

Synthesis, Structures, and Characterizations of $[ArTi(O-i-Pr)_3]_2$ and Efficient Room-Temperature Aryl-Aryl Coupling of Aryl Bromides with $[ArTi(O-i-Pr)_3]_2$ Catalyzed by the Economic Pd(OAc)_2/PCy_3 System

Hsu-Tang Yang,[†] Shuangliu Zhou,^{†,‡} Feng-Shuo Chang,[†] Chi-Ren Chen,[†] and Han-Mou Gau^{*,†}

[†]Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan, and [‡]Anhui Key Laboratory of Molecule-based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, People's Republic of China

Received May 29, 2009

The series of aryltris(2-propoxo)titanium reagents $[ArTi(O-i-Pr)_3]_2$ (Ar = Ph (1a), 2-MeC₆H₄ (1b), $4-MeC_6H_4$ (1c), $4-CIC_6H_4$ (1d), $4-TMSC_6H_4$ (1e), $4-CF_3C_6H_4$ (1f), $3,5-Me_2C_6H_3$ (1g)) was synthesized from reactions of the in situ prepared CITi(O-i-Pr)₃ with ArMgBr in THF. All compounds were characterized by NMR spectroscopy and elemental analyses. A variable-temperature ¹H NMR study of 1c suggested that compounds 1 are dimeric species in solution. The structures of complexes 1b,g were further determined by single-crystal X-ray analyses. X-ray diffraction studies confirmed that the aryltris(2propoxo)titanium complexes have a dimeric structure with a Ti₂O₂ core bridging through the oxygen atom of two 2-propoxide groups. The application of aryltris(2-propoxo)titanium reagents to cross-coupling with any bromides catalyzed by the catalytic system of 1 mol % Pd(OAc)₂ and 2 mol % PCy₃ was studied. Results show that aryltris(2-propoxo)titanium compounds are excellent reagents for aryl-aryl coupling reactions at room temperature and that the system works well for a wide range of arvl bromides regardless of the electronic or steric nature of the substituents on the aryl bromides. Couplings with pyridyl bromides under the mild reaction condition of room temperature were also demonstrated to afford products in high yields over 2-3 h. It is worth noting that couplings with 3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthylene proceeded smoothly also at room temperature over 3-5 h, affording products in excellent yields. The coupling reactions demonstrated in this study are highly efficient compared to the typical synthesis of 3,3'diaryl-2,2'-dimethoxy-1,1'-binaphthylenes via Suzuki couplings, which required higher catalyst loading under reaction conditions of longer reaction times (18–24 h in general) at elevated temperatures.

Introduction

The C-C cross-coupling reactions were first discovered in late 1960s and early 1970s,¹ and since then, many catalytic

systems using diversified coupling reagents, such as organoboron compounds,² organotin compounds,³ Grignard reagents,⁴ organozirconium or organozinc compounds,⁵ and others,⁶ have been developed. In the past 10 years, some efficient catalytic systems for coupling reactions of inert organic chlorides under milder reaction conditions and/ or at low catalyst loadings have been reported.⁷ Recent

^{*}To whom correspondence should be addressed. Fax: (886) 4-22862547. Tel: (886)4-22878615. E-mail: hmgau@dragon.nchu.edu.tw. (1) (a) Heck, R. F. J. Am. Chem. Soc. **1968**, *90*, 5518. (b) Tamura, M.; Kochi, J. J. Am. Chem. Soc. **1971**, *93*, 1485.

^{(2) (}a) Navarro, O.; Kelly, R. A.; Nolan, S. P. J. Am. Chem. Soc. 2003, 125, 16194. (b) Moore, L. R.; Shaughnessy, K. H. Org. Lett. 2004, 6, 225. (c) Dong, C.-G.; Hu, Q.-S. J. Am. Chem. Soc. 2005, 127, 10006. (d) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. J. Am. Chem. Soc. 2005, 127, 4685. (e) González-Bobes, F.; Fu, G. C. J. Am. Chem. Soc. 2006, 128, 5360. (f) Imao, D.; Glasspoole, B. W.; Laberge, V. S.; Crudden, C. M. J. Am. Chem. Soc. 2009, 131, 5024.

^{(3) (}a) Espinet, P.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4704. (b) Su, W.; Urgaonkar, S.; McLaughlin, P. A.; Verkade, J. G. *J. Am. Chem. Soc.* **2004**, *126*, 16433. (c) Powell, D. A.; Maki, T.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 510. (d) Chiappe, C.; Pieraccini, D.; Zhao, D.; Fei, Z.; Dyson, P. J. Adv. Synth. Catal. **2006**, *348*, 68.

^{(4) (}a) Martin, R.; Fürstner, A. Angew. Chem., Int. Ed. 2004, 43, 3955.
(b) Nagano, T.; Hayashi, T. Org. Lett. 2004, 6, 1297. (c) Yoshikai, N.; Mashima, H.; Nakamura, E. J. Am. Chem. Soc. 2005, 127, 17978.
(d) Bedford, R. B.; Betham, M.; Bruce, D. W.; Danopoulos, A. A.; Frost, R. M.; Hird, M. J. Org. Chem. 2006, 71, 1104. (e) Leleu, A.; Fort, Y.; Schneider, R. Adv. Synth. Catal. 2006, 348, 1086. (f) Wolf, C.; Xu, H. H. J. Org. Chem. 2008, 73, 162. (g) Manolikakes, G.; Knochel, P. Angew. Chem., Int. Ed. 2009, 48, 205. (h) Hartmann, C. E.; Nolan, S. P.; Cazin, C. S. J. Organometallics 2009, 28, 2915–2919.

^{(5) (}a) Wiskur, S. L.; Korte, A.; Fu, G. C. J. Am. Chem. Soc. 2004, 126, 82. (b) Stanetty, P.; Hattinger, G.; Schnürch, M.; Mihovilovic, M. D. J. Org. Chem. 2005, 70, 5215. (c) Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. J. Org. Chem. 2005, 70, 8503. (d) Huang, Z.; Qian, M.; Babinski, D. J.; Negishi, E.-I. Organometallics 2005, 24, 475. (e) Xu, H.; Ekoue-Kovi, K.; Wolf, C. J. Org. Chem. 2008, 73, 7638.

