

6. β -DIKETIMINATE-SUPPORTED TITANIUM AND VANADIUM DICHLORIDE COMPLEXES

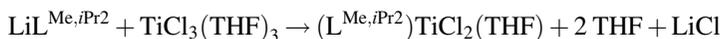
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General Procedures

All manipulations unless otherwise mentioned were performed under a nitrogen atmosphere using standard Schlenk line or glovebox techniques. THF was dried over Na/Ph₂CO and distilled into an evacuated vacuum flask equipped with a gas adapter and under a positive flow of N₂ or Ar. The THF-filled flask was transferred into the glovebox and stored over metallic Na (thin films). Anhydrous toluene and pentane were purchased from Aldrich in a sure-sealed reservoir (18 L) and dried by passing through two columns of activated alumina and a Cu Q-5 column under a pressure of N₂. Before use, a 5 mL aliquot of each solvent was tested, qualitatively, with a drop of Na/benzophenone ketyl radical in a THF solution (1–2 drops in 3–5 mL of solvent must give a blue to purple solution).¹ Celite was dried under reduced pressure at 180°C for 24 h. TiCl₃(THF)₃ was purchased from Strem and also prepared according to the literature procedure.² Solution magnetization measurements were determined by the method of Evans.^{3,4} C₆D₆ was degassed and dried over CaH₂ and then vacuum transferred to 4 Å molecular sieves. L^{Me,*i*Pr₂}H and the salt [L^{Me,*i*Pr₂}Li]_x (L^{Me,*i*Pr₂} = [ArNC(Me)]₂CH⁻, Ar = 2,6-*i*Pr₂C₆H₃) were synthesized using a slightly modified protocol (described herein).⁵ [L^{*t*Bu,*i*Pr₂}Li]_x (L^{*t*Bu,*i*Pr₂} = [ArNC(*t*Bu)]₂CH⁻, Ar = 2,6-*i*Pr₂C₆H₃) was synthesized using the method described herein for [L^{Me,*i*Pr₂}Li]_x.⁶

A. SYNTHESIS OF (L^{Me,*i*Pr₂})TiCl₂(THF)



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Procedure

Into a 350- or 500-mL thick-walled round-bottomed pressure vessel (Fig. 1) equipped with a large stir bar are loaded 100 mL of THF, $\text{TiCl}_3(\text{THF})_3$ (5.00 g, 0.014 mol), and $[\text{L}^{\text{Me},i\text{Pr}_2}\text{Li}]_x$ (5.94 g, 0.014 mol). The vessel is sealed inside the glovebox with a Teflon pin. After the mixing, the slurry becomes a green colored solution. The reaction mixture is transferred out of the glovebox and heated to reflux (80°C) for 12 h, during which time the solution color turns to deep green. After this time, the solution is brought into the glovebox, transferred to a 300-mL filter flask, and evaporated under reduced pressure. The green mass is extracted with 200 mL toluene, and the extract is filtered through Celite, which is then washed with toluene several times until the washed solution is nearly clear. The green filtrate is then reduced in volume until solid begins to form on the sides of the flask. The concentrated solution is capped with a large rubber stopper and stored at -35°C for 24 h to obtain deep green crystals and solid $(\text{L}^{\text{Me},i\text{Pr}_2})\text{TiCl}_2(\text{THF})$. To expedite drying of the materials, the crystals and solids are washed with 25 mL pentane and then dried under vacuum. The combined yield is 6.19 g (0.010 mol, 68%).

Anal. Calcd. for $\text{C}_{33}\text{H}_{49}\text{N}_2\text{OCl}_2\text{Ti}$: C, 65.13; H, 8.12; N, 4.60. Found: C, 65.10; H, 8.19; N, 4.60. $^1\text{H NMR}$ (23°C, 399.8 MHz, C_6D_6): δ 4.94 ($\Delta\nu_{1/2} = 73$ Hz), 3.50 ($\Delta\nu_{1/2} = 92$ Hz), 2.29 ($\Delta\nu_{1/2} = 47$ Hz), 1.67 ($\Delta\nu_{1/2} = 93$ Hz). $\mu_{\text{eff}} = 2.05(12)\mu_{\text{B}}$ (C_6D_6 , 298K, Evans' method). UV-vis (toluene (ϵ in $\text{M}^{-1}\text{cm}^{-1}$)): 427 (1359), 542 (368) nm. IR (Et_2O , CaF_2): 3088 (s), 3071 (s), 3029 (s), 3022 (m), 2963 (m), 1962 (m), 1962 (m), 1814 (m), 1560 (m), 1476 (s), 1464 (w), 1034 (s) cm^{-1} . mp decomp. $>200^\circ\text{C}$.

