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Direct palladium(0)-catalyzed amination of allylic alcohols with aminonaphthalenes

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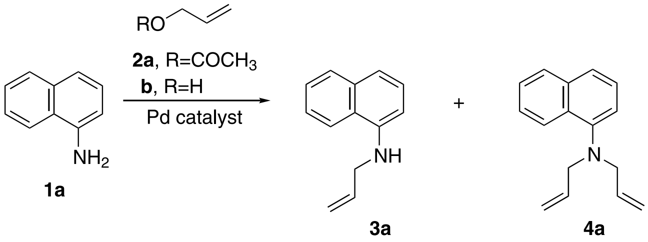
Abstract—The direct activation of C–O bonds in allylic alcohols by palladium complexes has been accelerated by carrying out the reactions in the presence of titanium reagents. The palladium-catalyzed amination of allylic alcohols using aminonaphthalenes gave *N*-allylic naphthylamines in good yields. The monoallylation products are formed in the main. © 2003 Elsevier Science Ltd. All rights reserved.

A principal goal of organometallic chemistry is the catalytic synthesis of organic compounds by using the chemistry of organic ligands covalently bound to transition metals. Most organometallic chemistry has focused on complexes with covalent metal–carbon or metal–hydrogen bonds. The platinum group transition metals, in particular palladium and rhodium, have been workhorse elements in many commercialized catalytic processes that include hydrogenations, hydroformylations, acetic acid production, and other C–C and C–H bond forming processes.[1] Although carbon–oxygen, carbon–nitrogen, or carbon–sulfur bonds are found in the majority of important organic molecules, catalytic organometallic chemistry that leads to the formation of carbon–heteroatom bonds is less common than that forming carbon–carbon and carbon–hydrogen bonds. Moreover, the construction of C–N bonds in amines using this chemistry is not common.[2] In large part, routes to the necessary reactive intermediates for such catalysis and the fundamental reactions required of such intermediates are poorly developed. A number of synthetic methods for the preparation of allylamines from alkene derivatives have been developed, but these require severe reaction conditions or several sequential reactions.[3] Transition metal η^3-allyl complexes, as well as transition metal σ-alkyl complexes, play important roles as active species and key intermediates in many reactions catalyzed by transition metal complexes.[4] Palladium-catalyzed allylation is an established, efficient, and highly stereo- and chemoselective method for C–C, C–N, and C–O bond formation, which has been widely applied to organic chemistry.[5] Although halides,[6] esters,[7] carbonates,[8] carbamates,[9] phosphates,[10] and related derivatives[11] of allylic alcohols have frequently been used as substrates, there have been only limited and sporadic reports dealing with the direct cleavage of the C–O bond in allylic alcohols on interaction with a transition metal complex.[12] Successful applications using allylic alcohols directly in catalytic processes are even more limited. This apparently stems from the poor capability of a nonactivated hydroxyl to serve as a leaving group.[13] We have recently reported our attempts and some successful applications of a process involving C–O bond cleavage with direct use of allylic alcohols catalyzed by palladium complexes.[14] In this paper, we wish to report a novel catalytic palladium complex, which mediates amination of allylic alcohols with aminonaphthalenes.

We treated a mixture of 1-aminonaphthalene (**1a**, 2.5 mmol) and allyl acetate (**2a**, 3.0 mmol) in the presence of Pd(OAc)$_2$ (1 mol%), PPh$_3$ (4 mol%), and molecular sieves (4 Å MS) (200 mg) in benzene under nitrogen, at room temperature for 3 h. *N*-Allyl-1-naphthylamine (**3a**) was formed in only 11% yield (Scheme 1). The



Scheme 1.

