temperature, forming a colorless oil. Trituration afforded a white powder, which was isolated by filtration and dried in vacuo (0.35 g, 95 %). ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 0.17$ (s, $SiCH_3$); ^{11}B NMR (96.29 MHz, CD_2Cl_2): $\delta = -15$ (borane signal not observed); see Figure 1 for the ^{19}F NMR spectrum; elemental analysis calcd for $C_{49}H_{57}B_2F_{24}N_3Si_6Zr$: C 41.3, H 4.0, N 2.9; found: C 41.2, H 3.9, N 2.8.

Generation of metallocenium cations from [Cp_2ZrMe_2] and **1**: Monomeric and dimeric metallocenium cations were generated in situ by adding a solution of **1** in C_6D_5Br to a solution of [Cp_2ZrMe_2] in a 1:1 or a 1:2 (**1**:Zr) stoichiometry. The solutions were then assayed by ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy; the results of the latter two were essentially identical to that found for **4**. ^{1}H NMR for $[Cp_2ZrCH_3(S)]^+[\mathbf{A'}/\mathbf{A}]^-$ (S = solvent; 200 MHz, C_6D_5Br, 25 °C): $\delta = 5.83$ (s, C_5H_5), 1.67 (br s, $B_{borate}CH_3$), 1.19 (br s, $B_{borane}CH_3$), 0.48 (s, $ZrCH_3$); ^{13}C NMR (100.61 MHz, C_6D_5Br): $\delta = 115.3$ (C_5H_5), 53.8 ($ZrCH_3$), 17.3 ($B_{borate}CH_3$), 15.0 ($B_{borane}CH_3$). ^{1}H NMR for $[(Cp_2ZrCH_3)_2(\mu\text{-}CH_3)]^+[\mathbf{A'}/\mathbf{A}]^-$ (200 MHz, C_6D_5Br, 25 °C): $\delta = 5.89$ (s, 20 H, C_5H_5), 1.67 (br s, $B_{borate}CH_3$ of **A**), 1.19 (br s, $B_{borane}CH_3$ of **A′**), 0.07 (s, 6 H, $ZrCH_3$), -1.05 (s, 3 H, $ZrCH_3Zr$).

Generation of metallocenium cations from [Cp_2ZrMe_2] and **3**: Ion pair **5** was generated in situ by mixing [Cp_2ZrMe_2] and diborane **3** in C_6D_5Br. ^{1}H NMR (200 MHz, C_6D_5Br, 25 °C): $\delta = 5.74$ (s, 10 H, C_5H_5), 0.36 (s, 3 H, $ZrCH_3$), 0.12 (br s, 3 H, $B_{borate}CH_3$); ^{19}F{^{1}H} NMR (C_6D_5Br, 25 °C): $\delta = -124.74$ (br m, 2 F), -133.8 and -136.8 (2 × br m, total 2 F, *o*-F), -134.4 (m, 2 F), -135.8 (br m, 2 F, *o*-F), -146.6 (br m, 2 F), -156.4 (t, J(F,F) = 20.7 Hz, *p*-F), -159.8 (br m, 2 F, *m*-F), -160.9 (br m, 1 F, *p*-F), -163.2 and -163.8 (2 × br m, total 2 F, *m*-F), -165.2 (br m, 2 F).

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[1] a) L. Li, T. J. Marks, *Organometallics* **1998**, *17*, 3996; b) Y.-X. Chen, C. L. Stern, S. Yang, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 12451; c) D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492; d) A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245.

[2] a) Y.-X. Chen, C. L. Stern, T. J. Marks *J. Am. Chem. Soc.* **1997**, *119*, 2582; b) M. Bochmann, M. J. Sarsfield, *Organometallics* **1998**, *17*, 5908.

[3] a) Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 6287, and references therein; b) R. E. v. H. Spence, W. E. Piers, Y. Sun, M. Parvez, L. R. MacGillivray, M. J. Zaworotko, *Organometallics* **1998**, *17*, 2459.

[4] a) P. A. Deck, C. L. Beswick, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 1772, and references therein; b) Y. Sun, R. E. v. H. Spence, W. E. Piers, M. Parvez, G. P. A. Yap, *J. Am. Chem. Soc.* **1997**, *119*, 5132; c) L. Luo, T. J. Marks, *Top. Catal.* **1999**, *7*, 97.

