Chapter One

COMPLEXES OF BULKY β-DIKETIMINATE LIGANDS

1. INTRODUCTION

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In the past decade, β-diketiminates[1] have experienced a dramatic renaissance.[2] These scaffolds are structurally analogous to the ubiquitous acac (acetylacetonate) ligand, forming a six-membered chelate ring with nitrogen atoms in place of the oxygen atoms of acac. Like the popular cyclopentadienyl ligand, the monoanionic β-diketiminate ligand forms complexes with a wide variety of main-group and d-block metals, lanthanides, and actinides.[2] Moreover, β-diketiminates often serve as a robust framework for supporting metal-containing functional groups owing to their relatively strong donating properties and chelating nature. As such, β-diketiminate complexes rarely suffer from decomplexation pathways that often plague monodentate ligands such as amides, amines, and neutral diimines. Although β-diketiminates typically bind in a bidentate fashion, the delocalization of charge about the NCCCN ring renders it possible for metals to coordinate to the face of the ligand with hapticities up to η^5. In such cases, the coordination geometry is highly dependent on both the metal and ligand substituents.[2]

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The availability of straightforward, multigram syntheses for many classes of β-diketiminates has generated widespread popularity of the ligand for coordination and organometallic chemistry. Prototypical β-diketimines with *N*-aryl substituents can be synthesized in one step from commercially available anilines and diones through simple condensation reactions.[1,3] β-Diketiminate ligands with aliphatic nitrogen substituents can also be prepared by related condensation routes, but often require harsh reagents such as oxonium salts for complete diimine formation.[4] More sterically encumbered derivatives possessing *tert*-butyl groups on the β-carbons of the NCCCN backbone require a multistep, but high-yielding, synthesis (described herein).[5] Other variants of the β-diketiminate scaffold have been recently discussed in a comprehensive review.[2]

This chapter focuses on the *N*-aryl β-diketiminates, which have a high degree of modularity of the R and R′ positions of the NCCCN backbone, and of the *N*-aryl *ortho* substituents (R″ and R‴) (Fig. 1, left). Steric and electronic factors can easily be fine-tuned via the R, R′, and R″ groups. For instance, the steric demands of the coordination wedge in β-diketiminatometal complexes (Fig. 1, right) can be modified by judicious choice of R and R″ substituents, while the electronic properties of the ligand are influenced predominantly by the backbone substituents R′, and to a lesser extent, R. In this chapter, we describe complexes of four different β-diketiminate ligands using a notation that specifies R and R″/R‴ substituents (R′ = H in all syntheses described here). Thus, $L^{Me,Me2}$ indicates R = R″ = Me and R‴ = H; $L^{Me,Me3}$ indicates R = R″ = R‴ = Me; $L^{Me,iPr2}$ indicates R = Me, R″ = ^{i}Pr, and R‴ = H; and $L^{tBu,iPr2}$ indicates R = ^{t}Bu, R″ = ^{i}Pr, and R‴ = H.

An important application for β-diketiminates is the generation of low-coordinate metal complexes. This propensity for stabilizing complexes with low coordination numbers has proven particularly useful for the isolation of systems with unprecedented oxidation states, especially low oxidation state main-group species.[6] Such complexes often serve as precursors for group-transfer reactions to

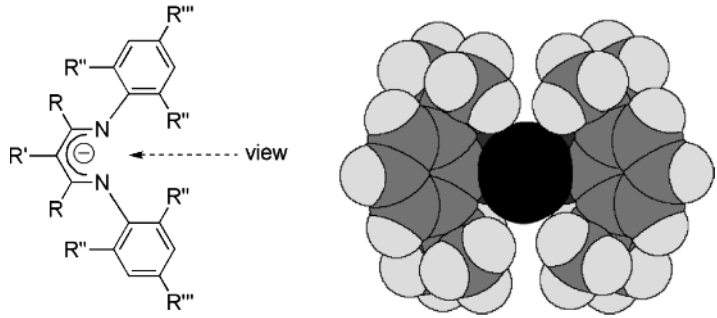

Figure 1. *Left*: General structure of a β-diketiminate ligand with aryl substituted nitrogen groups. *Right*: The coordination wedge of a metal complex with $L^{Me,iPr2}$ (R = Me, R′ = H, R″ = ^{i}Pr, R‴ = H), depicting how the R″ groups block the axial sites of the metal atom (shown in black).

afford reactive, metal-bound functional groups. Low-coordinate β-diketiminate complexes also play host to a variety of reactive functionalities including hydrides,[7] alkyls,[2,8] alkylidenes/carbenes,[9,10] alkylidynes,[11] imides/nitrenes and nitrides,[12–15] and phosphinidenes.[9,16] Many of these functionalities find application in catalysis such as copolymerization,[17] ring-opening polymerization,[18] alkene and alkyne polymerization,[5,8,11,19] olefin metathesis,[20] intramolecular hydroamination,[21] carboamination,[22] intermolecular hydrophosphination,[16c] carbene and nitrene group transfer,[9,10] and hydrodefluorination.[23] In biomimetic chemistry, β-diketiminate ligands have been used in type 1 ''blue'' copper sites,[24] the study of dioxygen activation by cobalt[10a] and copper,[25] the binding of nitric oxide by nickel,[26] and the binding of nitrogenase substrates to iron.[27]

In this chapter we collect representative procedures for the preparation of the most popular family of *N*-aryl β-diketiminate ligands, and of alkali metal and thallium salts that are especially useful precursors to transition metal complexes. We then describe the preparation of a series of useful β-diketiminato metal complexes with 3d transition metals from Sc to Zn, each of which serves as a template for further elaboration.

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2. β-DIKETIMINATE PRECURSORS $HL^{Me,Me3}$ and $TlL^{Me,Me3}$ ($L^{Me,Me3}$ = 2,4-BIS-(MESITYLIMIDO)PENTYL)

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The β-diketiminate ligand $HL^{Me,Me3}$ was first reported by Budzelaar via condensation of acetylacetone with 2,4,6-trimethylaniline in 12 N HCl at 120–140°C.[1] We find that the milder procedure below for $HL^{Me,Me3}$ adapted from Budzelaar's method for $HL^{Me,Me2}$ offers a simple workup and is also versatile for the synthesis of other $HL^{Me,R}$ derivatives.[2] We also include spectroscopic information for $HL^{Me,Me2}$ that was prepared analogously. The synthesis of the thallium derivative $TlL^{Me,Me3}$ was adapted from the published literature procedures for $TlL^{Me,Me2}$ and $TlL^{Me,Me3}$.[3,4]

General Procedures

Experiments requiring air-free techniques were carried out in a dry nitrogen atmosphere using a glovebox and/or standard Schlenk techniques. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passing through activated alumina columns.[5] Pentane was first washed with conc. HNO_3/H_2SO_4 to remove olefins, stored over $CaCl_2$, sparged with nitrogen, and then dried by passing through activated alumina columns.[5] Deuterated solvents were sparged with nitrogen, dried over activated 4 Å molecular sieves, and stored under nitrogen.

2,4,6-Trimethylaniline, 2,4-pentanedione, *p*-toluenesulfonic acid, and thallous acetate were purchased from Acros Organics. These reagents were used as received. Potassium hydride was obtained from Aldrich as a dispersion in mineral oil; using air-free techniques, it was filtered and washed with pentane to afford a dry powder.

A. 2,4-BIS-(MESITYLIMIDO)PENTANE ($HL^{Me,Me3}$)

$$\mathrm{MeC(O)CH_2C(O)Me} + 2\,2,4,6\text{-}\mathrm{Me_3C_6H_2NH_2} + \mathrm{HOTs} \rightarrow [\mathrm{H_2L^{Me,Me3}}]\mathrm{OTs} + 2\,\mathrm{H_2O}$$

$$[\mathrm{H_2L^{Me,Me3}}]\mathrm{OTs} + \mathrm{Na_2CO_3} \rightarrow \mathrm{HL^{Me,Me3}} + \mathrm{NaOTs} + \mathrm{NaHCO_3}$$

To a suspension of *p*-toluenesulfonic acid monohydrate (18.6 g, 0.098 mol) in 300 mL of toluene is added 2,4-pentanedione (9.75 g, 0.098 mol) and 2,4,6-trimethylaniline (26.6 g, 0.196 mol). Using a Dean–Stark trap, the mixture is refluxed with stirring for 4 h until no further water is collected. Cooling the resulting solution gives a solid, the protonated β-diketimine as its tosylate salt, which is filtered and the solid is air-dried. This solid is taken up in 300 mL of CH_2Cl_2 and stirred with 200 mL of saturated Na_2CO_3 solution for 1 h. The organic layer is separated and dried over $MgSO_4$. The volatiles are removed *in vacuo* to

yield a yellow oil.* Addition of 200 mL of ice-cold MeOH to the yellow oil followed by vigorous shaking for 1 min causes a white solid to precipitate. The slurry is stored at −35°C overnight to encourage further crystallization. The product is isolated by filtration, washed with cold methanol, and dried to yield 30.3 g (93%) of product.

^{1}H NMR ($CDCl_3$): δ 12.20 (s, 1, N-H), 6.89 (s, 4, Ar-H), 4.89 (s, 1, backbone-CH), 2.29 (s, 6, Ar-*p*-CH_3), 2.16 (s, 12, Ar-*o*-CH_3), 1.72 (s, 6, backbone-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.62, 141.81, 134.16, 132.46, 129.09, 93.93 (backbone-CH), 21.50 (Ar-*o*-CH_3), 20.96 (Ar-*p*-CH_3), 18.95 (backbone-CH_3).

Properties

The white microcrystalline solid forms colorless needles upon careful crystallization attempts. It is soluble in common organic solvents.

The β-diketimine $HL^{Me,Me2}$ may be prepared analogously by substituting 2,6-dimethylaniline for 2,4,6-trimethylaniline in the above synthesis.[3] ^{1}H NMR ($CDCl_3$): δ 12.17 (s, 1, N-H), 7.02 (d, 4, Ar-*m*-H), 6.93 (t, 2, Ar-*p*-H), 4.86 (s, 1, backbone-CH), 2.14 (s, 6, Ar-CH_3), 1.67 (s, 6, backbone-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.72, 143.69, 132.06, 127.67, 124.19, 93.20 (backbone-CH), 20.25 (Ar-*o*-CH_3), 18.29 (backbone-CH_3).

B. THALLIUM 2,4-BIS-(MESITYLIMIDO)PENTYL ($TlL^{Me,Me3}$)

$$HL^{Me,Me3} + KH \rightarrow KL^{Me,Me3} + H_2$$

$$KL^{Me,Me3} + TlOAc \rightarrow TlL^{Me,Me3} + KOAc$$

■ **Caution**. *Air-free procedures are required for use of potassium hydride, which can explosively generate hydrogen gas upon uncontrolled hydrolysis. Hydrogen gas is generated in the procedure and should not be performed in a sealed flask.*

Procedure

A solution of $HL^{Me,Me3}$ (8.00 g, 23.9 mmol) in 40 mL of THF is treated with 1.3 equiv. of dry KH (1.25 g, 31.1 mmol). The reaction is stirred overnight and then filtered through Celite to remove excess KH to yield a bright yellow filtrate. The filter cake is washed with a small amount of THF that is added to the filtrate; TlOAc (6.31 g, 23.9 mmol) is then added to this solution, which is stirred overnight in the

* The checkers obtained a solid at this step, which was treated identically and gave a 68% yield.

dark. The resulting dark green solution is filtered through Celite to yield a bright yellow filtrate. Removal of all volatiles *in vacuo* gives a dry yellow solid. Dissolving this solid in ca. 25 mL diethyl ether followed by chilling to −35°C results in the formation of yellow crystals, which are isolated by decanting the mother liquors to yield 8.50 g (66%) of the product after drying *in vacuo*.*

^{1}H NMR (C_6D_6): δ 6.86 (s, 4, Ar-H), 4.84 (s, 1, backbone-CH), 2.22 (s, 6, Ar-*p*-CH_3), 2.14 (s, 12, Ar-*o*-CH_3), 1.71 (s, 6, backbone-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.87, 147.28, 132.15, 130.39, 129.31, 100.12 (backbone-CH), 24.93 (Ar-*o*-CH_3), 21.36 (Ar-*p*-CH_3), 19.59 (backbone-CH_3).

Properties

The compound is both light and air sensitive and is best stored in the dark. Decomposition by light, air, or water results in black solutions or solids in which the free β-diketimine $HL^{Me,Me3}$ may be detected by observation of its N-*H* ^{1}H NMR signal at δ 12.20 (benzene-d_6). Thallium β-diketiminates exhibit low coordination numbers in the solid state.[6–8] Owing to their soft, relatively nonreducing nature and the insolubility of resulting metal halides, thallium reagents favor complete removal of the exchanged halide from the metal's coordination sphere; thallium β-diketiminates have found use as transmetallation agents in the preparation of Co,[9,10] Ni,[5,11] Cu,[4,12,13] and Au[14] β-diketiminate complexes.

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*The checkers obtained a yield of 48% from the first crop of crystals. Concentrating the mother liquor afforded additional crystals (total over 2 crops: 59%)

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3. β-DIKETIMINATE PRECURSORS $L^{Me,iPr2}H$, $[L^{Me,iPr2}Li]_x$, and $[L^{tBu,iPr2}K]_x$ ($L^{Me,iPr2}$=2,4-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)PENTYL; $L^{tBu,iPr2}$=2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO) HEPTYL)

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The following procedure has been slightly modified from the literature by inclusion of a few more synthetic details as well as an increment in the scale for consistency of yield.[4,5] Potassium salts of $L^{Me,iPr2}$ have been reported by Mair[6] and Winter[7] by using $KN(SiMe_3)_2$ and KH, respectively. Likewise, in Chapter 8, Roesky describes the synthesis of $L^{Me,iPr2}K$ from KH and $L^{Me,iPr2}H$. We have, however, encountered low yields and irreproducible results in syntheses that start from potassium diketiminate salts prepared in this way, presumably because of the variable quality of commercial KH. We describe here a reproducible and facile synthesis that uses benzylpotassium[3] as the potassium source, thus avoiding the use of potentially dubious KH and the hazards of explosion from the production of H_2 gas.