Properties

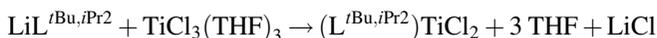
Complex $(\text{L}^{\text{Me},i\text{Pr}_2})\text{TiCl}_2(\text{THF})$ (deep green) is a close analogue of Budzelaar's nonsolvento complex $(\text{L}^{\text{Me},i\text{Pr}_2})\text{TiCl}_2$ (deep red-brown).⁶ Budzelaar reported that THF can be removed by repeated distillation of toluene solutions at 1 bar.⁶ Although $(\text{L}^{\text{Me},i\text{Pr}_2})\text{TiCl}_2(\text{THF})$ can be stored indefinitely under an inert atmosphere, it is recommended that samples be stored at -35°C in a well-sealed vial since traces of O_2 , moisture, or other oxidants (e.g., CCl_4) readily promote decomposition. Both the solvent-free and THF complexes have similar solubilities, being soluble in toluene, benzene, and THF, and insoluble in pentane and hexane. The complex is partially soluble in Et_2O . The complex gradually decomposes in CH_2Cl_2 . Decomposition to unidentified products also occurs when either complex is exposed to air, moisture, or halogenated solvents such as CCl_4 .

Related Complexes

Complex $(\text{L}^{\text{Me},i\text{Pr}_2})\text{TiCl}_2(\text{THF})$ can be alkylated to give the dimethyl derivative, $(\text{L}^{\text{Me},i\text{Pr}_2})\text{TiMe}_2$. When combined with $\text{B}(\text{C}_6\text{F}_5)_3$, the complex forms a highly active catalyst for the polymerization of propene and 1-hexene.⁶ Atactic polymers can be generated from the polymerization reactions.⁶ THF coordi-

nation to $(L^{\text{Me},i\text{Pr}2})\text{TiCl}_2$ does not seem to impede transmetallation reactions. Likewise, THF can be readily displaced when the alkyl substituent is sterically encumbering. For example, treatment of $(L^{\text{Me},i\text{Pr}2})\text{TiCl}_2(\text{THF})$ with 2 equiv of LiCH_2^tBu , $\text{LiCH}_2\text{SiMe}_3$, and LiNHAr ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) affords the four-coordinate Ti(III) products, $(L^{\text{Me},i\text{Pr}2})\text{Ti}(\text{CH}_2^t\text{Bu})_2$,⁷ $(L^{\text{Me},i\text{Pr}2})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$,⁸ and $(L^{\text{Me},i\text{Pr}2})\text{Ti}(\text{NHAr})_2$,⁹ respectively. Treatment of $(L^{\text{Me},i\text{Pr}2})\text{TiCl}_2(\text{THF})$ with 1 equiv of $\text{NaN}(\text{SiMe}_3)_2$ provides $(L^{\text{Me},i\text{Pr}2})\text{TiCl}[\text{N}(\text{SiMe}_3)_2]$ and free THF.¹⁰

B. SYNTHESIS OF $(L^{t\text{Bu},i\text{Pr}2})\text{TiCl}_2$



Procedure

In a 350- or 500-mL thick-walled glass round-bottomed pressure vessel (CHEMGLASS) in the glovebox, $\text{TiCl}_3(\text{THF})_3$ (1.3 g, 0.004 mol) is transferred into 30 mL of toluene, and the suspension cooled to -35°C . In a conical flask, $[\text{L}^{t\text{Bu},i\text{Pr}2}\text{Li}]_x$ (1.785 g, 0.004 mol) is taken up with 30 mL of toluene. The toluene solution of $[\text{L}^{t\text{Bu},i\text{Pr}2}\text{Li}]_x$ is transferred by a pipette to the suspension of $\text{TiCl}_3(\text{THF})_3$ in toluene. During the addition of the salt, the blue color of the $\text{TiCl}_3(\text{THF})_3$ suspension gradually changes to greenish brown. Upon completing the addition, the thick-walled reaction vessel (Fig. 1) is closed with a Teflon-coated cap. The reaction vessel is brought outside the glovebox and heated at 110°C for 3 days with vigorous stirring. Within 2 h of initial heating, the color of the solution changes to intense green. After completion of the reaction, the reaction vessel is brought back into the glovebox, the solution is filtered through a Celite bed, and the volume of the filtrate is reduced to ~ 20 mL until green microcrystals begin to form. After allowing the solution to warm up to the box temperature to redissolve the crystals, 25 mL of hexane is added and the solution is cooled to -35°C for 24 h. At this time, intense green microcrystals of $(L^{t\text{Bu},i\text{Pr}2})\text{TiCl}_2$ are separated after filtering the solution through a medium porosity frit, and the solids are washed with 10 mL of hexane to afford 1.27 g of product (0.002 mol, 58% yield).^{*} The filtrate from the first crystallization appears reddish in color. Reducing the volume of the latter solution to ~ 5 mL and subsequent cooling to -35°C over 12–16 h yields red crystals of $(L^{t\text{Bu},i\text{Pr}2})\text{Ti}=\text{NAr}(\text{Cl})$ (335 mg, 0.0004 mol, 12.5% yield).¹¹

