ROMP using heterocyclic carbenes bearing a hydride ligand. An improved synthesis of $RuCl_2(PR_3)_2$(=CHMe)

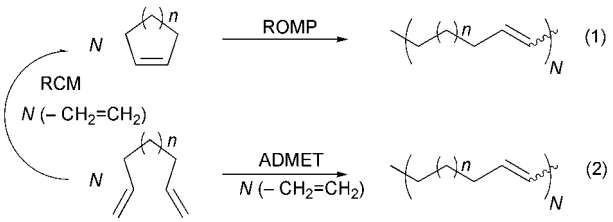
Joseph N. Coalter III and Kenneth G. Caulton*

Department of Chemistry, Indiana University, Bloomington, IN 47405-7102, USA

Received (in New Haven, CT, USA) 7th December 2000, Accepted 5th February 2001
First published as an Advance Article on the web 30th March 2001

The cyclic, heteroatom-stabilized carbene complexes $RuHCl(PR_3)_2[=C(X)C_3H_6]$ (R = Pr^i, Cy; X = O, NH) catalyze the ring-opening metathesis polymerization of 2-norbornene to give mainly (85%) *trans*-polynorbornene (M_w 1.1–2.0 × 10^5 g mol^{-1}) in arene solvent at 30–80 °C. Initiation is slow, but not dependent on free phosphine concentration because the catalyst has an empty coordination site *cis* to the carbene. Protonation of $RuHCl(PR_3)_2[=C(OR)R']$ species occurs at the hydride ligand, and the acidity of the resulting species leads to C–OR bond cleavage. This leads to facile conversion of $RuHClL_2[C(OEt)Me]$ to $RuCl_2L_2[=CHMe]$ and EtOH by HCl and, thus, a convenient new synthesis of a traditional metathesis catalyst whose carbene source is $H_2C=C(OEt)H$.

Although olefin metathesis represents a fairly young area of chemistry, its utility in a variety of processes, from drug development to industrial elastomer production, is enormous. Two related branches of this wide field, ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET), have grown enormously over the last decade due to extensive research into the mechanism of these polymerizations, now generally accepted to involve transition metal carbenes as chain carriers [eqn. (1) and (2)].[1,2] The former process, thermodynamically driven by the relief of ring strain, will constitute the focus of this work.

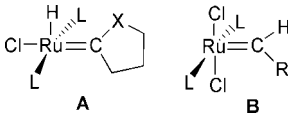


(1) (2)

The ROMP of 2-norbornene (NBE) has been exploited with numerous heterogeneous and homogeneous metal systems, though all are proposed to be initiated and propagated through *heteroatom-free* carbene ligands, either previously synthesized or generated *in situ*. No examples of ROMP of any monomer have been shown to be initiated by a heteroatom-bearing (traditionally termed Fischer-type) carbene. If fact, a now widespread method for *quenching* ROMP polymerization is to treat the system with vinyl ether to generate an inactive alkoxy substituted carbene through a metathesis event [eqn. (3)].[3] The carbene complexes **A** have a formal similarity to the commonly used carbene ruthenium dichloro species **B**, but the site preferences for ligands in a five-coordinate d^6 species lead to a fundamental difference between **A** and **B**: while **B** has no open coordination site *cis* to the carbene, **A** does. This might be an asset for species **A** functioning as an olefin metathesis catalyst, where the olefin substrate must bind *cis* to the carbene ligand. Indeed, a mechanistic study has shown that the most effective olefin

(3)