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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/Ph_2CO and distilled into an evacuated vacuum flask equipped with a gas adapter and under a positive flow of N_2 or Ar. The THF-filled flask was taken 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 N_2.[1] Before use, a 5mL 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). Celite was dried under reduced pressure at 180°C for 24 h. $TiCl_3(THF)_3$ was purchased from Strem and also prepared according to the literature procedure.[2] All ^1H NMR spectra were referenced to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 ppm). C_6D_6 was purchased from Cambridge Isotope Laboratories, degassed and dried over CaH_2, and then vacuum transferred to 4 Å molecular sieves. Benzylpotassium was prepared by a procedure reported in the literature.[3]

A. 2,4-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)PENTANE ($L^{Me,iPr2}H$)

$$\begin{aligned} &MeC(O)CH_2C(O)Me + 2\,2,6\text{-}(i\text{-}Pr)_2C_6H_3NH_2 + HCl \\ &\quad \rightarrow [H_2L^{Me,Me3}]Cl + 2H_2O \end{aligned}$$

$$[H_2L^{Me,iPr2}]Cl + Na_2CO_3 \rightarrow HL^{Me,iPr2} + NaCl + NaHCO_3$$

Procedure

Manipulations are performed in the air. In a two-neck 500-mL round-bottomed flask, 1,4-pentanedione (6.68 g, 0.067 mol) is mixed with 300 mL of ethanol and 2,6-diisopropylaniline (28.67 g, 0.162 mol). To the mixture is added 7.5 mL of conc. hydrochloric acid (~12 M) and the solution is refluxed with vigorous stirring at 100°C for 3 days. After 6 h, a white precipitate begins to form, but the reaction must be continued for the full 3 days for complete conversion. The slurry is allowed to cool to room temperature and then filtered. The filtered solid is dried under reduced pressure, and the filtrate is evaporated on a rotary evaporator. The dried mass is combined with the filtrate residue and the mixture is refluxed in 250 mL hexane at 80°C for 1 h. After cooling the mixture, the slurry is filtered, and the solid residue is treated with 300 mL of a saturated aqueous solution of Na_2CO_3 and 500 mL of CH_2Cl_2. The slurry is stirred until the solid dissolves, giving a yellowish organic solution and a pale yellow aqueous layer. The organic layer is separated

using a separatory funnel and the solution is dried over $MgSO_4$. The solution is filtered again and dried under reduced pressure to yield a slightly yellow residue that upon washing with 50 mL of cold methanol (−20°C) yields white $L^{Me,iPr2}H$ as a fluffy powder (21.42 g, 0.051 mol, 77% yield).* The compound is characterized by ^1H NMR spectroscopy that was compared with that reported in the literature.[5]

^1H NMR (C_6D_6): δ 12.44 (s, 1H, N-*H*), 7.14–7.09 (m, 6H, Ar-*H*), 4.85 (s, 1H, C*H*), 3.27 (m, 4H, C*H*$(CH_3)_2$), 1.63 (s, 6H, NC(C*H*$_3$)), 1.18 (d, $J_{H-H} = 7$ Hz, 12H, CH$(CH_3)_2$), 1.12 (d, $J_{H-H} = 7$ Hz, 12H, CH$(CH_3)_2$).

Properties

$L^{Me,iPr2}H$ is a white crystalline solid that is soluble in organic solvents including *n*-pentane and *n*-hexane. $L^{Me,iPr2}H$ is not soluble in water and is poorly soluble in other polar solvents such as MeOH and EtOH. Solids are indefinitely stable in air and readily form the iminium salt $[L^{Me,iPr2}H_2]Cl$ upon exposure to 12 M HCl. As a solid, $L^{Me,iPr2}H$ gradually turns pale yellow in air, but the material can be purified by recrystallization by concentrating an Et_2O solution followed by cooling to −20°C for >12 h. It is recommended, however, to store the pure white free base under an inert atmosphere (or under vacuum) to avoid gradual tainting.

B. LITHIUM 2,4-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)PENTYL ($[L^{Me,iPr2}Li]_x$)

$$HL^{Me,iPr2} + BuLi \rightarrow [L^{Me,iPr2}Li]_x + BuH$$

■ **Caution**. *Butyllithium is pyrophoric in air and should be handled exclusively under dry nitrogen or argon. This reaction is extremely exothermic, so the addition of n-BuLi should be performed at low temperatures and not be rushed.*

Procedure

In a 250-mL round-bottomed flask, $L^{Me,iPr2}H$ (5.00 g, 0.012 mol) is dissolved in 100 mL of hexane and the solution cooled to −35°C. To the cooled solution a 1.6 M *n*-BuLi solution in hexane (7.84 mL, 0.013 mol) is added dropwise, and the solution is stirred for 12 h at room temperature.

During the course of this time, a white precipitate gradually appears. The suspension is cooled to −35°C over 12 h, and the solid is collected by filtration, washed with 10 mL of cold hexane, and then dried under reduced pressure. The filtrate collected from the first batch is concentrated to ∼30 mL under reduced

* The checkers omitted the step where the residue was refluxed in hexane, obtaining a final yield of 72%.

pressure and the solution is cooled again to −35°C. After 12 h, a second batch of solid is collected via filtration, washed with cold hexane, and dried under reduced pressure. The combined yield for the two batches is 2.85 g (0.007 mol, 56% yield).* Compound $[L^{Me,iPr2}Li]_x$ is characterized by ^{1}H NMR spectroscopy by comparison to that reported in the literature.[4] The structural chemistry of lithium diketiminate complexes has been investigated.[4]

^{1}H NMR (C_6D_6): δ 7.21–7.18 (m, 6H, Ar-*H*), 4.90 (s, 1H, γ-C*H*), 3.15 (m, 4H, C*H*$(CH_3)_2$), 1.83 (s, 6H, NC(C*H*$_3$)), 1.21 (d, $J_{H-H} = 7$ Hz, 12H, CH(C*H*$_3)_2$), 1.18 (d, $J_{H-H} = 7$ Hz, 12H, CH(C*H*$_3)_2$).

Properties

Compound $[L^{Me,iPr2}Li]_x$ is a white amorphous solid, which is soluble in donor solvents such as Et_2O and THF. The salt has very low solubility in hydrocarbons such as *n*-pentane and *n*-hexane but can be dissolved in copious amounts of benzene and toluene. The compound $[L^{Me,iPr2}Li]_x$ decomposes rapidly in halogenated solvents and upon exposure to air. It is recommended that solids not be stored for extended periods of time, even if inside a glovebox. For the preparation of its transition metal derivatives, it is preferable to use fresh $[L^{Me,iPr2}Li]_x$ or generate it *in situ* before use. In the presence of donor solvents such as Et_2O and THF, $[L^{Me,iPr2}Li]_x$ forms yellow adducts.[4] The binding is exothermic, and it is therefore recommended to add the salt to the solution and not the reverse.

C. POTASSIUM 2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)HEPTYL ($[L^{tBu,iPr2}K]_x$)

$$L^{tBu,iPr2}H + KCH_2Ph \rightarrow [L^{tBu,iPr2}K]_x + PhMe$$

Procedure

■ **Caution**. *KCH_2Ph is a highly pyrophoric that should be handled only in an inert atmosphere. Upon contact with O_2 or H_2O, solid benzylpotassium will immediately deflagrate. This reaction to produce $[L^{tBu,iPr2}K]_x$ is extremely exothermic, so it is recommended that the addition of KCH_2Ph be performed slowly and at low temperatures.*

A solution of $L^{tBu,iPr2}H$ (2.15 g, 4.27 mmol) in 40 mL of diethyl ether is placed in a 250-mL round-bottomed flask and frozen in a cold well for 0.5 h. To the thawing solution is added benzylpotassium[3] (557 mg, 4.27 mmol) in portions. The

* The checkers performed the reaction on a larger scale (27 mmol) and obtained a yield of 75%.

suspension is slowly warmed to room temperature, and the orange solids gradually dissolve to give a yellow solution. After stirring the solution at room temperature for 1.5 h, removal of the ethereal solution affords a canary yellow solid, which is triturated with 25 mL of cold pentane and vacuum filtered through a porous frit to afford a pale yellow product. The product is further washed with 15 mL of cold pentane, dried, and stored at −37°C. Yield: 91% (2.10 g, 3.88 mmol).* ^{1}H NMR spectra of $[L^{tBu,iPr2}K]_x$ indicate the absence of solvent. The degree of aggregation of this material was not investigated.

^{1}H NMR (C_6D_6): δ 7.00 (d, 4H, $J = 7$ Hz, *m*-Ar-*H*), 6.81 (t, 2H, $J = 7$ Hz, *p*-Ar-*H*), 4.93 (s, 1H, α-*H*), 3.26 (m, 4H, C*H*$(CH_3)_2$, 1.37 (s, 18H, C(C*H*$_3)_3$), 1.32 (d, 12H, $J = 7$ Hz, CH(C*H*$_3)_2$, 0.94 (d, 12H, $J = 7$ Hz, CH(C*H*$_3)_2$). ^{13}C NMR (C_6D_6): δ 166.0 (ArN(C(CH$_3)_3$)*C*CH*C*(C(CH$_3)_3$)NAr), 151.4 (Ar), 144.8 (Ar), 135.7 (Ar), 133.2 (Ar), 123.4 (Ar), 118.1 (Ar), 89.6 (ArN(C(CH$_3)_3$)C*C*HC(C(CH$_3)_3$)NAr), 44.0 (ArN(*C*(CH$_3)_3$)CCHC(*C*(CH$_3)_3$)NAr), 32.5 (ArN(C(*C*H$_3)_3$)CCHC(C(*C*H$_3)_3$)NAr), 31.6 (Ar-2,6-(*C*H(CH$_3)_2$), 27.0 (Ar-2,6-(CH(*C*H$_3)_2$), 24.8 (Ar-2,6-(CH(*C*H$_3)_2$), 23.4 (Ar-2,6-(CH(*C*H$_3)_2$), 22.69 (Ar-2,6-(CH(*C*H$_3)_2$).

Properties

Compound $[L^{tBu,iPr2}K]_x$ is a pale yellow amorphous solid that is soluble in THF. The salt is insoluble in hydrocarbons such as *n*-pentane and *n*-hexane, and partially soluble in benzene, toluene, and Et_2O. Compound $[L^{tBu,iPr2}K]_x$ decomposes rapidly in halogenated solvents such as CH_2Cl_2 and CCl_4 and also upon exposure to air. It is also recommended that solids not be stored for extended periods of time, even if inside a glovebox. It is preferable to isolate fresh $[L^{tBu,iPr2}K]_x$ for subsequent use.

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* The checkers obtained a yield of 93% using the method described. The checkers also performed the reaction on a similar scale at room temperature and obtained a solid having identical properties, with a yield of 95%. It is difficult to remove the final traces of toluene from the solid under vacuum, as is evident from ^1H NMR spectra.

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4. β-DIKETIMINATE PRECURSORS $L^{tBu,iPr2}H$ AND $L^{tBu,iPr2}Li(THF)$ ($L^{tBu,iPr2}$=2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)HEPTYL)

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The β-diketiminate ligand with *tert*-butyl substituents on the backbone ($L^{tBu,iPr2}$) gives especially extreme hindrance in late transition metal complexes. Studies on the vanadium chemistry of bulky β-diketiminates showed that this ligand did not coordinate to vanadium or titanium.[1] Only under the right conditions can this ligand be coordinated to Ti(III), albeit in low yields.[2]

In iron(II) and nickel(II) complexes, the $L^{tBu,iPr2}$ ligand gives three-coordinate monomers $L^{tBu,iPr2}MCl$, even though $L^{Me,iPr}$ gives $[L^{Me,iPr2}M(\mu\text{-}Cl)]_2$ under identical conditions.[3] At first glance, this distinct increase in size may be surprising because the location of the large *t*-butyl groups is far from the metal binding site, and directed away from the metal. However, steric interactions between the *tert*-butyl groups and the neighboring 2,6-diisopropylphenyl groups push the latter toward the ''open'' side of the ligand and increase the extent to which the metal is blocked from additional ligands. This size difference has been shown by side-to-

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side comparison of three-coordinate iron alkyl complexes of the two diketiminate ligands.[4]

Because of the hindrance near the imine carbon atoms, the diimine $L^{tBu,iPr2}H$ cannot be synthesized through a double condensation, as in the other ligands. Budzelaar sidestepped this problem using a convergent synthesis that couples the two sides of the ligand.[1] Both sides derive from a common intermediate, an imine chloride which is prepared from pivaloyl chloride. Half of this imine chloride is methylated to give a methyl *tert*-butyl imine, which is then deprotonated and treated with the remaining half of the imine chloride to give the final ligand. The synthesis below, which is very little changed from that reported by Budzelaar, gives the ligand in a total yield of 58% in four steps.[1] The ^{1}H NMR spectrum of the final ligand has broad signals at room temperature, presumably from exchange between diimine and imine–enamine tautomers, which has a rate similar to the NMR timescale.

A method for preparing the lithium salt of this ligand is given here; please refer to the previous chapter to find a method for preparing the potassium salt of this ligand.

General Procedures

All materials were purchased from Aldrich and used as received, unless otherwise specified. NMR spectra are referenced to residual C_6D_5H at 7.16 ppm or $CHCl_3$ at 7.26 ppm. Solvents for the final two steps were dried by passing HPLC-grade solvents through columns of activated alumina and Cu Q-5 (Glass Contour Co.).

A. *N*-PIVALOYL-2,6-DIISOPROPYLANILIDE (DIPPNHC(O)^{t}Bu)

$$\begin{aligned} &Me_3C(O)Cl + 2,6\text{-}(i\text{-}Pr)_2C_6H_3NH_2 + Et_3N \\ &\quad \rightarrow 2,6\text{-}(i\text{-}Pr)_2C_6H_3NHC(O)CMe_3 + Et_3NHCl \end{aligned}$$

Procedure

2,6-Diisopropylaniline (97.5 g, 0.55 mol), triethylamine (70 mL, 0.50 mol), dichloromethane (200 mL), and a large stir bar are added to a 1000-mL round-bottomed flask to give a colorless solution. A solution of pivaloyl chloride (62 mL, 0.50 mol) in dichloromethane (200 mL) is added to a pressure-equalizing addition funnel, and this solution is added dropwise to the vigorously stirring aniline solution over 2 h. Although pivaloyl chloride is sensitive to water, predrying the triethylamine and dichloromethane is not required. The reaction is exothermic, so

slow addition is necessary. The solution has a pale pink or green color, and a white precipitate is evident. After stirring the mixture for an additional 30 min, the slurry is chilled to 0°C, and the fluffy solid is collected by filtration.* The solid is washed with diethyl ether (3 × 150 mL) to remove excess aniline and with copious amounts of water (4 × 200 mL) to remove triethylammonium chloride. Finally, the solid is dried under vacuum for at least 12 h to afford DIPPNH(C=O)(^{t}Bu) (121 g, 93% yield). Typical isolated yields are greater than 90%, and the product is stable to air and water. Purity is determined by ^{1}H NMR spectroscopy.

^{1}H NMR ($CDCl_3$): δ 7.29 (m, 2H, *p*-Ar), 7.15 (d, 2H, *m*-Ar, $J = 7.6$ Hz), 6.80 (br, 1H, N-*H*), 3.00 (sept, 2H, C*H*(CH_3)$_3$, $J = 6.8$ Hz), 1.36 (s, 9H, C(C*H*$_3$)$_3$), 1.18 (d, 12H, CH(C*H*$_3$)$_2$, $J = 6.8$ Hz).

