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Synthesis and reactivity of bis(heptamethylindenyl) yttrium (Ind^*_2Y) complexes containing alkyl and hydride ligands: crystal structure of $Ind^*_2YCl(THF)$

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Abstract

The syntheses and reactivities of yttrium alkyl and hydride complexes containing a sterically demanding, bis(heptamethylindenyl) ligand set are reported. The chloride complex $Ind^*_2YCl(THF)$ (**2,** Ind* = heptamethylindenyl) was prepared by the reaction of Ind*Na (**1,** 2 equiv) with YCl_3 in THF. Compound **2** was structurally characterized. Complex reaction mixtures were obtained when compound **2** was treated with $KSi(SiMe_3)_3$ or $(THF)_3LiSi(SiMe_3)_3$, although **2** reacted readily with MeLi to yield the methyl complex $Ind^*_2YMe(THF)$ (**3**). Treatment of **3** with H_2 or $PhSiH_3$ gave the base-stabilized hydride complex $Ind^*_2YH(THF)$ (**4**). The base-free chloride complex Ind^*_2YCl (**5**) was synthesized by the reaction of **1** (2 equiv) with YCl_3 in toluene. Treatment of **2** with $LiCH(SiMe_3)_2$ yielded the base-free alkyl complex $Ind^*_2YCH(SiMe_3)_2$ (**6**). No reaction was observed between **6** and CH_4, and complex reaction mixtures were obtained when **6** was treated with H_2 or $PhSiH_3$. However, when **6** was treated with H_2 in the presence of THF, the transient hydride Ind^*_2YH was trapped as complex **4**. The increased steric bulk of **6** leads to a slower reaction with $PhSiH_3$ as compared to $Cp^*_2YCH(SiMe_3)_2$ (**7**).

Keywords: Yttrium hydride complexes; Yttrium alkyl complexes; Heptamethylindenyl ligand; σ-Bond metathesis

1. Introduction

Alkyl and hydride complexes of the Group 3 transition metals are highly reactive and have been shown to mediate a number of chemical transformations [1,2]. Examples of these reactions include reductive cyclization of diolefins [3,4], dimerization of olefins [4,5] and alkynes [6], olefin polymerization [7,8], hydrosilylation [9,10], hydrocarbon activation [4,11–13], and alkane functionalization [14]. While active catalysts for these reactions can be monomeric or dimeric, mononuclear species tend to be more reactive. For example, Casey has observed that the bridging hydrides $[Cp^*_2YH]_2$ are much less reactive than the terminal hydride of Cp^*_2YH, and that dimer dissociation precedes olefin insertion for bulky substrates (such as 3-methyl-1-butene) [15]. In an effort to develop new compounds capable of enhanced reactivity toward σ-bond metathesis processes, we have targeted complexes containing ligands that are sterically demanding enough to destabilize dimeric species, while providing sufficient space at the metal center for the binding of small molecules.

In this contribution, we report yttrium complexes of the heptamethylindenyl (Ind*) ligand. While the initial preparation of this ligand was reported in 1981 [16], it has been employed with relatively few transition metals, lanthanides, and actinides [17]. With respect to Group 3 metals, the lanthanum complexes $Ind^*_nLaCl_{(3-n)}$ (Ind* = heptamethylindenyl, $n = 1$–3) have been reported [18]. In addition, yttrium alkyl and hydride complexes of the related 2,4,7-trimethylindenyl (Ind′) ligand have been described [5]. In this contribution, we present the synthesis and reactivity of a series of alkyl and hydride

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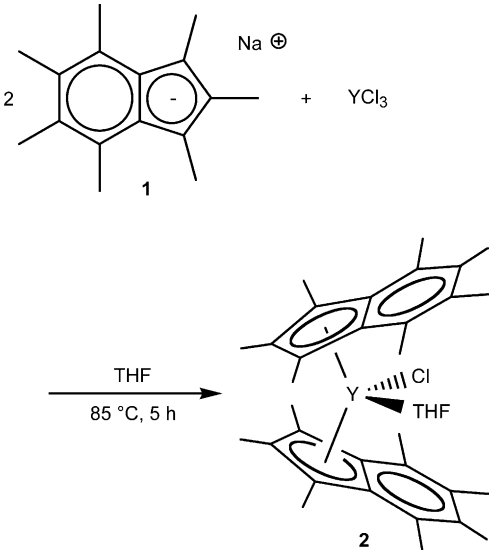
complexes of yttrium supported by a bis(heptamethylindenyl) ligand framework.

2. Results and discussion

2.1. Synthesis and reactivity of THF-containing complexes

Heptamethylindene (Ind*H) was prepared in 15 g quantities in 20% overall yield from tiglic acid and 1,2,3,4-tetramethylbenzene according to the method of O'Hare et al. [19]. A significant amount of unreacted 2,3,4,5,6,7-hexamethylindan-1-one was recovered in the last step of the synthesis. Treatment of Ind*H with excess NaH (5 equiv) in THF at reflux (three days) afforded Ind*Na (**1**) as a light yellow solid in 94% yield. Compound **1** is insoluble in aromatic or straight chain hydrocarbon solvents, but readily dissolves in THF. The ^{1}H NMR spectrum of **1** (in THF-d_8) contains four methyl group resonances, integrating in a 2:2:2:1 ratio. No stretches were observed for THF in the IR spectrum, and hydrolysis of a benzene-d_6 suspension yielded only Ind*H (by ^{1}H NMR spectroscopy), indicating that compound **1** is free of coordinated solvent.

Heating a THF solution of compound **1** (2 equiv) and YCl_3 at reflux for 5 h gave Ind*$_2$YCl(THF) (**2**) as an off-white solid in 74% yield (Eq. (1)). After removing the solvent in vacuo, the residue was extracted with toluene. Compound **2** was crystallized from toluene at −35 °C, but a more convenient purification procedure involves evaporation of the combined toluene extracts and washing the resulting solid with pentane. The ^{1}H NMR spectrum of complex **2** contains four resonances for the indenyl methyl groups. While the resonances at 1.88, 2.05, and 2.59 ppm appear as sharp singlets, the one at 2.57 ppm is broad (toluene-d_8). However, at 80 °C in toluene-d_8 solution, this resonance appears as a sharp singlet at 2.54 ppm. The broad indenyl methyl resonance is likely due to conformational fluxionality involving the Ind* ligands. The yttrium-bound THF was identified by the sharp ^{1}H NMR resonances at 0.93 and 2.86 ppm (benzene-d_6) and the strong IR absorbances at 859 and 1010 cm^{-1}. Addition of excess THF (5 equiv) to a benzene-d_6 solution of **1** does not sharpen the indenyl methyl resonance at 2.57 ppm at room temperature. All of the resonances of **1** remain unchanged, with the exception that the THF signals appear as broad singlets at 1.40 and 3.56 ppm (the chemical shifts for free THF). No resonance was observed for the bound THF. This suggests that rapid exchange occurs at room temperature between free and bound THF. Heating a THF solution of Ind*Li (2 equiv) and YCl_3 to reflux (90 °C bath) for 18 h resulted in a complex reaction mixture, with Ind*H as the major product. The resonances for complex **2** could not be identified in the ^{1}H NMR spectrum of the reaction mixture.



