Supporting Information

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An Alkylidyne Analogue of Tebbe's Reagent.

Trapping Reactions of a Titanium Neopentylidyne by incomplete and Complete 1,2 Additions

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Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in an M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under an argon atmosphere. Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column. Diethylether was dried by passage through a column of activated alumina. THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into a dry box. C₆D₆ and C₇D₈ were purchased from Cambridge Isotope Laboratory (CIL), degassed and vacuum transferred to 4 Å molecular sieves. THF-*d*₈ was purchased from CIL and used as received. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Li(PNP) (PNP = N[2-P(CHMe₂)2-4-methylphenyl]₂)[−]^[1] and (PNP)Ti=CH^tBu(CH₂^tBu) (**1**)^[2] were prepared according to the literature. B(OMe)₃ was dried by adding to the solution chunks of sodium metal and left to sit for two days forming a white solid on the bottom of the vial. The suspension is then filtered through two pipette columns of alumina to obtain a clear colorless liquid (8 mL). All other chemicals were used as received. CHN analyses were performed by Desert Analytics, Tucson, AZ or Midwest Microlabs, Indianapolis, IN. ¹H, ¹³C, ¹⁹F, ¹¹B and ³¹P

NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^1H and ^{13}C NMR are reported with reference to solvent resonances (residual $\text{C}_6\text{D}_5\text{H}$ in C_6D_6 , 7.16 ppm and 128.0 ppm). ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (aqueous solution, δ 0.0 ppm). ^{27}Al NMR chemical shifts are reported with respect to AlMe_3 (153.0 ppm). ^{11}B NMR chemical shifts are reported with respect to external BF_3 (0.0 ppm). X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2 (g) at low temperatures.^[3]

Preparation of (PNP)Ti[C(^tBu)Al(CH₃)₃] (**2**)

In a vial (PNP)Ti=CH^tBu(CH₂^tBu) (**1**) [88 mg, 0.142 mmol] was dissolved in pentane and cooled to 77 K. Room temperature $\text{Al}(\text{CH}_3)_3$ (~4 drops, excess) was added to the frozen solution. The solution was allowed to warm to room temperature and stirred for 1 hour. Upon thawing, the solution instantly turned to a deep-red color. The solution was dried under vacuum and the residue was extracted with hexane and filtered. The filtrate was reduced in volume under reduced pressure, and then cooled to $-35\text{ }^\circ\text{C}$. Red crystals of **2** [50 mg, 0.081 mmol, 57% yield] were collected.

For **2**: ^1H NMR (23 $^\circ\text{C}$, 399.8 MHz, C_6D_6): δ 7.38 (dd, 1H, C_6H_3), 6.90–7.03 (m, 3H, C_6H_3), 6.77–6.83 (m, 2H, C_6H_3), 2.82 (septet, 1H, CHMe_2), 2.25–2.36 (m, 3H, CHMe_2), 2.20 (s, 3H, $\text{C}_6\text{H}_3\text{--CH}_3$), 2.09 (s, 3H, $\text{C}_6\text{H}_3\text{--CH}_3$), 1.56–1.70 (m, 6H, CHMe_2), 1.26–1.37 (m, 6H, CHMe_2), 1.17 (dd, 3H, CHMe_2), 0.92 (s, 9H, Ti=CCMe_3), 0.69–0.76 (m, 6H, CHMe_2), 0.67 (t, 3H, $\text{Ti=C}^t\text{BuAl}(\text{Me}_2)(\mu\text{--CH}_3)$), 0.49 (dd, 3H, CHMe_2), 0.18 (s, 3H, $\text{Ti=C}^t\text{BuAl}(\text{Me}_2)(\mu\text{--CH}_3)$), 0.09 (s, 3H, $\text{Ti=C}^t\text{BuAl}(\text{Me}_2)(\mu\text{--CH}_3)$). ^{13}C NMR (23 $^\circ\text{C}$, 100.6 MHz, C_6D_6): δ 333.0 ($\text{Ti=C}^t\text{BuAl}(\text{Me}_2)(\mu\text{--CH}_3)$), 160.2 (d, C_6H_3), 153.2 (d,