[5] a) L. Jia, X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1994**, *13*, 3755; b) T. J. Marks, L. Jia, X. Yang (Northwestern University), US Patent 5447895, **1995**.

[6] V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins, T. B. Marder, *J. Am. Chem. Soc.* **1999**, *121*, 3244.

[7] Y. Sun, W. E. Piers, M. Parvez, *Can. J. Chem.* **1998**, *76*, 513.

[8] a) M. V. Metz, D. J. Schwartz, C. L. Beswick, C. L. Stern, T. J. Marks, *Inorganic Abstracts of the 217th ACS National Meeting* (Anaheim, CA), **1999**, abstract no. 15; b) M. H. Mcadon, P. N. Nickias, T. J. Marks, D. J. Swartz (Northwestern University and the Dow Chemical Co.) WO 99/06413, **1999**.

[9] M. D. Healey, D. A. Wierda, A. R. Barron, *Organometallics* **1988**, *7*, 2543.

[10] The use of MAD in combination with [Cp_2ZrMe_2] and methylaluminoxane (MAO) in ethylene polymerizations and as a cocatalyst in styrene polymerizations using Ti–alkoxide initiators has been reported: a) S. S. Reddy, S. Shashidhar, S. Sivaram, *Macromolecules* **1993**, *26*, 1180; b) S. S. Reddy, S. Shashidhar, *Eur. Polym. J.* **1997**, *33*, 583; for use of R_2Al(BHT) and related compounds as scrubbing agents, see R. K. Rosen, J. C. Stevens, J. C. Tracy (Dow Chemical Co.), WO 97/27228, **1997**.

[11] R. Andersen, *Inorg. Chem.* **1979**, *18*, 1724.

[12] A. D. Horton, J. de With, *Organometallics* **1997**, *16*, 5424.

[13] Crystal data for **4** ($C_{49}H_{57}B_2F_{24}N_3Si_6Zr$): $M_r = 1425.4$, monoclinic, space group $P2_1/c$, $a = 12.942(2)$, $b = 22.372(4)$, $c = 22.345(4)$ Å, $\beta = 95.403(4)°$, $V = 6441.0(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.470$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 275(2)$ K; of 35107 measured reflections, 15491 were unique, $R_{int} = 0.0361$; 9019 reflections with $I_{net} > 2.0\sigma(I_{net})$, $\mu = 3.87$ cm^{-1}, min./max. transmission 0.752 and 0.913, $R = 0.0441$ ($I > 2\sigma$), $Rw = 0.1069$ (F^2, all data), GOF = 0.922, no. of parameters 785, final difference map within ±0.52 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127481. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk.

[14] J. R. Galsworthy, M. L. H. Green, N. Maxted, M. Müller, *J. Chem. Soc. Dalton Trans.* **1998**, 387.

[15] a) M. Bochmann, S. L. Lancaster, *Angew. Chem.* **1994**, *106*, 1715; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1634; b) X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1991**, *10*, 840; c) S. Beck, M.-H. Prosenc, H. H. Brintzinger, R. Goretzki, N. Herfert, G. Fink, *J. Mol. Catal. A* **1996**, *111*, 67; d) K. Köhler, W. E. Piers, S. Xin, Y. Feng, A. M. Bravakis, A. P. Jarvis, S. Collins, W. Clegg, G. P. A. Yap, T. B. Marder, *Organometallics* **1998**, *17*, 3557.

[16] C. H. Lee, S. J. Lee, J. W. Park, K. H. Kim, B. Y. Lee, J. S. Oh, *J. Mol. Catal. A* **1998**, *132*, 231.

[17] Although degenerate Me exchange can occur between MAD and [Cp_2ZrMe_2] or the ion pair formed from [Cp_2ZrMe_2] and $B(C_6F_5)_3$, these processes are slow on the NMR time scale at 25 °C in [D$_8$]toluene. For quantitative studies on Me exchange between alkylmetallocenes and MAD in toluene, see A. R. Siedle, R. A. Newmarks, W. M. Lamanna, J. N. Schroepfer, *Polyhedron* **1990**, *9*, 301.

[18] The 2D ^{1}H–^{1}H EXSY spectra of the ion pair derived from [Cp_2ZrMe_2] and **1** in bromobenzene revealed the presence of weak crosspeaks between the ZrMe resonance and the neutral BMe resonance of the major counteranion, suggesting slow Me exchange under these conditions. The limited solubility of this ion pair in toluene precluded analogous experiments in this solvent.