Anal. Calcd. for $\text{C}_{35}\text{H}_{53}\text{N}_2\text{Cl}_2\text{Ti}$: C, 67.73; H, 8.61; N, 4.51. Found: C, 66.19; H, 8.63; N, 4.40. ¹H NMR (23°C , C_6D_6): δ 8.50 ($\Delta\nu_{1/2} = 25$ Hz), 5.06 ($\Delta\nu_{1/2} = 48$ Hz), 1.99 ($\Delta\nu_{1/2} = 127$ Hz). $\mu_{\text{eff}} = 1.98(9)\mu_{\text{B}}$ (C_6D_6 , 298K, Evans' method). UV–

^{*} Sometimes it is necessary to physically separate the red crystals of $(L^{t\text{Bu},i\text{Pr}2})\text{Ti}=\text{NAr}(\text{Cl})$ from the intensely green microcrystals of $(L^{t\text{Bu},i\text{Pr}2})\text{TiCl}_2$. To obtain reproducible recrystallization results, it is highly recommended to have a homogeneous solution prior to cooling.

vis (toluene, 25°C): 344 nm (3780 M⁻¹ cm⁻¹). IR (Nujol, CaF₂): 1363 (s), 1258 (m), 1212 (w), 1180 (w), 939 (w). mp 146(3)°C (the color changes from green to reddish during the melting process).

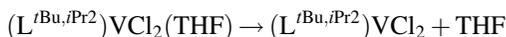
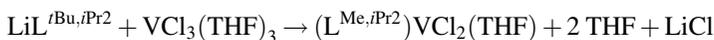
Properties

Complex (L^{*t*Bu,*i*Pr₂})TiCl₂ (intense green) is indefinitely stable at -35°C and in the absence of oxidants or protic media. This complex is soluble in toluene, benzene, THF, and Et₂O, but insoluble in pentane and hexane. Unlike (L^{*t*Bu,*i*Pr₂})TiCl₂(THF), (L^{*t*Bu,*i*Pr₂})TiCl₂ appears to be stable in CH₂Cl₂ over several hours at room temperature, but decomposition ensues after extended times.

Related Compounds

Complex (L^{*t*Bu,*i*Pr₂})TiCl₂ can be alkylated to the dimethyl derivative, (L^{*t*Bu,*i*Pr₂})TiMe₂, a precursor to the Ti(IV) complex (L^{*t*Bu,*i*Pr₂})TiMe₂(OTf) by AgOTf oxidation.¹² The latter complex is a convenient synthon to the phosphinidene, (L^{*t*Bu,*i*Pr₂})Ti=P[Trip](Me),¹³ via the treatment with LiPH[Trip] (Trip = 2,4,6-*t*Pr₃C₆H₂). Complex (L^{*t*Bu,*i*Pr₂})TiCl₂ can also be alkylated with 2 equiv of LiCH₂^{*t*}Bu to afford (L^{*t*Bu,*i*Pr₂})Ti(CH₂^{*t*}Bu)₂,¹² a precursor to the four-coordinate alkylidene complex (L^{*t*Bu,*i*Pr₂})Ti=CH^{*t*}Bu(OTf).¹² An alternative synthesis of (L^{*t*Bu,*i*Pr₂})TiCl₂ without formation of the imido impurity can be achieved using TiCl₃ instead of TiCl₃(THF)₃ in toluene.¹² The low yield of (L^{*t*Bu,*i*Pr₂})TiCl₂ (~23%), however, coupled with the expense in using TiCl₃ makes this process unattractive.

C. SYNTHESIS OF (L^{*Me,*i*Pr₂*})VCl₂



Procedure

The procedure for (L^{*Me,*i*Pr₂*})VCl₂ is a slight modification of the literature method.⁶ VCl₃(THF)₃¹⁴ (3.00 g, 0.008 mol) is slurried in 40 mL of THF and [L^{*Me,*i*Pr₂*}Li]_x (3.41 g, 0.008 mol) is dissolved in 30 mL of THF. Inside the glovebox, both solutions are loaded in a 350- or 500-mL heavy wall glass round-bottomed pressure vessel (Fig. 1, vide supra, CHEMGLASS), which is securely sealed with a Teflon cap. After mixing, the color of the solution gradually changes to red-brown. The mixture is transferred out of the glovebox and refluxed with stirring at 90°C for 30 min, upon which the solution rapidly turns to deep brown-red. The solution is cooled to room temperature, and then the flask is brought into the glovebox and transferred to a Schlenk flask. The volatiles are removed under reduced pressure inside the glovebox to yield a red-brown solid. The flask is sealed with a glass