C_6H_3), 132.8 (d, C_6H_3), 131.9 (d, C_6H_3), 131.8 (d, C_6H_3), 131.2 (d, C_6H_3), 127.4 (d, C_6H_3), 126.5 (d, C_6H_3), 123.0 (dd, C_6H_3), 119.4 (d, C_6H_3), 118.9 (d, C_6H_3), 114.7 (dd, C_6H_3), 55.0 (Ti=CCMe₃), 32.9 (q, Ti=CCMe₃), 25.1 (d, CHMe₂), 25.0 (d, CHMe₂), 24.9 (C₆H₃-CH₃), 25.8 (d, CHMe₂), 21.8 (d, CHMe₂), 21.6 (d, CHMe₂), 21.0 (d, CHMe₂), 20.7 (d, CHMe₂), 20.6 (d, CHMe₂), 20.5 (d, CHMe₂), 20.2 (AlMe₂), 19.5 (AlMe₂), 18.8 (C₆H₃-CH₃), 18.6 (d, CHMe₂), 18.0 (d, CHMe₂), 17.1 (d, CHMe₂), -1.40 (br s, Ti-CH₃-AlMe₂). ³¹P NMR (23 °C, 121.5 MHz, C₆D₆): δ 31.5 (d, J_{P-P} = 36 Hz), 15.3 (d, J_{P-P} = 36 Hz). ²⁷Al (25 °C, 130.24 MHz, C₇D₈): δ 56.7 ($\Delta\nu_{1/2}$ = 5890 Hz). Anal. Calcd. for C₃₄H₅₈NaIP₂Ti: C, 66.12; H, 9.46; N, 2.27. Found: C, 65.81; H, 9.77; N, 2.21.

Caution: trimethylaluminum spontaneously combusts in the presence of air or moisture. Special care must be taken to remove Al(CH₃)₃ collected in the vacuum trap. In general, the contents in the trap should be transferred cold (thawing from liquid N₂) rapidly to a safe vacuum hood. After several hours the contents in the trap are quenched with cold isopropanol.

Preparation of 2 from (PNP)Ti=CH^tBu(Ph) (3)

In a vial (PNP)Ti=CH^tBu(Ph) (3) [50 mg, 0.080 mmol] was dissolved in pentane and cooled to 77 K. Room temperature Al(CH₃)₃ (~4 drops, excess) was added to the frozen solution. The solution was allowed to warm to room temperature. Upon thawing, the solution instantly turned to a deep-red color. The solution was dried under vacuum (Caution: trimethylaluminum spontaneously combusts in the presence of air or moisture) and the residue was extracted with hexane and filtered. The filtrate was reduced in volume under reduced pressure, and then cooled to -35 °C. The reaction was quantitative

by ^1H and ^{31}P NMR spectroscopy. Spectral data matched an independently prepared sample of **2**.

Preparation of (PNP)Ti(C(^tBu)CC $_4\text{H}_4\text{NH}$) (4**) from **2****

In a J. Young tube [50 mg, 0.081 mmol] was dissolved in neat pyridine (~2 mL) and heated to 40 °C for 48 hours. The conversion to **4** was formed quantitatively by ^1H and ^{31}P NMR spectroscopy. The spectroscopic data matched an independently prepared sample of **4**.^[4]

Preparation of (PNP)Ti[C(^tBu)B(OCH $_3$) $_2$](OCH $_3$) (5**)**

In a vial (PNP)Ti=CH ^tBu (CH $_2^t\text{Bu}$) [67 mg, 0.108 mmol] was dissolved in neat B(OMe) $_3$ (~2 mL) and heated to 50 °C for 1 hour. The solution changed from green to red-brown. Upon completion of the reaction, the solution was dried under vacuum and the residue was extracted with pentane and filtered. The filtrate was reduced in volume under reduced pressure, and then cooled to -35 °C. Red-brown crystals of **5** [60 mg, 0.092 mmol, 86% yield] were collected.

