Reactivity of $[\{Y(C_5Me_5)(OC_6H_3Bu^t_2)(\mu\text{-}H)\}_2]$ with Terminal Alkenes and Alkynes: A Model for the First Insertion Step in Alkene Polymerization

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Terminal alkenes $H_2C{=}CHR$ (R = H, Me, Bu^n) react with $[\{Y(C_5Me_5)(OAr)(\mu\text{-}H)\}_2]$ **1** to give the μ-n-alkyl species *trans*-$[\{Y(C_5Me_5)(OAr)\}_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2R)]$ (R = H **2**, Me **3**, Bu^n **4**), respectively; $HC{\equiv}CSiMe_3$ reacts to give $[\{Y(C_5Me_5)(OAr)\}_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CSiMe_3)]$ **5**.

We have recently reported[1] the synthesis of the dimeric bridging hydride complex $[\{Y(C_5Me_5)(OAr)(\mu\text{-}H)\}_2]$ **1** (OAr = $OC_6H_3Bu^t_2$). Its reactivity was of interest to determine the influence of replacing a C_5Me_5 ligand in $[\{(C_5Me_5)_2MH\}_2]$ (M = Y,[2a] La,[2b] Ce,[2c] Nd,[2b] Sm,[2b,2d] Lu[2b,2e]) with the electronically different alkoxide ligand. In this contribution, initial reactivity studies of **1** with terminal alkenes and alkynes are described. The novel μ-hydrido μ-alkyl and μ-hydrido μ-acetylide species *trans*-$[\{Y(C_5Me_5)(OAr)\}_2(\mu\text{-}H)(\mu\text{-}X)]$ serve as models for the first insertion step in alkene polymerization.

Reaction of **1** with C_2H_4 (1 bar, 25 °C) leads to the rapid formation of polyethene (m.p. 127.6 °C), and the μ-ethyl species *trans*-$[\{Y(C_5Me_5)(OAr)\}_2(\mu\text{-}H)(\mu\text{-}CH_2Me)]$ **2** (Scheme 1). Only **2** is observed by ^1H NMR monitoring; the characteristic triplet of a $\mu\text{-}CH_2CH_2R$ {R = $(CH_2CH_2)_n\text{-}CH_2Me$} propagating chain does not replace the quartet of $\mu\text{-}CH_2Me$ (δ −0.08), despite the energy difference between μ-ethyl **2**, μ-n-butyl, μ-n-hexyl **4** (*vide infra*) *etc.* being likely to be very small. Thus, **1** is converted relatively slowly (from μ-H intensities of **1** and **2**; << 1 bar C_2H_4, C_6D_6, 1 h) to **2** only,

indicating that whilst initiation is slow, propagation is relatively fast. This is the opposite of that usually observed in alkene polymerization. Complex **2** does not react with propene.

