for their preparation is of great interest. Allene moieties can be prepared by alkylation of allenylmethyl halides with an appropriate carbanionic species,^[1e] by $\text{S}_{\text{N}}2'$ -type selective displacement of propargyl alcohol derivatives with organo-copper reagents,^[1e,3] and by intramolecular regio- and stereo-selective reduction of alkynes.^[4] The synthesis of allenes by metal-catalyzed cross-coupling reactions is an alternative method;^[5] however, some disadvantages are the inconvenient preparation of the reagents, limited substrate scope, and incompatibility of sensitive groups to the reaction conditions.^[6] Recently, several reports have described the synthesis of allenes with transition metal complexes.^[5] Despite this recent progress a method for the highly efficient and catalytic synthesis of substituted allenes is still needed. We have realized this goal (Scheme 1) as part of our continuing studies directed toward the development of efficient indium-mediated reactions.^{[7], [8]}

The catalytic activity of several palladium complexes was initially examined in the reaction of 1-iodonaphthalene with allenylindium. The best results were obtained with 4 mol %

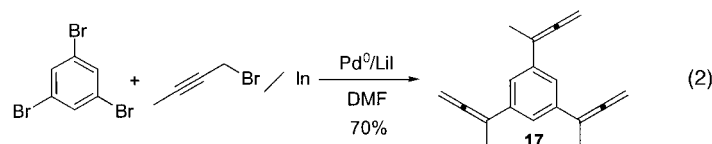
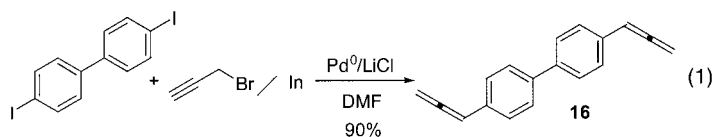


Scheme 1. Palladium-catalyzed cross-coupling reaction mediated by indium. Tf = trifluoromethanesulfonyl.

$[\text{Pd}(\text{PPh}_3)_4]$ in the presence of 3 equivalents of LiI in DMF at 100 °C under a nitrogen atmosphere (see Experimental Section), and 1-allenylnaphthalene was produced in quantitative yield (98 %) with complete regioselectivity (Table 1, entry 1). The allenylindium reagent generated in situ from the reaction of 1 equivalent of indium with 1.5 equivalents of propargyl bromide gave the best results as a coupling partner.^[9]

To demonstrate the efficiency and scope of the present method, we applied this catalytic system to a variety of propargyl halides and organic electrophiles. For the propargyl halides as coupling partners, the presence of various alkyl substituents at the α and γ positions had little effect on either the reaction rate or the product yield (Table 1). Under the optimized conditions, treatment of iodobenzene with 3-bromo-1-phenyl-1-butyne and indium gave selectively trisubstituted allene **2** in 80 % yield (entry 2). Varying the electron demand of the substituents on the arene did not diminish the efficiency and selectivity (entries 3, 7–9). It is noteworthy that protection of an oxo group and a hydroxy group on substrates is not necessary, as demonstrated by the reactions of 4-iodoacetophenone (entry 5) and 3-iodophenol (entry 6), respectively. Hetero substituents turned out to be compatible with the reaction conditions (entry 10). The method worked equally well with vinyl halides (entries 11 and 12) and imido-yl bromide (entry 13). Treatment of iodophenylacetylene with allenylindium produced 3-methyl-1-phenyl-3,4-pentadien-1-yne (**14**) in 91 % yield (entry 14). In the case of vinyl triflate, the desired product **15** was obtained in 90 % yield (entry 15). Surprisingly, no propargylic cross-coupling product is formed in any reactions.

We then applied the present method to polyhalogenated aromatic compounds to obtain polyallenyl-substituted arenes, which can be used effectively in material and polymer sciences. Reaction of 4,4'-diiodobiphenyl with two equivalents of allenylindium produced 4,4'-diallenylbiphenyl **16** in 90 % yield [Eq. (1)]. We were pleased to observe that treatment of



1,3,5-tribromobenzene with 1-bromo-2-butyne and indium selectively gave 1,3,5-tri(1'-methylallenyl)benzene (**17**) in 70 % yield [Eq. (2)]. On the basis of these results, unsym-

[*] Prof. Dr. P. H. Lee, K. Lee, D. Seomoon
Department of Chemistry, Kangwon National University
Chuncheon 200-701 (Korea)
Fax: (+82)33-253-7582
E-mail: phlee@kangwon.ac.kr

[**] This work was supported financially by the CMDS at KAIST. We thank Prof. Sungak Kim and Prof. Sukbok Chang of KAIST for helpful discussions and Hyosoon Ahn, Keuckchan Bang, and Dr. Sunyoung Sung for the preparation of starting materials and preliminary experiments.