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Why propene is not polymerized by $(Cp^*_2YH)_2$: reactions of yttrium alkyl complexes with alkenes produce allyl and vinyl yttrium complexes

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday and in recognition of his leading role in advancing organometallic chemistry in Spain

Abstract

Yttrium alkyl complexes Cp^*_2YR react with C–H bonds of alkenes to form either yttrium allyl complexes or yttrium vinyl complexes. Less substituted alkenes react faster, consistent with prior alkene coordination. The selectivity of the reaction of Cp^*_2YR with C–H bonds is allylic $CH_3 \gg$ vinyl C–H $\gg$ allylic CH_2. Propene is readily metallated by Cp^*_2YR giving the η^3-allyl complex $Cp^*_2Y(\eta^3\text{-}CH_2{-}{-}{-}CH{-}{-}{-}CH_2)$ which does not react further with propene. This explains why Cp^*_2YR (R = alkyl, H) complexes make poor propene polymerization catalysts.

Keywords: Alkene polymerization; Termination; Allyl complex; Vinyl complex

1. Introduction

Group III and lanthanide hydrides are highly active ethylene polymerization catalysts [1]. However, attempts to polymerize propene with bis(pentamethylcyclopentadienyl)lanthanide hydrides have resulted only in low molecular weight oligomers, presumably due to a high rate of chain termination relative to propagation. A recent theoretical study of propene polymerization using yttrium hydride catalysts concluded that propene polymerization by $(Cp^*_2YH)_2$ does not occur because the barrier for insertion of propene into the Y–H of Cp^*_2YH to form $Cp^*_2YCH_2CH_2CH_3$ is too large [2]. Our experimental result that propene reacts with $(Cp^*_2YH)_2$ at −80 °C to form $Cp^*_2YCH_2CH(CH_3)CH_2CH_2CH_3$ was apparently ignored and shows that this theoretical study clearly fails to reflect reality [3]. Given this discrepancy, we sought better understanding of the pathway(s) for termination in the polymerization of alkenes by $(Cp^*_2YH)_2$.

1-Alkene polymerization by Cp^*_2LaH was shown to terminate by formation of La-allyl complexes (Scheme 1) [1c]. Similarly, in an elegant study, Evans observed that the reaction of $(Cp^*_2SmH)_2$ with 1-alkenes terminates in formation of Sm–allyl complexes [4]. However, the reaction of Sc alkyls with 1-alkenes produces scandium vinyl complexes rather than scandium allyl complexes [5]. Here we report observation of both of these modes of metallation of alkenes by yttrium alkyl complexes. In addition, we explain why $(Cp^*_2YH)_2$ catalyzes the polymerization of ethylene, but not propene.

2. Results and discussion

2.1. Reaction of propene with $(Cp^*_2YH)_2$

Previously, we reported the mechanistic details of formation of yttrium alkyls from reaction of $(Cp^*_2YH)_2$

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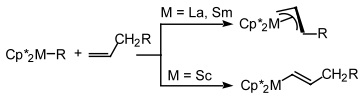


Scheme 1.

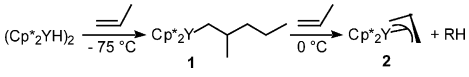
with alkenes [3b]. Overall, $(Cp^*_2YH)_2$ reacts with excess propene at −75 °C in methylcyclohexane-d_{14} to produce $Cp^*_2YCH_2CH(CH_3)CH_2CH_2CH_3$ (**1**) in >95% yield based on $CH_2(SiMe_3)_2$ internal standard. This complex does not insert another equivalent of propene (~0.1 M) up to 0 °C. At 0 °C, a new complex forms which we have identified as the η^3-allyl complex $Cp^*_2Y(\eta^3\text{-}CH_2\text{---}CH\text{---}CH_2)$ (**2**) (Scheme 2) [3b]. The ^{1}H-NMR spectrum of **2** shows inequivalent Cp* ligands and equivalent allyl termini, consistent with a symmetric η^3-allyl ligand.

We observe a similar reaction of propene with $Cp^*_2YCH_2CH(CH_3)CH_2CH_2CH(CH_3)_2$ (**3**). Compound **3** is prepared from the reaction of 3-methyl-1-butene with $(Cp^*_2YH)_2$ followed by treatment with propene [3]. When **3** is warmed to 0 °C in the presence of propene, π-allyl **2** is formed with concomitant liberation of $(CH_3)_2CHCH_2CH_2CH(CH_3)_2$.

These results suggest that the yttrium alkyl group acts to remove a hydrogen from propene. Compound **2** is unreactive toward further insertion of propene (0.05 M) at 90 °C, thus it is clear that propene polymerization by $(Cp^*_2YH)_2$ terminates by formation of $Cp^*_2Y(\eta^3\text{-}CH_2\text{---}CH\text{---}CH_2)$.