Titanium–Thiolate–Aluminum–Carbide Complexes by Multiple C–H Bond Activation[**]

Frédéric Guérin and Douglas W. Stephan[*]

Much of early transition metal thiolate chemistry is based on metallocene derivatives.[1] More recently, interest has focused on related monocyclopentadienyl analogues as such systems have proved to be more reactive, often affording novel reactivity and products.[2–13] For example, we have observed that CpTi–thiolate species undergo either *β*-C–H or C–S bond activation of the thiolate ligands depending on the reaction conditions.[3–7] An interesting aspect of early transition metal chemistry in general involves the perturba-

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tion of reactivity precipitated by judicious choice of ancillary ligands. In this regard, we have recently applied the notion of a steric and electronic analogy between cyclopentadienyl and phosphinimide ligands[14, 15] to develop effective ethylene polymerization catalysts.[16, 17] We have now combined these two approaches in the quest for unique reactivity of CpTi–thiolate complexes. Herein we describe the reactions of [Cp(iPr$_3$PN)Ti(SR)$_2$] with AlMe$_3$. The result is an unprecedented triple C–H bond activation of a methyl group to yield Ti–Al–carbide clusters.

The red compounds [Cp(iPr$_3$PN)Ti(SR)$_2$] (**1**: R = Ph, **2**: R = CH$_2$Ph) are readily prepared by reaction of [Cp(iPr$_3$PN)TiCl$_2$][16] with the lithium thiolates LiSPh or LiSCH$_2$Ph. These species are isolated in 64 and 75% yields, respectively. The ^{31}P{^{1}H} NMR spectra for **1** and **2** reveal single resonances at $\delta = 34.94$ and 31.55, respectively. The ^{1}H and ^{13}C{^{1}H} NMR data are unexceptional and are consistent with the formulations.

Compounds **1** and **2** react with excess AlMe$_3$. Monitoring of these reactions by ^{31}P{^{1}H} NMR spectroscopy shortly after mixing reveals the presence of three new resonances in addition to a signal from the starting material. When the reaction mixtures were left standing for 24 h at 25 °C, these signals were replaced by single resonances at $\delta = 54.09$ and 52.87, respectively, inferring the quantitative formation of new species **3** and **4**. These species were isolated in 83 and 74% yield, respectively. The ^{1}H NMR spectra of **3** and **4** reveal resonances attributable to two inequivalent thiolate ligands, a cyclopentadienyl and phosphinimide ligands. In addition, **3** and **4** exhibit five resonances between $\delta = 0.30$ and -0.32 attributable to methyl groups. The corresponding ^{13}C resonances for the ligand fragments are observed, whereas the signals for the methyl groups are extremely weak. This latter observation is consistent with aluminum-bound methyl groups.

On the basis of these NMR data, formulations incorporating a Ti and three Al atoms could be proposed, although the precise nature of the molecular structure remained unclear. For this reason, crystallographic studies of **3** and **4** were undertaken.[18] Despite repeated attempts to obtained suitable crystals of **3**, the structure solved for **3** was of less than desirable quality. Nonetheless, the data did permit the establishment of the molecular connectivity of **3**.

In contrast, high-quality crystals of **4** were obtained by recrystallization from benzene. The X-ray structural data for **3** and **4** confirmed that they are analogous and can be formulated as [CpTi(μ-SR)(μ-NPiPr$_3$)(C)(AlMe$_2$)$_2$(μ-SR)-AlMe] (**3**: R = Ph, **4**: R = CH$_2$Ph; Figures 1 and 2). In both of these molecules, the pseudo-"three-legged piano stool" coordination sphere of Ti comprises a cyclopentadienyl ring, a thiolate sulfur, a phosphinimide nitrogen, and a carbide carbon. Three aluminum atoms complete the bonding sphere of the carbide carbon atom. Bridging the titanium-bound thiolate and the carbide is an AlMe$_2$ moiety; a second AlMe$_2$ fragment on the carbide is coordinated to a second thiolate group, which also bridges to a third aluminum center. This last AlMe moiety is also bonded to the titanium-bound phosphinimide nitrogen atom. The majority of the metric parameters are unexceptional. The most interesting feature is the geometry about the carbide carbon atom. The Ti–carbide distance in **4** is 1.900(3) Å, which is significantly shorter than the terminal Ti–CH$_3$ distance in [Cp(tBu$_3$PN)TiMe{μ-CH$_3$B(C$_6$F$_5$)$_3$}] (2.123(5) Å).[16] This is attributed to the relative increase in the Lewis acidity of the Ti center as a result of the interaction of the S and N donors with Al. The geometry about the carbide is severely distorted tetrahedral. The Ti-C-Al2 and Al1-C-Al3 angles are 141.36(14)° and 123.08(13)°, respectively, in **4**. These distortions are consistent with the carbide being central to three fused four-membered rings, where the corresponding Ti-C-Al and Al-C-Al angles range from 86.6(7) to 97.0(6)°.