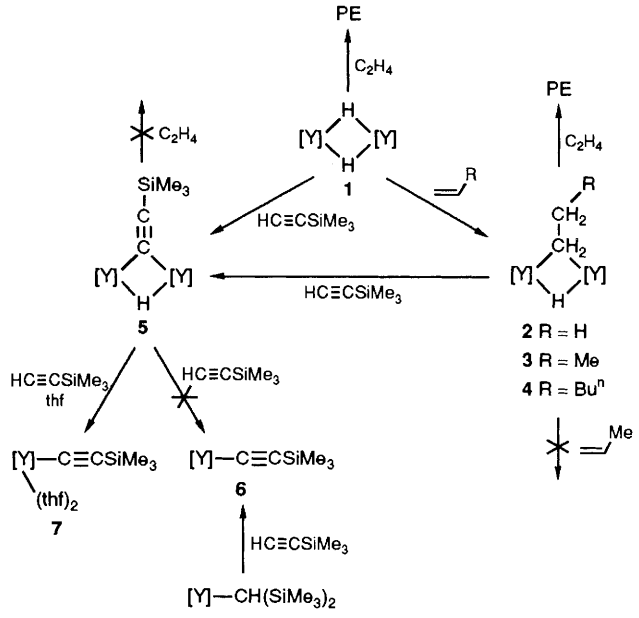
Compound **1** reacts with propene (5 bar, 16 h, 25 °C) to give *trans*-[{Y(C_5Me_5)(OAr)}$_2$(μ-H)(μ-CH_2CH_2Me)] **3**† selectively. In contrast to the reactivity observed with the bis-pentamethylcyclopentadienyl species [{(C_5Me_5)$_2$MH}$_2$],[2] the putative allyl [Y(C_5Me_5)(OAr)(η^3-CH_2CHCH_2)] is not formed. Reaction of [{Y(C_5Me_5)(OAr)(μ-D)}$_2$] {prepared from [Y(C_5Me_5)(OAr)CH($SiMe_3$)$_2$][1] and D_2} with propene yields, as expected, only [{Y(C_5Me_5)(OAr)}$_2$(μ-D)(μ-CH_2CHDMe)] (by ^{1}H and ^{13}C NMR), confirming the non-reversibility of insertion. In all reactions of **1** with terminal alkenes there is no evidence for μ-isoalkyl species. Complex **3** does not react further with propene.

To demonstrate that longer chain bridged alkyl species are not inherently unstable with respect to β-H elimination, the μ-n-hexyl species [{Y(C_5Me_5)(OAr)}$_2$(μ-$CH_2CH_2CH_2$-CH_2-CH_2Me)] **4** was prepared straightforwardly by reaction of **1** with an excess of hex-1-ene.‡ Complex **1** does not react with an excess of *trans*-hex-3-ene (70 °C, C_6D_6, 16 h); insertion and/or isomerization to **4** do not occur.

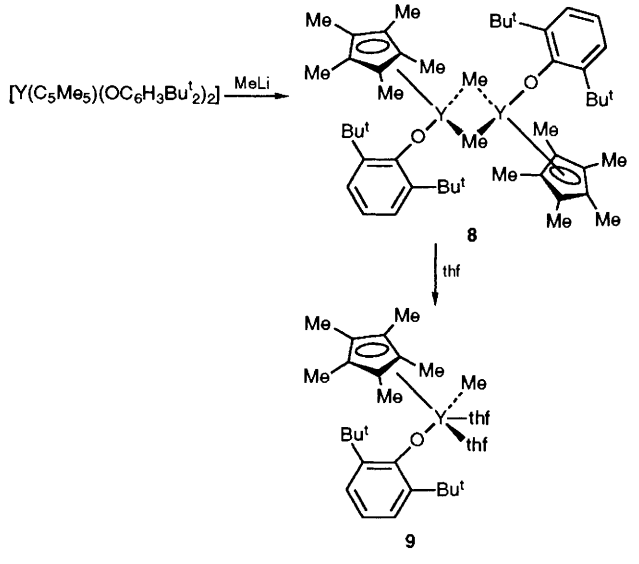
Bridged alkyl species **2–4** are stable to β-H elimination. Heating at 75 °C in C_6D_6 (sealed NMR tube) does not give **1** and the free alkene as expected, but instead yields [Y(C_5Me_5)(OAr)$_2$] as the only identifiable yttrium product.