2.2. Reaction of Cp^*_2YR with other alkenes

Reaction of $(Cp^*_2YH)_2$ with excess 2-methylpropene at −50 °C results in the formation of $Cp^*_2YCH_2CH(CH_3)_2$ (**4**) which is often contaminated with 5–10% of the allyl complex $Cp^*_2Y[\eta^3\text{-}CH_2{=}C(CH_3){=}CH_2]$ (**5**) [6]. Warming this solution of **4** and 2-methylpropene (0.2 M) to room temperature for 1 h results in the disappearance of **4** and the appearance of additional **5** (85% yield). At room temperature, the new complex **5** appears to have only two resonances, a singlet corresponding to a Cp* at δ 1.92 and a doublet at δ 2.11. However, cooling this solution to −50 °C results in the sharpening and appearance of additional peaks at δ 2.85 and 1.82 ppm, typical of terminal allyl hydrogens. Furthermore, the ^{13}C-NMR spectrum at −50 °C shows 2 Cp* resonances, indicative of η^3 binding of the allyl ligand. All data are consistent with the assignment of the product as $Cp^*_2Y[\eta^3\text{-}CH_2\text{---}C(CH_3)\text{---}CH_2]$ (**5**) [6].



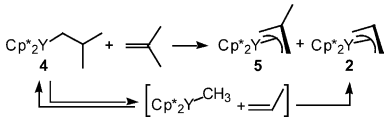
Scheme 2.

If lower concentrations of 2-methyl propene (0.04 M) are used to generate **5**, two products form. The major product **5** (65%) results from allylic activation of 2-methylpropene. In addition, a significant amount of η^3-allyl complex **2** (17%) is also observed. The appearance of **2** is likely a result of β-methyl elimination from **4** to form $(Cp^*_2YCH_3)_2$ and propene. The propene can then react with an yttrium alkyl to form the η^3-allyl complex **2** (Scheme 3). This hypothesis is in accord with the observation that $Cp^*_2LuCH_2CH(CH_3)_2$ undergoes facile β-methyl elimination [7]. Finally, the observation that the ratio of **5**:**2** increases with increasing concentration of 2-methylpropene suggests that the formation of **5** from **4** depends on [alkene].

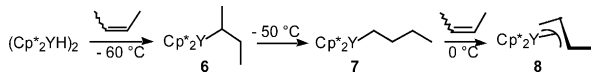
Allylic C–H activation is also observed when yttrium alkyls are treated with 2-butene. $(Cp^*_2YH)_2$ reacts with *cis*- or *trans*-2-butene to initially form $Cp^*_2YCH(CH_3)CH_2CH_3$ (**6**). When **6** is kept at −50 °C, the secondary alkyl complex **6** isomerizes to the primary alkyl complex $Cp^*_2YCH_2CH_2CH_2CH_3$ (**7**) ($t_{1/2}$ = 10 min) in 85±5% yield; in addition, the formation of $Cp^*_2Y(\eta^3\text{-}CH_2\text{---}CH\text{---}CHCH_3)$ (**8**) in 15±5% yield (presumably from reaction of **7** with 2-butene) is seen. Further warming to 0 °C results in complete conversion to **8** (Scheme 4). The ^{1}H-NMR spectrum of **8** at −60 °C shows two different Cp* resonances and four distinct allyllic resonances typical of a static η^3-allyl structure. The presence of small quantities of **8** when **7** is generated at −60 °C suggests that Cp^*_2YH is also capable of reacting with 2-butene to form **8**; the $t_{1/2}$ for the reaction of **7** with 2-butene at −60 °C is estimated to be >20 h.

2.3. Allyl coordination dynamics

Dynamic NMR spectra of metal allyl complexes have been extensively studied. Since η^3–η^1 allyl complex interconversion involves a formal dissociation of an alkene from a metal, the activation barriers for these processes have been used as a measure of the upper limit of alkene binding energy [8]. Two different Cp* resonances are seen in the ^{1}H-NMR spectrum of $Cp^*_2Y(\eta^3\text{-}CH_2\text{---}CH\text{---}CHCH_3)$ (**8**) at −60 °C. However, as the temperature is raised, these resonances broaden and eventually coalesce at −5 °C ($\Delta G^{\ddagger}$ = 13.6 (2) kcal mol^{-1}) and become a sharp singlet at 25 °C. The exchange of the Cp* environments of **8** is attributed to reversible alkene dissociation to from a transient η^1-allyl



Scheme 3.



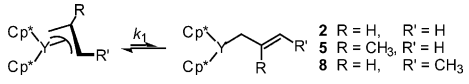
Scheme 4.

yttrium complex that undergoes rapid rotation about the Y–CH_2 bond (Scheme 5).