B. DIPPN=C(Cl)^{t}Bu

$$2,6\text{-}(i\text{-Pr})_2C_6H_3NHC(O)CMe_3 + PCl_5$$

$$\rightarrow 2,6\text{-}(i\text{-Pr})_2C_6H_3N{=}C(Cl)CMe_3 + HCl + POCl_3$$

Procedure

A 2000-mL three-necked flask containing a slurry of DIPPNH(C=O)(^{t}Bu) (121 g, 0.46 mol) in 1000 mL of benzene (predrying benzene is not necessary) is fitted with a glass stopper and two hose adapters. One hose attaches to a N_2 inlet, and the other is allowed to bubble through saturated sodium carbonate to neutralize gaseous HCl produced in the reaction. The headspace of the flask is purged with N_2 for 10 min, and the flow rate is reduced to a slow bubble. Solid PCl_5 (106 g, 0.51 mol) is added in small portions (5–10 g) over a 90-min period by opening the stoppered joint against a positive N_2 flow, adding the solid, and replacing the stopper. Slow addition of PCl_5 is necessary because the reaction is exothermic. During the course of the reaction all solids dissolve, and the solution develops a yellowish color. The mixture is stirred for an additional 1 h after the addition of PCl_5 is complete. The two hose adapters are removed from the flask and replaced with ground glass stoppers. The third neck is fitted with a distillation head and benzene and $POCl_3$ are removed by distillation directly from the reaction flask at ambient pressure under a N_2 atmosphere. (*Caution*: $POCl_3$ produces gaseous HCl upon contact with moisture or moist air.) The residue is then transferred into a smaller single-necked flask and chloroimine is distilled under vacuum (82°C,

* Using 2,6-diisopropylaniline from Acros Organics, the checkers conducted the reaction at a lower concentration and obtained a tacky product.

0.10 mbar) through a Vigreux column.* The product (100 g, 83%) is a colorless oil and is best stored under an atmosphere of N_2 to prevent reaction with moisture, which converts it to DIPPNH(C=O)(^{t}Bu). Purity is established by ^{1}H NMR spectroscopy. Occasionally, the distillate contains traces of DIPPNH(C=O)(^{t}Bu) (up to 10% based on ^{1}H NMR integration), in which case a second distillation through a Vigreux column is necessary.

^{1}H NMR ($CDCl_3$): δ 7.14 (m, 3H, *m*- and *p*-Ar), 2.74 (sept, 2H, C*H*$(CH_3)_2$, $J = 6.8$ Hz), 1.43 (s, 9H, C(C*H*$_3)_3$), 1.18 (d, 12H, CH(C*H*$_3)_3$, $J = 6.8$ Hz).

C. DIPPN=C(Me)^{t}Bu

$$2,6\text{-}(i\text{-Pr})_2C_6H_3N{=}C(Cl)CMe_3 + MeLi$$
$$\rightarrow 2,6\text{-}(i\text{-Pr})_2C_6H_3N{=}C(Me)CMe_3 + LiCl$$

Procedure

■ **Caution**. *Methyllithium is pyrophoric in air and should be handled exclusively under dry nitrogen or argon. This reaction is extremely exothermic, so the addition should be performed carefully at low temperatures.*

An oven-dried (150 °C) 500-mL Schlenk flask is charged with DIPPN=C(Cl)(^{t}Bu) (45.3 g, 0.16 mol), rigorously dry diethyl ether (200 mL), and a stir bar under a N_2 atmosphere to give a colorless solution, and the flask is sealed with a septum and removed from the glovebox. (It is easier to perform the reaction in a cold well in a drybox, if the equipment is available.) The solution is chilled to −78°C in a dry ice/acetone cold bath, and methyllithium (121 mL, 1.6 M solution in diethyl ether, 0.19 mol) is added to the stirring reaction mixture in ∼5-mL portions over 30 min.

The mixture is allowed to slowly warm and stirred at ambient temperature, upon which a white precipitate is observed. (*Caution*: A slow flow of N_2 through the septum and out to an oil bubbler is necessary to ensure that the reaction vessel does not develop pressure since the reaction is exothermic and the ether solvent is quite volatile.) After 12 h,† the mixture is exposed to air by removing the septum and ice (about 5 g) is carefully added in small portions until effervescence ceases.

Water (100 mL) is added, and the mixture is transferred to a separatory funnel where the aqueous layer is removed. The organic layer is extracted twice more with

* The checkers distilled at 125–127°C at 7 mbar.

† The checkers report that a 3-h reaction time is sufficient for full conversion.

water (2 × 100 mL), dried with anhydrous $MgSO_4$, and filtered through coarse filter paper. The volatile materials are removed under vacuum to afford a light yellow oil. Pure DIPPN=C(Me)(^{t}Bu) is distilled through a Vigreux column under vacuum (72°C, 0.02 mbar) as a colorless oil (36.0 g, 86%).* The oil is stable for months to air and moisture. Purity is established by ^{1}H NMR spectroscopy.

^{1}H NMR ($CDCl_3$): δ 6.97–7.09 (m, 3H, Ar-*H*), 2.68 (sept, 2H, C*H*$(CH_3)_2$, $J = 6.9$ Hz), 1.66 (s, 3H, CH_3), 1.28 (s, 9H, C(CH_3)$_3$), 1.13 (d, 6H, CH(CH_3)$_3$, $J = 6.9$ Hz), 1.11 (d, 6H, CH(CH_3)$_3$, $J = 6.9$ Hz).

D. 2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)HEPTANE ([DIPPN=C(^{t}Bu)]$_2$CH$_2$, $L^{tBu,iPr}H$)

$$2,6\text{-}(i\text{-Pr})_2C_6H_3N{=}C(Me)CMe_3 + BuLi$$
$$\rightarrow 2,6\text{-}(i\text{-Pr})_2C_6H_3N{=}C(CH_2Li)CMe_3 + BuH$$
$$2,6\text{-}(i\text{-Pr})_2C_6H_3N{=}C(Cl)CMe_3$$
$$+ 2,6\text{-}(i\text{-Pr})_2C_6H_3N{=}C(CH_2Li)CMe_3 \rightarrow L^{tBu,iPr}H + LiCl$$

Procedure

In a N_2 glovebox, an oven-dried (150°C) 500-mL Schlenk flask is charged with DIPPN=C(Me)(^{t}Bu) (48.6 g, 0.18 mol), rigorously dry diethyl ether (250 mL, pentane can also be used), dried *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (40 mL, 0.26 mol), and a stir bar to give a colorless solution. The solution is chilled to −78°C and *n*-butyllithium (76 mL, 2.5 M in hexanes, 0.19 mol) is added slowly in 5-mL portions over 15 min. (*Note*: Although using a glovebox cold well is convenient, sealing the flask with a septum, removing the flask from the glovebox, and chilling in a dry ice/acetone bath under dynamic N_2 is also appropriate.) The flask is sealed with a ground glass stopper and the stopcock is left open to allow butane to escape. The mixture is allowed to slowly warm to ambient temperature for 16 h. The mixture is then cooled to −78°C and a solution of DIPPN=C(Cl)(^{t}Bu) (50.4 g, 0.18 mol) in diethyl ether (50 mL) is added. The resulting slurry is allowed to slowly warm and stirred at ambient temperature for 18 h, whereupon the

* The checkers conducted the reaction at 0°C and did not distill the product. The crude product was assayed by ^1H NMR spectrum and was used in subsequent steps without further purification.

solution develops a yellowish color and a white precipitate forms. The mixture is removed from the glovebox and heated at reflux in an oil bath for 2 h under N_2. The slurry is cooled and exposed to air where it is carefully quenched with ice and water (200 mL). The mixture is transferred to a separatory funnel, and the aqueous layer is discarded. The organic layer is extracted twice more with water (2×200 mL), dried with anhydrous $MgSO_4$, and filtered through coarse filter paper. The volatile materials are removed under vacuum to afford a sticky yellow solid. This solid is dissolved in 400 mL of boiling hexanes, and the extract is slowly cooled to $-25°C$ to give colorless block-shaped crystals of $L^{t\mathrm{Bu},i\mathrm{Pr}}H$ in two crops (79.1 g, 87%).

When stored in air, $L^{t\mathrm{Bu},i\mathrm{Pr}}H$ slowly turns yellow over a period of weeks; therefore, keeping $L^{t\mathrm{Bu},i\mathrm{Pr}}H$ under an atmosphere of N_2 is appropriate for long-term storage. Purity is established by ^1H NMR spectroscopy.

^1H NMR ($CDCl_3$): δ 7.07–6.97 (m), 3.21 (br), 2.68 (br), 1.21 (s), 1.09 (s), 1.05 (br) ppm. The ^1H NMR spectrum of $L^{t\mathrm{Bu},i\mathrm{Pr}}H$ shows overlapped and broadened peaks due to the mixture of bis(imine) and imine–enamine tautomers. At 70°C in $CDCl_3$, the spectrum is better resolved. The major component (ca. 95%) is the bis(imine) tautomer: δ 7.04–6.92 (m, 6H, *m*- and *p*-Ar), 3.26 (s, 2H, α-CH_2), 2.61 (broad m, 4H, CH(CH_3)$_2$), 1.19 (d, 12H, CH(CH_3)$_3$, $J = 8$ Hz), 1.07 (s, 18H, C(CH_3)$_3$), 1.03 (d, 12H, CH(CH_3)$_3$, $J = 8$ Hz) ppm. The minor (ca. 5%) component is assigned to the imine–enamine tautomer: δ 11.0 (s, 1H, N-*H*), 5.43 (s, 1H, α-C*H*), 3.15 (sept, 1H, CH(CH_3)$_2$). The remaining alkyl and aryl resonances from the imine–enamine tautomer overlap with the major component.

E. LITHIUM 2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)HEPTYL ($L^{t\mathrm{Bu},i\mathrm{Pr}2}$Li, THF ADDUCT)

$$L^{t\mathrm{Bu},i\mathrm{Pr}2}H + \mathrm{BuLi} \rightarrow L^{t\mathrm{Bu},i\mathrm{Pr}2}\mathrm{Li(THF)} + \mathrm{BuH}$$

Procedure

■ **Caution**. *Butyllithium is pyrophoric in air and should be handled exclusively under dry nitrogen or argon. This reaction is extremely exothermic, so n-BuLi should be added slowly. It is important to vent the reaction. This manipulation is also possible outside of the glovebox by adding n-butyllithium through a septum and allowing butane to escape through an oil bubbler.*

In a N_2 glovebox, an oven-dried (150°C) 500-mL Schlenk flask is charged with $L^{t\mathrm{Bu},i\mathrm{Pr}}H$ (24.5 g, 54.6 mmol), anhydrous THF (150 mL), and a stir bar to

give a colorless solution. The flask is kept open while a solution of *n*-butyllithium (22.5 mL, 2.5 M solution in hexanes, 56.3 mmol) is slowly added to the stirring solution, causing effervescence and a color change to dark yellow-orange. Following addition of butyllithium, the mouth of the flask is sealed with a ground glass stopper and the stopcock is left open to allow additional butane to vent.

After stirring the solution for 30 min, the flask is closed, removed from the glovebox, and the solution is heated in a 60°C oil bath for 3 h. The volatile materials are removed in vacuum, leaving a yellow residue. The flask is returned to the glovebox. The solid is freed from any excess butyllithium by briefly shaking with pentane (100 mL) and decanting the supernatant. This wash is repeated with an additional portion of pentane (100 mL), and the yellow solid is dried under vacuum to give $L^{tBu,iPr2}$Li(THF) (26.6 g). Additional product is obtained by reducing the volume of the combined pentane washes to 30 mL and cooling to −45°C. This solid is collected on an oven-dried fritted glass funnel and washed with cold pentane (10 mL, −45°C) to obtain additional $L^{tBu,iPr2}$Li(THF) (2.60 g, combined yield 92%). Purity is established by ^{1}H NMR spectroscopy.

^{1}H NMR (C_6D_6): δ 6.94–7.03 (m, 6H, Ar-*H*), 5.25 (s, 1H, α-*H*), 3.49 (sept, 4H, C*H*$(CH_3)_2$, $J = 7.0$ Hz), 2.31 (br, 4H, OCH_2CH_2), 1.38 (s, 18H, $C(CH_3)_3$), 1.37 (d, 12H, $CH(CH_3)_2$, $J = 7.0$ Hz), 1.11 (s, 12H, $CH(CH_3)_2$, $J = 7.0$ Hz), 0.92 (br, 4H, OCH_2CH_2).

Properties

Solid $L^{tBu,iPr2}$Li(THF) is air and moisture sensitive but stable indefinitely when stored under N_2. It is suitable for most further syntheses, but recrystallization is recommended to ensure complete removal of traces of butyllithium before use with metal salts that are prone to reduction, for example, copper(I) derivatives.[5]

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5. SCANDIUM TRICHLORIDE TRIS(TETRAHYDROFURAN) AND β-DIKETIMINATE-SUPPORTED SCANDIUM CHLORIDE COMPLEXES

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General Procedures

All manipulations were performed either in an inert atmosphere glovebox or on a double manifold high-vacuum line equipped with Teflon needle valves.[1] Toluene and hexanes were dried and purified using the Grubbs/Dow purification system[2] and stored in evacuated bombs. Diethyl ether and benzene-d_6 were dried and stored over sodium/benzophenone ketyl. Compounds $[L^{Me,iPr2}Li]_x$[3–5] ($L^{Me,iPr2} = [ArNC(Me)]_2CH^-$, Ar = 2,6-^{i}Pr$_2C_6H_3$) and $[L^{tBu,iPr2}Li]_x$[5] ($L^{tBu,iPr2} = [ArNC(^t Bu)]_2CH^-$, Ar = 2,6-^{i}Pr$_2C_6H_3$) were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were referenced to $SiMe_4$ through the residual solvent signals.

A. SCANDIUM TRICHLORIDE TRIS(TETRAHYDROFURAN), $ScCl_3(THF)_3$[*]

$$Sc_2O_3 + 6\,HCl + 9\,H_2O \rightarrow 2\,ScCl_3(H_2O)_6$$

$$ScCl_3(H_2O)_6 + 6\,SOCl_2 + 3\,THF \rightarrow ScCl_3(THF)_3 + 6\,SO_2 + 12\,HCl$$

Procedures

■ **Caution**. *This reaction is extremely exothermic, so the $SOCl_2$/THF solution should be added carefully.*

$ScCl_3(THF)_3$ is prepared by a modified literature procedure.[6] A 1-L round-bottomed flask equipped with a condenser is charged with Sc_2O_3 (20.3 g,

[§] The checkers converted commercially available $ScCl_3(H_2O)_6$ (Strem Chemicals) to $ScCl_3(THF)_3$ using the protocol in Ref. 6. It should be noted that the checkers did not use a swivel frit, but rather, conducted manipulations inside a glovebox using a commercially available microporous frit (medium porosity).

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0.147 mol) and 6 M HCl (300 mL). The reaction mixture is heated at reflux for 3 h during which period the mixture changes from a cloudy white suspension to a clear yellow solution. The solvent is removed by rotary evaporation to give $ScCl_3(H_2O)_6$ as a thick yellow oil. A solution of $SOCl_2$ (350 mL) in THF (250 mL) is added dropwise to the oil over 2 h, during which time a large quantity of gas (HCl and SO_2) evolves. Precipitation of a white solid, followed by a gradual change to a clear yellow solution, also occurs during this period. The reaction mixture is then heated at 86°C for 18 h, and the solvent is removed by rotary evaporation to afford an oily yellow solid. The moisture-sensitive mixture is quickly attached to a swivel-frit[1] apparatus and evacuated. Et_2O (200 mL) is added to the residue, which is then stirred for 20 min and filtered. The fine white powder is washed with Et_2O (4×50 mL) and the solvent is removed *in vacuo*. Yield: 100.8 g, 0.274 mol, 93%. IR (neat):[6] 1004 (s), 846 (s) cm^{-1}.

Properties

The product is a fine white powder that must be stored under an inert atmosphere as it rapidly absorbs moisture from air.