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reaction, under reflux, increased the yields of products **3a** and *N*,*N*-diallyl-1-naphthylamine (**4a**) to 57 and 6%, respectively (entry 1 in Table 1). Similarly, the direct amination of allyl alcohol (**2b**) at 50°C gave **3a** in only 9% yield (entry 2). The palladium-catalyzed amination of allyl alcohol with 1-aminonaphthalene was investigated under various conditions. In the presence of 25 mol% of $Ti(OPr^i)_4$ at 50°C, the reaction gave **3a** in 80% yield (entry 3). Decreasing the amount of $Ti(OPr^i)_4$ afforded **3a** in only 32% yield (entry 4). Conversely, increasing the amount of $Ti(OPr^i)_4$ increased the yields of products (entry 5). The effect of addition of $Ti(OPr^i)_4$ to promote the palladium-catalyzed allyl–OH bond cleavage remarkably enhanced both the reaction rate and yield. The reaction, under reflux, increased the yields of **3a** and **4a** to ca. 80 and 17%, respectively (entry 6). The reaction did not occur in the absence of the palladium species (entry 7) or phosphine ligand (entry 8). Titanium reagents such as $Ti(OEt)_4$ (entry 9), $Ti(OBu)_4$ (entry 10), $Ti(OBu^i)_4$ (entry 11), and $Ti[O(CH_2)_{17}CH_3]_4$ (entry 12) were also effective for the allylation. $TiCl_4$ (entry 13) did not promote the reaction to any great extent. It is known that several factors, such as the solvent and nature of the nucleophile, can alter the product pattern in metal-catalyzed allylation.[15] At 50°C, six solvents were investigated, benzene, toluene, dioxane, DMF, CH_2Cl_2, and MeCN, with benzene and CH_2Cl_2 giving the best results (entries 3 and 14–18). A comparative study of different catalysts in benzene was reported. As the catalyst precursor, $Pd(OAc)_2$ (entry 6), $Pd(acac)_2$ (entry 19), $PdCl_2(MeCN)_2$ (entry 20), and $Pd(OCOCF_3)_2$ (entry 21) showed high catalytic activity. Other palladium complexes such as $Pd(PPh_3)_4$ (entry 22) and $PdCl_2$ (entry 23) were less active and gave lower yields. Many reports have indicated[16] that chloride ions can strongly influence the catalytic activity of palladium catalysts, and it seemed reasonable that this factor might be responsible for the low reactivity of $PdCl_2$ in the present system. But using $Pd(PPh_3)_4$ coordinated with PPh_3 as catalyst increased the yield of products (entry 24).

We also studied the influence of substituents on the aminonaphthalene on the reactivity of the amination of allyl alcohol (**2b**) using $Pd(OAc)_2$, PPh_3, and $Ti(OPr^i)_4$. The results collected in Table 2 showed that the nature of the substituent had an influence on the reaction rate and the product yield. The amination of allyl alcohol (**2b**) worked well with aminonaphthalenes containing electron-donating groups, giving generally high yields of the corresponding *N*-allylic compounds. Conversely, anilines having strong electron-withdrawing groups, such as the nitro group (entry 5), gave lower chemical yields. These differences in reactivity could be related to the nucleophilicity of the corresponding aminonaphthalene. 1-Amino-4-nitronaphthalene (**1f**) gave only monoallylated product **3f** in 70% yield (entry 5); the lower yield observed may arise from the nature of the nitro group. The more acidic 1-amino-4-nitronaphthalene is probably less reactive in attack on the π-allyl

Table 1. Reaction of 1-aminonaphthalene (**1a**) with allylic compounds (**2a**,**b**)[a]