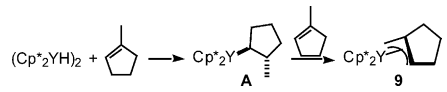
Related fluxional processes are seen for the η^3-allyl complexes **5** and **2**. In the ^{13}C-NMR spectra of $Cp^*_2Y[\eta^3\text{-}CH_2{-}{-}{-}C(CH_3){-}{-}{-}CH_2]$ (**5**), the Cp* resonances coalesce at −8 °C ($\Delta G^{\ddagger} = 12.8$ (2) kcal mol^{-1}) [9]. In the ^{1}H-NMR spectra of $Cp^*_2Y(\eta^3\text{-}CH_2CHCH_2)$ (**2**), the Cp* resonances coalesce at 44 °C ($\Delta G^{\ddagger} = 16.1$ (2) kcal mol^{-1}) [9]. Simulation of the temperature dependence of the Cp* line-broadening of **2** provides $\Delta H^{\ddagger} = 19.9$ (3) kcal mol^{-1} and $\Delta S^{\ddagger} = 12$ (2) eu. Extrapolation of the rate of η^3–η^1 interconversion to −5 °C shows that the rate of alkene dissociation from **2** at −5 °C is 0.28 s^{-1}. The rates of alkene dissociation (k_1) from **5** and **8** are 88 and 288 s^{-1}, respectively. This demonstrates that methyl substitution on the allyl ligand increases the rate of alkene dissociation by 300 for terminal carbon substitution and 1000 for center carbon substitution.

2.4. Selectivity of C–H activation and formation of yttrium vinyl complexes

Having shown that yttrium alkyls readily react with a variety of allylic methyl groups to form η^3-allyl complexes, we wanted to determine whether hydrogen abstraction from allylic methylene groups might occur as well. To do so, $(Cp^*_2YH)_2$ was treated with 1-methylcyclopentene to presumably give yttrium alkyl **A**, which might react with one of the two allylic methylene groups or the allylic methyl group of 1-methylcyclopentene. Reaction of $(Cp^*_2YH)_2$ with 1-methylcyclopentene at 0 °C results in formation of a single product $Cp^*_2Y(\eta^3\text{-}CH_2{-}{-}{-}C{-}{-}{-}CHCH_2CH_2CH_2)$ (**9**) in 85% NMR yield (Scheme 6). The structure of **9** was assigned based on the observation of a doublet in the ^{13}C-NMR spectrum at δ 50.77 ($J_{YC} = 12$ Hz; ^{89}Y has $I = 1/2$ and is 100% abundant) which was shown to be a CH_2 by a DEPT-135 NMR experiment. No evidence was obtained for complexes resulting from reaction at either of the methylene positions of 1-methylcyclopentene. This shows that the yttrium complex reacts very selectively with the CH_3 group of 1-methylcyclopentene. Although we have not investigated the complex **9** by low temperature NMR spectroscopy, the small Y–C coupling constant is characteristic of η^3-



Scheme 5.

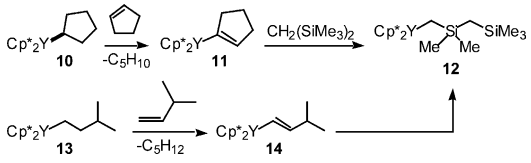


Scheme 6.

allyl binding; typical Y–C coupling constants for yttrium–alkyl bonds are 30–60 Hz whereas those of yttrium allyls are 2–10 Hz.

To test whether Cp^*_2YR complexes are capable of activating allylic methylene C–H bonds in the absence of allylic methyl groups, we chose to study the reaction of Cp^*_2YR and cyclopentene. The reaction between $(Cp^*_2YH)_2$ (0.015 M, containing 0.035 M $CH_2(SiMe_3)_2$ as an internal standard generated in the synthesis of $(Cp^*_2YH)_2$) and cyclopentene (0.12 M) was followed by ^{1}H-NMR spectroscopy. At −30 °C, cyclopentene inserts into the Y–H bond to form the cyclopentyl complex $Cp^*_2YCHCH_2CH_2CH_2CH_2$ (**10**) in quantitative yield ($t_{1/2}$ ~10 min). When the solution is warmed to 0 °C, a new Cp* resonance begins to grow at δ 1.83; at longer reaction times, this resonance gradually disappears. Concomitant with the formation of this new complex, a large singlet corresponding to cyclopentane grows in. Despite the transient nature of this new complex, ^{1}H and COSY NMR spectroscopies allow tentative assignment as the vinyl complex $Cp^*_2YC{=}CHCH_2CH_2CH_2$ (**11**). The observation of a single Cp* resonance down to −70 °C and a single alkene proton coupled to two different methylene groups is consistent with **11** and inconsistent with either an η^1- or η^3-allyl structure. Compound **11** is not stable and was only generated in varying quantities along with the ultimate product of the reaction $Cp^*_2YCH_2$-$Si(Me)_2CH_2Si(Me)_3$ (**12**) (Scheme 7). For example, at 86% conversion, the ratio of **11**:**12** is 3:2. The ratio of **11**:**12** is dependent on the initial concentration of alkene. Compound **12** forms as the result of metallation of $CH_2(SiMe_3)_2$ present from the hydrogenation of $Cp^*_2YCH(SiMe_3)_2$ to form $(Cp^*_2YH)_2$.