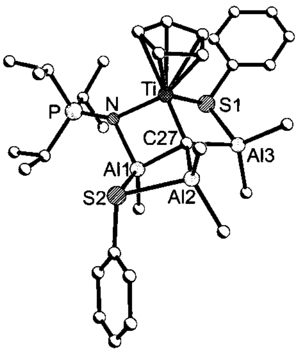


Figure 1. Molecular structure of **3**; hydrogen atoms have been omitted for clarity.

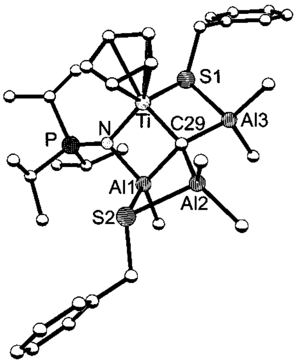
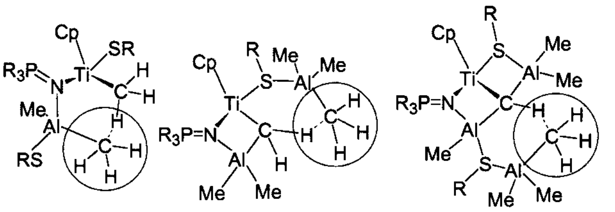


Figure 2. Molecular structure of **4**; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti–C2) 1.900(3), Ti–N 2.005(2), Ti–S1 2.4588(10), Al1–N 1.883(2), Al1–C29 2.002(3), Al1–S2 2.3599(12), Al2–C29 1.991(3), Al2–S2 2.4564(13), Al3–C29 2.001(3), Al3–S1 2.4103(12), P–N 1.604(2); C29-Ti-N 92.82(10), C29-Ti-S1 93.17(8), N-Ti-S1 104.53(6), N-Al1-S2 113.31(7), C29-Al1-S2 90.20(8), C29-Al1-Ti 45.07(8), P-N-Al1 131.25(13), P-N-Ti 141.24(13), Al1-N-Ti 87.07(9), Ti-C29-Al2 141.36(14), Ti-C29-Al3 96.68(12), Al2-C29-Al3 114.10(13), Ti-C29-Al1 86.69(10), Al2-C29-Al1 94.75(11), Al3-C29-Al1 123.08(13).

The mechanism of formation of **3** and **4** is unknown, although it is clear that there are several key steps involved. The observation of intermediate species upon addition of AlMe$_3$ to **1** or **2** suggests binding of the Lewis acid to the thiolate and/or phosphinimide ligands. Clearly, such adducts could lead to facile methyl-for-thiolate exchange, which is ultimately inferred by the nature of the product. Ligand-for-methyl exchange has been observed previously as in reactions of [CpTi(OAr′)$_2$Cl] with AlMe$_3$.[19] Subsequent C–H bond activating steps liberating methane are thought to result from the proximity of the ligand-bound AlMe fragments and the intermediate Ti-bound methyl group (Scheme 1).



Scheme 1. Possible geometries of intermediates affording C–H bond activation and methane elimination.