Entry	**2**	Catalyst	Titanium reagent	Solvent	Yield (%)[b] (**3a**:**4a**)
1	**2a**	$Pd(OAc)_2$-PPh_3	–	Benzene	63 (90:10)
2	**2b**	$Pd(OAc)_2$-PPh_3	–	Benzene[c]	9 (100:0)
3	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$	Benzene[c]	80 (100:0)
4	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$[d]	Benzene[c]	32 (100:0)
5	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$[e]	Benzene[c]	92 (99:1)
6	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$	Benzene	97 (82:18)
7	**2b**	PPh_3	$Ti(OPr^i)_4$	Benzene	0
8	**2b**	$Pd(OAc)_2$	$Ti(OPr^i)_4$	Benzene	0
9	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OEt)_4$	Benzene	95 (82:18)
10	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OBu)_4$	Benzene	94 (84:16)
11	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OBu^i)_4$	Benzene	96 (91:9)
12	**2b**	$Pd(OAc)_2$-PPh_3	$Ti[O(CH_2)_{17}CH_3]_4$	Benzene	92 (92:8)
13	**2b**	$Pd(OAc)_2$-PPh_3	$TiCl_4$	Benzene	8 (100:0)
14	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$	Toluene[c]	40 (100:0)
15	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$	Dioxane[c]	50 (100:0)
16	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$	DMF[c]	3 (100:0)
17	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$	CH_2Cl_2[c]	78 (99:1)
18	**2b**	$Pd(OAc)_2$-PPh_3	$Ti(OPr^i)_4$	MeCN[c]	57 (100:0)
19	**2b**	$Pd(acac)_2$-PPh_3	$Ti(OPr^i)_4$	Benzene	89 (92:8)
20	**2b**	$PdCl_2(MeCN)_2$-PPh_3	$Ti(OPr^i)_4$	Benzene	97 (93:7)
21	**2b**	$Pd(OCOCF_3)_2$-PPh_3	$Ti(OPr^i)_4$	Benzene	96 (87:13)
22	**2b**	$Pd(PPh_3)_4$	$Ti(OPr^i)_4$	Benzene	40 (100:0)
23	**2b**	$PdCl_2$-PPh_3	$Ti(OPr^i)_4$	Benzene	70 (100:0)
24	**2b**	$Pd(PPh_3)_4$-PPh_3	$Ti(OPr^i)_4$	Benzene	87 (86:14)

[a] Reaction conditions: **1a** (2.5 mmol), **2** (3.0 mmol), Pd catalyst (1 mol%), PPh_3 (4 mol%), titanium reagent (25 mol%), and 4 Å molecular sieves (200 mg) in a solvent were refluxed for 3 h.

[b] Isolated yield.

[c] Stirred at 50°C.

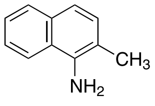
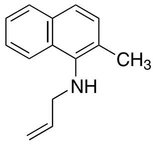
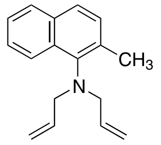
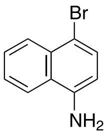
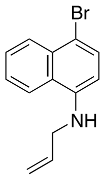
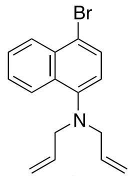
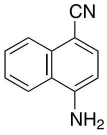
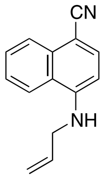
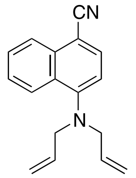
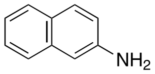
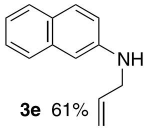
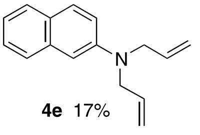
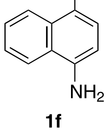
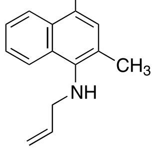
[d] 10 mol% of $Ti(OPr^i)_4$ was used.

[e] 50 mol% of $Ti(OPr^i)_4$ was used.

complex. Increasing the amount of **2b** also afforded only **3f** in 84% yield.