Cyclopentenyl complex **11** is the product of activation of a vinyl C–H bond. Once again there is no evidence for activation of the allylic methylene C–H bonds. Vinyl C–H activation is well known for reactions of related scandium alkyls with alkenes [5]. In contrast, Marks reported that Cp^*_2LaH reacts with cyclohexene to form an unstable complex which was tentatively assigned as the η^1-allyl complex $Cp^*_2LaCHCH{=}CHCH_2CH_2CH_2$ [1c]. In light of our observations, along with careful



Scheme 7.

examination of the Marks ^{1}H-NMR spectral data, we suggest that Marks product is more likely the La–vinyl complex $Cp^*_2LaCH{=}CHCHCH_2CH_2CH_2$.

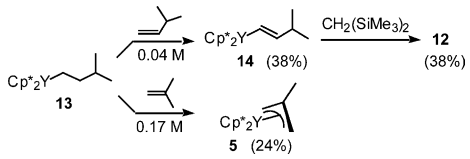
The thermodynamic product in the reaction of Cp^*_2YH with cyclopentene in the presence of $CH_2(SiMe_3)_2$ is **12**. Teuben has shown that $(Cp^*_2YH)_2$ catalyzes H–D exchange between C_6D_6 and $CH_2(SiMe_3)_2$ at room temperature, indicating that Cp^*_2YH can activate C–H bonds of $CH_2(SiMe_3)_2$. It appears that the formation of **12** is the result of activation of $CH_2(SiMe_3)_2$ by yttrium alkyls rather than yttrium hydride as there is no easy way to form Cp^*_2YH from cyclopentenyl complex **11**.

Consistent with the inability of Cp^*_2YR to react with allylic methylene groups, yttrium alkyls also failed to react with the hindered allylic methine C–H bond in 3-methyl-1-butene (Scheme 7). When $Cp^*_2YCH_2CH_2CH(CH_3)_2$ (**13**) is warmed to room temperature in the presence of excess 3-methyl-1-butene, metallation of the alkene occurs to give the yttrium vinyl complex *trans*-$Cp^*_2YCH{=}CHCH(CH_3)_2$ (**14**). Like **11**, complex **14** reacts with $CH_2(SiMe_3)_2$ to give **12**. Vinyl complex **14** was generated in ca 40% yield along with **13** (30%) and **12** (30%) and this mixture was cooled to −50 °C and characterized by ^{1}H, ^{13}C, DEPT-135, COSY, 1D TOCSY, HSQC and HMBC NMR spectroscopies. The ^{13}C-NMR spectrum shows a doublet at 184.5 ppm ($J_{YC} = 45$ Hz) due to coupling with ^{89}Y (100%, $I = 1/2$) indicative of an sp^2 carbon bound to yttrium. Furthermore, the *trans* substitution of the alkene is apparent from the large 22 Hz coupling between the alkene protons. Apparently substitution at the allylic position makes the hydrogen sterically less accessible leading to preferential activation of a vinyl hydrogen. Warming the solution back to room temperature converts the yttrium vinyl complex **14** completely to **12**.

This same type of reaction occurs when $Cp^*_2Y(\eta^1,\eta^2\text{-}CH_2CH_2CH(CH_3)CH{=}CH_2)$ (**15**) [10] is warmed to 20 °C for 10 min and $Cp^*_2YCH{=}CHCH(CH_3)CH_2CH_3$ (**16**) is formed in 78% yield (Scheme 8). This reaction appears to occur in an intramolecular fashion, but intermolecular pathways have not been ruled out.

2.5. Competition experiments

To investigate substrate selectivity, we chose to study alkene competition for Cp^*_2YR. When $Cp^*_2YCH_2CH_2CH(CH_3)_2$ (**13**) is warmed to 5 °C in the presence of 3-methyl-1-butene (0.04 M) and 2-methylpropene (0.17 M), **13** reacts three times with 3-methyl-1-butene (to give **14** and **12**) for every time it reacts with 2-methylpropene to give η^3-allyl complex **5** (Scheme 9). Taking concentrations into account, this indicates that 3-methyl-1-butene is 13 times more reactive than 2-methylpropene toward **13**. These experiments indicate that there is more to determining the selectivity than just the presence of an allylic methyl group; alkene binding to the metal is also important.



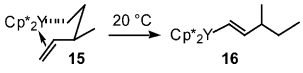
Scheme 9.