Despite the importance of alkylaluminum reagents as activators for early transition metal catalyst precursors, there is a paucity of well-defined products resulting from stoichiometric reactions of early transition metal compounds and Al reagents.[20] Of those known, perhaps the most familiar is the Tebbe reagent, $[Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2]$, obtained from the reaction of titanocene dichloride with $AlMe_3$.[21] Roesky et al. have described Zr–Al and Hf–Al clusters of the general formulae $[\{(Cp^*MMe)(\mu\text{-}F)_3AlMe_2\}_2]$ and $[(Cp^*M)_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)]$ derived from the reactions of Cp^*MF_3 with one and five equivalents of $AlMe_3$, respectively ($Cp^* = C_5Me_5$).[22, 23] Complexes **3** and **4** represent unique contributions to this class of compounds as they are rare examples in which a methyl carbon atom undergoes complete C–H bond activation.[24] This observation infers that transient Ti–methyl, Ti–methylene, and Ti–methine fragments remain accessible and yet the steric demands of the ancillary phosphinimide preclude oligomerization.

Experimental Section

1, **2**: These compounds were prepared in a similar fashion, thus only the preparation of **1** is detailed: To a solution of $[Cp(iPr_3PN)TiCl_2]$ (0.250 g, 0.698 mmol) in THF (10 mL) was added solid LiSPh (0.180 g, 1.550 mmol) at room temperature. The yellow solution turned dark red within 30 min. The solution was stirred for 12 h. The solvent was removed under vacuum, and the solid extracted with benzene (3 × 10 mL). The volume of the solution was reduced to 5 mL. A red microcrystalline solid was formed upon addition of hexanes (20 mL). Red solid **1** was isolated by filtration and dried under vacuum (0.225 g, 0.445 mmol, 64 %).

1: ^{1}H NMR (C_6D_6, 25 °C): $\delta = 8.04$ (d, 4H, SPh), 7.13 (t, 4H, SPh), 6.97 (t, 2H, SPh), 6.16 (s, 5H, Cp), 1.50 (d of sept, $^{2}J_{PH} = 11.6$ Hz, 3H, PC*H*Me$_2$), 0.81 (dd, $^{3}J_{PH} = 15.3$ Hz, 18H, PCH*Me*$_2$); ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): $\delta = 34.94$; ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): $\delta = 147.74$, 133.12, 124.26, 112.01, 25.84 (d, $^{1}J_{PC} = 55.5$ Hz, P*C*HMe$_2$), 16.65.

2: Yield 75 %. ^{1}H NMR (C_6D_6, 25 °C): $\delta = 7.57$ (d, 4H, SCH$_2$*Ph*), 7.20 (t, 4H, SCH$_2$*Ph*), 7.06 (t, 2H, SCH$_2$*Ph*), 6.27 (s, 5H, Cp), 4.70 (AB quart, 4H, $^{2}J_{HH} = 13.2$ Hz, SC*H*$_2$Ph), 1.62 (d of sept, $^{2}J_{PH} = 11.2$ Hz, 3H, PC*H*Me$_2$), 0.91 (dd, $^{3}J_{PH} = 15.1$ Hz, 18H, PCH*Me*$_2$); ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): $\delta = 31.55$; ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): $\delta = 144.87$, 129.00, 126.10, 110.86, 43.43, 26.10 (d, $^{1}J_{PC} = 56.4$ Hz, P*C*HMe$_2$), 16.83.

3, **4**: These compounds were prepared in a similar fashion, thus only the preparation of **3** is detailed. To a solution of **1** (0.200 g, 0.396 mmol) in hexane (10 mL) was added a solution of $AlMe_3$ in toluene (0.75 mL, 2.0 M, 1.500 mmol). A dark red solid precipitated over 24 h at room temperature. The solid was isolated by filtration and washed with hexane (3 × 15 mL). Recrystallization from benzene afforded dark red, crystalline **3** (0.220 g; 0.327 mol; 83 %).

3: ^{1}H NMR (C_6D_6, 25 °C): $\delta = 7.58$ (d, 2H, SPh), 7.55 (d, 2H, SPh), 7.05 (m, 4H, SPh), 6.95 (m, 2H, SPh), 6.18 (s, 5H, Cp), 1.80 (d of sept, $^{2}J_{PH} = 12.8$ Hz, 3H, PC*H*Me$_2$), 0.88 (dd, $^{3}J_{PH} = 13.7$ Hz, 9H, PCH*Me*$_2$), 0.85 (dd, $^{3}J_{PH} = 14.0$ Hz, 9H, PCH*Me*$_2$), 0.30 (s, 3H, AlMe), 0.17 (s, 3H, AlMe), 0.06 (s, 3H, AlMe), 0.04 (s, 3H, AlMe), −0.32 (s, 3H, AlMe); ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): $\delta = 54.09$; ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): $\delta = 140.02$, 133.78, 132.75, 131.70, 126.49, 126.13, 111.28, 26.67 (d, $^{1}J_{PC} = 56.4$ Hz, P*C*HMe$_2$), 16.72, −4.43, −5.76, −7.07.