P = Polymer chain

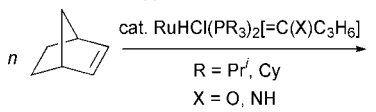


metathesis catalysis by **B** requires preliminary dissociation of phosphine, to open a coordination site *cis* to the carbene, and that a *cis* bidentate phosphine with a wide bite angle chelate,[4] which opens a site *cis* to the carbene, enhances catalyst activity; however, such phosphine dissociation from $RuCl_2L(PR_3)$(=CHR) is also the path to catalyst decomposition.[5] The *reason* for the geometry of **A** is the stability of the strong σ-donor hydride *trans* to an empty site. In other words, it is the *trans* effect of hydride. This causal description shows a potential flaw in the use of **A** for metathesis catalysis: will **A** bind the substrate with a reasonable K_{eq} *trans* to the hydride? We provide here some answers to these questions, and also report reaction chemistry that offers an attractive synthetic route to the metathesis catalyst $RuCl_2$(=CHMe)$(PPr^i_3)_2$, whose aliphatic-substituted carbene has been shown to be 2–3 times more active than the commonly used benzylidene derivatives for the initiation of metathesis events, such as cross metathesis (CM) with styrene-d_5 or 1-hexene.[6]

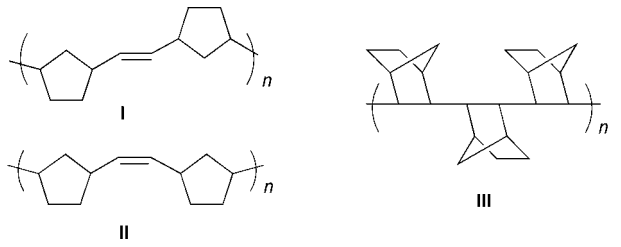
Results

ROMP of norbornene initiated by heterocyclic carbenes

General. Heterocyclic carbenes $RuHCl(PR_3)_2[=C(X)C_3H_6]$ (R = Pr^i, Cy; X = O, NH) are initiators for the catalytic ring-opening metathesis polymerization of 2-norbornene [eqn. (4)]. The identity of the heteroatom (O or N) does apparently affect turnover rates appreciably, with those of oxygen yielding higher activity, although the phosphine identity matters little. In all cases, the resulting *unsaturated* polymer is predominantly *trans* disposed (*ca.* 85% **I**, together with *cis* **II**), as is typical for other Ru based systems.[7,8] No evidence for production of Ziegler–Natta-type *saturated* polymer (**III**) was observed (expected for radical initiation or through Ru–H insertion reactivity).

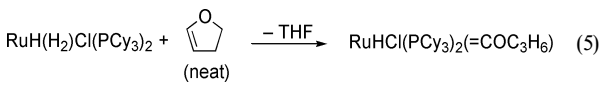


(4)



I II III

Catalyst synthesis. The least expensive of these precursors, $RuHCl(PCy_3)_2(=COC_3H_6)$, is readily prepared by treatment of $RuH(H_2)Cl(PCy_3)_2$ with excess 2,3-dihydrofuran [eqn. (5)]. This reaction is initiated by the dehydrogenation of $RuH(H_2)Cl(PCy_3)_2$ to form "$RuHCl(PCy_3)_2$" and THF, followed by isomerization of coordinated 2,3-dihydrofuran by this monohydride to form carbene[9,10] The *in situ* generation of "$RuHCl(PCy_3)_2$" was discussed previously,[11,12] and due to the propensity of this species to react intramolecularly with a PCy_3 C–H bond, the most efficient method of trapping it is to simply stir the $RuH(H_2)Cl(PCy_3)_2$ in neat vinyl ether. Washing the residue with pentane after removing the volatiles *in vacuo* gives the cyclic carbene in 92% yield. $RuH(H_2)Cl(PCy_3)_2$ is prepared using alcoholic solvent and wash medium, which must be completely removed (by a final wash with pentane before drying *in vacuo*) to avoid contamination of the $RuHCl(PCy_3)_2(=COC_3H_6)$ product with $RuHCl(CO)(PCy_3)_2$. All mechanistic studies and bulk polymer preparation (for GPC analysis) were performed using this inexpensive catalyst precursor.[13]



(5)