stopper, and then evacuated and brought out of the glovebox. The flask is then heated at 100°C for 45 min under dynamic vacuum on a Schlenk line. During the heating/vacuum process, the complex loses THF to afford a deep green solid. The flask is transferred into the glovebox, and the deep green mass is washed with 25 mL of hexane and then extracted with 200 mL of toluene. The toluene solution is filtered through a bed of Celite, rinsing the residue with 10 mL portions of toluene until the filtrate is almost colorless (approximately three portions). The volume of the deep green filtrate is reduced to ~50 mL until a solid begins forming on the sides of the flask. The solution is capped with a rubber stopper and cooled to -35°C for 2 days to obtain bright green crystals of $(L^{\text{Me},i\text{Pr}2})\text{VCl}_2$. After filtration, the green crystals are collected and dried under reduced pressure. The filtrate is then concentrated (~25 mL) and stored at -35°C for 1 day to afford a second batch of product, which is dried under vacuum. The combined yield is 3.29 g (0.006 mol, 76% yield).

^1H NMR (23°C, C_6D_6): δ 5.91 ($\Delta\nu_{1/2} = 123$ Hz), 3.64 ($\Delta\nu_{1/2} = 561$ Hz), 2.66 ($\Delta\nu_{1/2} = 194$ Hz). $\mu_{\text{eff}} = 2.90(1)\mu_{\text{B}}$ (C_6D_6 , 298K, Evans' method). UV-vis (toluene (ϵ in $\text{M}^{-1}\text{cm}^{-1}$)): 789 (260), 586 (287), 416 (2100), 319 (7973) nm. IR (Nujol, KBr plates) 1534 (m), 1340 (s), 1320 (s), 804 (m), 757 (w) cm^{-1} . mp decomp. >200°C.⁶

Properties

Complex $L^{\text{Me},i\text{Pr}2}\text{VCl}_2$ is a deep green material soluble in toluene, Et_2O , benzene, and THF. It has properties similar to $L^{\text{Me},i\text{Pr}2}\text{TiCl}_2(\text{THF})$, being insoluble in hexane and pentane. The complex gradually decomposes in CH_2Cl_2 . Complex $L^{\text{Me},i\text{Pr}2}\text{VCl}_2$ is readily oxidized by O_2 and reacts rapidly with water to afford intractable products.

Related Compounds

Complex $L^{\text{Me},i\text{Pr}2}\text{VCl}_2$ can be readily alkylated with 2 equiv of LiMe , Li^nBu , and LiCH_2^tBu to afford the corresponding bis-alkyl complexes $L^{\text{Me},i\text{Pr}2}\text{V}(\text{R})_2$ ($\text{R} = \text{Me}$, ^nBu , $^t\text{CH}_2\text{Bu}$ ¹⁵). Complex $L^{\text{Me},i\text{Pr}2}\text{V}(\text{Me})_2$ is not as active catalyst as the titanium analogue for the polymerization of propene and 1-hexene when activated with $\text{B}(\text{C}_6\text{F}_5)_3$.⁶ However, the alkyl derivative $L^{\text{Me},i\text{Pr}2}\text{V}(\text{CH}_2^t\text{Bu})_2$ is an excellent precursor to both vanadium(IV) alkylidene species¹⁵ and V(V) alkylidyne species such as $(L^{\text{Me},i\text{Pr}2})\text{V} \equiv \text{C}^t\text{Bu}(\text{OTf})$ ¹⁶ and $[(L^{\text{Me},i\text{Pr}2})\text{V} \equiv \text{C}^t\text{Bu}(\text{THF})][\text{BPh}_4]$.¹⁶ The latter complexes are prepared by a stepwise one-electron oxidation, followed by alkylation with $\text{LiCH}_2\text{SiMe}_3$, and then another one-electron oxidation with AgX ($\text{X} = \text{OTf}$ or BPh_4).¹⁶ Complex $(L^{\text{Me},i\text{Pr}2})\text{VCl}_2$ is also a convenient precursor to terminal and neutral vanadium nitride complexes.¹⁷

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7. β -DIKETIMINATE-SUPPORTED VANADIUM AND CHROMIUM CHLORIDE COMPLEXES

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General Procedures

All manipulations of compounds were carried out using standard Schlenk, vacuum line, and glovebox techniques. Pentane, diethyl ether, tetrahydrofuran, and toluene

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