(1)

X-ray quality crystals were obtained by slow evaporation of benzene-d_6 from a concentrated solution of **2**. The molecular structure is shown in Fig. 1, and important bond distances and angles are listed in Table 1. Due to a rapid decrease in intensity with increasing $(\mathrm{SIN}\theta)/\lambda$, data were integrated to 0.95 Å. As a result, the Ind* ring carbon atoms were refined isotropically, while the methyl, THF, chlorine, and yttrium atoms were refined anisotropically. The structure confirms the connectivity of the molecule, although meaningful distances and angles were determined only for those atoms refined with an anisotropic model. The Ind* ligands are oriented so that the six-membered rings are positioned

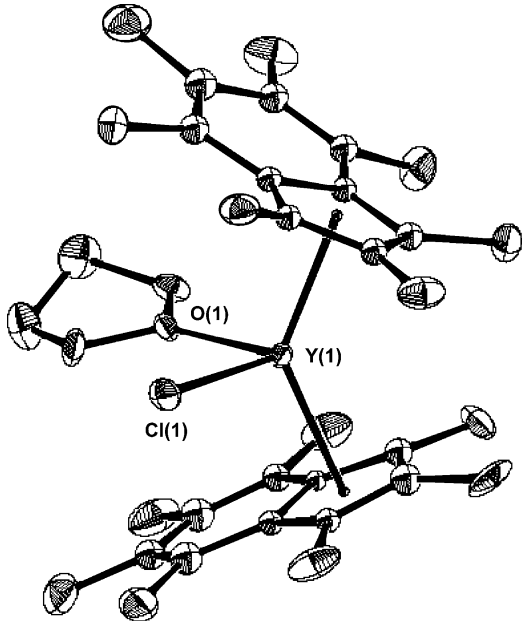


Fig. 1. ORTEP diagram of Ind*$_2$YCl(THF) (**2**).

Table 1
Selected bond lengths (Å) and angles (°) for Ind*$_2$YCl(THF) (**2**) and the two crystallographically independent molecules of Cp*$_2$YCl(THF)[a,20]

	2	Cp*$_2$YCl(THF)	
Bond lengths			
Y(1)–Cl(1)	2.572(2)	2.579(3)	2.577(3)
Y(1)–O(1)	2.330(5)	2.410(7)	2.410(7)
Y(1)–C(100)	2.4178(9)	2.382(1)	2.373(1)
Y(1)–C(101)	2.3984(8)	2.379(1)	2.388(1)
Bond angles			
Cl(1)–Y(1)–O(1)	88.0(1)	89.6(2)	90.5(2)
C(100)–Y(1)–C(101)	135.52(4)	136.2(4)	136.6(4)

[a] C(100) and C(101) represent the average of the *x*, *y*, and *z* coordinates of the Ind* ring carbons C(1)–C(5) and C(10)–C(14), respectively, and the Cp* ring carbons C(1)–C(5) and C(6)–C(10), respectively.

above and below the THF ligand. The creation of a "pocket" by the arrangement of the Ind* ligands is not unusual, and has been observed previously for thorium complexes reported by Parkin and coworkers [17]. Such Ind*$_2$Th complexes have been found to adopt a variety of conformations. The Ind*(centroid)-Y-Ind*(centroid) angle of **2** (135.52(4)°) is similar to the Cp*(centroid)-Y-Cp*(centroid) angles reported for the two crystallographically independent molecules of Cp*$_2$YCl(THF) (136.2(4)° and 136.6(4)°) [20]. In addition, while the Y–Cl bond distance of **2** (2.572(2) Å) is similar to the values reported for Cp*$_2$YCl(THF) (2.579(3) and 2.577(3) Å), the Y–O distance of **2** (2.330(5) Å) is slightly shorter than the Y–O bonds of Cp*$_2$YCl(THF) (2.410(7) and 2.410(7) Å).

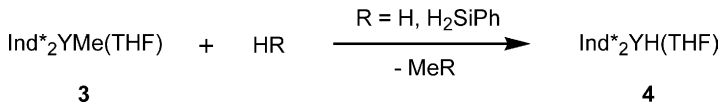
Several attempts were made to prepare a silyl derivative of the Ind*$_2$Y fragment by salt metathesis reactions of **2** with silyl anions. For example, a complex reaction mixture was observed by ^{1}H NMR spectroscopy when **2** was treated with KSi(SiMe$_3$)$_3$ (benzene-d_6, 29 h). The reaction progress exhibited no apparent sensitivity to ambient light, as the same product mixture was observed when the reaction was conducted in the dark. No reaction was observed between **2** and (THF)$_3$LiSi(SiMe$_3$)$_3$ at room temperature (benzene-d_6, two days), and heating the reaction mixture to 95 °C (17 h) gave rise to a complex mixture of products (by ^{1}H NMR spectroscopy).

An alkyl complex of the Ind*$_2$Y fragment was prepared by treating a THF solution of **2** with MeLi at −78 °C to afford Ind*$_2$YMe(THF) (**3**) as white crystals in 57% yield. The Y–Me group of **3** was clearly identified by a doublet in the ^{1}H NMR spectrum at −0.48 ppm ($J_{YH} = 2.3$ Hz), and a doublet in the ^{13}C{^{1}H}NMR spectrum at 25.5 ppm ($J_{YC} = 56$ Hz). These values are similar to the chemical shifts reported for the related complex Cp*$_2$YMe(THF) (^{1}H NMR: δ-0.66, ($J_{YH} = 2.3$ Hz); ^{13}C{^{1}H}NMR: δ 21.36 ($J_{YC} = 56.2$ Hz)) [21,22]. As for complex **2,** the ^{1}H NMR spectrum of **3** contains three sharp resonances and one broad resonance for the indenyl methyl groups. The yttrium-bound THF was identified by ^{1}H NMR and IR spectroscopy.