For **5**: ^1H NMR (23 °C, 399.8 MHz, C $_6\text{D}_6$): δ 7.38 (dd, 1H, C $_6\text{H}_3$), 7.19 (dd, 1H, C $_6\text{H}_3$), 6.87–6.91 (m, 3H, C $_6\text{H}_3$), 6.76 (br d, 1H, C $_6\text{H}_3$), 4.05 (s, 3H, Ti–OMe), 3.50 (s, 6H, Ti=C ^tBu B(OMe) $_2$), 2.32 (septet, 1H, CHMe $_2$), 2.21 (s, 3H, C $_6\text{H}_3$ –Me), 2.16 (s, 3H, C $_6\text{H}_3$ –Me), 2.12–2.50 (m, 2H, CHMe $_2$), 1.91 (septet, 1H, CHMe $_2$), 1.64 (s, 9H, Ti=CCMe $_3$), 1.29–1.36 (m, 6H, CHMe $_2$), 1.04–1.24 (m, 15H, CHMe $_2$), 0.90 (dd, 3H, CHMe $_2$). ^{13}C NMR (23 °C, 100.6 MHz, C $_6\text{D}_6$): δ 323.7 (Ti=CCMe $_3$), 162.3 (dd, C $_6\text{H}_3$), 160.0 (dd, C $_6\text{H}_3$), 132.4 (C $_6\text{H}_3$), 132.2 (C $_6\text{H}_3$), 132.0 (C $_6\text{H}_3$), 131.6 (C $_6\text{H}_3$), 124.7 (d, C $_6\text{H}_3$), 122.9

(d, C₆H₃), 122.4 (d, C₆H₃), 120.0 (d, C₆H₃), 119.4 (d, C₆H₃), 116.6 (d, C₆H₃), 63.0 (Ti-OMe), 51.9 (Ti=CCMe₃B(OMe)₂), 45.1 (Ti=CCMe₃), 36.6 (Ti=CCMe₃), 25.9 (d, CHMe₂), 23.1 (d, CHMe₂), 20.9 (C₆H₃-Me), 20.8 (C₆H₃-Me), 20.7 (d, CHMe₂), 20.6 (d, CHMe₂), 20.3 (d, CHMe₂), 20.1 (d, CHMe₂), 18.8 (d, CHMe₂), 18.4 (d, CHMe₂), 18.1 (d, CHMe₂), 18.0 (d, CHMe₂), 17.0 (d, CHMe₂), 15.8 (d, CHMe₂). ³¹P NMR (23 °C, 121.5 MHz, C₆D₆): δ 33.3 (d, J_{P-P} = 47 Hz), 30.0 (d, J_{P-P} = 47 Hz). ¹¹B NMR (23 °C, MHz, C₆D₆): 40.2 (Δν_{1/2} = 11,692 Hz).

References

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Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 6.0 suite¹ of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP²⁻⁵ functional and the 6-31G** basis set with no symmetry restrictions. Titanium was represented using the Los Alamos LACVP basis^{6,7}. The bond order is calculated using the definition of Mayer.⁸

The models used in this study consist of ~100 atoms, which represent the non-truncated substrates that were also used in the experimental work. Although a smaller model may also be able to reproduce the most important features of the studied reaction qualitatively, we chose to employ the large scale model to faithfully construct realistic model chemistry. These calculations challenge the current state of computational capabilities, whereas the numerical efficiency of the Jaguar program allows us to accomplish this task in a bearable time frame.

References

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S1. Optimized structure and bond order.

Selected bond lengths (in Å) and bond angles (in °):

Ti1-C5 1.798
C5-Al7 2.114
Al7-C8 2.182
Ti1-C8 2.298
Ti1-Al7 2.690
Ti1-H9 2.45
Ti1-H10 2.72
C8-H9 1.098
C8-H10 1.097
Ti1-C5-C6 155.5

Mayer bond order:

Ti1-C5 2.04
Ti1-C8 0.57
Ti1-N2 0.52
Al7-C5 0.48
Al7-C8 0.37
Al7-C(terminal CH₃) 0.92, 0.91

S2. Front orbitals.