X dependence of catalyst performance. As stated above, the nature of heteroatom X in eqn. (4) has a significant impact on the activity of these Ru systems for the polymerization of 2-norbornene. A sample of $RuHCl(PPr^i_3)_2[=C(X)C_3H_6]$ (X = NH) shows only 32% conversion of NBE to polymer after 30 min at 80 °C (0.47 M NBE, 25 : 1 NBE : Ru, C_6D_6). In contrast, the analogous species with X = O allows 85% conversion of NBE to polymer under similar conditions (30 min, 80 °C, 0.62 M NBE, 50 : 1 NBE : Ru, C_6D_6), even though a higher substrate-to-catalyst ratio was present. The ROMP of NBE is also initiated at room temperature using these carbenes, though reactions proceed more slowly. In this comparative study, >75% *loss* of catalyst precursor was found in solution by ^{31}P NMR after the elapsed time when X = NH, while when X = O, the catalyst precursor remains the dominant species (>95%) in solution after this same elapsed time. This suggests that the limiting factor in polymer production using these different catalyst precursors may be precursor decomposition *vs.* rate of initiation under the polymerization conditions rather than different propagation rates since the *same* propagating species, $RuHCl(PPr^i_3)_2[=CH(P)]$ (P = growing polymer chain) should be present in both systems but in different amounts. In addition, based on the large amount of catalyst precursor remaining when X = O, it is clear that the rate of propagation is much higher than that of initiation and that the entirity of polymer production is accomplished at the expense of very little catalyst precursor. In no case, however, was a discrete propagating species observed by ^1H or ^{31}P NMR during or following the polymerization process; the mechanistic implications of this are discussed later. However, it is already clear that norbornene does not bind *detectably* to Ru *trans* to hydride, thus answering one question posed in the introduction above.

Kinetic studies. With regard to the nature of the active species and mechanistic aspects of the polymerization process with these hydrido-chloro species, a kinetic study of polymerization rate *vs.* free phosphine concentration was performed. Remarkably, there was essentially *no* dependence of polymerization activity on free phosphine concentration. When $RuHCl(PCy_3)_2(=COC_3H_6)$ and 50 equiv. of NBE were combined in C_6D_6 in the presence of *ten equivalents* of excess PCy_3, the observed rate of monomer consumption at 50 °C was found to be suppressed by less than a factor of 1/2 (45%) relative to the control using $RuHCl(PCy_3)_2(=COC_3H_6)$ alone. A first-order rate dependence on NBE concentration was established (Fig. 1). Fig. 2 shows the olefinic region of the ^1H NMR spectra of one of these runs, where the production of unsaturated polymer and the previously specified *trans* : *cis* ratio (85 : 15) is evident. This *lack* of rate dependence on free phosphine is in stark contrast to dichloro systems initiated by $RuCl_2(PR_3)_2(=CHR)$, which were found to operate by a 95% dissociative mechanism, where the addition of *one equivalent* of free phosphine slowed propagation rates by a factor of 20.[14,15] Initial turnover rates for the hydrido-chloro species reported here are *ca.* 16 h^{-1} at 50 °C in the absence of free phosphine (0.26 M NBE, 50 : 1 NBE : Ru, C_6D_6).

While these turnover rates are substantially slower than for analogous dichloro systems,[3] they are not dramatically affected by temperature. This can be seen from the percent polymerization of NBE by $RuHCl(PCy_3)_2(=COC_3H_6)$ in fluorobenzene based on isolated yields of polynorbornene from

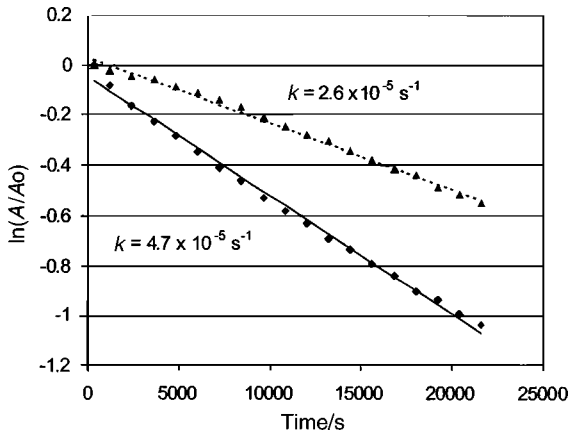


Fig. 1 First-order plot of norbornene (*A*) disappearance during its ROMP by $RuHCl(PCy_3)_2[=COC_3H_6]$ in the absence (◆) and presence (▲) of 10 equiv. added phosphine (lines —— and – – – are the fits). See text for details.