<sup>Babinski, D. 3., Rogishi, E.-I. Organometantics 2005, 27, 475 (c) Ad, 11,
Ekoue-Kovi, K.; Wolf, C. J. Org. Chem. 2008, 73, 7638.
(6) (a) Sahoo, A. K.; Oda, T.; Nakao, Y.; Hiyama, T. Adv. Synth.
Catal. 2004, 346, 1715. (b) Wolf, C.; Lerebours, R. Org. Lett. 2004, 6 1147.
(c) Goossen, L. J.; Zimmermann, B.; Knauber, T. Angew. Chem., Int. Ed.
2008, 47, 7103. (d) Alacid, E.; Nájera, C. Org. Lett. 2008, 10, 5011.
(e) Denmark, S. E.; Smith, R. C.; Chang, W.-T. T.; Muhuhi, J. M. J. Am.
Chem. Soc. 2009, 131, 3104.</sup>

^{(7) (}a) Littke, A. F.; Fu, G. C. Angew. Chem., Int. Ed. 2002, 41, 4176.
(b) Hu, Q.-S.; Lu, Y.; Tang, Z.-Y.; Yu, H.-B. J. Am. Chem. Soc. 2003, 125, 2856. (c) Bedford, R. B.; Blake, M. E.; Butts, C. P.; Holder, D. Chem. Commun. 2003, 466. (d) Miura, M. Angew. Chem., Int. Ed. 2004, 43, 2201.
(e) Zhou, L.; Miao, Q.; He, R.; Feng, X.; Bao, M. Tetrahedron Lett. 2007, 48, 7899. (f) Hoshi, T.; Nakazawa, T.; Saitoh, I.; Mori, A.; Suzuki, T.; Sakai, J.; Hagiwara, H. Org. Lett. 2008, 10, 2603. (g) So, C. M.; Yeung, C. C.; Lau, C. P.; Kwong, F. Y. J. Org. Chem. 2008, 73, 7803.

studies further extended C–C coupling to C–N,⁸ C–O,⁹ and other types of coupling reactions.¹⁰ Nowadays, coupling reactions have become practical synthetic techniques applicable to organic synthesis and to the synthesis of materials or bioactive compounds.¹¹ Palladium complexes of bulky and electron-rich phosphines¹² or N-heterocyclic carbenes (NHC's)¹³ are among the most effective catalysts. Recently, many catalysts with ligands other than the phosphine- or NHC-based compounds and catalytic systems with nickel,¹⁴ copper,¹⁵ or even iron¹⁶ metal centers have been established. Although many catalytic systems achieve high yields of coupling products, the specially tailored ligands, which are in general not commercially available, limit those systems for

(9) (a) Torraca, K. E.; Huang, X.; Parrish, C. A.; Buchwald, S. L. J. Am. Chem. Soc. 2001, 123, 10770. (b) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. J. Org. Chem. 2002, 67, 5553. (c) Vorogushin, A. V.; Huang, X.; Buchwald, S. L. J. Am. Chem. Soc. 2005, 127, 8146. (d) Goossen, L. J.; Goossen, K.; Stanciu, C. Angew. Chem., Int. Ed. 2009, 48, 3569.

(10) (a) Fernández-Rodríguez, M. A.; Shen, Q. L.; Hartwig, J. F. *Chem. Eur. J.* **2006**, *12*, 7782. (b) Maitro, G.; Vogel, S.; Sadaoui, M.; Prestat, G.; Madec, D.; Poli, G. Org. Lett. **2007**, *9*, 5493. (c) Kalek, M.; Stawinski, J. *Organometallics* **2007**, *26*, 5840. (d) Prokopcová, H.; Kappe, C. O. Angew. Chem., Int. Ed. **2008**, *47*, 3674. (e) Lee, J.-Y.; Lee, P. H. J. Org. Chem. **2008**, *73*, 7413.

(11) (a) Baudoin, O.; Cesario, M.; Guenard, D.; Gueritte, F. J. Org. Chem. 2002, 67, 1199. (b) Wegner, H. A.; Reisch, H.; Rauch, K.; Demeter, A.; Zachariasse, K. A.; De Meijere, A.; Scott, L. T. J. Org. Chem. 2006, 71, 9080. (c) Ji, N.; O'Dowd, H.; Rosen, B. M.; Myers, A. G. J. Am. Chem. Soc. 2006, 128, 14825. (d) Noguchi, H.; Hojo, K.; Suginome, M. J. Am. Chem. Soc. 2007, 129, 758.

(12) (a) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. J. Am. Chem. Soc. 1999, 121, 9550. (b) Littke, A. F.; Dai, C.; Fu, G. C. J. Am. Chem. Soc. 2000, 122, 4020. (c) Zapf, A.; Ehrentraut, A.; Beller, M. Angew. Chem., Int. Ed. 2000, 39, 4153. (d) Bedford, R. B. C.; Cazin, S. J.; Hazelwood, S. L. Angew. Chem., Int. Ed. 2002, 41, 4120. (e) Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. Angew. Chem., Int. Ed. 2002, 41, 4120. (e) Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. Angew. Chem., Int. Ed. 2002, 41, 4120. (e) Lau, C. P.; Kwong, F. Y. Org. Lett. 2007, 9, 2795. (g) So, C. M.; Lau, C. P.; Kwong, F. Y. Angew. Chem., Int. Ed. 2008, 47, 8059. (h) Moore, L. R.; Western, E. C.; Craciun, R.; Spruell, J. M.; Dixon, D. A.; O'Halloran, K. P.; Shaughnessy, K. H. Organometallics 2008, 27, 576.

(13) (a) Bourissou, D.; Guerret, O.; GabbaL, F. P.; Bertrand, G. Chem. Rev. 2000, 100, 39. (b) Jafarpour, L.; Nolan, S. P. Adv. Organomet. Chem.
2000, 46, 181. (c) Grasa, G. A.; Viciu, M. S.; Huang, J.; Zhang, C.; Trudell, M. L.; Nolan, S. P. Organometallics 2002, 21, 2866. (d) Herrmann, W. A. Angew. Chem., Int. Ed. 2002, 41, 1291. (e) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. Angew. Chem., Int. Ed. 2003, 42, 3690. (f) Navarro, O.; Kelly, R. A.III; Nolan, S. P. J. Am. Chem. Soc. 2003, 125, 16194. (g) Wang, J.-W.; Meng, F.-H.; Zhang, L.-F. Organometallics 2009, 28, 2334. (14) (a) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. J. Am. Chem. Soc. 1979, 101, 2246. (b) Saito, S.; Sakai, M.; Miyaura, N. Tetrahedron Lett. 1996, 37, 2993. (c) Dankwardt, J. W. Angew. Chem., Int. Ed. 2004, 43, 2428.

(d) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. J. Org. Chem. 2004, 69, 3474. (e) Xi, Z.; Liu, B.; Chen, W. J. Org. Chem. 2008, 73, 3954. (f) Tobisu, M.; Shimasaki, T.; Chatani, N. Angew. Chem., Int. Ed. 2008, 47, 4866.
(g) Quasdorf, K. W.; Tian, X.; Garg, N. K. J. Am. Chem. Soc. 2008, 130, 14422. (15) (a) Zhu, W.; Ma, D. W. Org. Lett. 2006, 8, 261. (b) Hintermann, L.;

(15) (a) Zhu, W., Ma, D. W. O'g. Lett. 2000, 6, 201. (b) Hintermann, E., Xiao, L.; Aurélie, L. Angew. Chem., Int. Ed. 2008, 47, 8246. (c) Li, J.-H.; Wang, D.-P. Eur. J. Org. Chem. 2006, 2063.