4: Yield 74 %. ^{1}H NMR (C_6D_6, 25 °C): $\delta = 7.27$ (d, 4H, SCH$_2$*Ph*), 7.13 (t, 4H, SCH$_2$*Ph*), 7.03 (t, 2H, SCH$_2$*Ph*), 6.26 (s, 5H, Cp), 3.85 (AB quart, $^{2}J_{HH} = 12.8$ Hz, 2H, SC*H*$_2$Ph), 3.75 (AB quart, $^{2}J_{HH} = 13.1$ Hz, 2H, SC*H*$_2$Ph), 1.64 (d of sept, $^{2}J_{PH} = 13.0$ Hz, 3H, PC*H*Me$_2$), 0.74 (dd, $^{3}J_{PH} = 14.8$ Hz, 9H, PCH*Me*$_2$), 0.57 (dd, $^{3}J_{PH} = 15.1$ Hz, 9H, PCH*Me*$_2$), 0.27 (s, 3H, AlMe), 0.11 (s, 3H, AlMe), −0.01 (s, 3H, AlMe), −0.07 (s, 3H, AlMe), −0.29 (s, 3H, AlMe); ^{31}P{^{1}H} NMR: (C_6D_6, 25 °C) $\delta = 52.87$; ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): $\delta = 141.16$, 129.02, 128.97, 127.04, 126.77, 110.123, 38.25, 32.61, 26.49 (d, $^{1}J_{PC} = 56.4$ Hz, P*C*HMe$_2$), 16.36 (d, $^{2}J_{PC} = 34.0$ Hz, PCH*Me*$_2$), 14.26, −4.75, −6.87, −7.15, −7.79.

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[1] T. T. Nadasdi, D. W. Stephan, *Coord. Chem. Rev.* **1996**, *147,* 147–208.

[2] Y. Huang, T. T. Nadasdi, D. W. Stephan, *J. Am. Chem. Soc.* **1994**, *116,* 5483–5484.

[3] Y. Huang, N. Etkin, R. H. Heyn, T. T. Nadasdi, D. W. Stephan, *Organometallics* **1996**, *15,* 2320–2330.

[4] T. T. Nadasdi, Y. Huang, D. W. Stephan, *Inorg. Chem.* **1993**, *32,* 347–356.

[5] A. V. Firth, D. W. Stephan, *Inorg. Chem.* **1997**, *36,* 1260–1262.

[6] A. V. Firth, D. W. Stephan, *Organometallics* **1997**, *16,* 2183–2188.

[7] A. V. Firth, D. W. Stephan, *Inorg. Chem.* **1998**, *37,* 4726–4731.

[8] K. Tatsumi, J. Takeda, Y. Sekiguchi, M. Kohsaka, A. Nakamura, *Angew. Chem.* **1985**, *97,* 355; *Angew. Chem. Int. Ed. Engl.* **1985**, *24,* 332–333.

[9] H. Kawaguchi, K. Tatsumi, *J. Am. Chem. Soc.* **1995**, *117,* 3885–3886.

[10] H. Kawaguchi, K. Yamada, J.-P. Lang, K. Tatsumi, *J. Am. Chem. Soc.* **1997**, *119,* 10346–10358.

[11] H. Kawaguchi, Y. Yamamoto, K. Asaoka, K. Tatsumi, *Organometallics* **1998**, *17,* 4380–4386.

[12] M. A. Mansour, M. D. Curtis, J. W. Kampf, *Organometallics* **1997**, *16,* 3363–3370.

[13] M. D. Curtis, S. H. Druker, L. Goossen, J. W. Kampf, *Organometallics* **1997**, *16,* 231–235.

[14] K. Dehnicke, F. Weller, *Coord. Chem. Rev.* **1997**, *158,* 103–169.

[15] K. Dehnicke, M. Krieger, W. Massa, *Coord. Chem. Rev.* **1999**, *182,* 19–65.

[16] D. W. Stephan, J. C. Stewart, F. Guerin, R. E. v. Spence, W. Xu, D. G. Harrison, *Organometallics* **1999**, *18,* 1116–1118.

