

Supplementary Information for

Amidate complexes of titanium and zirconium: a new class of tunable precatalysts for the hydroamination of alkynes

Chunyu Li, Robert K. Thomson, Bronwyn Gillon, Brian O. Patrick, and Laurel L. Schafer*

Department of Chemistry, the University of British Columbia, Vancouver, British Columbia, Canada. E-mail: schafer@chem.ubc.ca

Experimental Procedures.

General. All reactions were carried out using standard Schlenk line and glovebox techniques, under an atmosphere of nitrogen, unless stated otherwise. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under inert atmosphere. Hexanes and toluene were purified by passage through a column of activated alumina and degassed with nitrogen. C₆D₆ was degassed and dried over molecular sieves. Isopropyl acid chloride, benzoyl chloride, *t*-butyl amine and pentafluorobenzoyl chloride were purchased from Aldrich and used as received. Ti(NEt₂)₄, Ti(NMe₂)₄, Zr(NEt₂)₄ were purchased from Strem and used as received. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker 300 MHz Avance spectrometer at ambient temperature and chemical shifts are given relative to residual solvent or trifluoroacetic acid (¹⁹F). IR samples were prepared as Nujol mulls on KBr disks or KBr pellets and recorded on a BOMEM Michelson Series MB-100 FTIR spectrophotometer. Mass spectra were recorded on a Kratos MS-50 spectrometer using an electron impact (70 eV) source. Elemental analyses and single-crystal X-ray structure determinations were performed at the Department of Chemistry, University of British Columbia.

N-t-Butyl(*isopropyl*)amide, **1**.¹

Preparation of this compound has been previously reported, however its full spectroscopic characterization is provided here. ¹H NMR (C₆D₆, 300 MHz): δ 4.9 (br s, 1H, NH), 1.88 (sept, 1H, CHMe₂), 1.25 (s, 9H, C(CH₃)₃), 1.05 (d, 6H, CH(CH₃)₂). ¹³C NMR (C₆D₆, 300 MHz): δ 176.1, 50.7, 36.5, 29.1, 20.3. IR (KBr/Nujol, cm⁻¹): 3310 (w, NH), 1654 (s, CO), 1610 (m, CN).

*N-t*Butyl(phenyl)amide, **2**.²

¹H NMR (C₆D₆, 300 MHz): δ 7.73-6.97 (m, 5H, Ar-H), 5.48 (brs, 1H, N-H), 1.30 (s, 9H, C-(CH₃)₃). ¹³C NMR (C₆D₆, 75 MHz): δ 167, 137, 131, 128, 51.5, 29.1. MS(EI): *m/z* 177(M⁺). Anal. Calcd for C₁₁H₁₅NO: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.77; H, 8.55; N, 7.98.

***N*-*t*Butyl(pentafluorophenyl)amide, 3.**

A 250 mL round-bottomed flask equipped with stir bar was charged with 20 mL CH₂Cl₂, 5 mL (47.4 mmol) H₂N-C(CH₃)₃ and 3 mL (21.7 mmol) NEt₃. This solution was cooled to 0°C and 5 mL (21.7 mmol) of pentafluorobenzoyl chloride was added dropwise. The resultant mixture was warmed to room temperature with stirring, resulting in a white slurry. The reaction mixture was diluted with diethyl ether (50 mL) and then washed with 1M HCl (50 mL), 1M NaOH (50 mL) and brine (50 mL). The organic layer was dried over anhydrous MgSO₄ and evaporated to dryness *in vacuo* to give a white microcrystalline solid. The final product was purified and dried by sublimation yielding a white microcrystalline solid in 87% yield (5.0 g). Crystals suitable for X-ray diffraction were obtained from a CHCl₃ solution. ¹H NMR (CDCl₃, 300 MHz): δ 5.67 (s, 1H, NH), 1.40 (s, 9H, *t*-BuCH₃). ¹³C NMR (CDCl₃, 75 Hz): δ 156.4, 145.6, 143.6, 142.2, 140.2, 139.2, 135.8, 53.2, 28.5. ¹⁹F NMR (CDCl₃,): δ -142.7 (2F), -153.8 (1F), -161.3 (2F). MS(EI) *m/z*: 267(M⁺), 252(M⁺-CH₃). IR (KBr/Nujol, cm⁻¹): 3066 (w, NH), 1654.8(s, CO), 1566(m, CN). Anal. Calcd for C₁₁H₁₀ONF₅: C, 49.42; H, 3.77; N, 5.24; Found: C, 49.61; H, 3.80; N, 5.30.

General procedure for the preparation of bis(amidate)metal-bis(amido) complexes.

Example: Bis(*N*-*t*butyl(phenyl)amidate)zirconium-bis(diethylamido), Zr Complex of 2.