(16) (a) Fürstner, A.; Leitner, A. Angew. Chem., Int. Ed. 2002, 41, 609.
(b) Fürstner, A.; Leitner, A.; Mendez, M.; Krause, H. J. Am. Chem. Soc.
2002, 124, 13856. (c) Cahiez, G.; Habiak, V.; Duplais, C.; Moyeux, A. Angew. Chem., Int. Ed. 2007, 46, 4364. (d) Bistri, O.; Correa, A.; Bolm, C. Angew. Chem., Int. Ed. 2008, 47, 586. (e) Wen, J.; Zhang, J.; Chen, S.-Y.; Li, J.; Yu, X.-Q. Angew. Chem., Int. Ed. 2008, 47, 8897.

(17) (a) Blum, J.; Gelman, D.; Baidossi, W.; Shakh, E.; Rosenfeld, A.; Aizenshtat, Z. J. Org. Chem. **1997**, 62, 8681. (b) Blum, J.; Berlin, O.; Milstein, D.; Ben-David, Y.; Wassermann, B. C.; Schutte, S.; Schumann, H. Synthesis **2000**, 571. (c) Shenglof, M.; Gelman, D.; Molander, G. A.; Blum, J. Tetrahedron Lett. **2003**, 44, 8593. practical usage. In addition to the aforementioned coupling reagents, a few examples of coupling reactions between aryl halides and alkylaluminum reagents have been reported.¹⁷ However, conditions at high reaction temperatures and with high equivalents of alkylaluminum reagents were required to afford coupling products in satisfactory yields. Our recent paper demonstrated that the easily prepared AlAr₃(THF) compounds are efficient reagents for coupling reactions with aryl bromides or chlorides.¹⁸ One advantage of AlAr₃(THF) reagents is that an inorganic base, which is used as a promoter in many types of coupling reactions, is not required. Another advantage is that the economic palladium catalyst of the commercially available and relatively cheap PCy₃ ligand is good enough to induce coupling reactions of aryl chlorides or bulky aryl bromides under mild reaction conditions at room temperature or ≤ 60 °C. However, a drawback of the AlAr₃-(THF) reagents is that only one aryl group out of the three aryls is consumed in the coupling reactions. Hayashi et al. first established that organotitanium compounds in refluxing THF could be used as coupling reagents while employing palladium catalysts of chiral ferrocene-based phosphine-amine ligands to afford coupling products in good to excellent yields.¹⁵ Couplings of ArTi(OEt)₃ with anyl bromides or chlorides were later demonstrated by Knochel and co-workers using nickel complexes of NHC's at room temperature, giving coupling products in moderate to excellent yields.²⁰ ArTi(O-i-Pr)₃ reagents were also used as aryl nucleophiles in a few examples of asymmetric reactions reported by Seebach and a co-worker²¹ and by Hayashi et al.²² In comparison with AlAr₃(THF) reagents, ArTi(OR)₃ compounds are aryl-economic reagents, since the sole aryl nucleophile is consumed in the reactions. Despite the scarce application of aryltitanium compounds, the higher reactivity of the titanium metal center compared to the boron or the zinc metal center makes ArTi(OR)₃ compounds attractive nucleophilic reagents in catalytic reactions.²¹

Although ArTi(O-i-Pr)₃ were prepared and used in catalytic reactions, there has been no detailed information on the synthesis and on the solution and solid-state structures of aryltitanium complexes. To explore applications of aryltitanium compounds as practical reagents in catalysis, we herein report the synthesis, characterizations, and structures of ArTi(O-*i*-Pr)₃ compounds. In solution, a binuclear [ArTi- $(O-i-Pr)_2(\mu-O-i-Pr)]_2$ species was suggested by a variabletemperature ¹H NMR study and was further confirmed by solid-state structural studies. Coupling reactions of [ArTi(Oi-Pr)₂(μ -O-i-Pr)]₂ with a wide variety of aromatic bromides were examined by employing the economic Pd(OAc)₂/PCy₃ catalytic system. Aryl-aryl coupling products were obtained at room temperature in a short reaction time of 0.5 h, except for products derived from bulky aryl bromides or pyridyl bromides, for which longer reaction times of 3-7 h were required to afford products in satisfactory yields. It is worth noting that this study also demonstrates efficient syntheses of 3,3'-diaryl-2,2'-dimethoxy-1,1'-binaphthylenes compared to the typical synthesis of 3,3'-diaryl-substituted BINOLs,

^{(8) (}a) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. J. Am. Chem. Soc. **2003**, 125, 6653. (b) Chen, Y.-J.; Chen, H.-H. Org. Lett. **2006**, 8, 5609. (c) Hill, L. L.; Moore, L. R.; Huang, R. C.; Craciun, R.; Vincent, A. J.; Dixon, D. A.; Chou, J.; Woltermann, C. J.; Shaughnessy, K. H. J. Org. Chem. **2006**, 71, 5117. (d) Biscoe, M. R.; Fors, B. P.; Buchwald, S. L. J. Am. Chem. Soc. **2008**, 130, 6686. (e) Fors, B. P.; Watson, D. A.; Biscoe, M. R.; Buchwald, S. L. J. Am. Chem. Soc. **2008**, 130, 13552. (f) Zhu, L. B.; Li, G. C.; Luo, L.; Guo, P.; Lan, J. B.; You, J. S. J. Org. Chem. **2009**, 74, 2200.

⁽¹⁸⁾ Ku, S.-L.; Hui, X.-P.; Chen, C.-A.; Kuo, Y.-Y.; Gau, H.-M. Chem. Commun. 2007, 3847.

⁽¹⁹⁾ Han, J. W.; Tokunaga, N.; Hayashi, T. Synlett 2002, 871.

⁽²⁰⁾ Manolikakes, G.; Dastbaravardeh, N.; Knochel, P. Synlett 2007, 2077.

⁽²¹⁾ Weber, B.; Seebach, D. Tetrahedron 1994, 50, 7473.

^{(22) (}a) Hayashi, T.; Tokunaga, N.; Yoshida, K.; Han, J. W. J. Am. Chem. Soc. 2002, 124, 12102. (b) Yoshida, K.; Hayashi, T. J. Am. Chem. Soc. 2003, 125, 2872.



Figure 1. Variable-temperature ¹H NMR spectra of compound 1c in toluene- d_8 in the isopropoxy and the tolyl methyl regions at (a) 20 °C, (b) -30 °C, and (c) -60 °C.





which required in general higher catalyst loadings and longer reaction times of 18-24 h at elevated temperatures. Coupling reactions of 3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthylenes with [ArTi(O-*i*-Pr)₂(μ -O-*i*-Pr)]₂ proceeded smoothly at room temperature in 3-5 h, giving excellent yields of 3,3'-diaryl-2,2'-dimethoxy-1,1'-binaphthylenes which can be converted to the 3,3'-diaryl-substituted BINOLs.