To assess the role of alkene binding, $Cp^*_2YCH_2CH(CH_3)CH_2CH_2CH_2CH_3$ (**17**) (0.018 M) was prepared by the treatment of *n*-butyl complex **7** with propene and then its reaction with a mixture of propene (0.05 M) and 2-butene (0.13 M) was studied. Both alkenes have allylic methyl groups, but propene binds to yttrium better. At 24 °C, complex **17** reacted to form a 56:44 ratio of **2** (0.01 M) and **8** (0.008 M) (Scheme 10). Taking concentrations into account, this indicates that **17** reacts with propene at least three times more rapidly than with 2-butene. The more rapid reaction of the better binding alkene suggests that activation occurs from an alkene complex.

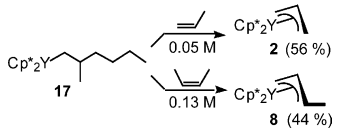
2.6. Alkene oligomerization activity

Since we found a large preference for reaction of yttrium alkyls with allylic methyl C–H bonds compared with crowded allylic methylene or methine C–H bonds, we decided to compare the oligomerization activity of $(Cp^*_2YH)_2$ toward propene, 1-butene, and 1-hexene. While these three alkenes have similar energies of binding to yttrium [11], 1-butene and 1-hexene lack reactive allylic methyl groups that promote the termination process. Consequently, we anticipated that 1-butene and 1-hexene might be better substrates for yttrium catalyzed alkene oligomerization [12].

As mentioned, the reaction of $(Cp^*_2YH)_2$ with propene ultimately results in formation of the η^3-allyl yttrium complex **2**. ^{1}H-NMR spectroscopic studies have shown that at 24 °C each Cp^*_2YH monomer consumes about four equivalents of propene to make the allyl complex. This indicates that on average propene is trimerized, because one equivalent of propene becomes the allyl ligand of termination product **2**.



Scheme 8.



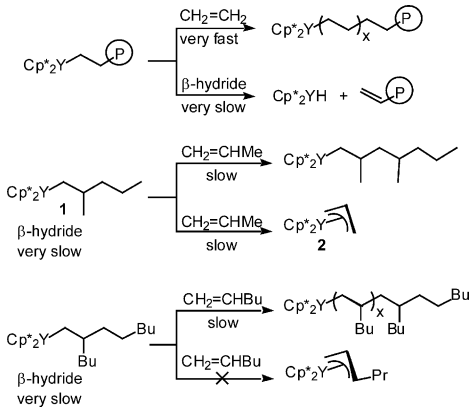
Scheme 10.

1-Butene and 1-hexene react to higher conversions than propene. When 1-butene (0.55 M) is allowed to react with $(Cp^*_2YH)_2$ (0.05 M) or $Cp^*_2YCH_2CH_2CH(CH_3)_2$ (0.08 M) at room temperature, all of the 1-butene is consumed within 40 min and no allyl complex **8** is observed. Similarly, when $(Cp^*_2YH)_2$ (0.01 M) is treated with 1-hexene (0.62 M) half of the 1-hexene is consumed within 60 min at 27 °C (TOF $\sim 16\ h^{-1}$). Analysis of the same solution after standing overnight shows that about 0.02 M 1-hexene did not react and that alkyl peaks corresponding to oligo-1-hexene grew [13]. These experiments show that 1-alkenes that lack allylic methyl groups are better substrates for yttrium catalyzed oligomerization due to slower rates of termination.

2.7. Summary

Yttrium alkyls react with alkenes either through insertion [3] of the alkene into the Y–C bond or by reaction with a C–H bond of the alkene. The reactivity of C–H bonds decreases in the order of allylic-$CH_3 \gg$ vinyl C–H $\gg$ allyl CH_2. Additionally, the reactivity of alkenes toward Cp^*_2YR depends on the ability of the alkene to coordinate to yttrium. Finally, oligomerization of propene is readily terminated by rapid reaction of Cp^*_2YR with propene to give the η^3-allyl complex **2** which does not react further with propene.

The results reported here clarify why $(Cp^*YH)_2$ is a uniquely bad catalyst for propene oligomerization while it rapidly polymerizes ethylene and is effective for giving high oligomers of 1-hexene (Scheme 11). For ethylene polymerization, the insertion of ethylene into a straight chain yttrium alkyl is very rapid because of the high reactivity of both ethylene and the unbranched alkyl. β-Hydride elimination is the principal mode available for termination and is very slow relative to chain growth. For propene, chain extension is slower both because propene is less reactive than ethylene and because the β-methyl substituted growing alkyl is about 200 times less reactive than straight chain alkyls. Chain termination by abstraction of an allylic methyl C–H from propene to give η^3-allyl yttrium complex **2** is much faster than termination by β-hydride elimination and occurs at about the same rate as propene insertion. For 1-hexene, chain extension is expected to be about as fast as for propene, but termination is much slower because 1-hexene has only unreactive allylic methylene hydrogens and no reactive allylic methyl groups. The net result is that alkene consumption in reactions with $(Cp^*YH)_2$ follows the unusual order ethylene $\gg$ 1-hexene $\gg$ propene.