[17] D. W. Stephan, F. Guerin, R. E. v. Spence, L. Koch, X. Gao, S. J. Brown, J. W. Swabey, Q. Wang, W. Xu, P. Zoricak, D. G. Harrison, *Organometallics* **1999**, *18,* 2046–2048.

[18] Diffraction experiments were performed on a Siemens SMART System CCD diffractometer, and structures were solved employing the SHELX-TL software package. Crystal data for **3** ($C_{38}H_{57}Al_3NPS_2Ti$): $M_r = 751.8$, space group $P2_1/n$, $a = 12.100(3)$, $b = 23.018(7)$, $c = 15.648(3)$ Å, $\beta = 90.75(2)°$, $V = 4357.8(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.146$ g cm^{-3}, $\mu = 0.414$ cm^{-1}, 3859 data, 395 parameters, GOF = 1.798, $R_1 = 0.1326$, $R_w = 0.3052$. Crystal data for **4** ($C_{34}H_{55}Al_3NPS_2Ti$): $M_r = 701.7$, space group $P2_1/n$, $a = 10.065(2)$, $b = 15.340(3)$, $c = 26.120(7)$ Å, $\beta = 93.24(2)°$, $V = 4027(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.158$ g cm^{-3}, $\mu = 0.444$ cm^{-1}, 7031 data, 379 parameters, GOF = 0.884, $R_1 = 0.0406$, $R_w = 0.1158$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127820 (**3**) and CCDC-127821 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: (+44)1223-336-033; e-mail:-deposit@ccdc.cam.ac.uk).

[19] A. V. Firth, J. C. Stewart, A. J. Hoskin, D. W. Stephan, *J. Organomet. Chem.* **1999**, in press.

[20] G. J. P. Britsovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111,* 448–468; *Angew. Chem. Int. Ed.* **1999**, *38,* 429–447.
[21] F. N. Tebbe, R. L. Harlow, *J. Am. Chem. Soc.* **1980**, *102,* 6151–6153.
[22] A. Herzog, H. W. Roesky, Z. Zak, M. Noltemeyer, *Angew. Chem.* **1994**, *106,* 1035; *Angew. Chem. Int. Ed. Engl.* **1994**, *33,* 967–968.
[23] A. Herzog, H. W. Roesky, F. Jäger, A. Steiner, M. Noltemeyer, *Organometallics* **1996**, *15,* 909–917.
[24] a) M. R. Kopp, B. Neumüller, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1246; b) M. R. Kopp, B. Neumüller, *Z. Anorg. Allg. Chem.* **1999**, *625*, 739; c) R. Hillwig, K. Harms, K. Dehnicke, *Z. Naturforsch. B* **1997**, *52*, 145.

Enantioselective Addition of Allylic Trimethoxysilanes to Aldehydes Catalyzed by *p*-Tol-BINAP · AgF**

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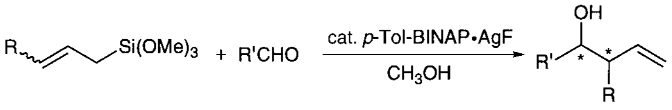
Allylic trialkoxysilanes are known as reactive allylic silanes since they form pentacoodinate silicates by reaction with nucleophiles.[1] These allylic silicates are sometimes utilized for allylation of carbonyl compounds under basic conditions,[2] but as far as we know there are no reports on asymmetric reactions of these reagents. We report here the first example of asymmetric addition of allylic trimethoxysilanes to aldehydes catalyzed by the *p*-Tol-BINAP · AgF complex [Eq. (1); BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl; *p*-Tol-BINAP = 2,2′-bis(di-*p*-tolylphosphanyl)-1,1′-binaphthyl].[3]



(1)