B. SCANDIUM 2,4-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)PENTYL DICHLORIDE TETRAHYDROFURAN, ($L^{Me,iPr2}$)$ScCl_2$(THF)

$$ScCl_3(THF)_3 + L^{Me,iPr2}Li \rightarrow (L^{Me,iPr2}Li)ScCl_2(THF) + 2\,THF + LiCl$$

A 250-mL round-bottomed flask is attached to a swivel-frit[1] assembly and charged with $[L^{Me,iPr2}Li]_x$ (5.00 g, 11.8 mmol) and $ScCl_3(THF)_3$ (5.00 g, 13.6 mmol).* Toluene (90 mL) is vacuum distilled into the evacuated flask at −78°C, and the mixture is heated with stirring at reflux for 16 h. During this period, the solution gradually changes from almost colorless to pale yellow. The reaction mixture is hot filtered to remove LiCl and excess $ScCl_3(THF)_3$, and the toluene is removed from the filtrate *in vacuo*. The residue is sonicated for 10 min in hexanes (60 mL), followed by cold (−78°C) filtration.** After exposure to vacuum for 6 h, ($L^{Me,iPr2}$)$ScCl_2$(THF) is isolated in 94% yield (6.72 g, 11.1 mmol).

Anal. Calcd. for $C_{33}H_{49}N_2Cl_2OSc$: C, 65.44; H, 8.15; N, 4.63. Found: C, 65.35; H, 8.61; N, 4.61. ^{1}H NMR (benzene-d_6): δ 7.21 (m, 6H, C_6H_3), 5.32 (s, 1H, CH), 3.56 (sp, 4H, C*H*Me_2, $J_{HH} = 6.8$ Hz), 3.48 (m, 4H, OCH_2CH_2), 1.65 (s, 6H, NCMe), 1.48

* The checkers performed the same reaction inside an N_2 filled glovebox equipped with a cold well. Similar yields were obtained as long as the glassware is oven dried and the N_2 atmosphere contains <1 ppm of O_2 and is virtually free of moisture

** The checkers performed an alternative method to sonication by vigorously stirring the mixture for 5–6 hours in 80–100 mL of hexanes. Similar yields were obtained.

(m, 4H, OCH_2CH_2), 1.39 (d, 12H, $CHMe_2$, $J_{HH} = 6.8$ Hz), 1.17 (d, 12H, $CHMe_2$, $J_{HH} = 6.8$ Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 162.3 (NCMe), 143.3 (C_{ipso}), 143.3, 126.6, 124.2 (C_6H_3), 99.8 (CH), 28.6 ($CHMe_2$), 25.0, 24.7 ($CHMe_2$), 24.4 (Me).

Properties

Complex $(L^{Me,iPr2})ScCl_2(THF)$ is an off-white solid that is soluble in most organic solvents, such as diethyl ether, THF, hexanes (slightly), toluene, and bromobenzene; however, prolonged exposure to chlorinated solvents such as dichloromethane or chloroform results in decomposition. Although $(L^{Me,iPr2})ScCl_2(THF)$ rapidly decomposes upon exposure to even trace air or moisture, samples can be stored indefinitely under an inert atmosphere.

Related Compounds

Complex $(L^{Me,iPr2})ScCl_2(THF)$ can be alkylated by reaction with lithium or potassium reagents. With LiMe, the resulting complex retains one THF molecule $(L^{Me,iPr2})ScMe_2(THF)$, but larger groups (e.g., $LiCH_2EMe_3$ (E = C, Si), KCH_2Ph) afford THF-free complexes.[7] It is also possible to remove THF directly from $(L^{Me,iPr2})ScCl_2(THF)$ via heating to 130°C under dynamic vacuum (10^{-4} Torr) for 18 h. The resultant chloride-bridged dimer, $[(L^{Me,iPr2})ScCl_2]_2$, is largely insoluble in alkane solvents, although reaction with LiMe to yield the methyl-bridged complex $[(L^{Me,iPr2})ScMe_2]_2$ proceeds in toluene.[8]

C. SCANDIUM 2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)HEPTYL DICHLORIDE, $(L^{tBu,iPr2})ScCl_2$

$$ScCl_3(THF)_3 + L^{tBu,iPr2}Li \rightarrow (L^{tBu,iPr2})ScCl_2 + 3\,THF + LiCl$$

Method A: A thick-walled round-bottomed pressure vessel (Fig.1) equipped with a Teflon valve[1] is charged with $[L^{tBu,iPr2}Li]_x$ (11.1 g, 21.9 mmol) and $ScCl_3(THF)_3$ (9.38 g, 25.7 mmol) and evacuated.* Toluene (400 mL) is condensed into the vessel, which is then sealed and heated at 110°C for 3 days. It is necessary that the mixture be constantly stirred. Quiescent mixtures generally require an additional 3–4 days. During this time, the color changes from pale to deep yellow.** The

* The checkers performed the same reaction inside an N_2 filled glovebox equipped with a heating stir plate and obtained similar yields.

** Minute quantities of water (usually from inadequately dried $ScCl_3(THF)_3$) will cause a black or dark green color during early stages of the reaction. Such colors are generally supplanted by the usual deep yellow as time progresses. If dark colors are observed during (or persist throughout) the reaction, the normal workup protocol outlined above will still give the desired product, albeit in somewhat lower yields.

Figure 1. Heavy-walled reactor used in this procedure.

reaction mixture is transferred via cannula into a 500 mL round-bottomed flask, which is attached to a swivel-frit[1] apparatus. A hot filtration is performed to remove LiCl, and excess $ScCl_3(THF)_3$, followed by removal of toluene under reduced pressure.* The bright yellow residue is sonicated for 10 min in hexanes (100 mL) and cooled to −78°C, and the slurry is filtered. The resultant yellow solid is dried under vacuum for 12 h to afford $(L^{tBu,iPr2})ScCl_2$ in 86% yield (11.7 g, 18.9 mmol).

Method B: The above method is used with the exception that the reaction mixture is heated at 180°C for approximately 30 min and $(L^{tBu,iPr2})ScCl_2$ is obtained in 68% yield.

Anal. Calcd. for $C_{35}H_{53}N_2Cl_2Sc$: C, 68.06; H, 8.65; N, 4.54. Found: C, 68.54; H, 7.98; N, 4.92. ^{1}H NMR (benzene-d_6): δ 7.05 (m, 6H, C_6H_3), 6.01 (s, 1H, CH), 3.10 (sp, 4H, C*H*Me$_2$, $J_{HH} = 6.8$ Hz), 1.43 (d, 12H, CH*Me*$_2$, $J_{HH} = 6.8$ Hz), 1.26 (d, 12H, CH*Me*$_2$, $J_{HH} = 6.8$ Hz), 1.17 (s, 18H, NCCMe$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 174.3 (N*C*CMe$_3$), 142.8 (C_{ipso}), 141.1, 127.0, 124.3 (C_6H_3), 90.8 (CH), 44.7 (*C*Me$_3$), 32.3 (C*Me*$_3$), 29.9 (*C*HMe$_2$), 26.9, 24.4 (CH*Me*$_2$).

Properties

Complex $(L^{tBu,iPr2})ScCl_2$ is a pale yellow solid that is soluble in most organic solvents, such as diethyl ether, THF, hexanes (slightly), toluene, and bromobenzene. Unlike $(L^{Me,iPr2})ScCl_2(THF)$, $(L^{tBu,iPr2})ScCl_2$ does not retain THF, although it does share a similar sensitivity toward air and moisture.

* The checkers performed the reaction inside an N_2 filled glovebox equipped with a cold well and filtered the product using an oven dried medium porosity filter frit. Similar yields were obtained.

Related Compounds

Complex ($L^{tBu,iPr2}$)$ScCl_2$ can be dialkylated using a wide array of Grignard and lithium reagents.[6] Substitution of only one chloride group can be accomplished by reaction with $LiCH_2SiMe_3$ at $-78°C$ to afford ($L^{tBu,iPr2}$)$ScCl(CH_2SiMe_3)$.[7] Alternatively, it is possible to prepare ($L^{tBu,iPr2}$)ScCl(Me) by the ligand redistribution of ($L^{tBu,iPr2}$)$ScCl_2$ and ($L^{tBu,iPr2}$)$ScMe_2$. Upon reaction with methylalumoxane (MAO) or $B(C_6F_5)_3$, ($L^{tBu,iPr2}$)$ScMe_2$ is an active ethylene polymerization catalyst.[9] If activated with MAO, complex ($L^{tBu,iPr2}$)$ScCl_2$ is also catalytically active; however, larger polydispersities and lower activity, in comparison to the dimethyl analogue, are observed.[9]

Acknowledgments

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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/Ph_2CO and distilled into an evacuated vacuum flask equipped with a gas adapter and under a positive flow of N_2 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 N_2. 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. $TiCl_3(THF)_3$ 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] C_6D_6 was degassed and dried over CaH_2 and then vacuum transferred to 4 Å molecular sieves. $L^{Me,iPr2}H$ and the salt $[L^{Me,iPr2}Li]_x$ ($L^{Me,iPr2} = [ArNC(Me)]_2CH^-$, Ar = 2,6-^{i}Pr$_2C_6H_3$) were synthesized using a slightly modified protocol (described herein).[5] $[L^{tBu,iPr2}Li]_x$ ($L^{tBu,iPr2} = [ArNC(^tBu)]_2CH^-$, Ar = 2,6-^{i}Pr$_2C_6H_3$) was synthesized using the method described herein for $[L^{Me,iPr2}Li]_x$.[6]

A. SYNTHESIS OF $(L^{Me,iPr2})TiCl_2(THF)$

$$LiL^{Me,iPr2} + TiCl_3(THF)_3 \rightarrow (L^{Me,iPr2})TiCl_2(THF) + 2\,THF + LiCl$$

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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, $TiCl_3(THF)_3$ (5.00 g, 0.014 mol), and $[L^{Me,iPr2}Li]_x$ (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 $(L^{Me,iPr2})TiCl_2(THF)$. 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 $C_{33}H_{49}N_2OCl_2Ti$: C, 65.13; H, 8.12; N, 4.60. Found: C, 65.10; H, 8.19; N, 4.60. ^{1}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). $\mu_{eff} = 2.05(12)\mu_B$ (C_6D_6, 298K, Evans' method). UV–vis (toluene (ε in $M^{-1}\,cm^{-1}$)): 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°C.

Properties

Complex $(L^{Me,iPr2})TiCl_2(THF)$ (deep green) is a close analogue of Budzelaar's nonsolvento complex $(L^{Me,iPr2})TiCl_2$ (deep red-brown).[6] Budzelaar reported that THF can be removed by repeated distillation of toluene solutions at 1 bar.[6] Although $(L^{Me,iPr2})TiCl_2(THF)$ 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 $(L^{Me,iPr2})TiCl_2(THF)$ can be alkylated to give the dimethyl derivative, $(L^{Me,iPr2})TiMe_2$. When combined with $B(C_6F_5)_3$, 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 $(L^{Me,iPr2})TiCl_2$ does not seem to impede transmetallation reactions. Likewise, THF can be readily displaced when the alkyl substituent is sterically encumbering. For example, treatment of $(L^{Me,iPr2})TiCl_2(THF)$ with 2 equiv of $LiCH_2{}^tBu$, $LiCH_2SiMe_3$, and LiNHAr (Ar = 2,6-$^iPr_2C_6H_3$) affords the four-coordinate Ti(III) products, $(L^{Me,iPr2})Ti(CH_2{}^tBu)_2$,[7] $(L^{Me,iPr2})Ti(CH_2SiMe_3)_2$,[8] and $(L^{Me,iPr2})Ti(NHAr)_2$,[9] respectively. Treatment of $(L^{Me,iPr2})TiCl_2(THF)$ with 1 equiv of $NaN(SiMe_3)_2$ provides $(L^{Me,iPr2})TiCl[N(SiMe_3)_2]$ and free THF.[10]

B. SYNTHESIS OF $(L^{tBu,iPr2})TiCl_2$

$$LiL^{tBu,iPr2} + TiCl_3(THF)_3 \rightarrow (L^{tBu,iPr2})TiCl_2 + 3\,THF + LiCl$$

Procedure

In a 350- or 500-mL thick-walled glass round-bottomed pressure vessel (CHEMGLASS) in the glovebox, $TiCl_3(THF)_3$ (1.3 g, 0.004 mol) is transferred into 30 mL of toluene, and the suspension cooled to −35°C. In a conical flask, $[L^{tBu,iPr2}Li]_x$ (1.785 g, 0.004 mol) is taken up with 30 mL of toluene. The toluene solution of $[L^{tBu,iPr2}Li]_x$ is transferred by a pipette to the suspension of $TiCl_3(THF)_3$ in toluene. During the addition of the salt, the blue color of the $TiCl_3(THF)_3$ 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 $(L^{tBu,iPr2})TiCl_2$ 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 $(L^{tBu,iPr2})Ti{=}NAr(Cl)$ (335 mg, 0.0004 mol, 12.5% yield).[11]

Anal. Calcd. for $C_{35}H_{53}N_2Cl_2Ti$: 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). $\mu_{eff} = 1.98(9)\mu_B$ (C_6D_6, 298K, Evans' method). UV–

* Sometimes it is necessary to physically separate the red crystals of $(L^{tBu,iPr2})Ti{=}NAr(Cl)$ from the intensely green microcrystals of $(L^{tBu,iPr2})TiCl_2$. 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, CaF_2): 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 ($L^{tBu,iPr2}$)$TiCl_2$ (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 Et_2O, but insoluble in pentane and hexane. Unlike ($L^{tBu,iPr2}$)$TiCl_2$(THF), ($L^{tBu,iPr2}$)$TiCl_2$ appears to be stable in CH_2Cl_2 over several hours at room temperature, but decomposition ensues after extended times.

Related Compounds

Complex ($L^{tBu,iPr2}$)$TiCl_2$ can be alkylated to the dimethyl derivative, ($L^{tBu,iPr2}$)$TiMe_2$, a precursor to the Ti(IV) complex ($L^{tBu,iPr2}$)$TiMe_2$(OTf) by AgOTf oxidation.[12] The latter complex is a convenient synthon to the phosphinidene, ($L^{tBu,iPr2}$)Ti=P[Trip](Me),[13] via the treatment with LiPH[Trip] (Trip = 2,4,6-$^{i}Pr_3C_6H_2$). Complex ($L^{tBu,iPr2}$)$TiCl_2$ can also be alkylated with 2 equiv of $LiCH_2{}^{t}Bu$ to afford ($L^{tBu,iPr2}$)Ti($CH_2{}^{t}Bu)_2$,[12] a precursor to the four-coordinate alkylidene complex ($L^{tBu,iPr2}$)Ti=$CH{}^{t}Bu$(OTf).[12] An alternative synthesis of ($L^{tBu,iPr2}$)$TiCl_2$ without formation of the imido impurity can be achieved using $TiCl_3$ instead of $TiCl_3(THF)_3$ in toluene.[12] The low yield of ($L^{tBu,iPr2}$)$TiCl_2$ (∼23%), however, coupled with the expense in using $TiCl_3$ makes this process unattractive.