In the ^{1}H NMR spectra the μ-H resonance in **2–4** appears as a triplet at δ 5.30–5.35, J_{YH} = 39–41 Hz. In the ^{1}H NMR spectrum for **3** at 25 °C,† the μ-propyl group displays resonances at δ 1.32 (Me), 0.94 ($C_\beta 2$) and 0.02 ($C_\alpha H_2$). At −80 °C the $C_\alpha H_2$ resonance splits into two broad resonances at δ 0.76 and −0.70. The μ-alkyls **2–4** show diastereotopic α-CH_2 resonances implying idealised C_2, rather than C_{2v}, geometry, indicating a mutually *trans*-geometry for the attendant ligands. Activation parameters for exchange of the two diastereotopic $C_\alpha H_2$ hydrogens were calculated based on coalescence for a simple two-site exchange model, $\Delta G^\ddagger$ (at −23 °C) = 46.4 ± 2 kJ mol^{-1}. This is similar to that calculated for [{$Et_2Si(C_5H_4)(C_5Me_4)$M}$_2$(μ-H)(μ-CH_2CH_2R)] (M = Y, Lu).[3] As previously proposed,[3] diastereotopic $C_\alpha H_2$ equilibration is *not* achieved by μ-propyl group rotation about the μ-H, μ-C_α axis in **3**; instead inversion at a planar μ-C_α has to be invoked. The carbons of the μ-propyl group in **3** are temperature invariant in the ^{13}C NMR spectrum and resonate at† δ 48.5 ($C_\alpha H_2$), 23.4 ($C_\beta H_2$) and 21.0 (Me). The magnitudes of J_{YC} and J_{CH} are characteristic of bent μ-alkyl groups.[3,4]

A different reaction pathway is observed between **1** and terminal alkynes. Instead of insertion into a Y–H bond, protonolysis occurs with $Me_3SiC{\equiv}CH$ with loss of H_2 (^{1}H NMR) to give the μ-acetylide [{Y(C_5Me_5)(OAr)}$_2$(μ-H)(μ-C≡$CSiMe_3$)] **5**, with the μ-acetylide moiety resonating at δ (^{13}C) 165.7 (t, J_{YC} = 25.0 Hz, μ-C_α) and 136.1 (t, J_{YC} = 2.7 Hz, C_β). Although the geometry of **5** cannot be determined unequivocally by NMR spectroscopy, we assume the C_5Me_5 ligands to be mutually *trans* as in **2–4**.



Scheme 1 [Y] = Y(C_5Me_5)(OAr); PE = polyethene



Scheme 2

In compounds **2–5** the second μ-H is significantly kinetically deactivated. Similar trends have been reported.[3] For example, **5** which contains a (presumably inert) μ-acetylide, as well as a μ-hydride, does not react with ethene. Neither does **5** react with excess of $Me_3SiC{\equiv}CH$ (5 equiv., 25 °C, 16 h) to give [Y(C_5Me_5)(OAr)C≡$CSiMe_3$] **6**, although this can be prepared from [Y(C_5Me_5)(OAr){$CH(SiMe_3)_2$}][1] and $HC{\equiv}CSiMe_3$. Complex **5** is cleaved by tetrahydrofuran (thf) only in the presence of excess of $Me_3SiC{\equiv}CH$ to give the monomeric terminal acetylide species [Y(C_5Me_5)(OAr)(C≡$CSiMe_3$)(thf)$_2$] **7**. The analogous [Y(C_5Me_5)$_2$(C≡$CSiMe_3$)(OEt_2)] has been prepared.[2a] Complex **3** reacts with

† NMR data for **3**: ^{1}H NMR (C_6D_6, 25 °C): δ 7.35 (br 't', 4H, H_m), 6.85 (t, 2H, H_p), 5.30 (t, 1H, J_{YH} = 39.5 Hz, μ-H), 1.97 (s, 30H, C_5Me_5), 1.65 (br, s, 18H, CMe_3), 1.56 (br s, 18H, CMe_3), 1.32 (t, 3H, *J* 7.3 Hz, Me), 0.94 (br, 2H, $C_\beta H_2$) and 0.02 (t, 2H, *J* 8.5 Hz, $C_\alpha H_2$); ^{13}C NMR (C_6D_6, 10 °C): δ 160.5 (virtual t, J_{YC} = 2.3 Hz, C_{ipso}), 137.6 and 136.1 (s, C_o), 127.4 (d, C_m), 125.0 (d, C_m), 119.9 (s, C_5Me_5), 117.8 (d, C_p), 48.5 (tt, J_{YC} = 19.7 Hz, J_{CH} = 105 Hz, $C_\alpha H_2$), 35.6 and 35.3 (s, CMe_3), 33.9 and 31.5 (q, CMe_3), 23.4 (t, J_{YC} = 2.0 Hz, $C_\beta H_2$), 21.0 (Me) and 11.9 (q, C_5Me_5). **8**, ^{1}H NMR (C_6D_6, 25 °C': δ 7.35 (d, 4H, H_m), 6.85 (t, 2H, H_p), 1.90 (s, 30H, C_5Me_5), 1.55 (s, 36H, CMe) and −0.076 (t, 6H, J_{YH} = 3.8 Hz, μ-Me); ^{13}C NMR (C_6D_6–CD_2Cl_2, 25 °C): δ 162.2 (s, C_{ipso}), 137.8 (s, C_o), 125.9 (d, C_m), 121.1 (s, C_5Me_5), 117.6 (d, C_p), 35.9 (s, CMe_3), 33.0 (q, CMe_3), 30.92 (qt, J_{CH} = 104 Hz, J_{YC} = 28 Hz, μ-Me) and 12.4 (q, C_5Me_5). Satisfactory elemental analyses were obtained for compounds **2–9**.