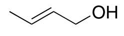
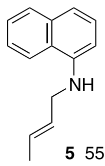
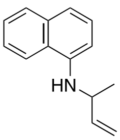
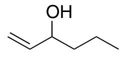
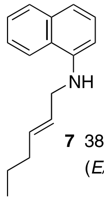
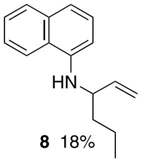
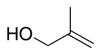
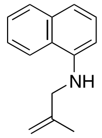
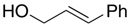
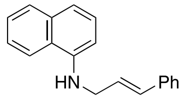
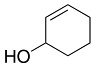
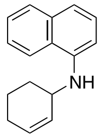
The results for amination of a number of allylic alcohols **2c**–**g** with 1-aminonaphthalene (**1a**) using Pd(OAc)$_2$, PPh$_3$, Ti(OPr^i)$_4$ and 4 Å MS are summarized in Table 3. Amination of crotyl alcohol (**2c**) gave mixtures of stereo- and regioisomeric aminonaphthalenes **5** and **6** in yields of 55 and 38%, respectively (entry 1, in Table 3). These products may all be derived from the same π-allyl intermediate which can be attacked at either the C-1 or C-3 position. The 92:8 *E*/*Z* ratio of **5** was determined by GC, the product *E* alkene arising from the more thermodynamically stable *syn* π-allyl complex. The reaction is considered to proceed via π-allylpalladium intermediates. The loss of the stereochemistry of the starting alcohol **2c** is due to a rapid $\sigma \leftrightarrows \eta^3 \leftrightarrows \sigma$ interconversion of the π-allyl intermediate compared to the rate of amination of this intermediate. We also noticed that the allylic alcohol **2d** reacted with **1a** to give mixtures of stereo- and regioisomeric aminonaphthalenes **7** and **8**, as expected from attack of the aminonaphthalene on the two allylic termini of the π-allylpalladium species (entry 2). With 2-substituted alcohol **2e**, monoalkylated product was obtained (entry 3). Alcohol **2f** which is prone to give the product having the olefin conjugated with the phenyl group did give selectively the conjugated product **10**, showing that the phenyl group acts as a regiocontrolling element (entry 4). However, the alcohol **2g** with a bulkier substituent R was found to be less reactive showing a decrease in the product yield (entry 5).

Table 2. Reaction of aminonaphthalenes (**1b**–**f**) with allyl alcohol (**2b**)[a]

entry	1	yield[b]	
1	 **1b**	 **3b** 79%	 **4b** 2%
2	 **1c**	 **3c** 83%	 **4c** 8%
3	 **1d**	 **3d** 83%	 **4d** 1%
4	 **1e**	 **3e** 61%	 **4e** 17%
5	 **1f**	 **3f** 70% (84%)[c]	

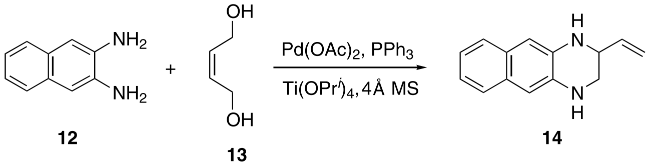
[a] Reaction conditions: **1** (2.5 mmol), **2b** (3.0 mmol), Pd(OAc)$_2$ (1 mol%), PPh$_3$ (4 mol%), Ti(OPr^i)$_4$ (25 mol%), and 4 Å molecular sieves (200 mg) in benzene were refluxed for 3 h. [b] Isolated yield. [c] 12.0 mmol of **2b** was used.

Table 3. Reaction of 1-aminonaphthalene (**1a**) with allylic alcohols (**2c**–**g**)[a]

entry	2	yield[b]	
1	 **2c**	 **5** 55% (*E*/*Z*=92/8)[c]	 **6** 38%
2	 **2d**	 **7** 38% (*E*/*Z*=98/2)[c]	 **8** 18%
3	 **2e**	 **9** 52%	
4	 **2f**	 **10** 91%	
5	 **2g**	 **11** 18%	

[a] Reaction conditions: **1a** (2.5 mmol), **2** (3 mmol), Pd(OAc)$_2$ (1 mol%), PPh$_3$ (4 mol%), Ti(OPr^i)$_4$ (25 mol%), and 4 Å molecular sieves (200 mg) in benzene were refluxed for 3 h. [b] Isolated yield. [c] Determined by GC.

We studied the extension of this reaction for the construction of benzo[*g*]quinoxaline. When a mixture of 2,3-diaminonaphthalene (**12**, 1 mmol) and 2-butene-1,4-diol (**13**, 1.2 mmol) was refluxed in the presence of catalytic amounts of Pd(OAc)$_2$ (0.01 mmol), PPh$_3$ (0.04 mmol), Ti(OPr^i)$_4$ (0.8 mmol), and molecular sieves (4 Å MS) (200 mg) in benzene (5 mL), under nitrogen for 3 h, 1,2,3,4-tetrahydro-2-vinylbenzo[*g*]quinoxaline **14** was formed in 90% yield (Scheme 2). This cyclization pro-



Scheme 2.

ceeds through tandem allylic substitution reactions between 2,3-diaminonaphthalene and 2-butene-1,4-diol via π-allylpalladium intermediates.