Initial reactivity studies with **3** centered on examining σ-bond metathesis processes involving H–H and Si–H bonds. Compound **3** reacted rapidly with H_2 (1 atm) at room temperature in toluene to give Ind*$_2$YH(THF) (**4**) as a yellow crystalline solid in 42% yield (Eq. (2)). Monitoring an NMR tube scale reaction of complex **3** with H_2 (1 atm) in benzene-d_6 (room temperature, 17 min) revealed complete conversion to **4** and the formation of CH_4 (0.28 equiv in solution). In contrast to the spectra of **2** and **3**, the ^{1}H NMR spectrum of compound **4** contains one sharp resonance (18 H) and four broad resonances (6 H each) for the indenyl methyl groups. The terminal hydride ligand was clearly identified by a doublet at 6.04 ppm ($J_{YH} = 82.0$ Hz) in the ^{1}H NMR spectrum and by a very strong IR absorbance at 1322 cm^{-1} ($\nu_{YD} = 942$ cm^{-1}). These values are similar to those reported for Cp*$_2$YH(THF) (^{1}H NMR: 6.17 ppm ($J_{YH} = 81.74$ Hz); $\nu_{YH} = 1295$ cm^{-1}) [12]. In contrast, the bridging hydride ligands of [Cp*$_2$YH]$_2$ and [Ind′$_2$YH]$_2$ were found at 2.68 ppm (dd) [12] and 2.69 ppm (t) [5], respectively. Furthermore, the upfield ^{1}H NMR shifts for the bridging hydride ligands of [Cp$_2$YH (THF)]$_2$ (2.02 ppm (t)) and [(C$_5$H$_4$Me)$_2$YH(THF)]$_2$ (2.31 ppm (t)) indicate that terminal vs. bridging ligation has greater influence than coordinated solvent on the chemical shift of the hydride ligand [23].

Complex **3** reacted rapidly with $PhSiH_3$ (1 equiv) at room temperature (benzene-d_6, 12 min) to yield **4** and $PhMeSiH_2$ (1 equiv, Eq. (2)). With excess $PhSiH_3$ (10 equiv), $PhMeSiH_2$ (1 equiv) formed immediately and broad signals were observed in the ^{1}H NMR spectrum for the hydride ligand, bound THF, and unreacted $PhSiH_3$, presumably because of exchange between the Y–H and Si–H (of unreacted $PhSiH_3$) groups in solution on the NMR time scale [24,25]. After 6.5 h, 3.6 equiv of $PhSiH_3$ were consumed and 0.64 equiv of $(PhSiH_2)_2$ had formed (relative to a Cp_2Fe internal standard). For comparison, $PhMeSiH_2$ was also observed as a product in the reaction of Cp*$_2$YMe(THF) with $PhSiH_3$ [26–28]. The reactions of both complex **3** and Cp*$_2$YMe(THF) with $PhSiH_3$ were very rapid at room temperature, indicating that the increased steric bulk of the Ind* ligand (vs. Cp*) does not significantly affect reactivity with small substrates such as $PhSiH_3$. An attempt was made to prepare a silyl derivative of Ind*$_2$Y by using *o*-$MeOC_6H_4SiH_3$ in place of $PhSiH_3$. This silane had been previously employed to synthesize and trap silyl complexes of samarium [29] and lutetium [30] in related reactions. However, when **3** was treated with *o*-$MeOC_6H_4SiH_3$ (benzene-d_6, room temperature), slow conversion to **4** and *o*-$MeOC_6H_4SiH_2Me$ (0.80 equiv) was observed over the course of 7 h. Methane

(0.14 equiv in solution) was also found in the reaction mixture, along with trace quantities of unidentified silanes. No resonances which could be attributed to $Ind^*_2YSiH_2$ (*o*-$MeOC_6H_4$) were observed.



(2)

2.2. Synthesis and reactivity of base-free complexes

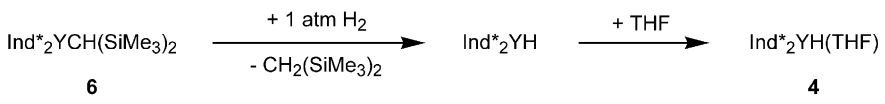
With the goal of preparing a coordinatively unsaturated, monomeric, base-free yttrium hydride complex, we sought methods to synthesize compounds of the Ind^*_2Y fragment in the absence of donor solvents. Heating a toluene suspension of **1** (2 equiv) and YCl_3 at reflux (130 °C bath) for 15.5 h provided the base-free yttrium chloride complex Ind^*_2YCl (**5**) as orange crystals in 19% yield. This product was not observed in the complex reaction mixture obtained from heating a toluene suspension of Ind*Li (2 equiv) and YCl_3 to reflux (125 °C bath) for three days. In contrast to complexes **2**–**4**, compound **5** contains four sharp indenyl methyl resonances in its ^1H NMR spectrum at room temperature. The analogous base-free pentamethylcyclopentadienyl complex, $Cp^*_2Y(\mu\text{-}Cl)YClCp^*_2$, was prepared in high yield by sublimation of $Cp^*_2YCl(THF)$ (or alternatively $Cp^*_2YCl_2M(THF)_2$, M = K, Li [31]) at 210–230 °C (0.03 mm Hg) [32]. When **2** was sublimed under similar conditions (200 °C, 0.02 mm Hg), Ind*H was the only identifiable product. Attempts to prepare silyl derivatives using complex **5** were unsuccessful. For example, complex reaction mixtures were observed upon treatment of **5** with $KSi(SiMe_3)_3$ at room temperature in benzene-d_6 (18 min) or cyclohexane-d_{12} (19 min).

Given the low (unoptimized) yield of **5,** efforts to prepare base-free alkyl and hydride complexes were focused on the treatment of **2** with bulky alkylating reagents. Warming a diethyl ether solution of **2** and $LiCH(SiMe_3)_2$ from −78 to 0 °C afforded $Ind^*_2YCH(SiMe_3)_2$ (**6**) as a yellow crystalline solid in 27% yield. The ^1H NMR spectrum of **6** contains eight sharp singlets for the indenyl methyl groups, indicating inequivalent Ind* ligand environments. The YCH group was observed as a doublet at −0.37 ppm (J_{YH} = 2.3 Hz), and the $SiMe_3$ groups appeared as a sharp singlet at 0.03 ppm. The related complexes $Cp^*_2YCH(SiMe_3)_2$ (**7**) [33] and $Ind'_2YCH(SiMe_3)_2$ [5] also have inequivalent Cp* and Ind′ ligand environments, with YCH resonances at −0.10 ppm (J_{YH} = 2.3 Hz) and 0.16 ppm (J_{YH} = 2.7 Hz), respectively.