Scheme 11.

3. Experimental

3.1. General

All compounds were manipulated under inert atmosphere using standard Schlenk and glove box techniques. All reactions were performed in 1.9 ml medium-walled J. Young Teflon stopcock valved, 5 mm OD NMR tubes. Proton NMR spectra were obtained on Varian Unity 500 or Bruker Avance-360 spectrometers. Characterization of unstable compounds was aided by DEPT-90, DEPT-135, 1D TOCSY and ^1H COSY, $^1H-^{13}C$ HMQC, and $^1H-^{13}C$ HMBC spectroscopies. $^1H-^1H$ and $^1H-^{13}C$ couplings are indicated by ↔.

Methylcyclohexane-d_{14} (Cambridge Isotopes) and pentane-d_{12} (Cambridge Isotopes) were distilled from sodium–potassium alloy. Alkenes (Aldrich) and H_2 (Liquid Carbonic) were used as received. $Cp^*_2YCH(SiMe_3)_2$ was prepared by a known procedure [14]. Preparations of compounds **1**, **3**, **4**, **6**, **7**, **13**, and **17** have been reported [3]. $Cp^*_2Y(\eta^3\text{-}CH_2\text{---}CH\text{---}CH_2)$ [4b,4c] and $Cp^*_2Y(\eta^3\text{-}CH_2\text{---}C(CH_3)\text{---}CH_2)\cdot MgCl_2$ [6] have previously been prepared through reaction of the appropriate allyl Grignard reagent with $(Cp^*_2YCl)_2$.

3.2. Synthesis of $(Cp^*_2YH)_2$ [14]

$Cp^*_2YCH(SiMe_3)_2$ was dissolved in methylcyclohexane-d_{14} (350–400 μl) in a resealable medium walled J. Young NMR tube. This solution was degassed by three freeze–pump–thaw cycles and 1 atm. H_2 was added at −196 °C. The solution was warmed to room temperature (r.t.) (3–4 atm. H_2) and shaken for 5 min, giving $(Cp^*_2YH)_2$ and $CH_2(SiMe_3)_2$. This solution was degassed by three freeze–pump–thaw cycles and then frozen in liquid nitrogen before addition of alkenes.

3.3. $Cp^*_2Y(\eta^3\text{-}CH_2\text{---}CH\text{---}CH_2)$ (2)

Propene (0.056 mmol) was measured using a monometer and added to $(Cp^*_2YH)_2$ (7 μmol) in 350 μl methylcyclohexane-d_{14} at −196 °C. This mixture was

warmed to −50 °C where formation of $Cp^*_2YCH_2CH(CH_3)CH_2CH_2CH_3$ (**1**) was observed by ^{1}H-NMR spectroscopy. Further warming to 0 °C resulted in formation of **2** (>90% yield). ^{1}H-NMR (500 MHz, 0 °C, $C_6D_{11}CD_3$) δ 6.81 (ddd, $J_{YH}=1.5$, $J_{syn}=9.5$ Hz, $J_{anti}=15.2$ Hz, CH), 3.28 (dd, $J_{YH}=1.5$, $J_{anti}=15.2$ Hz, C*H*H), 1.95 (d, $J_{syn}=9.5$ Hz, CH*H*), 1.93 (s, C_5Me_5), 1.87 (s, C_5Me_5). ^{13}C {^{1}H}-NMR (125.7 MHz, 0 °C, $C_6D_{11}CD_3$) δ 156.99 (d, $J_{YC}=2$ Hz, ↔ 6.81, CH), 115.53 (C_5Me_5), 115.38 (C_5Me_5), 67.60 (d, $J_{YC}=4.0$ Hz, ↔ 3.28, 1.95, CH_2), 9.92 (C_5Me_5), 9.55 (C_5Me_5).

3.4. $Cp^*_2Y[\eta^3$-CH_2---$C(CH_3)$---$CH_2]$ (**5**)

Isobutylene (0.098 mmol) was measured using a monometer and added to $(Cp^*_2YH)_2$ (7 μmol) in 350 μl methylcyclohexane-d_{14} at −196 °C. This mixture was warmed to −50 °C where formation of $Cp^*_2YCH_2CH(CH_3)_2$ (**4**) was observed by ^{1}H-NMR spectroscopy. Further warming to 0 °C resulted in formation of **5** (85% yield). ^{1}H-NMR (360 MHz, −35 °C, $C_6D_{11}CD_3$) δ 3.17 (d, $J\sim1.5$ Hz, C*H*H), 2.07 (d, $J=3.5$ Hz, CH_3), 1.92 (s, C_5Me_5), 1.82 (CH*H*). ^{13}C{^{1}H}-NMR (90 MHz, −35 °C, $C_6D_{11}CD_3$) δ 168.68 (C_{quat}), 115.98 (C_5Me_5), 115.27 (C_5Me_5), 62.81 (d, $J_{YC}=4.8$ Hz, ↔ 3.17, 1.82, CH_2), 27.63 (↔ 2.07, CH_3), 10.02 (C_5Me_5).