Results and Discussion

Synthesis and Characterizations of Aryltris(2-propoxo)titanium Complexes. Aryltitanium compounds of [ArTi-(O-*i*-Pr)₂(μ -O-*i*-Pr)]₂ (Ar = Ph (1a), 2-MeC₆H₄ (1b), 4-MeC₆-H₄ (1c), 4-ClC₆H₄ (1d), 4-TMSC₆H₄ (1e), 4-CF₃C₆H₄ (1f), 3,5-Me₂C₆H₃ (1g)) were synthesized easily in good yields from reactions of the in situ prepared ClTi(O-*i*-Pr)₃ with 1 mol equiv of ArMgBr in THF at 0 °C over 3 h (Scheme 1).²³ The ayrltris(2-propoxo)titanium complexes 1a-g are soluble in hydrocarbons and crystallize from hexanes as pale yellow crystalline solids. Though complexes 1a-g are sensitive to moisture, they can be stored under a dry nitrogen atmosphere for months. These complexes were characterized by ¹H and ¹³C NMR spectroscopic studies and by elemental



Figure 2. Molecular structure of 1b. Selected distances (Å) and angles (deg): Ti(1)-O(1)=1.955(2), Ti(1)-O(2)=1.774(2), Ti(1)-O(3)=1.794(2), Ti(1)-O(1A)=2.087(2), Ti(1)-C(1)=2.134(4); O(1)-Ti(1)-O(2)=99.13(9), O(2)-Ti(1)-O(3)=101.87(10), O(1)-Ti(1)-O(3)=121.90(10), O(1)-Ti(1)-O(1A)=73.07(9), O(2)-Ti(1)-O(1A)=168.70(9), O(3)-Ti(1)-O(1A)=89.30(10), O(1)-Ti(1)-C(1)=120.56(14), O(1A)-Ti(1)-C(1)=85.24(12), O(2)-Ti(1)-C(1)=92.05(12), O(3)-Ti(1)-C(1)=112.10(15). Hydrogen atoms are omitted for clarity.



Figure 3. Molecular structure of 1g. Selected distances (Å) and angles (deg): Ti(1)-O(1) = 1.936(2), Ti(1)-O(2) = 1.784(1), Ti(1)-O(3) = 1.800(2), Ti(1)-O(1A) = 2.103(2), Ti(1)-C(1) = 2.118(2); O(1)-Ti(1)-O(2) = 101.14(6) O(2)-Ti(1)-O(3) = 102.82(7), O(1)-Ti(1)-O(3) = 122.46(6), O(1)-Ti(1)-O(1A) = 73.78(6), O(2)-Ti(1)-O(1A) = 167.53(6), O(3)-Ti(1)-O(1A) = 89.39(6), O(1)-Ti(1)-C(1) = 120.23(8), O(1A)-Ti(1)-C(1) = 84.14(7), O(2)-Ti(1)-C(1) = 88.90(7), O(3)-Ti(1)-C(1) = 111.76(8). Hydrogen atoms are omitted for clarity.

analyses. The ¹H and ¹³C NMR spectra reveal only one set of 2-propoxide signals at ambient temperature. However, it is well-known that titanium(IV) alkoxides aggregate to form dimers²⁴ or oligomers²⁵ both in solution and in the solid

⁽²³⁾ Weidmann, B.; Widler, L.; Olivero, A. G.; Maycock, C. D.; Seebach, D. *Helv. Chim. Acta* **1981**, *64*, 357.

^{(24) (}a) Gau, H.-M.; Lee, C.-S.; Lin, C.-C.; Jang, M.-K.; Ho, Y.-C.;
Kuo, C.-N. J. Am. Chem. Soc. 1996, 118, 2936. (b) Wu, Y.-T.; Ho, Y.-C.;
Lin, C.-C.; Gau, H.-M. Inorg. Chem. 1996, 35, 5948. (c) Armistead, L. T.;
White, P. S.; Gagné, M. R. Organometallics 1998, 17, 4232. (d) You, J.-S.;
Shao, M.-Y.; Gau, H.-M. Organometallics 2000, 19, 3368. (e) Balsells, J.;
Davis, T. J.; Carroll, P.; Walsh, P. J. J. Am. Chem. Soc. 2002, 124, 10336.
(f) Wu, K.-H.; Gau, H.-M. Organometallics 2003, 22, 5193. (g) Wu, K.-H.;
Gau, H.-M. Organometallics 2004, 23, 580.

⁽²⁵⁾ Wright, D. A.; Williams, D. A. Acta Crystallogr. 1968, B24, 1107.

Table 1. Optimizations of Reaction Conditions for Coupling of 4-Methoxybromobenzene with Phenyltris(2-propoxo)titanium^a



entry	amt of Pd(OAc) ₂ (mol %)	ligand (amt (mol %))	solvent	time (h)	yield $(\%)^b$	
1			toluene	0.5	0	
2	1		toluene	0.5	3	
3	1	$PCy_3(2)$	toluene	0.5	≥99	
4	1	$PPh_3(2)$	toluene	0.5	trace	
5	1	$P(p-tolyl)_3(2)$	toluene	0.5	12	
6	1	$PCy_2Ph(2)$	toluene	0.5	54	
7	1	$P(t-Bu)_3(2)$	toluene	0.5	83	
8	1	$PCy_3(2)$	CH_2Cl_2	0.5	15	
9	1	$PCy_3(2)$	hexane	0.5	14	
10	1	$PCy_3(2)$	Et_2O	0.5	97	
11	1	$PCy_3(2)$	THF	0.5	trace	
12^{c}	1	$PCy_3(2)$	toluene	0.5	97	
13^{d}	1	$PCy_3(2)$	toluene	0.5	94	
14	0.5	$PCy_3(1)$	toluene	2	95	
15	0.25	$PCy_3(0.5)$	toluene	2	97	
16	0.1	PCy ₃ (0.2)	toluene	2	58	

^{*a*} 1.0 mmol of 4-methoxyphenyl bromide/1.3 mmol of PhTi(O-*i*-Pr)₃. ^{*b*} Yields were average values of two runs determined by ¹H NMR by comparing integrations of the methoxy ¹H signals of **2a** and **3a**. ^{*c*} 1.2 mmol of PhTi(O-*i*-Pr)₃. ^{*d*} 1.1 mmol of PhTi(O-*i*-Pr)₃.

state. Thus, a variable-temperature ¹H NMR study of 1c in toluene- d_8 was conducted. The ¹H NMR spectra in the isopropoxy region and the tolyl methyl region are presented in Figure 1. At 20 °C, a broad methine peak at 4.76 ppm and an isopropoxy methyl doublet at 1.26 ppm are observed (Figure 1a). The tolyl methyl singlet appears at 2.18 ppm. At -30 °C, the broad methine signal splits into two broad peaks at 5.02 and 4.88 ppm with a peak ratio of 1:2. The isopropoxy methyl doublet also splits into two broad signals at 1.30 and 1.20 ppm with a peak ratio of 2:1 (Figure 1b). The observation of two sets of isopropoxy ¹H signals in a 2:1 ratio suggests that complex 1c is a dimeric species of $[(4-MeC_6 H_4$)Ti(O-*i*-Pr)₂(μ -O-*i*-Pr)]₂ with the two metal centers bridging through two isopropoxy ligands. At -60 °C, the two methine signals become a septet and a broad peak, and the isopropoxy methyl resonances develop into two doublets (Figure 1c). The isopropoxy methine and methyl signals in ratios of 1 are resonances of terminal 2-propoxide ligands and the resonances in ratios of 1 arise from the bridging alkoxides. In contrast, the tolyl methyl peak remains a singlet at temperatures from 20 to -60 °C.