We have shown that palladium(0)-catalyzed amination of allylic alcohols using aminonaphthalenes is a simple and efficient route for C–N bond formation. The addition of $Ti(OPr^i)_4$ to promote the palladium-catalyzed allyl–OH bond cleavage remarkably enhanced both the reaction rate and yield. The amination of allylic alcohols worked well with aminonaphthalenes, generally giving good yields of the corresponding *N*-allylic naphthylamines. When the allylic alcohol is unsubstituted **2b**, the reaction is relatively fast, and high yields of the desired products are obtained. If the alcohol (and thus the π-allyl complex) is substituted, good chemical yields are still obtained, but the reaction proceeds more slowly, and mixtures of isomers are obtained.

Acknowledgements

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References

1. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
2. One reaction of this type is the hydroamination of alkenes and alkynes. For leading references see the following nine citations: (a) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800; (b) Pez, G. P.; Galle, J. E. *Pure Appl. Chem.* **1985**, *57*, 1917; (c) catalysis with a low-valent arylamido complex has been reported, although turnover numbers are not high: Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738 and references cited therein; (d) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108; (e) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716; (f) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708; (g) McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459; (h) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753; (i) Brunet, J.; Commenges, G.; Neibecker, D.; Philippot, K. *J. Organomet. Chem.* **1994**, *469*, 221.
3. Gilson, M. S.; Bradshaw, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 919.
4. For instance: (a) Chiusoli, G. P.; Salerno, G. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R.; Patai, S., Eds.; John Wiley & Sons: Chichester, UK, 1985; Vol. 3, Chapter 3.1, p. 143; (b) Tsuji, J. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R.; Patai, S., Eds.; John Wiley & Sons: Chichester, UK, 1985; Vol. 3, Chapter 3.2, p. 163; (c) Sato, F. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R.; Patai, S., Eds.; John Wiley & Sons: Chichester, UK, 1985; Vol. 3, Chapter 3.3, p. 200; (d) Bäckvall, J. E. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, p. 135.
5. (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985; (b) Goldeski, S. A. Nucleophiles with Allyl-Metal Complexes. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 4, Chapter 3.3; (c) Harrington, P. J. Transition Metal Allyl Complexes: Pd, W, Mo-Assisted Nucleophilic Attack. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12, Chapter 8.2; (d) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: New York, 1995.
6. (a) Connell, R. D.; Rein, T.; Åkermark, B.; Helquist, P. *J. Org. Chem.* **1988**, *53*, 3845; (b) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1065.
7. (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385; (b) Backvall, J. E. *Acc. Chem. Res.* **1983**, *16*, 335; (c) Tsuji, M.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140; (d) Tsuji, M.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140; (e) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173; (f) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38; (g) Tsuji, J. *Synthesis* **1990**, 739; (h) Trost, B. M. *Pure Appl. Chem.* **1992**, *64*, 315; (i) Backvall, J. E. *Pure Appl. Chem.* **1992**, *64*, 429; (j) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089; (k) Giambastiani, G.; Poli, G. *J. Org. Chem.* **1998**, *63*, 9608; (l) Uozumi, Y.; Danjo, H.; Hayashi, T. *J. Org. Chem.* **1999**, *64*, 3384.
8. (a) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, *23*, 4809; (b) Trost, B. M.; Hung, M. H. *J. Am. Chem. Soc.* **1983**, *105*, 7757; (c) Takahashi, T.; Jinbo, Y.; Kitamura, K.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5921; (d) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523; (e) Stary, I.; Kocovsky, P. *J. Am. Chem. Soc.* **1989**, *111*, 4981; (f) Stary, I.; Zajicek, J.; Kocovsky, P. *Tetrahedron* **1992**, *48*, 7229; (g) Goux, C.; Massacret, M.; Lhoste, P.; Sinou, D. *Organometallics* **1995**, *14*, 4585; (h) Deardorff, D. R.; Savin, K. A.; Justman, C. J.; Karanjawala, Z. E.; Sheppeck, J. E., II; Hager, D. C.; Aydin, N. *J. Org. Chem.* **1996**, *61*, 3616; (i) Moreno-Manas, M.; Morral, L.; Pleixats, R. *J. Org. Chem.* **1998**, *63*, 6160.
9. (a) Minami, I.; Ohashi, Y.; Shimizu, I.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 2449; (b) Minami, I.; Yuhara, M.; Tsuji, J. *Tetrahedron Lett.* **1987**, *28*, 2737; (c) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1987**, *28*, 4837.
10. (a) Ziegler, F. E.; Kneisley, A.; Wester, R. T. *Tetrahedron Lett.* **1986**, *27*, 1221; (b) Ziegler, F. E.; Wester, R. T. *Tetrahedron Lett.* **1986**, *27*, 1225; (c) Ziegler, F. E.; Cain, W. T.; Kneisley, A.; Stirchak, E. P.; Wester, R. T. *J. Am. Chem. Soc.* **1988**, *110*, 5442.