C. SYNTHESIS OF ($L^{Me,iPr2}$)VCl_2

$$LiL^{tBu,iPr2} + VCl_3(THF)_3 \rightarrow (L^{Me,iPr2})VCl_2(THF) + 2\,THF + LiCl$$

$$(L^{tBu,iPr2})VCl_2(THF) \rightarrow (L^{tBu,iPr2})VCl_2 + THF$$

Procedure

The procedure for ($L^{Me,iPr2}$)VCl_2 is a slight modification of the literature method.[6] $VCl_3(THF)_3$[14] (3.00 g, 0.008 mol) is slurried in 40 mL of THF and $[L^{Me,iPr2}Li]_x$ (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 $(L^{Me,iPr2})VCl_2$. 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).

^{1}H 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). $\mu_{eff} = 2.90(1)\mu_B$ (C_6D_6, 298K, Evans' method). UV–vis (toluene (ε in $M^{-1}\,cm^{-1}$)): 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 $L^{Me,iPr2}VCl_2$ is a deep green material soluble in toluene, Et_2O, benzene, and THF. It has properties similar to $L^{Me,iPr2}TiCl_2(THF)$, being insoluble in hexane and pentane. The complex gradually decomposes in CH_2Cl_2. Complex $L^{Me,iPr2}VCl_2$ is readily oxidized by O_2 and reacts rapidly with water to afford intractable products.

Related Compounds

Complex $L^{Me,iPr2}VCl_2$ can be readily alkylated with 2 equiv of LiMe, Li^{n}Bu, and LiCH$_2$^{t}Bu to afford the corresponding bis-alkyl complexes $L^{Me,iPr2}V(R)_2$ (R = Me,[6n] Bu,[6] $CH_2{}^tBu$[15]). Complex $L^{Me,iPr2}V(Me)_2$ is not as active catalyst as the titanium analogue for the polymerization of propene and 1-hexene when activated with $B(C_6F_5)_3$.[6] However, the alkyl derivative $L^{Me,iPr2}V(CH_2{}^tBu)_2$ is an excellent precursor to both vanadium(IV) alkylidene species[15] and V(V) alkylidynes such as $(L^{Me,iPr2})V{\equiv}C^tBu(OTf)$[16] and $[(L^{Me,iPr2})V{\equiv}C^tBu(THF)][BPh_4]$.[16] The latter complexes are prepared by a stepwise one-electron oxidation, followed by alkylation with $LiCH_2SiMe_3$, and then another one-electron oxidation with AgX (X = OTf or BPh_4).[16] Complex $(L^{Me,iPr2})VCl_2$ 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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were distilled from purple Na benzophenone ketyl solutions. C_6D_6 was predried with sodium and stored under vacuum over 4 Å molecular sieves. NMR spectra were referenced to the residual protons of the solvent ($C_6D_5H = 7.15$ ppm, $CDHCl_2 = 5.32$ ppm). Molar magnetic susceptibilities were corrected for diamagnetism using Pascal constants.

Butyllithium was purchased as a 1.6 M solution in hexane from Aldrich. VCl_3 (anhydrous) and $CrCl_3$ (anhydrous) were purchased from Strem. $VCl_3(THF)_3$[1] and $CrCl_3(THF)_3$[2] were prepared according to the literature procedures. $HL^{Me,Me2}$ was prepared according to Budzelaar's method (see Section 2A).[3]

A. SYNTHESIS OF $L^{Me,Me2}VCl_2$

$$HL^{Me,Me2} + BuLi \rightarrow LiL^{Me,Me2} + BuH$$

$$LiL^{Me,Me2} + VCl_3(THF)_3 \rightarrow L^{Me,Me2}VCl_2(THF) + LiCl + 2\,THF$$

Procedure

A solution of 10.0 g (32.6 mmol) of $HL^{Me,Me2}$ in 100 mL of diethyl ether is prepared in a 250-mL Schlenk flask. The solution is cooled to −30°C and then treated with 20.42 mL (32.6 mmol) of 1.6 M *n*-butyllithium in hexane. The mixture is allowed to warm to room temperature and the yellow solution thus obtained is added to a 500-mL flask containing a red slurry of 12.18 g (32.6 mmol) of $VCl_3(THF)_3$ in 200 mL of THF. The resulting dark red-brown solution is stirred overnight at room temperature giving a dark green solution. The solution is evaporated to dryness; the residue is triturated three times with 20 mL of diethyl ether to give a green solid, discarding the ether. The residue is then extracted three times with toluene totaling ca. 200 mL, and the combined extract is filtered through Celite, rinsing with ca. 10 mL of toluene. The resultant solution is concentrated to approximately one-third of its original volume and left to crystallize at −30°C to afford red-brown crystals. Yield: 10.50 g (75%).

Anal. Calcd. for $C_{21}H_{25}N_2Cl_2V$: C, 59.03%; H, 5.90%; N, 6.49%; Cl, 16.59%. Found: C, 59.06%; H, 5.85%; N, 6.42%; Cl, 16.33%. ^1H NMR (CD_2Cl_2): δ 8.1, 7.5 (vb, 22H), −2.5 (b, 3H). IR (KBr): 3015 (w), 2918 (m), 1534 (s), 1467 (m), 1376 (m), 1323 (s), 1234 (m), 1170 (w), 1094 (w), 1020 (w), 866 (w), 772 (s), 416 (m) cm^{-1}. EI-MS *m/z* (%): 426.0 (100) [M^+], 391.1 (8.3)[M^+ − Cl]. UV–vis (toluene): λ_{max} (ε in $M^{-1}\,cm^{-1}$) 415 (1773), 561 (409), 758 nm (460). $\mu_{eff} = 3.1$ (1)μ_B (294K). mp 268–270°C.

Properties

$L^{Me,Me2}VCl_2$ is soluble in THF, toluene, and dichloromethane but essentially insoluble in ether and pentane. In the β-diketiminato complexes $LVCl_2$, the nature of the *N*-aryl substituents determines the affinity of the complex for THF. For instance, the parent *N*-phenyl-substituted β-diketiminate is isolated as a bis(THF) solvate $L^{Me,Me2}VCl_2(THF)_2$,[4] whereas $L^{Me,Me2}VCl_2$, $L^{Me,Me3}VCl_2$,[3] and $L^{Me,iPr2}VCl_2$[3] may be isolated THF-free. As outlined in the entry for $L^{Me,iPr2}VCl_2$ (described herein), β-diketiminato vanadium dihalide complexes have been explored as precatalysts for α-olefin polymerization and may be alkylated to give dialkyls LVR_2.

B. SYNTHESIS OF $L^{Me,Me2}CrCl_2(THF)_2$

$$HL^{Me,Me2} + BuLi \rightarrow LiL^{Me,Me2} + BuH$$

$$LiL^{Me,Me2} + CrCl_3(THF)_3 \rightarrow L^{Me,Me2}CrCl_2(THF) + LiCl + 2\,THF$$

Procedure

$HL^{Me,Me2}$ (1.0 g, 3.27 mmol) is dissolved in 50 mL of THF and the solution was cooled to −30°C. *n*-Butyllithium (2.0 mL of 1.6 M in hexanes, 3.27 mmol) is slowly added to this solution, and this mixture is stirred for another 30 min and allowed to warm to room temperature. The resultant solution of $LiL^{Me,Me2}$ is then slowly added over 3 h at room temperature to a slurry of $CrCl_3(THF)_3$ (1.224 g, 3.27 mmol) in 150 mL of THF. The color of the solution changes from purple to red-brown. After stirring the solution at room temperature overnight, the THF is removed and the solid is extracted with three 30-mL portions of toluene. The solution is then filtered through Celite, rinsing with ca. 20 mL toluene. The toluene is then removed *in vacuo* and the solid is dissolved in ca. 40 mL THF and refiltered through Celite. The resulting THF solution is concentrated to 20 mL *in vacuo* and allowed to crystallize overnight at −30°C. A dark red microcrystalline powder is isolated by filtration. After washing with ca. 5 mL cold THF and drying under vacuum, 1.45 g (76%) of the product is isolated.

Anal. Calcd. for $C_{29}H_{41}N_2O_2CrCl_2$: C, 60.84%; H, 7.22%; N, 4.89%. Found: C, 60.71%; H, 7.03%; N, 5.38%. ^{1}H NMR (C_6D_6): δ 40.7 (vb, 6H), 13.3 (vb, 4H), 9.4 (vb, 4H), 3.8 (b, 8H), 1.4 (b, 8H), −4.2 (vb, 2H) ppm. IR (KBr): 3050 (w), 3014 (m), 2965 (s), 2925 (s), 2869 (s), 1520 (vs), 1459 (vs), 1448 (vs), 1377 (vs), 1259 (m), 1242 (m), 1177 (s), 1096 (m), 1015 (m), 1005 (m), 879 (s), 850 (s), 762 (s) cm^{-1}. UV–vis (Et_2O): λ_{max} (ε in $M^{-1}\,cm^{-1}$) 656 (224), 506 (815), 476 (945),

407 (5300). $\mu_{eff} = 4.0(1)\mu_B$ (294K). mp 208–209°C. Mass spectrum *m/z* (%): 427 (4.14) [M^+ − 2THF], 392 (17.3) [M^+ − Cl, 2THF], 356 (17.6) [M^+ − 2Cl, 2THF].

Properties

$L^{Me,Me2}CrCl_2(THF)_2$ is soluble in THF and partially soluble in toluene, benzene, and ether. The solution is red-brown in THF, toluene, and benzene, but changes to a yellow color in ether.

Related Compounds

β-Diketiminato chromium halide and alkyl complexes have been explored as precatalysts for alkene polymerization.[4–7] For instance, $L^{Me,Me2}CrCl_2(THF)_2$ reacts with alkyllithium reagents to give $L^{Me,Me2}CrMe_2(THF)$ and $L^{Me,Me2}Cr(CH_2SiMe_3)_2$.[7] These dialkyls may be converted to alkyl cations such as $[L^{Me,iPr2}Cr(CH_2SiMe_3)(OEt_2)]^+$ that serves as a living ethylene polymerization catalyst.[7] In addition, hydrogenation of $L^{Me,Me2}Cr(CH_2SiMe_3)_2$ produces the stable alkyl hydride complex $[L^{Me,Me2}Cr]_2(\mu\text{-}CH_2SiMe_3)(\mu\text{-}H)$.[8] The bulkier $L^{Me,iPr2}$ ligand has been used to prepare the highly reactive synthons to the two-coordinate $L^{Me,iPr2}Cr$ fragment $[L^{Me,iPr2}Cr]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$[9] and $[L^{Me,iPr2}Cr]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-toluene})$,[10] which participate in a variety of interesting reactions such as oxidation by O_2 to give the d^1 dioxo complex $L^{Me,iPr2}Cr(O)_2$.

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8. β-DIKETIMINATE-SUPPORTED MANGANESE AND ZINC COMPLEXES

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A two-step procedure is employed based on the literature procedure for $L^{Me,iPr2}MnI(THF)$, which first generates the potassium salt $KL^{Me,iPr2}$ prior to its reaction with MnI_2.[1] The preparation of the potassium salt of the β-diketimine $HL^{Me,iPr2}$ was first reported by Mair and coworkers from $HL^{Me,iPr2}$ and $KN(SiMe_3)_2$ in relatively low yield (27%).[2] Winter and coworkers have reported a related THF adduct from KH.[3] Here, the same reagents in diethyl ether give a base-free potassium salt that was used to introduce $L^{Me,iPr2}$ into manganese and zinc complexes.

General Procedures

All reactions were performed using standard Schlenk and drybox techniques. All the solvents except dichloromethane (P_4O_{10}) were distilled from sodium under dry nitrogen. 12 M HCl, MnI_2, ZnI_2, and BuLi in hexane were purchased from Aldrich.

A. $L^{Me,iPr2}MnI(THF)$

$$HL^{Me,iPr2} + KH \rightarrow KL^{Me,iPr2} + H_2$$

$$KL^{Me,iPr2} + MnI_2 + THF \rightarrow L^{Me,iPr2}MnI(THF) + KI$$

■ **Caution**. *Air-free procedures are required for use of potassium hydride, which can explosively generate hydrogen gas upon uncontrolled hydrolysis. Hydrogen gas is generated in the procedure and should not be performed in a sealed flask.*

Step 1: A suspension of KH (0.18 g, 4.5 mmol) and $HL^{Me,iPr2}$ (1.67 g, 4.00 mmol) in diethyl ether (50 mL) is stirred at room temperature for 3 days. After filtration, the light yellow filtrate is concentrated to ca. 10 mL and stored at −26°C for 24 h to afford crystalline solid. Yield: 1.59 g (87%).

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^{1}H NMR (C_6D_6): δ 7.08 (d, $J = 8.0$ Hz, 4H, Ar*H*), 6.96 (t, $J = 8.0$ Hz, 2H, Ar*H*), 4.74 (s, 1H, C*H*), 3.29 (sept, $J = 7.2$ Hz, 4H, C*H*$(CH_3)_2$), 3.29 (sept, $J = 7.2$ Hz, 4H, C*H*$(CH_3)_2$), 1.81 (s, 6H, CH_3), 1.19 (d, $J = 6.8$ Hz, 12H, CH(CH_3)$_2$), 1.00 (d, $J = 6.8$ Hz, 12H, CH(CH_3)$_2$).

Step 2: A solution of $KL^{Me,iPr2}$ (0.91 g, 2.0 mmol) in THF (10 mL) is added to a suspension of MnI_2 (0.62 g, 2.0 mmol) in THF (35 mL) at −78°C. The mixture is allowed to warm to room temperature and stirred for 14 h. The precipitate is removed by filtration. The yellow filtrate is concentrated to ca. 5 mL and stored at −26°C for 24 h to give yellow crystals. Yield: 1.17 g (87%).*

Anal. Calcd. for $C_{33}H_{49}IMnN_2O$ (670.84): C, 59.03; H, 7.30; N, 4.17. Found: C, 58.95; H, 7.24; N, 4.16. EI-MS: *m/z* (%) 599 (100) $[LMnI]^+$. UV–vis (THF, nm ($cm^{-1}\,M^{-1}$)) 439 (93), 461 (64). mp 379–381°C. IR (KBr, Nujol mull, cm^{-1}): 1624 (w), 1552 (w), 1520 (m), 1314 (m), 1262 (m), 1174 (w), 1100 (w), 1024 (m), 935 (w), 870 (w), 852 (w), 794 (m), 757 (w), 721 (w), 600 (vw), 524 (w), 468 (vw).

Properties

$L^{Me,iPr2}MnI(THF)$ is soluble in THF and toluene and sparingly soluble in Et_2O and *n*-pentane. The bound THF ligand may be readily removed by refluxing in toluene (see below) and may be displaced by other Lewis bases such as a *N*-heterocyclic carbene ligand.[1]

B. THE THF-FREE DIMER $(L^{Me,iPr2}MnI)_2$

$$L^{Me,iPr2}MnI(THF) \rightarrow L^{Me,iPr2}MnI + THF$$

A solution of $L^{Me,iPr2}MnI(THF)$ (1.34 g, 2 mmol) in toluene (40 mL) is refluxed for 0.5 h. All volatiles are removed *in vacuo* and bright yellow microcrystals are obtained. Yield: 1.15 g (96%).

Anal. Calcd. for $C_{58}H_{82}I_2Mn_2N_4$ (1197.68): C, 58.11; H, 6.84; N, 4.67. Found: C, 58.34; H, 6.92; N, 4.85. EI-MS: *m/z* 599 (100) $[LMnI]^+$. IR (KBr, Nujol mull, cm^{-1}): 1657 (w), 1625 (w), 1552 (w), 1262 (m), 1097 (m), 1023 (m), 875 (w), 800 (m), 722 (w), 659 (w), 536 (w), 468 (w) cm^{-1}. mp 271–273°C (dec).