Treatments of **6** with H_2 (1 atm) at room temperature in benzene-d_6 or cyclohexane-d_{12}, both in the presence and absence of ambient room light, resulted in complex reaction mixtures. In each case, $CH_2(SiMe_3)_2$ was observed as the only product with a $SiMe_3$ group, but no evidence for a Y–H group was found (by ^1H NMR spectroscopy). No adduct formation was observed upon treatment of **6** with THF (benzene-d_6, room temperature, two days), but the subsequent addition of H_2 (1 atm) resulted in complete conversion to **4** (Scheme 1). This suggests that the base-free hydride complex that is formed (Ind_2^*YH) is highly reactive, but can be trapped by THF to yield the base-stabilized complex **4**.

No reaction was observed between **6** and CH_4 (1 atm) at 70 °C (3 h), and prolonged heating at 110 °C (four days) simply led to thermal decomposition of the yttrium complex to a mixture of unidentified products. No doublets for a Y–Me group were observed, and the same product resonances were observed in both the presence and absence of CH_4. The reaction of **6** with $PhSiH_3$ (benzene-d_6, room temperature, 5 h) led to a complex reaction mixture which contained $CH_2(SiMe_3)_2$. However, when the reaction was monitored by ^1H NMR spectroscopy after 1.5 h, the $PhSiH_3$ resonance at 4.24 ppm appeared broad, and a small doublet at 4.38 ppm (J_{YH} = 3 Hz) was found which might be attributed to the yttrium silyl complex $Ind^*_2YSiH_2Ph$.

The relative reactivity of yttrium complexes of the bis(heptamethylindenyl) ligand set was determined by a qualitative rate comparison of the reactions of complexes **6** and $Cp^*_2YCH(SiMe_3)_2$ (**7**) with $PhSiH_3$. Equimolar quantities of **6** and **7** were dissolved separately in benzene-d_6 (0.7 ml). Phenylsilane (1 equiv) was then added to each solution via syringe, and the reaction progress was monitored at room temperature by ^1H NMR spectroscopy (relative to a Cp_2Fe internal standard). After 13 min, only 40% of complex **7** remained, and all of the $PhSiH_3$ had been consumed. In contrast, 83% of complex **6** remained and $PhSiH_3$ (approximately 1 equiv) was observed in the reaction mixture. After 75 min, 29% of **7** and 75% of **6** (along with $PhSiH_3$) were present in the respective reaction mixtures. Complex **7**



Scheme 1.

reacted rapidly, but not stoichiometrically, with complete conversion of the $PhSiH_3$ and formation of $CH_2(SiMe_3)_2$ along with a mixture of yttrium-containing products. After 7 h, 19% of **7** was still present. The sub-stoichiometric consumption of $PhSiH_3$ in the reaction of **7** might be attributed to the formation of silane oligomers, or to the reaction of $PhSiH_3$ with yttrium products in the reaction mixture. However, no additional silane or yttrium products could be identified. In addition, the slow disappearance of **7** after the initial consumption of $PhSiH_3$ might be due to the reaction of complex **7** with silane, or with yttrium-containing by-products. In contrast, complex **6** reacted stoichiometrically with $PhSiH_3$, leading to complete consumption of the reagents and formation of $CH_2(SiMe_3)_2$ (95% yield) after 7 h. Thus, the increased steric bulk of the Ind* ligand appears to significantly slow the reactivity of **7** (relative to the analogous alkyl complex **6**) toward a σ-bond metathesis reaction with $PhSiH_3$.

3. Concluding remarks

In an effort to develop new, highly reactive reagents and catalysts for σ-bond metathesis processes, we have investigated alkyl and hydride complexes of the sterically demanding Ind^*_2Y fragment. While complexes of this ligand have been reported for a number of transition metals, lanthanides, and actinides [17], this is the first report of the preparation of alkyl and hydride derivatives of a Group 3 metal containing this ligand. Our initial studies indicate that while some of the reactivity of the alkyl and hydride complexes of the Ind^*_2Y fragment is similar to that observed for compounds of the Cp^*_2Y and Ind'_2Y fragments, there are some notable differences. One is the absence of a stable, base-free hydride complex of the Ind* ligand. Whereas the base-free hydrides $[Cp^*_2YH]_2$ and $[Ind'_2YH]_2$ are stable, isolable compounds [5,12], the increased steric bulk of the Ind* ligand appears to result in more reactive hydride complexes that decompose, possibly via the transient, monomeric Ind^*_2YH. In addition, the increased steric bulk of $Ind^*_2YCH(SiMe_3)_2$ (**6**) leads to a slower reaction with $PhSiH_3$ as compared to $Cp^*_2YCH(SiMe_3)_2$ (**7**). Continuing investigations are focused on the synthesis of silyl complexes of the Ind^*_2Y fragment for use in studies of σ-bond metathesis reactions.

4. Experimental procedures

4.1. General procedures

All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox unless otherwise noted. Dry, oxygen free solvents were used unless otherwise indicated. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and saturated $NaHCO_3$. Pentane was then dried over $MgSO_4$, stored over activated 4 Å molecular sieves, and distilled from potassium benzophenone ketyl under a nitrogen atmosphere. Thiophene impurities were removed from toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Toluene was then dried over $MgSO_4$ and distilled from potassium under a nitrogen atmosphere. Tetrahydrofuran, diethyl ether, and hexanes were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Benzene-d_6, toluene-d_8, tetrahydrofuran-d_8, and cyclohexane-d_{12} were purified and dried by vacuum distillation from sodium/potassium alloy.