In a 50 mL round-bottomed Schlenk flask equipped with stir bar, 4.18 mL (11.3 mmol) of Zr(NEt₂)₄ was added to 4.00 g (22.6 mmol) of **2** dissolved in 25 mL of toluene and cooled to -78°C. The solution was allowed to stir while warming to room temperature. The yellow-orange reaction mixture was evaporated to dryness *in vacuo*, and the remaining orange solid was washed with hexanes. The hexanes soluble portion was evaporated to dryness *in vacuo*, giving a yellow-orange oily solid, which was subsequently redissolved in pentane, filtered and evaporated to dryness to give 5.31 g of the yellow-orange powder in 80% yield. ¹H NMR (C₆D₆, 300 MHz): δ 7.40 (d, 4H, Ar-*H*), 7.06 – 7.00 (m, 6H, Ar-*H*), 3.85 – 3.74 (m, 8H, N-(CH₂CH₃)₂), 1.30 – 1.22 (m, 30H total, C-(CH₃)₃, N-(CH₂CH₃)₂). MS(EI): *m/z* 514 (M⁺-NEt₂), 443 (M⁺-2NEt₂). IR (KBr, cm⁻¹): 1636 (m, CO), 1549 (s, CN). Satisfactory elemental analysis could not be obtained. See attached spectrum.

Bis(*N*-*t*butyl(isopropyl)amidate)zirconium-bis(diethylamido), Zr Complex of 1.

Yield: 76%. ¹H NMR (C₆D₆, 300 MHz): δ 3.66 (q, 8H, N(CH₂CH₃)₂), 2.50 (sept, 2H, CH(CH₃)₂), 1.22 (m, 30H, N(CH₂CH₃)₂, C(CH₃)₃), 1.16 (d, 12H, CH(CH₃)₂). IR(KBr/Nujol, cm⁻¹): 1610 (m, CO). MS(EI): *m/z* 622(M⁺). Satisfactory elemental analysis and single crystals of this material could not be obtained due to the extreme solubility and oily nature of the material obtained. See attached spectrum.

Bis(*N*-*t*butyl(isopropyl)amidate)titanium-bis(diethylamido), Ti Complex of 1.

Yield: 75%. ¹H NMR (C₆D₆, 300 MHz): δ 3.98 (br m, 8H, N(CH₂CH₃)₂), 2.52 (sept, 2H, CH(CH₃)₂), 1.24 (s, 18H, C(CH₃)₃), 1.16 (t, 12H, N(CH₂CH₃)₂), 1.15 (d, 12 H, CH(CH₃)₂). Satisfactory elemental analysis and single crystals of this material could not be obtained due to the extreme solubility and oily nature of the material obtained. See attached spectrum.

Bis(*N*-*t*butyl(phenyl)amidate)titanium-bis(dimethylamido), Ti complex of 2.

Yield: 79%. ¹H NMR (C₆D₆, 300 MHz): δ 7.39-7.04 (m, 10H total, Ar-*H*), 3.62 (s, 12H, N-(CH₃)₂), 1.28 (s, 18H, C-(CH₃)₃). MS(EI): *m/z* 488 (M⁺), 444 (M⁺-NMe₂), 400 (M⁺-2NMe₂), 343 (M⁺-(2NMe₂ + ^tBu)). Anal. Calcd for C₂₆H₄₀N₄O₂Ti: C, 63.93; H, 8.25; N, 11.47. Found: C, 63.72; H, 8.26; N, 11.10.

Bis(*N*-*t*butyl(perfluorophenyl)amidate)titanium-bis(diethylamido), Ti Complex of 3.

Yield: 70%. ¹H NMR (C₆D₆, 300MHz): δ 4.16 (8H, N(CH₂CH₃)₂), 1.21 – 1.00 (m, 30H, C(CH₃)₃, N(CH₂CH₃)₂). ¹⁹F NMR (C₆D₆, 282 MHz): δ -138.2(2F), -153.4(1F), -161.2(2F). IR(KBr/Nujol cm⁻¹): 1656 (s, CO), 1518(m, CN). MS(EI) *m/z*: 653(M⁺-NEt₂), 580(M⁺-2NEt₂). Anal. Calcd for C₃₀H₃₈O₂N₄F₁₀Ti: C, 49.70; H, 5.24; N, 7.73; Found: C, 49.81; H, 5.56; N, 7.78. Recrystallization from dry pentane gave crystals suitable for X-ray crystallography.