Properties and Related Compounds

The product is soluble in toluene and insoluble in Et_2O and pentane. This dimeric β-diketiminato manganese iodide complex as well as its chloride-bridged relative

* The checkers obtained yellow crystals from one crystallization with a yield of 53%.

$(L^{Me,iPr2}MnCl)_2$[4] can be alkylated with MeLi and arylated with PhLi to give the dinuclear $(L^{Me,iPr2}Mn)_2(\mu\text{-}Me)_2$ or the three-coordinate $L^{Me,iPr2}MnPh$.[4,5]. A related trinuclear species $L^{Me,iPr2}Mn(\mu\text{-}Cl)_2Mn(\mu\text{-}Cl)_2MnL^{Me,iPr2}$ undergoes related reaction with allylmagnesium chloride to yield the four-coordinate $L^{Me,iPr2}Mn(CH_2CH{=}CH_2)(THF)$ and with phenylethynyl lithium to give $(L^{Me,iPr2}Mn)_2(\mu\text{-}CCPh)_2$.[6] Reduction of $(L^{Me,iPr2}MnI)_2$ yields the highly reactive ferromagnetically coupled dimer $(L^{Me,iPr2}Mn)_2$ with a Mn–Mn distance of 2.721(1) Å.[7,8] This novel Mn^I–Mn^I dimer reacts with dioxygen to form the bis(μ-oxo) species $(L^{Me,iPr2}Mn)_2(\mu\text{-}O)_2$.[7]

C. $L^{Me,iPr2}ZnCl_2Li(OEt_2)_2$

$$HL^{Me,iPr2} + BuLi + Et_2O \rightarrow LiL^{Me,iPr2}(Et_2O) + BuH$$

$$LiL^{Me,iPr2}(Et_2O) + ZnCl_2 + Et_2O \rightarrow L^{Me,iPr2}ZnCl_2Li(Et_2O) + LiCl$$

■ **Caution**. *Butyllithium is pyrophoric in air and should be handled exclusively under dry nitrogen or argon.*

This two-step procedure uses the ether adduct of the lithium salt $L^{Me,iPr2}Li(OEt_2)$[9,10] in the reaction with $ZnCl_2$ to give the "ate" complex $L^{Me,iPr2}ZnCl_2Li(OEt_2)_2$.[12]

Step 1: $HL^{Me,iPr2}$ (8.00 g, 19.1 mmol) is dissolved in rapidly stirred Et_2O (70 mL), and the resulting solution is treated with 12.0 mL of a 1.6 M *n*-BuLi solution in hexane. Upon completion of the addition, the solution is allowed to warm to room temperature and stirred for 12 h. The solution is concentrated to approximately 20 mL under reduced pressure until the product precipitates, which redissolves with mild heating. Cooling for 24 h at ca. −20°C affords $L^{Me,iPr2}Li(OEt_2)$ as colorless crystals. mp 138–139°C. Yields range between 75% and 90%.

^{1}H NMR ($CDCl_3$): δ 7.02 (m, 6H, Ar*H*), 4.62 (s, 1H, C*H*), 3.13 (sept, $J = 6.8$ Hz, 4H, C*H*$(CH_3)_2$), 2.92 (quad, $J = 6.8$ Hz, 4H, ether-CH_2), 1.72 (s, 6H, CH_3), 1.21 (d, $J = 7.2$ Hz, 12H, CH(CH_3)$_2$), 1.07 (d, $J = 7.2$ Hz, 12H, CH(CH_3)$_2$), 0.61 (t, $J = 6.8$ Hz, 6H, ether-CH_3). ^{7}Li NMR (C_6D_6): δ 1.61.

Step 2: To a suspension of $ZnCl_2$ (395 mg, 2.90 mmol) in Et_2O (10 mL) is slowly added a solution of $L^{Me,iPr2}LiOEt_2$ (1.44 g. 2.90 mmol) in Et_2O (10 mL) at −35°C. The mixture is allowed to warm to room temperature and then stirred for additional 3 h and then filtered. The solution is concentrated to 10 mL and cooled overnight at −35°C to yield colorless crystals. Yield: 1.36 g (67%).*

* The checkers note that closely related procedures have been reported to give the halide-free monomer $L^{Me,iPr2}ZnCl$, though two attempts at checking gave only the LiCl adduct $L^{Me,iPr2}ZnCl_2Li(OEt_2)_2$ in comparable yields to that described above.

Anal. Calcd. for $C_{37}H_{61}Cl_2LiN_2O_2Zn$ (709.15): C, 62.67; H, 8.67; N, 3.95. Found: C, 62.46; H, 8.81; N, 4.19. ^{1}H NMR ($CDCl_3$): δ 7.17 (m, 6H, Ar*H*), 5.10 (s, 1H, C*H*), 3.47 (quad, $J = 7.2$ Hz, 8H, ether-CH_2), 2.98 (sept, $J = 6.8$ Hz, 4H, C*H*(CH_3)$_2$), 1.81 (s, 6H, CH_3), 1.25 (d, $J = 6.8$ Hz, 12H, CH(CH_3)$_2$), 1.20 (t, $J = 7.2$ Hz, 12H, ether-CH_3), 1.16 (d, $J = 6.8$ Hz, 12H, CH(CH_3)$_2$); ^{13}C NMR (C_6D_6): δ 170.1, 142.1, 141.5, 126.3, 123.6, 95.3, 65.8, 28.2, 24.2, 23.6, 23.2, 15.2.

Properties

$L^{Me,iPr2}Li(OEt_2)$ is readily soluble in ether, THF, and hydrocarbons as well as halogenated solvents such as CH_2Cl_2. $L^{Me,iPr2}ZnCl_2Li(OEt_2)_2$ is soluble in THF, ether, and aromatic solvents, sparingly soluble in CH_2Cl_2, and essentially insoluble in pentane. The Et_2O coordinated to Li is somewhat labile. Titration of the solid with other solvents such as $CDCl_3$ results in a gradual loss of Et_2O. This β-diketiminate has been reported to be isolated as the three-coordinate complex $L^{Me,iPr2}ZnCl$ via careful crystallization.[11,12]

Related Compounds

Both $L^{Me,iPr2}ZnCl$ and $L^{Me,iPr2}ZnCl_2Li(OEt_2)_2$ serve as platforms for subsequent modification. Three-coordinate alkyl complexes $L^{Me,iPr2}Zn$-R may be formed by alkylation with alkyllithium reagents. Monoethyl complexes may also be prepared by use of $ZnEt_2$ with the free ligand HL.[13,14] Reaction of $L^{Me,Me2}ZnMe$ with Me_3SnF gives the fluoride-bridged dimer $(L^{Me,Me2}Zn)_2(\mu\text{-}F)_2$, which can be converted to the hydride-bridged dimer $(L^{Me,Me2}Zn)_2(\mu\text{-}H)_2$ upon reaction with Et_3SiH.[15] The lithium halide-bridged adducts $LZnX_2Li(OEt_2)$ are also synthetically useful in the preparation of thiolate-bridged dimers $(L^{Me,Me2}Zn)_2(\mu\text{-}SR)_2$.[16] β-Diketiminato zinc complexes have been investigated as catalysts for epoxide/CO_2 copolymerization[13,14,17–19] and ring-opening lactide polymerization.[20–23] The related $L^{Me,iPr2}ZnI_2Li(OEt_2)_2$ can be reduced by potassium metal to give the unusual Zn^I–Zn^I dimer $(L^{Me,iPr2}Zn)_2$ with a Zn−Zn bond distance of 2.3586(7) Å.[24]

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9. IRON 2,4-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)PENTYL CHLORIDE ($L^{Me,iPr2}FeCl$)

Submitted by BRYAN D. STUBBERT[*] and PATRICK L. HOLLAND[*]
Checked by DEBASHIS ADHIKARI[†] and DANIEL J. MINDIOLA[†]

General Techniques

All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in a glovebox maintained at or below 1 ppm of O_2 and

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Figure 1. Reaction flask used in this procedure.

H_2O. Glassware was dried at 150°C overnight. Pentane and toluene were purified by passing through activated alumina and Q-5 columns from Glass Contour Co. Deuterated THF was first dried over CaH_2, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Celite was dried overnight at 200°C under vacuum. The iron starting material $FeCl_2(THF)_{1.5}$ was synthesized by the method of Kern,[1] by heating anhydrous $FeCl_2$[2] to reflux overnight in THF and subsequently removing volatile materials *in vacuo*.* $[L^{Me,iPr2}Li]_x$ was prepared using the method described herein.

$$FeCl_2(THF)_{1.5} + [L^{Me,iPr2}Li]_x \rightarrow L^{Me,iPr2}Fe(\mu\text{-}Cl)_2FeL^{Me,iPr2} + LiCl$$

Procedure

In a glovebox, a 100-mL thick-walled flask with a resealable Teflon valve (Fig. 1) is charged with a magnetic stir bar and $[L^{Me,iPr2}Li]_x$ (2.38 g, 5.60 mmol). Toluene (40 mL) is added to dissolve the solid, forming a pale yellow solution, and while stirring at 25°C, solid $FeCl_2(THF)_{1.5}$ (1.32 g, 5.72 mmol) is added to the solution in several portions. An immediate color change from pale yellow to light red is observed during the $FeCl_2(THF)_{1.5}$ addition. The flask is then sealed and moved from the glovebox to the Schlenk line where it is heated in an oil bath, gradually raised from 25 to 100°C. After 18 h, the red-orange suspension is allowed to cool and is evaporated to dryness. The oil bath is then heated to 40°C, and the orange solid is

* The checkers prepared $FeCl_2(THF)_{1.5}$ by Sohxlet extraction of anhydrous $FeCl_2$ with THF over the course of 2 weeks.

dried *in vacuo* for an additional 30–60 min to ensure complete removal of THF. The flask is then returned to the glovebox, and the solids are washed with pentane (3×10 mL) to remove unreacted $LiL^{Me,iPr}$. The orange powder obtained after drying this material *in vacuo*, $[L^{Me,iPr}FeCl]_2 \cdot 2LiCl$, is normally recovered in $\geq 95\%$ yield and is commonly used in later syntheses without further purification (because later steps typically involve pentane extractions, the LiCl is filtered off at that stage). *Note*: Contact of $[L^{Me,iPr}FeCl]_2 \cdot 2LiCl$ with THF or Et_2O results in the formation of the etherate complexes $L^{Me,iPr}FeCl_2Li(THF)_2$ and $L^{Me,iPr}FeCl_2Li(Et_2O)_2$, which may not be suitable for some later syntheses. The etherate complexes can be desolvated, regenerating $[L^{Me,iPr}FeCl]_2 \cdot 2LiCl$, by dissolving the yellow solids in toluene and heating at 100°C for 12 h and evacuating to dryness.

The by-product LiCl can be removed by Soxhlet extraction. The insoluble orange powder obtained above is slurried in pentane (3×20 mL) and collected by gravity filtration in a glass thimble consisting of a coarse glass frit with a 0.5-cm pad of predried Celite. The thimble containing the washed orange solid is then placed in the Soxhlet extractor fitted with a 200-mL round-bottomed flask containing a large magnetic stir bar and toluene (150 mL) on the lower end and a condenser with a resealable Teflon valve. (*Note*: It is beneficial to measure the antechamber and assembled Soxhlet extraction apparatus prior to loading in the glovebox, because the assembled apparatus may be quite long. If the assembled apparatus is too long, the condenser can be attached to the flask outside the box with a vigorous flow of N_2). Under a N_2 atmosphere on the Schlenk line, the apparatus is heated in a 140°C oil bath. Most of the LiCl-free material is extracted into hot toluene in 3–4 h; however, completely colorless extracts are not observed until >12 h. After 24 h, the red suspension is evacuated to dryness, leaving a solid orange residue. In the glovebox, the residue is washed with pentane (3×10 mL) and dried *in vacuo*, affording LiCl-free $[L^{Me,iPr}FeCl]_2$ in 82% yield (2.34 g, 2.30 mmol). Purity is determined by ^{1}H NMR spectroscopy.

^{1}H NMR (THF-d_8): δ 17.6 (4H), 4.9 (12H), 3.3 (4H), −6.8 (12H), −38.3 (2H), −67.9 (6H), −78.9 (1H).

Properties

$[L^{Me,iPr2}FeCl]_2$ is insoluble in alkane solvents, poorly soluble in Et_2O and toluene, and soluble in THF. It reacts slowly with CH_2Cl_2. Additional characterization in noncoordinating solvents is limited by low solubility. It is sensitive to air and moisture.

Related Compounds

This compound is a precursor to a wide variety of three- and four-coordinate iron(II) complexes, including alkyl, aryl, hydride, sulfido, amido, and fluoride

complexes.[3] Abstraction of chloride with borane[4] gives cationic iron(II) complexes with weak coordination of solvent or counterion. Reduction to an iron(I) dinitrogen complex provides a pathway to iron(I) alkyne, alkene, carbonyl, isocyanide, arene, and phosphine complexes, as well as a reactive iron(III) imido complex.[3]

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10. IRON 2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)HEPTYL CHLORIDE ($L^{tBu,iPr2}FeCl$)

Submitted by KAREN P. CHIANG[*] and PATRICK L. HOLLAND[*]
Checked by DEBASHIS ADHIKARI[†] and DANIEL J. MINDIOLA[†]

General Techniques

All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in a glovebox maintained at or below 1 ppm of O_2 and H_2O. Glassware was dried at 150°C overnight. NMR spectra are referenced to residual C_6D_5H at 7.16 ppm. Pentane and toluene were purified by passing through activated alumina and Q-5 columns from Glass Contour Co. Deuterated benzene was first dried over CaH_2, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Celite was dried overnight at 200°C under vacuum. The iron starting material $FeCl_2(THF)_{1.5}$ was synthesized by the method of Kern,[1] by heating a THF slurry of anhydrous $FeCl_2$[2]

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at reflux overnight and subsequently removing volatile materials *in vacuo*.*

$$KL^{tBu,iPr2} + FeCl_2(THF)_{1.5} \rightarrow L^{tBu,iPr2}FeCl$$

Procedure

Solid $KL^{tBu,iPr2}$ (0.50 g, 0.919 mmol), $FeCl_2(THF)_{1.5}$ (0.2022 g, 0.919 mmol), and toluene (25 mL) are added to a 150-mL Schlenk flask (see Fig. 1 in Section 9). The charged flask is removed from the glovebox, and the reaction mixture is heated in an oil bath at 100°C for 18 h during which time it turns very dark red in color. The solution is then cooled to room temperature, returned to the glovebox, and filtered through Celite. The filtrate is concentrated to 8 mL, whereupon some red solid begins to form. The sample is warmed to ca. 40°C to redissolve the solid, and slowly cooled to −35°C overnight to afford dark red crystals. The supernatant is decanted and the red solid is washed with 2 mL of pentane to remove trace $L^{tBu,iPr2}H$, leaving $L^{tBu,iPr2}FeCl$ (0.5306 g, 97%). The overall purity is best gauged by UV–vis spectroscopy.