NMR spectra were recorded at 500.132 MHz (^1H), 61.423 MHz (^2H), 125.759 MHz (^{13}C), or 132.298 MHz (^{23}Na) using a Bruker DRX-500 (^1H, ^{13}C, ^{23}Na) or AMX-400 (^2H) spectrometer. ^1H and $^2H\{^1H\}$ NMR spectra were referenced internally by the residual solvent signal relative to tetramethylsilane. $^{13}C\{^1H\}$ NMR spectra were referenced internally by the ^{13}C NMR signal of the NMR solvent relative to tetramethylsilane. ^{23}Na NMR spectra were referenced relative to an NaCl (in H_2O) external standard. In some cases, distortionless enhancement by polarization transfer (DEPT) was used to assign the ^{13}C NMR resonances as CH_3, CH_2, CH, or C groups. Heteronuclear multiple quantum coherence (HMQC) was used to identify ^1H,^{13}C coupling, heteronuclear multiple bond correlation (HMBC) was used to identify some ^{13}C NMR resonances, and total correlation spectroscopy (TOCSY) was used to identify some coupled ^1H NMR systems. All spectra were recorded at room temperature (~22 °C) unless otherwise indicated. Infrared spectra were recorded as KBr pellets using a Mattson FTIR spectrometer at a resolution of 4 cm^{-1}. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

All chemicals were purchased from Aldrich, Fluka, or Cerac and used without further purification. Hydrogen was purchased from Praxair and deuterium was purchased from Airgas. The compounds Ind*H [19], $LiCH(SiMe_3)_2$ [34], $Cp^*_2YCH(SiMe_3)_2$ (**7**) [33], $KSi(SiMe_3)_3$ [35–37], and $(THF)_3LiSi(SiMe_3)_3$ [38] were prepared as reported in the literature.

4.2. Synthesis of Ind*Na (*1*)

THF (100 ml) was added to solid Ind*H (4.911 g, 22.9 mmol) and NaH (2.776 g, 116 mmol) to give a gray suspension which was heated at reflux for three days (90 °C bath). After cooling to room temperature, the bright, yellow–green reaction mixture was filtered, and the remaining solid was extracted with THF (2 × 80 ml) to

give a gold-colored solution. Evaporation of the combined THF extracts gave a yellow crystalline solid, which was washed with hexanes (3×40 ml, until the washings appeared colorless) and dried in vacuo to afford **1** as a light yellow solid (5.067 g, 94%). ^{1}H NMR (tetrahydrofuran-d_8): δ 2.17 (s, 6H, C_9Me_7), 2.21 (s, 3H, C_9Me_7), 2.62 (s, 6H, C_9Me_7), 2.63 (s, 6H, C_9Me_7). $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8): 12.4 ($C_9\mathit{Me}_7$), 15.8 ($C_9\mathit{Me}_7$), 16.7 ($C_9\mathit{Me}_7$), 18.2 ($C_9\mathit{Me}_7$), 95.9 (C_9Me_7), 117.5 (C_9Me_7), 122.4 (C_9Me_7), 123.7 (C_9Me_7), 124.8 (C_9Me_7). $^{23}Na\{^1H\}$ NMR (tetrahydrofuran-d_8): δ −26.5. IR (KBr, cm^{-1}): 421 (w), 556 (vw), 607 (vw), 667 (vw), 721 (vw), 763 (vw), 809 (w), 898 (vw), 962 (w), 1005 (m), 1029 (m), 1058 (m), 1092 (m), 1116 (m), 1163 (m), 1185 (vw), 1290 (m), 1355 (m), 1374 (m), 1384 (m), 1447 (s), 1576 (vw), 1629 (w), 2727 (m), 2864 (vs), 2911 (vs), 2962 (vs). Anal. Calc. for $C_{16}H_{21}Na$: C, 81.32; H, 8.96. Found: C, 81.07; H, 9.10.

4.3. Synthesis of Ind*$_2$YCl(THF) (2)

A solution of **1** (2.037 g, 8.62 mmol) in THF (50 ml) was added to a suspension of YCl_3 (0.843 g, 4.32 mmol) in THF (50 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and then heated at reflux (85 °C bath) for 5 h. After cooling the cloudy, light-yellow reaction mixture to room temperature, the solvent was removed in vacuo to provide a pale, light-yellow solid. The solid was extracted with toluene (4×35 ml) and the extracts were filtered to give a yellow solution. Removal of the solvent in vacuo gave a light-yellow, crystalline solid, which was washed with pentane (30 ml) to provide **2** as an off-white powder (1.975 g, 74%). Alternatively, the combined toluene extracts can be concentrated and cooled to −35 °C to afford off-white crystals of **2**. ^{1}H NMR (benzene-d_6): δ 0.93 (p, 4H, $J = 4$ Hz, THF), 1.88 (s, 6H, C_9Me_7), 2.04 (s, 12H, C_9Me_7), 2.59 (v broad s, 12H, C_9Me_7), 2.62 (s, 12H, C_9Me_7), 2.86 (t, 4H, $J = 6$ Hz, THF). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 11.7 ($C_9\mathit{Me}_7$), 15.8 (broad s, $C_9\mathit{Me}_7$), 16.8 ($C_9\mathit{Me}_7$), 18.5 ($C_9\mathit{Me}_7$), 25.8 (THF), 72.4 (THF), 106.6 (broad s, C_9Me_7), 110.8 (broad s, C_9Me_7), 127.3 (broad s, C_9Me_7), 130.5 (d, $J_{CY} = 1.4$ Hz, C_9Me_7). IR (KBr, cm^{-1}): 406 (m), 497 (vw), 558 (vw), 578 (vw), 622 (w), 672 (w), 707 (w), 743 (vw), 763 (vw), 814 (w), 859 (s, THF), 913 (vw), 925 (vw), 974 (w), 1010 (s, THF), 1060 (m), 1094 (w), 1119 (w), 1171 (w), 1247 (vw), 1294 (m), 1312 (w), 1384 (s), 1450 (s), 1583 (w), 1630 (w), 2726 (m), 2870 (vs), 2905 (vs), 2963 (vs). Anal. Calc. for $C_{36}H_{50}ClOY$: C, 69.39; H, 8.09. Found: C, 69.38; H, 8.20.