3.5. $Cp^*_2Y(\eta^3$-CH_2---CH---$CHCH_3)$ (**8**)

2-Butene (0.058 mmol) was measured using a monometer and added to $(Cp^*_2YH)_2$ (9.6 μmol) in 400 μl methylcyclohexane-d_{14} at −196 °C. This mixture was warmed to 0 °C resulting in formation of **8** (>90% yield). ^{1}H-NMR (360 MHz, −50 °C, $C_6D_{11}CD_3$) δ 6.51 (td, $J_{anti}=14$ Hz, $J_{syn}=10$ Hz, CH_2CH), 3.93 (dq, $J=6$ Hz, $J_{anti}=14$ Hz, C*H*CH_3), 2.58 (d, $J_{anti}=14$ Hz, C*H*H), 1.91 (s, C_5Me_5), 1.87 (s, C_5Me_5), 1.43 (d, $J=10$ Hz, CH*H*), 1.30 (d, $J=6$ Hz, CH_3). ^{13}C{^{1}H}-NMR (90 MHz, −50 °C, $C_6D_{11}CD_3$) δ 153.16 (↔ 6.51, CH), 115.07 (C_5Me_5), 114.98 (C_5Me_5), 81.21 (↔ 3.93, *C*HCH$_3$), 60.96 (d, $J_{YC}=8$ Hz, ↔ 2.58, 1.43, CH_2), 15.75 (↔ 1.30, CH_3), 10.00 (C_5Me_5), 9.89 (C_5Me_5).

3.6. $Cp^*_2Y(\eta^3$-CH_2---C---$CHCH_2CH_2CH_2)$ (**9**)

1-Methylcyclopentene (21 μmol) was measured using a monometer and added to $(Cp^*_2YH)_2$ (7 μmol) in 350 μl methylcyclohexane-d_{14} at −196 °C. This mixture was warmed to 0 °C and monitored by ^{1}H-NMR spectroscopy (about 4 h) for the formation of **9** (85% yield based on $CH_2(SiMe_3)_2$ internal standard). ^{1}H-NMR (500 MHz, 0 °C, $C_6D_{11}CD_3$) δ 4.24 (br s, CH), 2.68 (br t, $J\sim7.7$ Hz, CCH_2), 2.11 (br t, $J=7.0$, $CHCH_2CH_2$), 1.90 (s, C_5Me_5), 1.80 ($CH_2CH_2CH_2$). ^{13}C{^{1}H}-NMR (125.7 MHz, 0 °C, $C_6D_{11}CD_3$) δ 115.84 (s, C_5Me_5), 115.82 (C), 84.32 (↔ 4.24, CH), 50.77 (↔ 2.01, $J_{YC}=11.9$ Hz, YCH_2), 38.81 (↔ 2.68, CCH_2), 31.33 (↔ 2.11, $CHCH_2$), 22.81 (↔ 1.80, $CH_2CH_2CH_2$), 10.63 (C_5Me_5).

3.7. $Cp^*_2YCHCH_2CH_2CH_2CH_2$ (**10**)

Cyclopentene (0.090 mmol) was measured using a monometer and added to $(Cp^*_2YH)_2$ (11 μmol) in 400 μl methylcyclohexane-d_{14} at −196 °C. This mixture was warmed to −40 °C and shaken to give a solution of **10** (80–95% yield based on $CH_2(SiMe_3)_2$ internal standard). ^{1}H-NMR (500 MHz, −60 °C, $C_6D_{11}CD_3$) δ 1.88 (s, C_5Me_5), 1.80 (m, β-C*H*H), 1.79 (m, γ-C*H*H), 1.50 (m, γ-CH*H*), 1.00 (m, CH), 0.50 (m, β-CH*H*). ^{13}C{^{1}H}-NMR (125.7 MHz, −60 °C, $C_6D_{11}CD_3$) δ 116.04 (s, C_5Me_5), 53.05 (d, $J_{YH}=39.7$ Hz, YCH), 35.66 (↔ 0.50, ↔ 1.80, β-CH_2), 29.16 (↔ 1.50, ↔ 1.79, γ-CH_2), 10.85, ($C_5(CH_3)_5$).