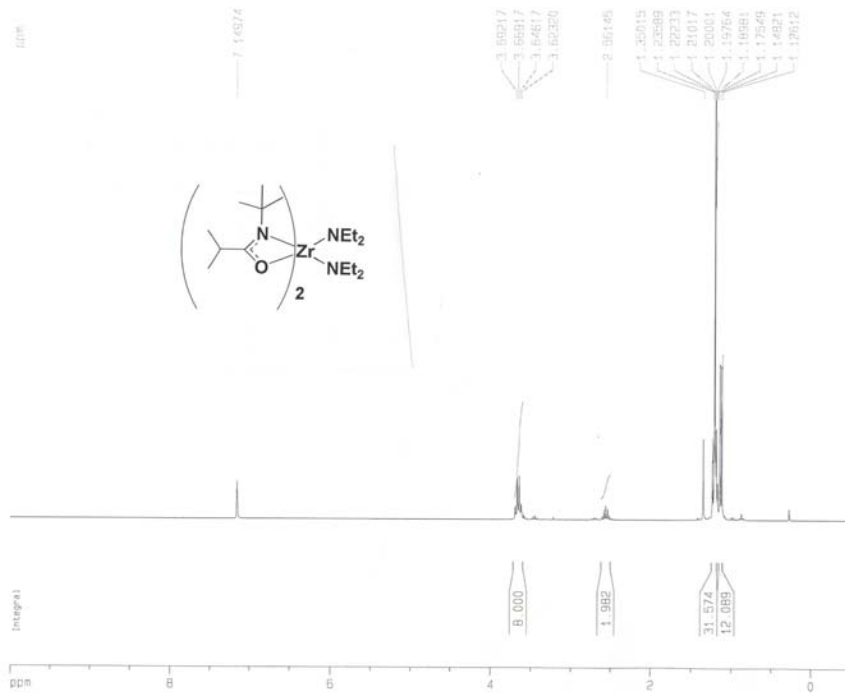
General Procedure For Hydroamination Reactions

All hydroamination reactions were performed on NMR tube scale using sealable NMR tubes. The NMR tube was loaded with 5 or 10 mol percent of the catalyst dissolved in C₆D₆ and the aminoalkyne or amine/alkyne mixture was added by pipette. The tube was sealed (and heated to 75°C with the Zr based catalyst) and the reaction progress was monitored by ¹H NMR spectroscopy. Yields were determined by integration against the internal standard 1,3,5-trimethoxybenzene.

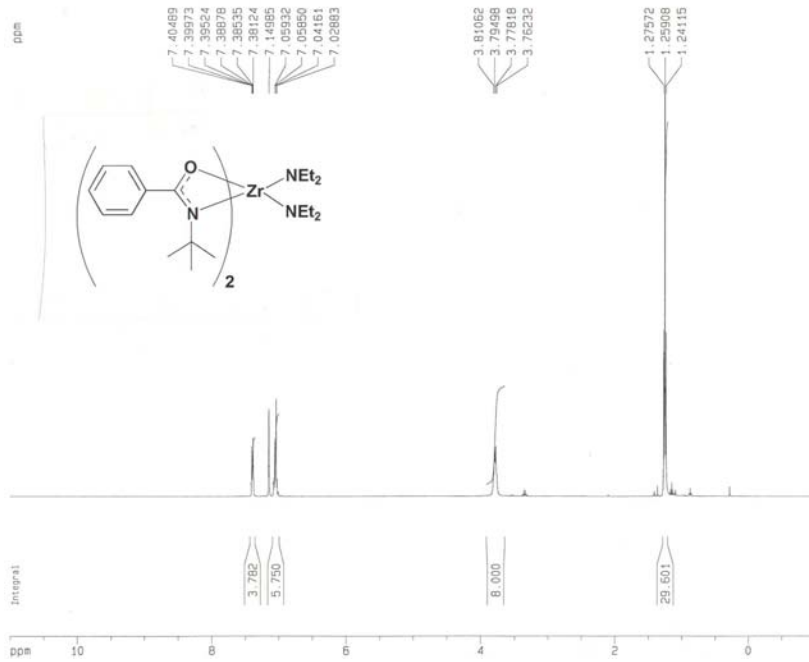
Example: In a Teflon valved sealable NMR tube 1.9 mg of Zr Complex of **2** and 1.2 mg of 1,3,5-trimethoxybenzene were dissolved in 1 mL of C₆D₆. To this solution 10.2 mg of 1-amino-5-phenylpenta-4-yne (**4**) was added via pipette. The NMR tube was sealed and heated to 75°C. ¹H NMR spectra were recorded at 2 hour intervals to monitor the progress of the reaction. Products were identified by comparing with literature data.^{3,4}

References.

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- ² A. D. Nikolic, N. Perisic-Janjic, N. L. Kobilarov, and S. D. Petrovic, *J. Mol. Struc.*, 1984, **114**, 161.
- ³ P. L. McGrane, M. Jensen, and T. Livinghouse, *J. Am. Chem. Soc.*, 1992, **114**, 5459.
- ⁴ Y. Shi, J. T. Ciszewski, and A. L. Odom, *Organometallics*, 2001, **20**, 3967.



[tBu (NO) Ph] 2Zr (NEt₂)₂ in C₆D₆



Current Data Parameters
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 PROCNO 1

F2 - Acquisition Parameter
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