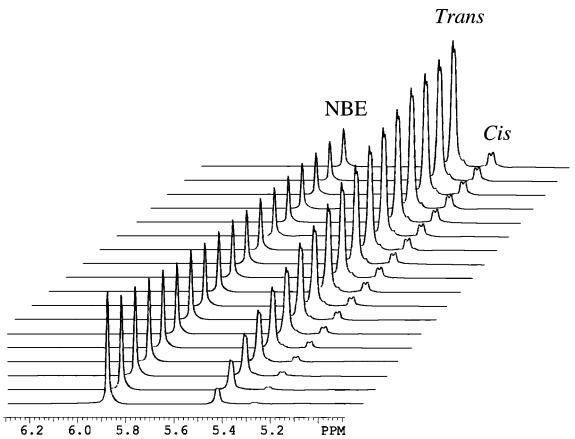


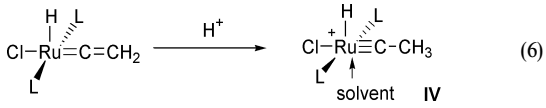
Fig. 2 Time evolution of the ^1H NMR spectra during ROMP of norbornene by $RuHCl(PCy_3)_2[=COC_3H_6]$ in C_6D_6 at 50 °C. Total elapsed time is 6 h and the interval between spectra is 20 min.

reaction mixtures held at different temperatures. Although solutions of the runs at 60 °C did thicken noticeably faster than those at held at 30 °C, after 4 h the percent conversion of 500 equiv. of NBE (0.21 M NBE, C_6H_5F) to polymer is the same within experimental error at both temperatures. Results from duplicate experiments gave 76 and 77% isolated polymer yields at 30 °C, while at 60 °C the comparable yields were 77 and 81%. These data indicate that ROMP occurs faster in C_6H_5F than in C_6H_6 with this system since, in all cases, over 375 turnovers occurred in 4 h (*ca.* 94 h^{-1} averaged), regardless of the temperature (*vs.* 16 h^{-1} initial rate in C_6D_6 at 50 °C).[16]

Analysis of these polymers by gel permeation chromatography (GPC) showed them to be of high molecular weight (110–200 kg mol^{-1}) compared to those obtained from the dichlorides $RuCl_2(Bu^t{}_2PCH_2PBu^t{}_2)$(=CHR) (5 kg mol^{-1})[17] and $RuCl_2(PPh_3)_2$(=CHR) (32–42 kg mol^{-1}),[3] and similar to those from dichlorides with wide bite angle phosphine chelates, such as $RuCl_2[R_2P(CH_2)_4PR_2]$(=CHR′) (80–188 kg mol^{-1}; R = Ph, Cy),[4] but much lower than those from the halide-free initiators $Ru[R_2P(CH_2)_nPR_2]$(olefin)(=CHR′) (210–381 kg mol^{-1}; R = Cy; n = 1–3) and Ru(cod)(olefin)(=CHR′) (790 kg mol^{-1}).[18] This data should not be overinterpreted, since living systems, which commonly show low polydispersity indexes (1–1.5; PDI = M_w/M_n), normally have a linear dependence of M_n relative to substrate-to-catalyst ratio;[19] this data is included in Table 1. It is clear, however, that the hydrido-chloro and dichloro systems presented above show dramatically lower molecular weights than halide-free systems, likely due to a (±2) difference in formal oxidation state at Ru. A large PDI index, such as that obtained using $RuHCl(PCy_3)_2(=COC_3H_6)$ (Table 1), can result from slow initiation rates *vs.* those of propagation.[17] In brief, slow initiation leads to metal centers beginning polymer growth at many different times and at very different remaining monomer concentrations. Slow initiation has been attributed to conjugation of a system with that of the carbene ligand,[3] and the conjugation of Ru=C with OR in this heteroatom-bearing carbene may be viewed as an extreme of this phenomenon. Certainly the fact that the initiating and the propagating carbenes are so differently substituted is at the origin of the very different initiation and propagation rates.