Molecular Structures of Complexes 1b,g. The complexes 1b,g were subjected to single-crystal X-ray analyses, and the molecular structures of both 1b (Figure 2) and 1g (Figure 3) reveal a dimeric geometry with a Ti_2O_2 core bridging through the oxygen atom of two isopropoxy groups. The titanium metal centers in 1b,g adopt a five-coordinate distorted-trigonal-bipyramidal environment. The bridging isopropoxy oxygen atoms bond to the two metal centers asymmetrically with a Ti(1)-O(1) bond distance of 1.955(2) Å in complex 1b, being shorter than the Ti(1A)-O(1) distance of 2.087(2) Å. Similarly, the Ti(1)-O(1) distance of 2.103(2) Å. The terminal Ti(1)-O(2) (1.774(2) Å) and Ti(1)-O(3) (1.794(2) Å) bond lengths in complex 1b are much shorter than the

(26) Johnson, A. L.; Davidson, M. G.; Mahon, M. F. Dalton Trans. 2007, 5405. distances of the bridging Ti–O bonds, and the same results are also observed in complex **1g** and the titanium complexes $[Ti(O-i-Pr)_2(\mu-O-i-Pr)(C_6F_5)]_2^{26}$ and $[Ti(ONp)_3(\mu-ONp)]_2$ (Np = neopentyl).²⁷ The Ti(1)–C(1) bond distance of 2.134(4) Å in complex **1b** is slightly longer than that of 2.118(2) Å in complex **1g** but shorter than that of 2.177(2) Å in $[Ti(O-i-Pr)_2(\mu-O-i-Pr)(C_6F_5)]_2$, indicating the steric and electronic effects of aryl ligands. In comparison with [Ti-O-(bridging) bond distances in**1b** $,g and <math>[Ti(ONp)_3(\mu-ONp)]_2$ are comparable despite the replacement of one alkoxide ligand on each titanium metal center in $[Ti(OR)_3(\mu-OR)]_2$ with an aryl ligand in **1b**,g.

Coupling Reactions of Aryl Bromides with Aryltris(2-pro**poxo**)titanium. Coupling reactions of aryl bromides with aryltris(2-propoxo)titanium were then examined. Reaction conditions were optimized using 4-methoxybromobenzene as a substrate and 1.3 equiv of PhTi(O-i-Pr)₃ as a phenyl source, and the results are summarized in Table 1. It was found that both the Pd source and the phosphine ligand were mandatory for successfully performing the reaction, as trace or even no product was formed in the absence of either one or both of them (entries 1 and 2). For palladium/phosphine catalytic systems, the choice of phosphine ligands was crucial for coupling reactions (entries 3-7). In this case, sterically hindered phosphine ligands, such as PCy_3 and $P(t-Bu)_3$, were highly active in attaining the coupling product 3a in high yields of >99% (entry 3) and 83% (entry 7) at room temperature over a short reaction time of 0.5 h, respectively. Having found the optimum catalyst of 1 mol % Pd(OAc)₂ along with 2 mol % PCy₃, further investigations were made for the choice of the solvent (entries 8-11). Both toluene (entry 3) and diethyl ether (entry 10) were the best choices. Reactions in other solvents such as CH_2Cl_2 (entry 8), hexane (entry 9), and THF (entry 11) afforded trace amounts or low

⁽²⁷⁾ Boyle, T. J.; Alam, T. M.; Mechenbier, W. R.; Scott, B. L.; Ziller, J. W. Inorg. Chem. **1997**, *36*, 3293.

Table 2. Coup	ing Reactions of	Aryl Bromides	s with Aryltris(2-p	opoxo)titanium R	Reagents Catalyzed	l by the Pd(OAc) ₂ /	PCy ₃ System ^{<i>a</i>,<i>b</i>}
---------------	------------------	---------------	---------------------	------------------	--------------------	---------------------------------	--

∠Br

1 mol% Pd(OAc)₂

	Br + ArTi(O- <i>i</i> -Pr) ₃				2 mol%	2 mol% PCy ₃						
			R	1.	.3 equiv	toluene ((1 mL)	, rt R				
			2					3				
Entry	Substrate	Ar	Time (h)	Product	Yield(%) ^c	En	try	Substrate	Ar	Time (h)	Product	Yield(%) ^c
1	MeO-Br	Ph	0.5	3a	95	1	14		Ph	3	3n	75
2	MeS-Br	Ph	0.5	3b	93	1	15	Br	Ph	2	30	70
3	Br	Ph	1	3c	97	1	.6 ^f	N MeO-	2-MeC ₆ H ₄	0.5	3p	93
4	Br	Ph	2	3d	87	1	17	MeO-	4-MeC ₆ H ₄	0.5	3q	96
5 ^d	Br	Ph	3	3e	94	1	18	MeO-	4-ClC ₆ H ₄	1	3r	95
						1	19	MeO-Br	4-Me ₃ SiC ₆ H ₄	1	3s	94
6 ^{<i>d</i>}	Br	Ph	4	3f	90			Br				
7 ^d	Br	Ph	7	3g	72	20	0 ^{e,g}	OMe OMe Br	Ph	3	3t	97
8	F-	Ph	1	3h	94	21	1 6.8	Br	DI-	2	(5) 24	00
9 ^e	Cl-Br	Ph	0.5	3i	91	21	1.0		Pn	3	(S) -31	90
10^e	NC-	Ph	3	3ј	97			Br				
11^e	O ₂ N-S-Br	Ph	4	3k	73	22	e,g,h	OMe	4-CF ₃ C ₆ H ₄	5	(S)- 3u	93
12 ^e	Br	Ph	0.5	31	97			Br Br				
13	Br	Ph	3	3m	96	23 [¢]	e,g,h,i	OMe OMe Br	3,5-Me ₂ C ₆ H ₃	5	(S) -3v	95