3.8. $Cp^*_2YC{=}CHCH_2CH_2CH_2)$ (**11**)

A solution of **10** was prepared as described above and warmed to r.t. The ^{1}H-NMR spectra showed the formation of **11**, which is not stable at r.t. and eventually forms **12**. Despite its transient nature, we were able to obtain ^{1}H and COSY spectra of **11**. ^{1}H-NMR (500 MHz, 25 °C, $C_6D_{11}CD_3$) δ 4.38 (br t, $J\sim1.4$ Hz, ↔ 2.53, ↔ 2.25, C=C*H*), 2.53 (dt, $J=1.4$, 7.0 Hz, ↔ 4.38, ↔ 1.82, CCH_2), 2.25 (m, ↔ 4.38, ↔ 1.82, $CHCH_2$), 1.83 (s, C_5Me_5), 1.82 (m, ↔ 2.53, ↔ 2.25, CCH_2CH_2).

3.9. $Cp^*_2YCH_2Si(CH_3)_2CH_2Si(CH_3)_3$ (**12**)

The solution of **10** and cyclopentene reacted at r.t. overnight to form **12** (70–85%). ^{1}H-NMR (500 MHz, 25 °C, $C_6D_{11}CD_3$) δ 1.91 (C_5Me_5), 0.05 (s, $Si(CH_3)_3$), 0.02 (s, $Si(CH_3)_2$), −0.44 (d, $J_{YH}=3.4$ Hz, YCH_2), −0.74 (d, $J_{YH}=1$ Hz, $SiCH_2Si$). ^{13}C{^{1}H}-NMR (125.7 MHz, 25 °C, $C_6D_{11}CD_3$) δ 116.26 (s, C_5Me_5), 22.14 (d, $J_{YH}=39.7$ Hz, ↔ −0.44, YCH_2), 9.62, ($C_5(CH_3)_5$), 3.48 (↔ −0.74, $SiCH_2Si$), 2.89 (↔ 0.02, $Si(CH_3)_2$), 0.83 (↔ 0.05, $Si(CH_3)_3$).

3.10. $Cp^*_2YCH{=}CHCH(CH_3)_2$ (**14**)

3-Methyl-1-butene (48 μmol) was measured using a monometer and added to $(Cp^*_2YH)_2$ (6 μmol) in 350 μl methylcyclohexane-d_{14} at −196 °C. This mixture was warmed to 0 °C and monitored by ^{1}H-NMR spectroscopy for the formation of **14** (40% yield) and **12** (30% yield). ^{1}H-NMR (500 MHz, 0 °C, $C_6D_{11}CD_3$) δ 7.37 (dd, $J_{YC}=1.5$, $J_{HH}=22.0$ Hz, YCH), 4.10 (dd, $J=4.2$, 22.0, YCHC*H*), 2.31 (m, C*H*$(CH_3)_2$), 1.84 (s, C_5Me_5), 1.01 (d, $J=6.8$ Hz, $CH(CH_3)_2$). ^{13}C{^{1}H}-NMR (125.7 MHz, 0 °C, $C_6D_{11}CD_3$) δ 184.52 (δ, $J_{YC}=44.6$ Hz, ↔

7.37, YCH), 137.10 (↔ 4.10, YCHC*H*), 116.29 (s, C_5Me_5), 33.27 (↔ 2.31, $CH(CH_3)_2$), 21.78 (↔ 1.01, $CH(CH_3)_2$), 9.87 (↔ 1.84, C_5Me_5).

3.11. $Cp^*_2YCH{=}CHCH(CH_3)CH_2CH_3$ (16)

A solution of $Cp^*_2Y[\eta^1,\eta^2\text{-}CH_2CH_2CH(CH_3)CH{=}CH_2]$ [10] was warmed to 10 °C for 20 min to yield a pale yellow solution of **16** (78% yield based on $CH_2(SiMe_3)_2$ internal standard). ^{1}H-NMR (500 MHz, 0 °C, $C_6D_{11}CD_3$) δ 6.61 (ddd, $J = 15.3$ Hz, $J_{YH} = 4$ Hz, $J = 3$ Hz, YCH=C*H*), 6.11 (ddd, $J = 15.3$ Hz, $J_{YH} = 2.5$ Hz, $J = 2$ Hz, YC*H*), 2.20 (m, C*H*CH_3), 1.91 (s, C_5Me_5), 1.28 (m, C*H*HCH_3), 1.10 (m, CH*H*CH_3), 0.96 (t, $J = 7.3$ Hz, CH_2CH_3), 0.73 (d, $J = 6.7$ Hz, CHC*H*$_3$). ^{13}C{^{1}H}-NMR (126 MHz, 0 °C, $C_6D_{11}CD_3$) δ 183.7 (d, $J_{YC} = 60$ Hz, ↔ 6.11, YCH), 146.6 (d, $J_{YC} = 3.4$ Hz, ↔ 6.61, YCH*C*H), (C_5Me_5), 118.0 (C_5Me_5), 43.2 (↔ 2.20, *C*HCH$_3$), 27.7 (↔ 1.28, 1.10, *C*H$_2$CH$_3$), 15.4 (↔ 0.73, CH*C*H$_3$), 11.6 (CH$_2$*C*H$_3$), 11.2 (C_5Me_5).

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