We initially adopted the complex (*R*)-BINAP · AgF[4] as a chiral catalyst for asymmetric allylation, anticipating that the fluoride ion would activate the trialkoxysilanes.[5] In fact, treatment of benzaldehyde (1 equiv) with allyltrimethoxysilane (1 equiv) in MeOH in the presence of (*R*)-BINAP · AgF (10 mol %) at −20 °C for 4 h gave the corresponding *R*-enriched homoallylic alcohol in 72 % yield and with 91 % *ee*. In contrast, when (*R*)-BINAP · AgOTf ($Tf = F_3CSO_2$) was used as catalyst, the racemic homoallylic alcohol was obtained in only 5 % yield. Results of the (*R*)-BINAP · AgF-catalyzed asymmetric allylation with various solvents and optimization of the reaction conditions are listed in Table 1. Among the solvents tested, alcohols proved to be effective for the reaction, and MeOH provided the best result (entries 1–6), while no reaction occurred in THF because AgF is insoluble in this solvent (entry 5). It is noteworthy that as the alcohol becomes bulkier, the enantioselectivity gradually decreases (entries 1–3). Several reaction temperatures were examined, and allylation at −20 °C gave a satisfactory result with respect to both chemical yield and the *ee* of the product (entries 1, 7, and 8). Further improvement in the yield and enantioselectivity was achieved when 1.5 equivalents of allyltrimethoxysilane were introduced (entries 1, 9, and 10). We also attempted to decrease the amount of catalyst and found that the reaction proceeded in high yield without any loss of enantioselectivity when only 3 mol % of (*R*)-BINAP was present (entries 10–12).[6] Employment of (*R*)-*p*-Tol-BINAP[7] furnished *ee* values similar to those obtained with (*R*)-BINAP (compare entries 12 and 13).

Table 1. Enantioselective allylation of benzaldehyde with allyltrimethoxysilane and BINAP · AgF as catalyst.[a]

Entry	Solvent	[(*R*)-BINAP] [mol %]	[AgF] [mol %]	*T* [°C]	Yield[b] [%]	*ee*[c] [%]
1	MeOH	10	10	−20	72	91
2	EtOH	10	10	−20	86	82
3	*i*PrOH	10	10	−20	64	39
4	$HOCH_2CH_2OH$	10	10	0	33	60
5	THF[d]	10	10	−20	< 1	–
6	CH_3CN	10	10	−20	5	< 1
7	MeOH	10	10	−40	37	93
8	MeOH	10	10	0	75	86
9[e]	MeOH	10	10	−20	77	90
10[f]	MeOH	10	10	−20	82	93
11[f]	MeOH	6	10	−20	92	94
12[f]	MeOH	3	5	−20	84	93
13[f,g]	MeOH	3	5	−20	80	94

[a] Unless otherwise noted, the reaction was carried out with (*R*)-BINAP · AgF as catalyst, allyltrimethoxylsilane (1 equiv), and benzaldehyde (1 equiv) in the specified solvent at temperature *T* for 4 h. [b] Yield of isolated product. [c] Determined by HPLC analysis (Chiralcel OD-H, Daicel Chemical Industries, Ltd.). [d] AgF did not dissolve in THF. [e] 1.2 equivalents of allyltrimethoxysilane were used. [f] 1.5 equivalents of allyltrimethoxysilane were used. [g] (*R*)-*p*-Tol-BINAP was used.

Optimal conditions were established for MeOH as solvent at −20 °C, and we then employed these conditions in catalytic enantioselective addition of allyltrimethoxysilane to typical aromatic and *α*,*β*-unsaturated aldehydes (Table 2). All reac-

Table 2. Enantioselective allylations of various aldehydes with (*R*)-*p*-Tol-BINAP · AgF as catalyst.[a]

Entry	Aldehyde	Yield[b] [%]	*ee* [%][c] (config.)
1[d]	PhCHO	80	94 (*R*)
2	(*E*)-PhCH=CHCHO	93	78 (*R*)
3	2-furyl-CHO	70	83 (*R*)
4	1-naphthyl-CHO	81	92 (*R*)
5	4-MeOC_6H_4CHO	67	93 (*R*)
6	4-BrC_6H_4CHO	90	93[e]

[a] Unless otherwise specified, the reaction was carried out with allyltrimethoxylsilane (1.5 equiv) and aldehyde (1 equiv) in the presence of a chiral silver(I) catalyst prepared from (*R*)-*p*-Tol-BINAP (6 mol %) and AgF (10 mol %) in MeOH at −20 °C for 4 h. [b] Yield of isolated product. [c] Determined by HPLC analysis (Chiralcel OD-H or OJ, Daicel Chemical Industries, Ltd.). [d] 3 mol % of (*R*)-*p*-Tol-BINAP and 5 mol % of AgF were used. [e] The absolute configuration is unknown.

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