HOMO

HOMO-2

HOMO-7

LUMO

S3. Optimized Structure

Ti	-0.009449920	0.021181709	0.009479058
P	1.731123400	1.237214229	-1.584964029
P	-0.337230226	-2.231942222	1.468850318
C	2.816821256	1.635078621	-0.156978205
C	3.648913037	2.759005719	-0.056912830
C	4.435352468	2.997908625	1.072708091
C	5.340852364	4.204699963	1.164971663
C	4.354542851	2.071698081	2.124862378
C	3.534331098	0.953079896	2.049257234
C	2.750597361	0.700567448	0.905681595
N	1.876974532	-0.406325728	0.797078091
C	2.351008166	-1.666488135	1.194190458
C	3.725904481	-2.001693214	1.201835122
C	4.162185128	-3.265717899	1.575151589
C	3.266391331	-4.275344314	1.957029628
C	3.758153229	-5.648678171	2.353029989
C	1.906649171	-3.955907911	1.933750462
C	1.436186624	-2.687661827	1.561281991
C	2.840552454	0.038918104	-2.551440084
C	2.068388448	-0.837938998	-3.550046997
C	4.067450967	0.700877182	-3.193439402
C	1.621450360	2.815499776	-2.598799721
C	0.895281409	3.918481756	-1.812855492
C	0.918411110	2.563099337	-3.944176659
C	-0.879316825	-2.049302641	3.275345767
C	0.091022652	-1.102660291	4.000637533
C	-1.031306133	-3.361880509	4.057264131
C	-1.178433667	-3.813984075	0.875234429
C	-0.598345244	-4.326637453	-0.453599912
C	-2.700535281	-3.621814636	0.783304412
C	-0.938802103	1.321912217	0.833266824
C	-1.168391017	2.430043656	1.862955037
C	0.173147183	2.837980349	2.514211180
C	-1.785774854	3.694368486	1.216551169
C	-2.132064551	1.938554092	2.972068910
Al	-2.528550382	0.833238019	-0.472429859
C	-3.035118525	2.162096621	-1.877091884
C	-4.109851961	-0.023600086	0.404311318
C	-1.453704109	-0.662960150	-1.641338033
H	3.696332547	3.468020171	-0.879637693
H	5.250935622	4.840818398	0.279119273
H	6.394169769	3.911853144	1.256984842
H	5.102057440	4.819706809	2.041053907
H	4.941626968	2.236663579	3.026347388
H	3.487016125	0.259858004	2.883568386
H	4.455185329	-1.254405829	0.907558916
H	5.230232111	-3.477057654	1.560859963
H	4.511418459	-5.593433640	3.148207590
H	2.939468815	-6.277637340	2.716086151
H	4.224643182	-6.170819219	1.507721051
H	1.191251015	-4.727846328	2.207885151
H	3.187542631	-0.615177356	-1.742237699
H	1.224758680	-1.348355732	-3.075986402
H	2.734615811	-1.606424523	-3.960290077
H	1.677585292	-0.262511968	-4.395056696
H	4.744767570	-0.067251829	-3.586195512
H	3.790135038	1.347797249	-4.033180007
H	4.629571371	1.299883877	-2.470579254
H	2.650040395	3.140059240	-2.803429164
H	0.866636347	4.838640467	-2.409218655

H	1.386090284	4.146195314	-0.863309827
H	-0.134785610	3.623730781	-1.594812149
H	0.814699581	3.509349319	-4.488161229
H	-0.088278048	2.156916286	-3.798020537
H	1.475482108	1.875943368	-4.586610034
H	-1.856719695	-1.555965278	3.204567138
H	-0.307712411	-0.842302409	4.988188902
H	1.064344826	-1.583028004	4.146210079
H	0.250659840	-0.178318257	3.441748252
H	-0.083481804	-3.909319564	4.102886940
H	-1.327758445	-3.140247813	5.089803606
H	-1.792593173	-4.025008498	3.636504376
H	-0.972298859	-4.573089263	1.639481662
H	-3.176925344	-4.558325660	0.469021425
H	-3.143174115	-3.332224575	1.741327791
H	-2.961974277	-2.850242337	0.053282777
H	0.485808179	-4.457535010	-0.406935817
H	-1.044723502	-5.298184665	-0.697229980
H	-0.825423925	-3.651779373	-1.284734335
H	0.874696039	3.209725941	1.761656697
H	0.648117726	1.989425488	3.014347190
H	0.019439583	3.629306014	3.260012241
H	-1.145282664	4.084401413	0.420456549
H	-2.771040925	3.491088858	0.784254015
H	-1.910075920	4.484611105	1.968223215
H	-3.108530019	1.665711736	2.560312496
H	-1.727926190	1.062014278	3.485958928
H	-2.288287379	2.727557547	3.719779949
H	-3.623201720	1.681735333	-2.672899339
H	-3.663945824	2.969180008	-1.477888033
H	-2.177598921	2.643688901	-2.364237201
H	-4.788995043	0.731839999	0.824113229
H	-4.711805609	-0.603699321	-0.311015988
H	-3.848141054	-0.700761361	1.226749546
H	-1.016560352	-1.654935849	-1.464373071
H	-2.478208199	-0.902090738	-1.958480493
H	-0.960647211	-0.239007052	-2.524387519

S4. Computed components

E(SCF) (eV, LACVP**) -64454.820