^a Conditions: substrate (1 mmol), ArTi(O-i-Pr)₃ (1.3 mmol), Pd(OAc)₂ (0.01 mmol), PCy₃ (0.02 mmol). ^b Procedure A. ^c Isolated yield from average values of two runs. ^d Conditions: ArTi(O-i-Pr)₃ (1.5 mmol). ^e Procedure B. ^f Procedure C. ^g Conditions: substrate (0.5 mmol), ArTi(O-i-Pr)₃ (1.3 mmol). h^{2} mL of toluene. i^{i} Yield obtained after converting to 3,3'-bis(3,5-dimethylphenyl)-2,2'-binaphthol ((S)-4v).

yields of **3a**. For further optimization of reaction conditions, toluene was selected as the solvent. Tuning amounts of PhTi(O-i-Pr)₃ to 1.2 and 1.1 equiv decreased the yield of 3a to 97% and 94% (entries 12 and 13). To examine the efficiency of the catalytic system, catalyst loadings were decreased to 0.5 and 0.25 mol %. The reactions still afforded 3a in excellent yields of 97 and 95% over 2 h (entries 14 and 15). However, the coupling reaction catalyzed by a system of 0.1 mol % of Pd(OAc)₂ and 0.2 mol % of PCy₃ produced the product 3a in a lower yield of 58% over 2 h (entry 16). This study shows that an inorganic base is not required as a promoter while using the phenyltris(2-propoxo)titanium reagent.

The generality of coupling reactions of substituted aryl bromides with aryltris(2-propoxo)titanium reagents was demonstrated using 1 mol % of Pd(OAc)₂ and 2 mol % of PCy_3 , and the results are given in Table 2. The catalytic system was compatible with a wide range of aryl bromides, regardless of the electronic nature or the steric effect of the

substituents on the aryl groups. For examples, yields of coupling products ranged from 87 to 97% (entries 1-5) for electron-rich substrates such as 4-methoxybromobenzene, 4-bromothioanisole, 4-methylbromobenzene, 2-methylbromobenzene, and 3,5-dimethylbromobenzene. For aryl bromides bearing an electron-withdrawing substituent such as 4-chlorobromobenzene, 4-fluorobromobenzene, and 4-bromobenzonitrile, coupling products were obtained in 91-97% yields (entries 8-10). However, a lower yield of 73%(entry 11) was obtained for 4-nitrobromobenzene, probably due to a higher affinity of the nitro group for the titanium reagent, which retarded the access of the substrate to the catalytic metal center. For sterically hindered 2,4-dimethylbromobenzene (entry 6) and 1-bromonaphthylene (entry 13), coupling products were obtained in 90 and 96% yields. The system also works well for the most sterically hindered 2,6-dimethylbromobenzene, affording the product 3g in a satisfactory 72% yield using 1.5 equiv of PhTi(O-i-Pr)₃ over a longer reaction time of 7 h (entry 7). It is worth noting that

Scheme 2. Typical Synthesis of 3,3'-Diaryl-2,2'-dimethoxy-1,1'binaphthylenes and Their Conversion to 3,3'-Diaryl BINOLs



heterocyclic bromides such as 2- and 3-bromopyridine were also tolerated in this system, and the coupling products **3n**,**o** were obtained in satisfactory yields of 75% and 70% (entries 14 and 15) over reaction times of 2 and 3 h, respectively.²⁸ Coupling reactions of 4-methoxybromobenzene with different aryltitanium compounds, such as $(2-\text{MeC}_6\text{H}_4)\text{Ti}(\text{O}-i-\text{Pr})_3$ (**1b**), $(4-\text{MeC}_6\text{H}_4)\text{Ti}(\text{O}-i\text{-Pr})_3$ (**1c**), $(4-\text{ClC}_6\text{H}_4)\text{Ti}(\text{O}-i-\text{Pr})_3$ (**1d**), and $(4-\text{Me}_3\text{SiC}_6\text{H}_4)\text{Ti}(\text{O}-i\text{-Pr})_3$ (**1e**), were also evaluated, and coupling products were obtained in 93– 96% yields over reaction times of 0.5–1 h (entries 16–19).

Recently, applications of 3,3'-diaryl-2,2'-binaphthols or their derivatives to metal-catalyzed asymmetric reactions^{29,30} or organocatalysis³¹ have attracted much attention. In general, 3,3'-diaryl-2,2'-binaphthols were prepared via Suzuki couplings in two synthetic protocols: (1) coupling of 3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthylene with arylboronic acid³² and (2) coupling of 3,3'-bis(dihydroxyborane)-2,2'-dimethoxy-1,1'-binaphthylene with aryl bromide³³ (Scheme 2). Both reaction routes required catalyst loadings of 2-5 mol %, elevated temperatures in refluxing solvents, and longer reaction times of 18-24 h in general. In this study, we carried out coupling reactions of 3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthylene (**2s**) with ArTi(O-*i*-Pr)₃, employing a catalytic system of 2 mol % of Pd(OAc)₂ and 4 mol % of PCy₃. The coupling reaction of racemic **2s** with

(31) (a) McDonald, N. T.; Schau, S. E. J. Am. Chem. Soc. **2003**, 125, 12094. (b) Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. Angew. Chem., Int. Ed. **2004**, 43, 1566. (c) Storer, R. I.; Carrera, D. E.; Ni, Y.; MacMillian, D. W. C. J. Am. Chem. Soc. **2006**, 128, 84. (d) Guo, Q.-X.; Liu, H.; Guo, C.; Luo, S.-W.; Gu, Y.; Gong, L.-Z. J. Am. Chem. Soc. **2007**, 129, 3790. (e) Liu, H.; Dagousset, G.; Masson, G.; Retailleau, P.; Zhu, J. J. Am. Chem. Soc. **2009**, 131, 4596.

(33) Simonsen, K. B.; Gothelf, K. V.; Jørgensen, K. A. J. Org. Chem. 1998, 63, 7536. PhTi(O-*i*-Pr)₃ proceeded smoothly at room temperature to afford the coupling product **3s** in an excellent 97% yield over 3 h (entry 20). Couplings of chiral (*S*)-**2s** with the aryltitanium reagents **1a**,**f**,**g** were also demonstrated. Similarly, the reactions took place at room temperature over 3 or 5 h, affording corresponding chiral 3,3'-diaryl-2,2'-dimethoxy-1,1'-binaphthylenes in excellent yields (entries 21-23). The above compounds can be converted to the 3,3'-diaryl-2,2'-binaphthols for further applications to asymmetric catalysis.

The mechanism of coupling reactions of aryl bromides with ArTi(O-*i*-Pr)₃ is believed to be similar to that of the Suzuki coupling reaction, except that there is no requirement of a base to promote the reaction. The reaction probably starts with the reaction of Pd(OAc)₂ with 2 equiv of ArTi(O*i*-Pr)₃ in the presence of PCy₃ to give a (PCy₃)₂PdAr₂ species followed by a reductive elimination process of the diaryl species, giving an active Pd(0) species of Pd(PCy₃)₂.¹⁶ An oxidative addition of RX to the Pd(0) species furnishes a Pd(II) intermediate of (PCy₃)₂Pd(R)X. Due to the high reactivity of ArTi(O-*i*-Pr)₃, the transmetalation process proceeds directly to afford the transmetalated intermediate (PCy₃)₂Pd(R)(Ar), which subsequently undergoes a reductive elimination of R–Ar and regenerates the active species.