UV–vis (toluene): 559 nm (626 M^{-1} cm^{-1}). ^1H NMR (C_6D_6, 500 MHz): δ 104 (s, 1H, α-H), 42 (s, 18H, ^{t}Bu), 2.6 (s, 4H, *m*-aryl), −27 (s, 12H, ^{i}Pr methyl), −108 (s, 4H, ^{i}Pr methine), −111 (s, 12H, ^{i}Pr methyl), −115 (s, 2H, *p*-aryl). Trace water results in a small amount of $L^{tBu,iPr}H$, which is observed as white solid and appears in the ^1H NMR spectrum at 1–2 ppm.

Properties

$L^{tBu,iPr}FeCl$ is very soluble in THF and toluene, somewhat soluble in diethyl ether, and poorly soluble in pentane. It decomposes in CH_2Cl_2 in a few hours. It is extremely sensitive to moisture and air. Coordinating solvents such as THF and acetonitrile form yellow 1 : 1 adducts.

Related Compounds

This compound is a precursor to a wide variety of three- and four-coordinate iron (II) complexes, including alkyl, aryl, hydride, oxo, hydroxo, amido, and fluoride complexes.[3,4] Reduction to an iron(I) dinitrogen complex provides a pathway to iron(I) complexes.[4]

Acknowledgments

This work was supported by the National Science Foundation (CHE-0112658) and the Alfred P. Sloan Foundation (Research Fellowship).

* The checkers prepared $FeCl_2(THF)_{1.5}$ through a Soxhlet extraction of anhydrous $FeCl_2$ with THF over 2 weeks.

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11. COBALT 2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)HEPTYL CHLORIDE ($L^{tBu,iPr2}CoCl$)

Submitted by KEYING DING,[*] THOMAS R. DUGAN,[*] and PATRICK L. HOLLAND[*]
Checked by DEBASHIS ADHIKARI[†] and DANIEL J. MINDIOLA[†]

The following reaction was originally conducted in THF solution using $LiL^{tBu,iPr2}$, in which case the product is $L^{tBu,iPr2}Co(\mu\text{-}Cl)_2Li(ether)_2$, which is four-coordinate at cobalt and has mixed coordination of Et_2O and THF at the lithium ion.[1] By using $TlL^{tBu,iPr2}$ instead as the diketiminate source, the authors obtained the three-coordinate $L^{tBu,iPr2}CoCl$. Here, the lithium salt is used but in hot toluene, the LiCl precipitates, and the three-coordinate monomer is obtained. This method eliminates the need for using the thallium salt.

General Procedures

Manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in a glovebox maintained at or below 1 ppm of O_2 and H_2O. Glassware was dried at 150°C overnight. NMR spectra are referenced to residual C_6D_5H at 7.16 ppm. Pentane and toluene were purified by passing through activated alumina and Q-5 columns from Glass Contour Co. Deuterated benzene was first dried over CaH_2, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Celite was dried overnight at 200°C under vacuum. The cobalt starting material $CoCl_2(THF)_{1.5}$ was synthesized by the method of Kern,[2] by heating anhydrous $CoCl_2$ (Sigma) to reflux overnight in THF and subsequently removing volatile materials *in vacuo*.

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$$L^{tBu,iPr2}Li(THF) + CoCl_2(THF)_{1.5} \rightarrow L^{tBu,iPr2}CoCl + LiCl$$

Procedure

In the glovebox, blue $CoCl_2(THF)_{1.5}$[1] (705 mg, 2.96 mmol) is added to a 500-mL resealable flask (see Fig. 1 in Section 9) containing a pale yellow solution of $L^{tBu,iPr2}$Li(THF) (1.72 g, 2.96 mmol) in toluene (100 mL) and a stir bar, causing a slow color change to blue-brown. The flask is sealed, taken out of the glovebox, and heated in an oil bath, which is gradually heated to 100°C. After stirring for 18 h, the flask is returned to the glovebox, and the brown mixture is filtered through 1 cm of Celite.* The filtrate is concentrated to 40 mL and cooled at −35°C for 1 day to give brown-purple crystals. The supernatant solution is removed and the crystals are dried under vacuum to give 1.23 g of a brown-purple solid. Reducing the volume of the supernatant solution to 18 mL, adding 10 mL of pentane, and cooling to −35°C yields 0.25 g of additional crystals. The combined solids are washed with pentane to remove traces of $L^{tBu,iPr2}$Li(THF) and $L^{tBu,iPr}$H. Combined yield: 84%.

^{1}H NMR (400 MHz, C_6D_6): δ 59.9 (4H, *m*-aryl), 27.2 (18H, ^{t}Bu), −2.7 (12H, ^{i}Pr methyl), −45.4 (2H, *p*-aryl), −56.5 (4H, ^{i}Pr methine), −83.0 (12H, ^{i}Pr methyl), −89.3 (1H, α-*H*).

Properties

Purity is evaluated using ^{1}H NMR spectroscopy. Solid samples of $L^{tBu,iPr2}$CoCl are brown-purple in color. $L^{tBu,iPr2}$CoCl is soluble in tetrahydrofuran, CH_2Cl_2, and toluene, somewhat soluble in diethyl ether, and poorly soluble in pentane. The compound is extremely sensitive to moisture and air. $L^{tBu,iPr2}$CoCl has been used as a precursor to a three-coordinate cobalt(II) methyl complex.[1]

* In more recent work after submission and independent checking, we have seen that some batches of $CoCl_2(THF)_{1.5}$ give incomplete conversion to $L^{tBu,iPr}$CoCl (evident from significant amounts of light blue material in the crude product). If this is a problem, a variant can be used as follows. A mixture of $CoCl_2$ (749 mg, 5.77 mmol, Strem) and THF (200 mL) is heated to reflux overnight under N_2 to give a blue solution, and concentrated to 100 mL under vacuum. A pale yellow solution of $L^{tBu,iPr}$Li(THF) (2.90 g, 5.71 mmol) in THF (70 mL) is added, and the green mixture is heated at 70 °C for 4 h. The olive-green mixture is stirred overnight at room temperature. Volatile materials are removed under reduced pressure, giving a brown residue consisting primarily of $L^{tBu,iPr2}Co(\mu\text{-}Cl)_2Li(THF)_2$. Toluene (125 mL) is added, and the mixture is heated at 100 °C overnight (this step dissociates THF and precipitates the LiCl). After cooling to room temperature, volatile materials are again removed to give a dark purple residue. The solid is dried under dynamic vacuum at 100 °C for 3 hours to remove all traces of THF. The resulting solid is extracted with toluene (150 mL), and the mixture is filtered through a pad of Celite to remove a gray solid. Volatile materials are removed from the purple filtrate to give a semi-crystalline purple solid. This solid is washed with cold pentane (60 mL, precooled to −40 °C) and collected to give 1.898 g (55.8% yield) of $L^{tBu,iPr}$CoCl as a fine purple powder.

Acknowledgments

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12. β-DIKETIMINATE-SUPPORTED NICKEL(II) AND NICKEL(I) COMPLEXES OF $L^{ME,ME3}$ ($L^{ME,ME3}$=2,4-BIS-(MESITYLIMIDO)PENTYL)

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Checked by SARA S. ROCKS† and PATRICK L. HOLLAND†

General Procedures

All experiments were carried out in a dry nitrogen atmosphere using a glovebox and/or standard Schlenk techniques. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passing through activated alumina columns.[1] Pentane was first washed with concentrated HNO_3/H_2SO_4 to remove olefins, stored over $CaCl_2$, sparged with nitrogen, and then dried by passing through activated alumina columns.[1] Dry toluene was stored over activated 4 Å molecular sieves. Deuterated solvents were sparged with nitrogen, dried over activated 4 Å molecular sieves, and stored under nitrogen.

Thallous acetate and 2,4-lutidine were purchased from Acros. Anhydrous nickel(II) iodide was purchased from Strem. These reagents were used as received.

A. $L^{Me,Me3}$NiI(2,4-LUTIDINE)

$$TlL^{Me,Me3} + NiI_2 + 2,4\text{-}Me_2C_5H_3N \rightarrow L^{Me,Me3}NiI(2,4\text{-}Me_2C_5H_3N) + TlI$$

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Procedure

This synthesis is based on a reported procedure.[2] A sample of $TlL^{Me,Me3}$ (3.00 g, 5.58 mmol) in 100 mL THF is added to a stirring solution of anhydrous NiI_2 (1.74 g, 5.58 mmol) in 60 mL THF containing 3 equiv of 2,4-lutidine (1.95 mL, 16.74 mmol), and the resulting heterogeneous solution retains the dark green/black color of the NiI_2. The slurry is stirred overnight. The yellow precipitate of TlI is removed by filtering through Celite, and the filtrate is concentrated to 50 mL and cooled at −35°C overnight. The mother liquor is removed, and the residue is washed with a few milliliters of cold pentane to yield 1.922 g of green/black crystals. The volume of the mother liquor is reduced to 15 mL and cooled again to yield a second crop of crystals (0.698 g) with a combined yield of 75%.* The crystals can be crushed into a fine powder and dried *in vacuo* to give a THF-free sample.

Anal. Calcd. for $C_{30}H_{38}N_3INi$: C, 57.55; H, 6.07; N, 6.71. Found: C, 57.82; H, 6.04; N, 6.65. ^1H NMR (C_6D_6, 400 MHz, 25°C): δ 93.5 (s, 1, 2,4-lut-*ArH*), 47.5 (s, 6, Ar-*p-Me*), 34.8 (s, 12, Ar-*o-Me*$_2$), 32.7 (s, 4, *m*-Ar-*H*), −4.2 (br s, 3, 2,4-lut-*Me*), −11.3 (br s, 3, 2,4-lut-*Me*), −46.6 (s, 6, backbone-*Me*), −118.1 (s, 1, 2,4-lut-*ArH*). The backbone-*H* and one 2,4-lut-*ArH* cannot be observed in the ^1H NMR spectrum. $\mu_{eff} = 2.38$ B.M. (C_6D_6 solution). UV–vis (CH_2Cl_2 ($M^{-1}\,cm^{-1}$)): 527 (562) and 676 (507) nm.

Properties

$L^{Me,Me3}$NiI(2,4-lutidine) is very soluble in CH_2Cl_2 and THF, soluble in toluene, and much less soluble in pentane or diethyl ether. In the absence of a neutral donor ligand, β-diketiminato(II) nickel halide species have a strong tendency to dimerize through bridging halogen groups. For instance, the tetrahedral bridged dimers $(L^{Me,Me2}Ni)_2(\mu\text{-}Cl)_2$[3] and $(L^{Me,iPr2}Ni)_2(\mu\text{-}Cl)_2$[4] have been structurally characterized.

Related Compounds

β-Diketiminato monohalide-lutidine species have been used in the synthesis of monoalkyl complexes with Grignard reagents to give [(β-diketiminate)Ni(R)(2,4-lutidine)] (R = CH_2CH_3 and $CH_2CH_2CH_3$).[3] These square planar alkyl complexes dissociate 2,4-lutidine to give the crystallographically characterized β-agostic complexes with the formula $L^{Me,Me2}$NiR, which are models for intermediates in Ni-catalyzed polymerization of alkenes.[5]

B. $L^{Me,Me3}$Ni(2,4-LUTIDINE)

$$TlL^{Me,Me3} + NiI_2 + 2,4\text{-}Me_2C_5H_3N \rightarrow L^{Me,Me3}NiI(2,4\text{-}Me_2C_5H_3N) + TlI$$

$$L^{Me,Me3}NiI(2,4\text{-}Me_2C_5H_3N) + Na \rightarrow L^{Me,Me3}Ni(2,4\text{-}Me_2C_5H_3N) + NaI$$

Procedure

This one-pot procedure is based on a published synthesis that employed $NiCl_2$.[6] A solution of $TlL^{Me,Me3}$ (2.50 g, 4.65 mmol) in 20 mL THF is added to a suspension of NiI_2 (1.46 g, 4.65 mmol) and 2,4-lutidine (0.50 g, 4.65 mmol) in ca. 20 mL THF. The reaction is stirred at room temperature overnight and then filtered through Celite to yield a dark green solution.* A 0.5% w/w Na/Hg amalgam (21.4 g of amalgam = 0.107 g Na, 4.65 mmol Na) is added to the solution and stirred vigorously for 3 h. The resulting red solution is decanted away from the remaining amalgam and filtered through Celite. The volatiles are removed over 3 h *in vacuo* and the red solid is taken up in 40 mL of Et_2O. The solution is again filtered through Celite to remove any remaining NaI and then concentrated *in vacuo* to a volume of about 10 mL. The solution is cooled to −35°C overnight to give deep red crystals. A second crop of crystals is isolated to yield a total of 1.29 g (57%) of product after drying.

UV–vis (Et_2O with added lutidine, nm ($M^{-1}\,cm^{-1}$)): 396 (5200) and 488 (3300). $\mu_{eff} = 2.00$ B.M. (C_6D_6 with ca. 10 equiv added 2,4-lutidine). EPR (toluene with ca. 10 equiv added lutidine, 77K, frozen glass): $g = 2.437, 2.131, 2.068$.

Properties

$L^{Me,Me3}$Ni(2,4-lutidine) is very soluble in aliphatic and aromatic hydrocarbons as well as diethyl ether and THF. 2,4-Lutidine is added during the characterization owing to the lability of this ligand. The nickel(I) compound is extremely reactive toward halogenated solvents as well as oxygen and water. For instance, blue-green $L^{Me,Me3}$NiCl(2,4-lutidine) forms upon exposure to CH_2Cl_2 and a green hydroxo species $(LNi)_2(\mu\text{-}OH)_2$ forms upon exposure to dioxygen.[7]

Related Compounds

Nickel(I) β-diketiminates LNi(2,4-lutidine) react with nitric oxide to give stable three-coordinate nitrosyls LNi(NO) ($L = L^{Me,Me2}$ and $L^{Me,Me3}$).[8] Depending on their steric bulk, these β-diketiminate complexes react with CO to give either dimeric $(L^{Me,Me3}Ni)_2(\mu\text{-}CO)_2$[6] or T-shaped three-coordinate $L^{Me,iPr2}Ni(CO)$[9] derivatives. Addition of adamantyl azide (N_3Ad) to LNi(2,4-lutidine) gives the dinickel nitrene $(L^{Me,Me2}Ni)_2(\mu\text{-}NAd)$ as well as the terminal $L^{Me,Me3}$-Ni=NAd, which undergoes nitrene group transfer to nucleophiles such as $CNBu^t$.[6] A related β-diketiminato nickel(I) complex $(L^{Me,iPr2}Ni)_2(\mu\text{-toluene})$[10] also reacts

* The checkers filtered their product through Celite twice to remove TlI.

with organoazides to give reactive nickel nitrene intermediates[11] as well as allows for the isolation of a nickel(II) superoxo complex $L^{Me,iPr2}Ni(\eta^2\text{-}O_2)$.[12]

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13. NICKEL 2,4-BIS-(2,6-DIISOPROPYLPHENYLIMIDO) PENTYL CHLORIDE DIMER, $[L^{Me,iPr2}Ni(\mu\text{-}Cl)]_2$

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Checked by STEFAN WIESE[†] and TIMOTHY H. WARREN[†]

General Procedures

All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in a glovebox maintained at or below 1 ppm of O_2 and H_2O. Glassware was dried at 150 °C overnight. NMR spectra are referenced to residual $CDHCl_2$ at 5.31 ppm. UV–vis spectra were measured using screw-cap