4.4. Synthesis of Ind*$_2$YMe(THF) (3)

A solution of MeLi in diethyl ether (1.6 M, 0.34 mmol) was added to a solution of compound **2** (0.202 g, 0.324 mmol) in THF (20 ml) at −78 °C. After stirring the reaction mixture at −78 °C for 1 h, the cold bath was removed and the mixture was allowed to warm to room temperature over the course of 1 h. The solvent was then removed in vacuo to leave behind an off-white oily foam which was extracted with toluene (2×15 ml) and the extracts were filtered to give a light yellow solution. The solution was concentrated to ~5 ml and cooled to −35 °C to afford white crystals, which were isolated by filtration and washed with pentane (5 ml) to afford compound **3** (0.111 g, 57%). ^{1}H NMR (benzene-d_6): δ −0.48 (d, 3H, $J_{YH} = 2.3$ Hz, YMe), 0.89 (p, 4H, $J = 3$ Hz, THF), 1.85 (s, 6H, C_9Me_7), 2.06 (s, 12H, C_9Me_7), 2.55 (broad s, 12H, C_9Me_7), 2.56 (s, 12H, C_9Me_7), 2.59 (t, 4H, $J = 6$ Hz, THF). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 11.6 ($C_9\mathit{Me}_7$), 15.4 ($C_9\mathit{Me}_7$), 16.8 ($C_9\mathit{Me}_7$), 18.5 ($C_9\mathit{Me}_7$), 25.4 (THF), 25.5 (d, $J_{YC} = 56$ Hz, YMe), 70.4 (THF), 105.1 (broad s, C_9Me_7), 107.4 (broad s, C_9Me_7), 126.2 (broad s, C_9Me_7), 126.3 (C_9Me_7), 129.0 (broad s, C_9Me_7). IR (KBr, cm^{-1}): 503 (m), 577 (vw), 613 (vw), 623 (w), 674 (vw), 728 (vw), 743 (vw), 813 (w), 862 (s, THF), 903 (vw), 912 (vw), 925 (vw), 972 (w), 1013 (s, THF), 1060 (m), 1086 (m), 1119 (w), 1138 (vw), 1173 (w), 1214 (vw), 1245 (w), 1294 (s), 1358 (m), 1383 (s), 1407 (m), 1450 (s), 1583 (w), 2587 (vw), 2724 (m), 2901 (vs), 2956 (vs). Anal. Calc. for $C_{37}H_{53}OY$: C, 73.73; H, 8.86. Found: C, 73.48; H, 8.66.

4.5. Synthesis of Ind*$_2$YH(THF) (4)

Compound **3** (0.091 g, 150 μmol) was dissolved in toluene (20 ml), and the resulting solution was transferred to a 50 ml reaction vessel. The solution was degassed, H_2 (1 atm) was admitted, and the reaction solution was stirred at room temperature. After 1 h, the light, yellow–orange reaction mixture was filtered, concentrated to ~5 ml, and cooled to −35 °C to provide yellow crystals. The crystals were washed with pentane (~3 ml) and were dried in vacuo to obtain **4** (0.037 mg, 42%). This reaction was not optimized and the low isolated yield of **4** was likely due to the small reaction scale. ^{1}H NMR (benzene-d_6): δ 0.89 (m, $J = 1.5$ Hz, THF), 2.04 (s, 18H, C_9Me_7), 2.49 (broad s, 6H, C_9Me_7), 2.65 (broad s, 6H, C_9Me_7), 2.65 (hidden m, 4H, THF), 2.75 (broad s, 6H, C_9Me_7), 2.88 (broad s, 6H, C_9Me_7), 6.04 (d, 1H, $J_{YH} = 82.0$ Hz, YH). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 12.1 ($C_9\mathit{Me}_7$), 15.2 (broad s, $C_9\mathit{Me}_7$), 16.8 ($C_9\mathit{Me}_7$), 17.0 (broad s, $C_9\mathit{Me}_7$), 18.3 ($C_9\mathit{Me}_7$), 24.9 (THF), 69.2 (THF), 103.4 (broad s, C_9Me_7), 109.3 (broad s, C_9Me_7), 125.2 (broad s, C_9Me_7), 125.8 (broad s, C_9Me_7), 126.1 (broad s, C_9Me_7), 126.5 (broad s, C_9Me_7), 127.9 (broad s, C_9Me_7), 128.9 (C_9Me_7), 129.0 (C_9Me_7), 129.7 (C_9Me_7). IR (KBr, cm^{-1}): 413 (m), 468 (m), 557 (w), 577 (w), 624 (m), 652 (s), 707 (vw), 728 (vw), 743 (vw), 813 (w), 842 (m), 852 (m), 865 (m), 904 (vw), 921 (vw), 971 (m), 1011 (s, THF), 1059 (m), 1092 (m), 1120 (m), 1177 (m), 1295 (vs), 1322 (s, broad, ν_{YH}),

1331 (s), 1355 (s), 1378 (s), 1449 (vs), 1583 (w), 1630 (vw), 1656 (vw), 2725 (m), 2869 (vs), 2903 (vs), 2966 (vs). Anal. Calc. for $C_{36}H_{51}OY$: C, 73.45; H, 8.73. Found: C, 73.27; H, 8.96.

4.6. Synthesis of Ind*$_2$YD(THF) (4-d)

An essentially identical procedure to that used to prepare **4** (substituting D_2 for H_2) yielded yellow crystals of compound **4-*d*** (16.1 mg, 38%). Selected data: $^2H\{^1H\}$ NMR (benzene): δ 6.08 (d, $J_{YD} = 12.6$ Hz, YD). IR (KBr, cm^{-1}): 942 (m, broad, ν_{YD}). Anal. Calc. for $C_{36}H_{50}DOY$: C, 73.32; H, 8.72. Found: C, 73.07; H, 8.87.

4.7. Synthesis of Ind*$_2$YCl (5)

Toluene (40 ml) was added to solid **1** (0.511 g, 2.16 mmol) and YCl_3 (0.211 g, 1.08 mmol) to give a yellow suspension. After heating at reflux (130 °C bath) for 15.5 h, the orange reaction mixture was cooled to room temperature and was filtered. The orange solid left behind was extracted with toluene (2×15 ml) and the extracts were filtered. The orange solution obtained from the extraction was then concentrated to ~10 ml and cooled to −35 °C to afford orange crystals of **5** (0.114 g, 19%). ^1H NMR (benzene-d_6): δ 1.90 (s, 6H, η^5-C_9Me_7), 2.03 (s, 12H, C_9Me_7), 2.35 (s, 12H, η^5-C_9Me_7), 2.39 (s, 12H, C_9Me_7). $^{13}C\{^1H\}$ NM (benzene-d_6): δ 11.6 (η^5-$C_9\mathit{Me}_7$), 14.5 (η^5-$C_9\mathit{Me}_7$), 16.8 ($C_9\mathit{Me}_7$), 18.0 ($C_9\mathit{Me}_7$), 108.4 (d, $J_{CY} = 1.4$ Hz, η^5-C_9Me_7), 126.2 (d, $J_{CY} = 1.6$ Hz, η^5-C_9Me_7), 127.2 (C_9Me_7), 127.8 (C_9Me_7), 130.8 (d, $J_{CY} = 0.7$ Hz, η^5-C_9Me_7). IR (KBr, cm^{-1}): 408 (m), 557 (w), 576 (w), 612 (w), 626 (w), 651 (m), 729 (w), 764 (vw), 813 (vw), 904 (vw), 973 (w), 1007 (m), 1023 (m), 1063 (m), 1095 (m), 1121 (w), 1172 (vw), 1293 (m), 1383 (s), 1448 (s), 1582 (w), 1630 (w), 2726 (m), 2869 (vs), 2912 (vs), 2959 (vs). Anal. Calc. for $C_{32}H_{42}ClY$: C, 69.75; H, 7.68. Found: C, 69.99; H, 7.65.