Conclusion

In summary, the series of aryltris(2-propoxo)titanium reagents [ArTi(O-i-Pr)₂(µ-O-i-Pr)]₂ were synthesized and characterized. Both solution ¹H NMR and solid-state X-ray diffraction studies show that the aryltris(2-propoxo)titanium complexes have a dimeric structure with a Ti_2O_2 core bridging through the oxygen atom of two isopropoxy groups. These aryltitanium reagents exhibit extremely high efficiency in cross-coupling reactions with aryl bromides, and depending on the arylbromide substrate, the commercially available and economic catalytic system of 0.25 mol % of $Pd(OAc)_2$ and 0.5 mol % of PCy_3 is effective enough to induce coupling reactions at room temperature over 2 h. The Pd(OAc)₂/PCy₃ system works well for a wide range of aryl bromides, regardless of the electronic nature or the steric effect of the substituents on the aryl groups, and there is no requirement of an inorganic base as a promoter. In addition, couplings of pyridyl bromides with PhTi(O-i-Pr)3 afford aryl-substituted pyridine products in satisfactory yields over 2-3 h. Coupling reactions of 4-methoxybromobenzene with a variety of aryltris(2-propoxo)titanium reagents are demonstrated to provide the coupling products in excellent yields. Most importantly, this study also demonstrates efficient syntheses of 3,3'-diaryl-modified BINOL ligands compared to the typical synthesis that was conducted in refluxing solvent over much longer reaction times.

Experimental Section

General Remarks. All syntheses and manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Solvents were dried by refluxing for at least 24 h over P_2O_5 (dichloromethane) or sodium/benzophenone (THF, *n*-hexane, or toluene) and were freshly distilled prior to use. Ti(O-*i*-Pr)₄ and TiCl₄ were obtained from Aldrich and freshly distilled prior to use. Aryl bromides and magnesium turnings were used directly or purified using standard procedures. ¹H NMR spectra were obtained with a Varian Inova Unity-600 (600 MHz) or a Varian Mercury-400 (400 MHz) spectrometer, and ¹³C NMR spectra were recorded

^{(28) (}a) Billingsley, K. L.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4695. (b) Yang, D. X.; Colletti, S. L.; Wu, K.; Song, M. Y.; Li, G. Y.; Shen, H. C. *Org. Lett.* **2009**, *11*, 381. (c) Molander, G. A.; Canturk, B.; Kennedy, L. E. *J. Org. Chem.* **2009**, *74*, 973.

⁽²⁹⁾ For reviews see: (a) Pu, L.; Yu, H. Chem. Rev. 2001, 101, 757.
(b) Chen, Y.; Yekta, S.; Yudin, A. K. Chem. Rev. 2003, 103, 3155.
(c) Kočoský, P.; Vyskočil, S; Smrčina, M. Chem. Rev. 2003, 103, 3213.

 ^{(30) (}a) Huang, W.-S.; Pu, L. J. Org. Chem. 1999, 64, 4222. (b) Costa,
 A. M.; Jimeno, C.; Gavenonis, J.; Carroll, P. J.; Walsh, P. J. J. Am. Chem. Soc. 2002, 124, 6929. (c) Wu, T. R.; Shen, L.; Chong, J. M. Org. Lett. 2004, 6, 2701. (d) Harada, T.; Kanda, K. Org. Lett. 2006, 8, 3817.

^{(32) (}a) Huang, W.-S.; Hu, Q.-S.; Pu, L. J. Org. Chem. 1998, 63, 1364.
(b) Wipf, P.; Jung, J.-K. J. Org. Chem. 2000, 65, 6319.

Article

with the Varian Mercury-400 instrument (100.70 MHz). ¹H and ¹³C chemical shifts were measured relative to tetramethylsilane as the internal reference. Elemental analyses were performed using a Heraeus CHN-O-RAPID instrument.

Typical Procedures for the Preparation of ArTi(O-i-Pr)₃. A two-necked 250 mL round-bottomed flask equipped with a condenser, a magnetic stir bar, and an addition funnel was charged with magnesium turnings (2.40 g, 100 mmol), and the flask was evacuated under reduced pressure for 2 h. Under a nitrogen atmosphere, 100 mL of THF was added to the flask and aryl bromide (120 mmol) in 50 mL of THF was transferred into the addition funnel. The THF solution of aryl bromide was added slowly to the reaction flask, and the reaction mixture was controlled under gentle reflux using an ice bath if necessary. After the reaction was complete, the resulting Grignard reagent was cooled to 0 °C. In another two-necked 500 mL roundbottomed flask under a nitrogen atmosphere, to a solution of Ti(O-*i*-Pr)₄ (22.4 mL, 75.0 mmol) in 50 mL of THF at 0 °C was added TiCl₄ (2.8 mL, 25.0 mmol). The resulting solution was warmed to room temperature and stirred for 30 min, giving a ClTi(O-i-Pr)₃ solution (100 mmol). The ClTi(O-i-Pr)₃ solution was cooled to 0 °C, and to this solution was transferred the icecold Grignard solution via a cannula. The reaction mixture was warmed to room temperature and was allowed to react for 3 h. The volatile material was removed completely under reduced pressure, and under a nitrogen atmosphere, the residue was extracted with *n*-hexane (3×200 mL). The combined hexane solution was concentrated and was cooled to -20 °C, furnishing a crystalline product of the aryltris(2-propoxo)titanium species.

PhTi(O-*i***-Pr)₃ (1a).** Pale yellow crystalline solid. Yield: 21.8 g (72.1%). Mp: 73–75 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.58–7.52 (m, 2H, Ar*H*), 7.13–7.09 (m, 3H, Ar*H*), 4.58 (m, 3H, OC*H*), 1.30 (d, J = 6.0 Hz, 18 H, C*H*₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 186.6, 132.6, 126.6, 126.4, 77.5, 25.9 ppm. Anal. Calcd for C₃₀H₅₂O₆Ti₂: C, 59.61; H, 8.67. Found: C, 59.16; H, 9.06.

(2-MeC₆H₄)Ti(O-*i*-Pr)₃ (1b). Pale yellow crystals. Yield: 20.6 g (65.1%). Mp: 80–82 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, J = 6.8 Hz, 1H, ArH), 7.04–6.89 (m, 3H, ArH), 4.69 (m, 3H, OCH), 2.52 (s, 3H, CH₃), 1.27 (d, J = 6.0 Hz, 18 H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 187.5, 140.1, 134.5, 127.7, 127.2, 123.3, 77.6, 26.1, 25.0 ppm. Anal. Calcd for C₃₂H₅₆O₆Ti₂: C, 60.76; H, 8.92. Found: C, 60.27; H, 8.50.