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cuvettes. Pentane, diethyl ether, and toluene were purified by passing through activated alumina and Q-5 columns from Glass Contour Co. Deuterated dichloromethane was first dried over CaH_2, and then vacuum transferred into a storage container. Celite was dried overnight at 200°C under vacuum. $NiCl_2(THF)_x$ is prepared by refluxing anhydrous $NiCl_2$ (Strem),[*,1] in dry tetrahydrofuran under nitrogen for 24 h.[2] The amount of THF coordinated to Ni varies from 0.1 to 0.7, and the stoichiometry of this starting material is obtained through the gravimetric determination of Ni^{2+} content with dimethylglyoxime.[3]

$$[L^{Me,iPr2}Li]_x + NiCl_2(THF)_{0.4} \rightarrow L^{Me,iPr2}Ni(\mu\text{-}Cl)_2NiL^{Me,iPr2} + LiCl$$

Procedure

Tan $NiCl_2(THF)_{0.4}$ (335 mg, 2.11 mmol) and $[L^{Me,iPr2}Li]_x$ (888 mg, 2.09 mmol) are placed in a 100-mL resealable flask (see Fig. 1 in Section 9), and toluene (~30 mL) is added to produce a tan colored slurry. The flask is closed, and the reaction mixture is heated and stirred at 100°C. After 24 h, the dark blue reaction mixture is cooled to room temperature, and the solvent is removed under reduced pressure. Under a nitrogen atmosphere, CH_2Cl_2 (30 mL) is added to the residue, and the mixture is filtered through 3 cm of Celite. The dark blue solution is concentrated to 18 mL and cooled to −45°C, which yields the first crop of blue crystals (254 mg). A second crop of crystals (228 mg) is obtained by reducing the volume of the supernatant to 6 mL and cooling to −45°C. The solids are washed with pentane to remove traces of $L^{Me,iPr2}H$ and $LiL^{Me,iPr2}$. Combined yield: 482 mg (45%).[†]

^{1}H NMR (CD_2Cl_2, 500 MHz, 25°C): δ 58 (4H, C*H*$(CH_3)_2$ or *m*-Ar), 36 (4H, C*H*$(CH_3)_2$ or *m*-Ar), 9.7 (12H, CH(C*H*$_3$)$_2$), 8.5 (12H, CH(C*H*$_3$)$_2$), −27 (2H, *p*-Ar), −90 (6H, CH_3), −282 (1H, backbone-*H*). UV–vis (CH_2Cl_2, ε in $M^{-1}\,cm^{-1}$): 575 (680), 765 (2800) nm. UV–vis (toluene, ε in $M^{-1}\,cm^{-1}$): 580 (1200), 740 (2800) nm.

Properties

Solid samples of $[L^{Me,iPr2}NiCl]_2$ are dark blue, and the purity can be tested by ^{1}H NMR spectroscopy in CD_2Cl_2. $[L^{Me,iPr2}NiCl]_2$ is very soluble in CH_2Cl_2,

[*] Although commercial material was used here without special precautions, it is uncertain that commercial "anhydrous" $NiCl_2$ is completely free of water. Methods have been reported for removing trace moisture from $NiCl_2$ using anhydrous HCl: see Ref. 1.

[†] The checkers observed a dark green solution after heating, and the green CH_2Cl_2 solution yielded blue crystals in a yield of 40%. These crystals had spectroscopic properties identical to those described above. The reaction failed with some sources of nickel(II) chloride.[*]

soluble in toluene, and slightly soluble in pentane and diethyl ether. It reacts with tetrahydrofuran to give a purple solution of the adduct $L^{Me,iPr2}Ni(Cl)(THF)$, with UV–vis (THF, ε in $M^{-1}\,cm^{-1}$): 520 (1300), 670 (830) nm.[2]

Related Compounds

$[L^{Me,iPr2}NiCl]_2$ has been used as a precursor to a nickel(II) amido complex, and to an unusual T-shaped nickel(I)-carbonyl complex.[4] The analogous bromide complex has been used as an ethylene polymerization catalyst,[5] and as a source of nickel(I) for group-transfer and bond activation reactions (described in more detail in Section 12).

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14. BIS[COPPER 2,4-BIS-(2,4,6-TRIMETHYLPHENYLIMIDO) PENTYL] TOLUENE, $(L^{Me,Me3}Cu)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_7H_8)$

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Checked by KAREN P. CHIANG[†] and PATRICK L. HOLLAND[†]

Following Sadighi's use of copper(I) *tert*-butoxide in the synthesis of a fluorinated β-diketiminato copper(I) complex,[1] a two-step procedure is employed beginning

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with a recently reported preparation for copper(I) *tert*-butoxide,[2] which is then combined with $HL^{Me,Me3}$ to give $[L^{Me,Me3}Cu]_2(\mu$-benzene).[3] Copper(I) *tert*-butoxide is first prepared by a modification of the original procedure, which employed $LiOBu^t$ and anhydrous CuCl. This preparation gave the tetrameric [CuO-*tert*-Bu]$_4$ when crystallized from hexane or benzene.[4] Additionally, an octameric structure [CuO-*tert*-Bu]$_8$ has been observed in the reaction of mesitylcopper(I) with *tert*-butanol after crystallization from toluene.[5]

General Procedures

Experiments were carried out in a dry nitrogen atmosphere using a glovebox and/or standard Schlenk techniques. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passing through activated alumina columns.[6] Pentane was first washed with conc. HNO_3/H_2SO_4 to remove olefins, stored over $CaCl_2$, sparged with nitrogen, and then dried by passing through activated alumina columns.[6] Dry toluene was purchased from Aldrich and was stored over activated 4 Å molecular sieves. All deuterated solvents were sparged with nitrogen, dried over activated 4 Å molecular sieves, and stored under nitrogen. Potassium *tert*-butoxide was purchased from Acros. Anhydrous copper(I) iodide was purchased from Strem.

A. COPPER *tert*-BUTOXIDE

$$\text{KO-}tert\text{-Bu} + \text{CuI} \rightarrow \text{CuO-}tert\text{-Bu} + \text{KI}$$

Procedure

A chilled (−35°C) solution of commercial potassium *tert*-butoxide (1.95 g, 17.4 mmol) in 20 mL THF is added to a suspension of anhydrous copper(I) iodide (3.00 g, 15.79 mmol) in 25 mL of THF. The mixture is stirred overnight at room temperature. The resulting solution is then filtered through Celite to remove the precipitated KI followed by removal of all volatiles from the filtrate *in vacuo* to give a brown-yellow residue. Addition of ca. 5 mL of cold pentane allows the isolation of a pale yellow solid from this residue by filtration and dried *in vacuo* to afford 1.69 g (78%) of pale yellow copper(I) *tert*-butoxide.

^{1}H NMR (benzene-d_6): δ 1.31 (s, ^{t}Bu). $^{13}C\{^1H\}$ NMR (benzene d_6): δ 72.6 *C* (CH_3), 35.8 (*C*H_3).

B. BIS[COPPER 2,4-BIS-(2,4,6-TRIMETHYLPHENYLIMIDO) PENTYL] TOLUENE

$$2\,\text{CuO-}tert\text{-Bu} + 2\,\text{HL}^{\text{Me,Me3}} + \text{C}_6\text{H}_5\text{Me} \rightarrow [\text{L}^{\text{Me,Me3}}\text{Cu}]_2(\text{C}_6\text{H}_5\text{Me}) + 2\,tert\text{-BuOH}$$

Procedure

To a stirring solution of copper(I) *tert*-butoxide (1.250 g, 9.150 mmol) in 20 mL toluene is added a solution of $\text{HL}^{\text{Me,Me3}}$ (2.550 g, 7.620 mmol) in 20 mL of toluene. After stirring for 3 h, the dark brown solution is filtered through Celite, and the volatile materials are removed *in vacuo* to give a yellow brown, slightly oily residue. This residue is triturated with a small amount of pentane to reveal a yellow solid, which is then recrystallized by extraction into pentane (ca. 5–10 mL) containing a small amount of toluene (1–2 mL) followed by chilling to −35°C. Filtration affords 2.85 g (85%) of the dinuclear product as a yellow solid in two crops.

^{1}H NMR (benzene-d_6): major species: δ 6.92 (br s, 4, Ar-*H*), 4.79 (s, 1, backbone-C*H*), 2.27 (s, 6, Ar-*p*-CH_3), 2.03 (s, 12, Ar-*p*-CH_3), 1.67 (s, 6, backbone-*CH3*). ^{13}C{^{1}H} NMR (benzene d_6): 162.7, 148.3, 131.8, 130.3, 128.9, 94.5 (backbone-*C*H), 23.2, 21.1, 18.8, 18.7. Minor species: δ 6.81 (s, 8, Ar-H), 4.76 (s, 2, backbone C-*H*), 2.24 (s, 12, Ar-*p*-CH3), 1.89 (s, 24, Ar-*o*-CH_3), 1.58 (s, 12, backbone-CH_3).

Properties

The β-diketiminato copper(I) complex is a pale yellow solid that is freely soluble in benzene, toluene, chlorobenzene, THF, and acetonitrile while partially soluble in diethyl ether and pentane. In solution, the toluene ligand dissociates. When dissolved in benzene, for example, the NMR spectrum exhibits signals for both $\text{L}^{\text{Me,Me3}}$Cu(benzene) (major species) and $[\text{L}^{\text{Me,Me3}}\text{Cu}]_2$(benzene) (minor species). The copper(I) complex reacts slowly with chloroform and dichloromethane, resulting in a gradual darkening of the solution to purple.

Related Compounds

Reaction with oxygen leads to formation of brown $(\text{L}^{\text{Me,Me3}}\text{Cu})_2(\mu\text{-OH})_2$, presumably through the intermediacy of a dicopper(III) bis(μ-oxo) species $(\text{L}^{\text{Me,Me3}}\text{Cu})_2(\mu\text{-O})_2$.[7–9] More hindered β-diketiminato copper(I) complexes such as $\text{L}^{t\text{Bu},i\text{Pr2}}$Cu(MeCN) react with dioxygen to give the crystallographically characterized Cu(III) side-on peroxo complex $\text{L}^{t\text{Bu},i\text{Pr2}}\text{Cu}(\eta^2\text{-O}_2)$.[10] Employing the diazoalkane N=N=CPh$_2$, $[(\text{L}^{\text{Me,Me3}})\text{Cu}]_2$(μ-benzene) may be used for the

synthesis of dicopper and terminal carbenes $[(L^{Me,Me3})Cu]_2(\mu\text{-}CPh_2)$[2] and $(L^{Me,Me3})Cu{=}CPh_2$.[11] Similarly, this copper(I) complex reacts with the organoazide N=N=NAr (Ar = 3,5-$Me_2C_6H_3$) to give the discrete dicopper nitrene $[(L^{Me,Me3})Cu]_2(\mu\text{-NAr})$, which undergoes nitrene group transfer to nucleophiles such as $CNBu^t$.[12] Related Cu(I) β-diketiminates have been used for catalytic nitrene group transfer to alkenes with PhI=NTs to afford aziridines.[13] Moreover, the related $[(L^{Me,Cl_2})Cu]_2(\mu\text{-benzene})$ may be prepared similarly from HL^{Me,Cl_2} and copper(I) *tert*-butoxide and serves as an active C-H amination catalyst with N_3Ad, formally inserting the NAd moiety into C-H bonds.[2]

^{1}H NMR spectra in benzene-d_6 indicate a mixture of dinuclear $\{L^{Me,Me3}Cu\}_2(\mu\text{-benzene})$ and mononuclear $L^{Me,Me3}Cu(\text{benzene})$ along with free toluene (δ 7.13–7.02 (m, 5, toluene-Ar), 2.10 (s, 3, toluene-CH_3)).[2] $K_{eq} = [\{L^{Me,Me3}Cu\}(\text{benzene})]^2/[\{L^{Me,Me3}Cu\}_2(\mu\text{-benzene})]$ was about 0.5 M at 25°C with the mononuclear species predominating under typical NMR concentrations (0.01–0.1 M).

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15. COPPER 2,4-BIS-(2,6-DIISOPROPYLPHENYLIMIDO) PENTYL CHLORIDE ($L^{Me,iPr2}CuCl$)

Submitted by PATRICK L. HOLLAND*
Checked by MARIE M. MELZER† and TIMOTHY H. WARREN†

This compound was the first example of a three-coordinate complex of copper(II) outside a protein environment, and it is a precursor to other three-coordinate copper(II) complexes.[1] The chloride ligand in this complex has been substituted with thiolate and phenolate ligands to give mimics of type 1 copper sites[1,2] and of reduced galactose oxidase,[3] respectively. Itoh and Tolman have examined the influence of diketiminate substitution pattern on the copper(II) chemistry.[4]

General Procedures

All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in a glovebox maintained at or below 1 ppm of O_2 and H_2O. Glassware was dried at 150°C overnight. UV–vis spectra were measured using screw-cap cuvettes. Pentane and dichloromethane were purified by passing through activated alumina and Q-5 columns. Celite was dried overnight at 200°C under vacuum. Anhydrous $CuCl_2$ was purchased from Aldrich and converted to the THF adduct by the method of Kern.[5]

$$L^{Me,iPr2}Li + CuCl_2(THF)_{0.8} \rightarrow L^{Me,iPr2}CuCl + LiCl$$

Procedure

Orange $CuCl_2(THF)_{0.8}$ (158 mg, 0.822 mmol) is added to a scintillation vial containing a pale yellow solution of $[L^{Me,iPr2}Li]_x$ (see Section 3, 351 mg, 0.827 mmol) in tetrahydrofuran (7 mL), causing an immediate color change to red-brown.‡ After stirring the reaction solution for 1.5 h, the solvent is evaporated under reduced pressure. The residue is extracted with CH_2Cl_2 (15 mL), and the mixture is filtered through 1 cm of Celite. The volume of the filtrate is reduced to 5 mL, and 2 mL of pentane is added before cooling to −40°C to give one crop of

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‡ When the checkers added $LiL^{Me,iPr2}$ to a solution of $CuCl_2(THF)_{0.8}$, it turned dark green.

crystals (101 mg). Adding 7 mL of pentane to the filtrate and cooling yields a second crop of solid (155 mg), and reducing the volume of supernatant to 3 mL and cooling yields a third crop of solid (96 mg). The solids are washed with pentane to remove traces of $L^{Me,iPr2}H$ and $L^{Me,iPr2}Li$. The combined yield is 352 mg (82.9%). The purity is verified by UV–vis spectroscopy.

UV–vis (0.3–0.4 mM solutions in CH_2Cl_2, ε in $M^{-1}\,cm^{-1}$): 507 (4100), 835 nm (650).

Properties

Solid samples of $L^{Me,iPr2}CuCl$ are purple-brown in color. It can also be characterized by its EPR spectrum at 77 K ($g_{\|}$ 2.20, $A_{\|}$ $130 \times 10^{-4}\,cm^{-1}$, $g_{\perp}$ 2.05, $A_{\perp}$ $8 \times 10^{-4}\,cm^{-1}$). $L^{Me,iPr}CuCl$ is highly soluble in CH_2Cl_2 and tetrahydrofuran, somewhat soluble in toluene, poorly soluble in MeCN, and insoluble in diethyl ether and pentane.

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