‡ The steric hindrance afforded by the ancillary ligands in **1** is demonstrated by the lack of reaction between **1** and an excess of styrene or $Me_3SiCH{=}CH_2$ (> 10 equiv., C_6D_6, 25 °C); furthermore, **1** reacts surprisingly slowly (days) with an excess of ArOH (3 equiv.) to afford [Y(C_5Me_5)(OAr)$_2$].

$Me_3SiC{\equiv}CH$, not to give the μ-propyl μ-acetylide $[\{Y(C_5Me_5)(OAr)\}_2(\mu\text{-}CH_2CH_2Me)(\mu\text{-}C{\equiv}CSiMe_3)]$, but affords **5**, the more basic μ-alkyl clearly being more susceptible to protonolysis than μ–H.

The synthesis and α-alkene polymerization activity of $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)Sc(PMe_3)\}_2(\mu\text{-}H)_2]$,[5] $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)Sc\}_2(\mu\text{-}CH_2CH_2Me)_2]$[5] and $[\{Y(C_5H_4R)_2(\mu\text{-}R')\}_2]$ (R = H, Me, $SiMe_3$; R′ = Me, Bu^n)[6] were taken as evidence to support polymerization *via* an $M(\mu\text{-}R')_2M$ intermediate. To determine if this was a possibility here, the bis μ-Me species $[\{Y(C_5Me_5)(OAr)(\mu\text{-}Me)\}_2]$ **8**† was prepared from $[Y(C_5Me_5)(OAr)_2]$ and MeLi (1 equiv.) (Scheme 2). It reacts very slowly with ethene and not at all with an excess of propene (*ca.* 10 equiv., 25 °C, after several days). A similar lack of reactivity for $[\{Sc(C_5Me_5)(O\text{-}C_6H_3Bu^t_2\text{-}3,5)Me\}_2]$[7] was attributed to the presence of robust, apparently bridging alkoxides. We find this highly unlikely. In **8**, it is the *influence*[1] of the *terminal* alkoxides that results in the signficantly kinetically deactivated μ-Me group.

Although only μ-hydrido μ-alkyl species have been observed and isolated, and it was therefore tempting to propose that propagation occurs *via* dimeric $[\{Y(C_5Me_5)(OAr)\}_2(\mu\text{-}H)(\mu\text{-}CH_2R)]$, a low concentration of an (undetected) monomer {probably $[Y(C_5Me_5)(OAr)X]$ (X = H or CH_2R)} being the active catalyst seems probable. We have shown that in $[Y(\mu\text{-alkyl})(\mu\text{-}H)Y]$ **2–4** and $[Y(\mu\text{-}Me)_2Y]$ **8**, both the μ-alkyl and μ-hydride are significantly kinetically deactivated with respect to their terminal counterparts. The absence of a binuclear chelating ligand system[3] suggests that reversible dissociation to active monomer(s) may be facile, though the dimer dominates the equilibrium. Further work is currently addressing this possibility.

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