(4-MeC₆H₄)Ti(O-*i*-Pr)₃ (1c). Pale yellow crystalline solid. Yield: 21.8 g (68.9%). Mp: 78–79 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.00 (d, J = 7.6 Hz, 2H, Ar*H*), 6.94 (d, J = 7.6 Hz, 2H, Ar*H*), 4.64 (sept, J = 6.0 Hz, 3H, OC*H*), 2.26 (s, 3H, CH₃), 1.28 (d, J = 6.0 Hz, 18H, OCH(CH₃)₂) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 182.9, 136.2, 133.1, 126.9, 77.3, 26.1, 21.5 ppm. ¹H NMR (600 MHz, toluene- d_8 , -60 °C): δ 7.76 (d, J = 7.2 Hz, 2H, Ar*H*), 7.12 (d, J = 7.2 Hz, 2H, Ar*H*), 5.05 (sept, J = 6.0 Hz, 12H, OCH(CH₃)₂), 1.25 (d, J = 5.4 Hz, 12H, OCH(CH₃)₂), 1.25 (d, J = 5.4 Hz, 6H, OCH(CH₃)₂) ppm. Anal. Calcd for C₃₂H₅₆O₆Ti₂: C, 60.76; H, 8.92. Found: C, 60.85; H, 9.15.

(4-ClC₆H₄)Ti(O-*i*-Pr)₃ (1d). Pale yellow crystalline solid. Yield: 22.6 g (67.1%). Mp: 84–86 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, J = 6.8 Hz, 2H, Ar*H*), 7.09 (d, J = 6.8 Hz, 2H, Ar*H*), 4.66 (sept, J = 6.0 Hz, 3H, OC*H*), 1.26 (d, J = 6.0 Hz, 18H, OCH(CH₃)₂) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 184.3, 133.6, 131.6, 126.1, 77.7, 25.7 ppm. Anal. Calcd for C₃₀H₅₀O₆Cl₂-Ti₂: C, 53.51; H, 7.48. Found: C, 53.50; H, 7.79.

(4-TMSC₆H₄)Ti(O-*i***-Pr)₃ (1e). Pale yellow crystalline solid. Yield: 28.1 g (75.0%). Mp: 92–93 °C. ¹H NMR (400 MHz, CDCl₃): \delta 7.58 (d, J = 7.6 Hz, 2H, Ar***H***), 7.30–7.28 (m, 2H, Ar***H***), 4.63 (sept, J = 6.4 Hz, 3H, OC***H***), 1.29 (d, J = 6.4 Hz, 18H, OCH(CH₃)₂), 0.22 (s, 9H, Si(CH₃)₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): \delta 185.9, 138.9, 132.7, 131.3, 77.5, 26.2, –1.1 ppm. Anal. Calcd for C₃₆H₆₈O₆Si₂Ti₂: C, 57.74; H, 9.15. Found: C, 57.66; H, 9.00.** (4-CF₃C₆H₄)Ti(O-*i*-Pr)₃ (1f). Pale yellow crystalline solid. Yield: 29.6 g (79.9%). Mp: 101–103 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J*=7.6 Hz, 2H, Ar*H*), 7.35 (d, *J* = 8.0 Hz, 2H, Ar*H*), 4.74 (m, 3H, OC*H*), 1.22 (d, *J* = 6.4 Hz, 18H, OCH-(CH₃)₂) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 132.2, 125.8, 123.1, 122.6, 77.7, 25.3 ppm. Anal. Calcd for C₃₂H₅₀F₆O₆Ti₂: C, 51.91; H, 6.81. Found: C, 52.25; H, 6.96.

(3,5-Me₂C₆H₃)Ti(O-*i*-Pr)₃ (1g). Pale yellow crystals. Yield: 23.1 g (69.9%). Mp: 85–86 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.09 (s, 2H, ArH), 6.69 (s, 1H, ArH), 4.64 (sept, J = 6.0 Hz, 3H, OCH), 2.16 (s, 6H, CH₃), 1.20 (d, J = 6.0 Hz, 18H, OCH(CH₃)₂) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 185.6, 135.1, 130.8, 128.7, 77.4, 26.2, 21.4 ppm. Anal. Calcd for C₃₄H₆₀O₆Ti₂: C, 61.82; H, 9.16. Found: C, 61.45; H, 9.59.

X-ray Crystallography. Suitable crystals of complexes **1b**,g were mounted under a dinitrogen atmosphere in sealed capillaries. Diffractions were performed on an Oxford Gemini S diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å): temperature 100(2) K; φ and ω scan technique; SADABS effects and empirical absorption applied in the data corrections. All structures were solved by direct methods (SHELXTL-97),³⁴ completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on F^2 (SHELXTL-97). See the Supporting Information for crystallographic data.

General Procedures for Coupling Reactions. Procedure A. Aryltris(2-propoxo)titanium (1.30 mmol) in 0.8 mL of toluene was added to a solution of $Pd(OAc)_2$ (0.010 mmol) and PR_3 (0.020 mmol) in 0.2 mL of toluene under a dry nitrogen atmosphere, followed by the addition of liquid aryl bromide (1.00 mmol). The mixture was stirred at room temperature for a given period of time and quenched with 10 mL of water. The solution was extracted with dichloromethane (3 × 30 mL). The combined organic phase was dried over MgSO₄ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography to give the coupling product.

Procedure B. Solid aryl bromide (1.00 mmol), $Pd(OAc)_2$ (0.010 mmol), and PR_3 (0.020 mmol) were placed in a reaction vessel under a dry nitrogen atmosphere, and $ArTi(O-i-Pr)_3$ (1.30 mmol) in 1 mL of toluene was added. The mixture was stirred at room temperature for a given period of time and quenched with 10 mL of water. The solution was extracted with dichloromethane (3 × 30 mL). The combined organic phase was dried over MgSO₄ and concentrated to dryness under reduced pressures. The residue was purified by column chromatography to give the coupling product.

Procedure C. A solution of $Pd(OAc)_2$ (0.010 mmol) and PR_3 (0.020 mmol) in 1 mL of toluene was transferred to a reaction vessel containing $ArTi(O-i-Pr)_3$ (1.30 mmol) followed by addition of liquid aryl bromide (1.00 mmol). The mixture was stirred at room temperature for a given period of time and quenched with 10 mL of water. The solution was extracted with dichloromethane (3 × 30 mL). The combined organic phase was dried over MgSO₄ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography to give the coupling product.

Acknowledgment. Financial support under Grant No. NSC 96-2113-M-005-007-MY3 from the National Science Council of Taiwan, Republic of China, is appreciated.

Supporting Information Available: Text and figures giving chromatographic conditions yields, and ¹H NMR spectroscopic data of coupling products and CIF files giving X-ray crystallographic data for structure determinations of complexes **1b.g.** This material is available free of charge via the Internet at http:// pubs.acs.org.

⁽³⁴⁾ Sheldrick, G. M. SHELXTL, Version 5.10; Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.