4.8. Synthesis of Ind*$_2$YCH(SiMe$_3$)$_2$ (6)

Chilled (−78 °C) diethyl ether (30 ml) was added to solid **2** (0.176 g, 0.282 mmol) and $LiCH(SiMe_3)_2$ (0.068 g, 0.33 mmol) to give an off-white suspension which was stirred at −78 °C for 1 h. The reaction flask was then transferred to an ice bath. After stirring at 0 °C for 1 h, the solvent was removed from the bright yellow reaction mixture in vacuo (at 0 °C) to leave behind a light yellow solid. The solid was extracted with cold (0 °C) toluene (2×10 ml) and the extracts were filtered to give a bright yellow solution. The solution was concentrated to ~5 ml and cooled to −35 °C to afford bright yellow crystals of **6** (0.051 g, 27%). ^1H NMR (benzene-d_6): δ −0.37 (d, 1H, $J_{YH} = 2.3$ Hz, YCH), 0.03 (s, 18H, $(SiMe_3)_2$), 1.83 (s, 3H, η^5-C_9Me_7), 2.11 (s, 6H, C_9Me_7), 2.13 (s, 6H, C_9Me_7), 2.18 (d, 3H, $J_{YH} = 1$ Hz, η^5-C_9Me_7), 2.23 (s, 6H, C_9Me_7), 2.25 (s, 6H, C_9Me_7), 2.38 (s, 6H, C_9Me_7), 2.44 (s, 6H, C_9Me_7). $^{13}C\{^1H\}$ NMR (benzene-d_6): 5.0 ($(SiMe_3)_2$), 11.9 (η^5-$C_9\mathit{Me}_7$), 14.8 (η^5-$C_9\mathit{Me}_7$), 14.9 ($C_9\mathit{Me}_7$), 15.7 ($C_9\mathit{Me}_7$), 16.9 ($C_9\mathit{Me}_7$), 17.0 ($C_9\mathit{Me}_7$), 18.1 ($C_9\mathit{Me}_7$), 18.6 ($C_9\mathit{Me}_7$), 27.5 (d, $J_{YC} = 35.2$ Hz, YCH), 107.2 (d, $J_{YC} = 1.5$ Hz, η^5-C_9Me_7), 107.7 (d, $J_{YC} = 1.5$ Hz, η^5-C_9Me_7), 126.9 (C_9Me_7), 127.3 (C_9Me_7), 128.8 (d, $J_{YC} = 0.7$ Hz, C_9Me_7), 129.0 (C_9Me_7), 129.1 (d, $J_{YC} = 0.7$ Hz, C_9Me_7), 129.4 (C_9Me_7), 131.6 (d, $J_{YC} = 1.2$ Hz, η^5-C_9Me_7), 137.2 (d, $J_{YC} = 1.2$ Hz, η^5-C_9Me_7). IR (KBr, cm^{-1}): 407 (m), 557 (m), 583 (m), 604 (m), 669 (m), 697 (m), 720 (w), 762 (m), 837 (vs), 853 (vs), 903 (w), 971 (w), 1007 (m), 1032 (m), 1060 (w), 1094 (w), 1120 (w), 1172 (vw), 1185 (vw), 1241 (m), 1254 (m), 1293 (w), 1383 (m), 1449 (s), 1582 (w), 1630 (w), 2727 (w), 2870 (vs), 2908 (vs), 2946 (vs). Anal. Calc. for $C_{39}H_{61}Si_2Y$: C, 69.40; H, 9.11. Found: C, 68.35; H, 8.78.

4.9. Reactivity comparison of Ind*$_2$YCH(SiMe$_3$)$_2$ (6) and Cp*$_2$YCH(SiMe$_3$)$_2$ (7) with PhSiH$_3$

Complexes **6** (12 mg, 18 μmol) and **7** (9 mg, 20 μmol) were dissolved separately along with Cp_2Fe (3 mg, 20 μmol) in benzene-d_6 (0.7 ml), and the resulting solutions were transferred to NMR tubes fitted with J. Young Teflon stoppers. Phenylsilane (2.4 μl, 19 μmol) was then added to each NMR tube via syringe, and reaction progress was monitored by ^1H NMR spectroscopy at room temperature relative to the Cp_2Fe internal standard.

4.10. X-ray single crystal structure determination of 2

4.10.1. X-ray crystal structure determination of 2

Crystals suitable for X-ray diffraction were obtained by slow evaporation of solvent from a concentrated benzene-d_6 solution of **2**. A colorless, rod-like crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. X-ray diffraction measurements were made on a Siemens SMART diffractometer with a CCD area detector, using graphite-monochromated MoKα radiation. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range $4.38° < 2\theta < 40.65°$. The orientation matrix gave a primitive, monoclinic cell with dimensions described below. Data were collected for 10 s frames. The frame data were integrated using the program SAINT [39]. An empirical absorption correction based on measurements of multiply redundant data was performed using the program SADABS [40]. In addition, XPREP [41] clearly indicated the space group was $P2_1/n$ (#14). Equivalent reflections were merged. The data

were corrected for Lorentz and polarization effects. The structure was solved using the teXsan crystallographic software package of the Molecular Structure Corporation, using direct methods (SIR92), and expanded with Fourier techniques.