11. Imidoesters: (a) Schenck, T. G.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2058. Xanthates: (b) Auburn, P. R.; Wheland, J.; Bosnich, B. *J. Chem. Soc., Chem. Commun.* **1986**, 146. Nitrogroups: (c) Ono, N.; Hamamoto, I.; Kamimura, A.; Kaji, A. *J. Org. Chem.* **1986**, *51*, 3734; (d) Tamura, R.; Kai, Y.; Kakihama, M.; Hayashi, K.; Tsuji, M.; Nakamura, T.; Oda, D. *J. Org. Chem.* **1986**, *51*, 4375; (e) Tamura, R.; Kato, M.; Saegusa, K.; Kakihama, M.; Oda, D. *J. Org. Chem.* **1987**, *52*, 4121; (f) Tamura, R.; Kamimura, A.; Ono, N. *Synthesis* **1991**, 423. Sulfones: (g) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979.
12. (a) Lumin, S.; Falck, J. R.; Capdevila, J.; Karara, A. *Tetrahedron Lett.* **1992**, *33*, 2091; (b) Tsay, S.; Lin, L. C.; Furth, P. A.; Shum, C. C.; King, D. B.; Yu, S. F.; Chen, B.; Hwu, J. R. *Synthesis* **1993**, 329; (c) Masuyama, Y.; Kagawa, M.; Kurusu, Y. *Chem. Lett.* **1995**, 1121; (d) Hirai, Y.; Shibuya, K.; Fukuda, Y.; Yokoyama, H.; Yamaguchi, S. *Chem. Lett.* **1997**, 221.
13. (a) Stary, I.; Stara, I. G.; Kocovsky, P. *Tetrahedron Lett.* **1993**, *34*, 179; (b) Stary, I.; Stara, I. G.; Kocovsky, P. *Tetrahedron* **1994**, *50*, 529.
14. (a) Yang, S. C.; Chung, W. H. *Tetrahedron Lett.* **1999**, *40*, 953; (b) Yang, S. C.; Hung, C. W. *J. Org. Chem.* **1999**, *64*, 5000; (c) Yang, S. C.; Tsai, Y. C. *Organometallics* **2001**, *20*, 763.
15. (a) Fiaud, J. C.; Legros, J. Y. *J. Org. Chem.* **1990**, *55*, 4840; (b) Yamaguchi, A.; Shima, T.; Yamagishi, T.; Hida, M. *Tetrahedron Lett.* **1990**, *31*, 5049; (c) Yamaguchi, A.; Shima, T.; Yamagishi, T.; Hida, M. *Tetrahedron: Asymmetry* **1991**, *2*, 663; (d) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 4089; (e) Trost, B. M.; Krueger, A. C.; Bunt, R. C.; Zambrano, J. *J. Am. Chem. Soc.* **1996**, *118*, 6520.
16. (a) Milstein, D. *Organometallics* **1982**, *1*, 888; (b) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630; (c) Bäckvall, J. E.; Bystrom, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619; (d) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033; (e) Yang, S. C.; Shea, F. R.; Hung, C. W. *J. Chin. Chem. Soc.* **1998**, *45*, 779.