The structure consists of one molecule of **2** per asymmetric unit. Due to a rapid decrease in intensity with increasing (SINθ)/λ, data were integrated to 0.95 Å. As a result, the Ind* ring carbon atoms were refined isotropically, while the methyl, THF, chlorine, and yttrium atoms were refined anisotropically. C(100) and C(101) were added as the centroids of the η^5-heptamethylindenyl ligands, defined as the average of the x, y, and z coordinates of carbons C(1)–C(5) and C(10)–C(14), respectively. All hydrogen atoms were refined isotropically in geometrically calculated positions. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a p-factor to downweight the intense reflections. Crystallographic data are summarized below.

4.10.2. Crystal data for **2**

Colorless, rod-like crystal of dimensions $0.31 \times 0.12 \times 0.05$ mm; air and moisture sensitive; $C_{36}H_{50}ClOY$, $M_w = 623.14$ g/mol; $a = 8.962(1)$ Å, $b = 24.325(7)$ Å, $c = 14.649(4)$ Å, $\beta = 100.267(2)°$, $V = 3142(1)$ Å^3; monoclinic, $P2_1/n$ (#14), $Z = 4$; Siemens SMART CCD, MoKα ($\lambda = 0.71069$ Å), ω-scan (0.3° per frame), 10.0 s per frame; 11,475 reflections were measured of which 3966 were unique; $R_{int} = 0.088$; empirical absorption correction; $R = 0.045$, $R_w = 0.045$; 1899 observations ($I > 3.00\sigma(I)$), 262 variables; full-matrix least-squares refinement on F^2. Hydrogen atoms were refined isotropically in geometrically calculated positions.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 218988 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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References

[1] A.J. Hoskin, D.W. Stephan, Coord. Chem. Rev. 233–234 (2002) 107.
[2] W.E. Piers, D.J.H. Emslie, Coord. Chem. Rev. 233–234 (2002) 131.
[3] E.E. Bunel, B.J. Burger, J.E. Bercaw, J. Am. Chem. Soc. 110 (1988) 976.
[4] W.E. Piers, P.J. Shapiro, E.E. Bunel, J.E. Bercaw, Synlett (1990) 74.
[5] W.P. Kretschmer, S.I. Troyanov, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 17 (1998) 284.
[6] R. Duchateau, C.T. van Wee, J.H. Teuben, Organometallics 15 (1996) 2291.
[7] E.B. Coughlin, J.E. Bercaw, J. Am. Chem. Soc. 114 (1992) 7606.
[8] K.C. Hultzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 228.
[9] T.I. Gountchev, T.D. Tilley, Organometallics 18 (1999) 5661.
[10] A.A. Trifonov, T.P. Spaniol, J. Okuda, Organometallics 20 (2001) 4869.
[11] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.
[12] K.H. den Haan, Y. Wielstra, J.H. Teuben, Organometallics 6 (1987) 2053.
[13] M. Booij, B.-J. Deelman, R. Duchateau, D.S. Postma, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 3531.
[14] A.D. Sadow, T.D. Tilley, Angew. Chem. Int. Ed. 42 (2003) 803.
[15] C.P. Casey, J.A. Tunge, T.-Y. Lee, D.W. Carpenetti, Organometallics 21 (2002) 389.
[16] T.K. Miyamoto, M. Tsutsui, L.-B. Chen, Chem. Lett. (1981) 729.
[17] T.M. Trnka, J.B. Bonanno, B.M. Bridgewater, G. Parkin, Organometallics 20 (2001) 3255.
[18] M. Tsutsui, L.-B. Chen, D.E. Bergbreiter, T.K. Miyamoto, J. Am. Chem. Soc. 104 (1982) 855.
[19] D. O'Hare, J.C. Green, T. Marder, S. Collins, G. Stringer, A.K. Kakkar, N. Kaltsoyannis, A. Kuhn, R. Lewis, C. Mehnert, P. Scott, M. Kurmoo, S. Pugh, Organometallics 11 (1992) 48.
[20] W.J. Evans, J.W. Grate, K.R. Levan, I. Bloom, T.T. Peterson, R.J. Doedens, H. Zhang, J.L. Atwood, Inorg. Chem. 25 (1986) 3614.
[21] K.H. den Haan, Y. Wielstra, J.J.W. Eshuis, J.H. Teuben, J. Organomet. Chem. 323 (1987) 181.
[22] K.H. den Haan, J.L. de Boer, J.H. Teuben, J. Organomet. Chem. 327 (1987) 31.
[23] W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 104 (1982) 2008.
[24] T.D. Tilley, Acc. Chem. Res. 26 (1993) 22.
[25] H.-G. Woo, J.F. Walzer, T.D. Tilley, J. Am. Chem. Soc. 114 (1992) 7047.
[26] N.S. Radu, T.D. Tilley, A.L. Rheingold, J. Organomet. Chem. 516 (1996) 41.
[27] N.S. Radu, T.D. Tilley, A.L. Rheingold, J. Am. Chem. Soc. 114 (1992) 8293.
[28] M.P. Engeler, T.D. Tilley, unpublished results.
[29] I. Castillo, T.D. Tilley, J. Am. Chem. Soc. 123 (2001) 10526.
[30] I. Castillo, T.D. Tilley, Organometallics 20 (2001) 5598.
[31] W.J. Evans, T.T. Peterson, M.D. Rausch, W.E. Hunter, H. Zhang, J.L. Atwood, Organometallics 4 (1985) 554.
[32] K.H. den Haan, J.H. Teuben, J. Organomet. Chem. 322 (1987) 321.
[33] K.H. den Haan, J.L. de Boer, J.H. Teuben, A.L. Spek, B. Kojic-Prodic, G.R. Hays, R. Huis, Organometallics 5 (1986) 1726.
[34] A.H. Cowley, R.A. Kemp, Synth. React. Inorg. Met.-Org. Chem. 11 (1981) 591.
[35] C. Kayser, R. Fischer, J. Baumgartner, C. Marschner, Organometallics 21 (2002) 1023.

[36] C. Kayser, C. Marschner, Monatshefte für Chemie 130 (1999) 203.
[37] C. Marschner, Eur. J. Inorg. Chem. (1998) 221.
[38] G. Gutekunst, A.G. Brook, J. Organomet. Chem. 225 (1982) 1.
[39] SAX Area-Detector Integration Program, V4.024, Siemens Industrial Automation, Inc., Madison, WI, 1995.
[40] G.M. Sheldrick, Siemens Area Detector Absorption Corrections, Siemens Industrial Automation, Inc., Madison, WI, 1996.
[41] SHELXTL Crystal Structure Determination Package, Siemens Industrial Automation, Inc., Madison, WI, 1995.