Protonation of $RuHCl(PR_3)_2[=C(E)R]$ [E = OR′, N(H)R′]: novel routes to dichloro carbenes $RuCl_2(PR_3)_2$(=CHMe)

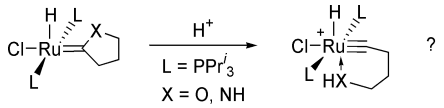
A recent publication showed that protonation of hydrido vinylidene complexes $RuHCl(PR_3)_2(=C=CH_2)$ with acids of weakly coordinating anions [eqn. (6)] yielded cationic carbynes (**IV**), although these species quickly decomposed in solution.[20] Despite their fleeting lifetime, they were shown to be very active species for ROMP of low-strain cyclo-olefins and had the ability to incorporate electron-poor monomers into block copolymers of these ROMP products. These cationic carbynes are "redox isomers" of the cationic carbenes $[RuCl(solvent)(PR_3)_2\{=CH(CH_3)\}]^+$ [shown in the hypothetical equilibrium of eqn. (7)], which may undergo ROMP without the need for phosphine dissociation, since the loss of one chloride {relative to dichloride $RuCl_2(PR_3)_2[=CH(CH_3]$} allows a *cis* disposition of the active carbene ligand and incoming monomer without rearrangement (other than loss of a labile solvent molecule).



(6)

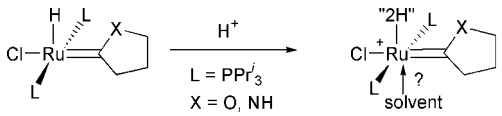
(7)

From these observations, the proposal that the heterocyclic carbene hydrido complexes in eqn. (4) might serve as efficient precursors to carbynes analogous to **IV** was investigated [eqn. (8)]. These proposed "pendant tail" cationic carbynes, however, offer the possibility of added stability by intramolecular (and entropy conserving) stabilization through a pendant donor rather than through coordinated solvent. On the other hand, the species $RuHCl(PR_3)_2[=C(X)C_3H_6]$ offer multiple potential protonation sites in the form of hydride, chloride, and carbene (X) donor functionalities, which could lead to alternate products.



(8)

When carbenes $RuHCl(PPr^i{}_3)_2[=C(X)C_3H_6]$ are treated in THF-d_8 with equimolar $[H(OEt_2)_2][BAr'_4]$, where Ar = 3,5-$(CF_3)_2C_6H_3$, the primary products are not cationic carbyne complexes, but result instead from protonation of the hydride to generate cationic compounds $[Ru(\text{“}2H\text{”})Cl(PPr^i{}_3)_2\{=C(X)C_3H_6\}]^+$ whose empty orbital may be stabilized by a solvent donor [eqn. (9)]. This is most evident in the ^1H NMR spectra, where a new high-field signal that integrates for *two* protons at −8.6 or −9.8 ppm (for X = O and NH, respectively) appears. All other expected ^1H signals are slightly displaced from those of the parent monohydrides, indicating no ring opening, and both ^{31}P NMR resonances are singlets. These new cationic species decompose unselectively at 25 °C in THF-d_8 over a period of minutes to hours, so no ^{13}C NMR acquisition was attempted. Likewise, $T_{1(min)}$ measurements were not performed, so the nature of these two metal-bound H moieties (as H_2 or two hydrides) is uncertain, and they will simply be referred to as "2H". Acyclic $RuHCl(P^iPr_3)_2[=C(Me)OEt]$ behaves similarly when protonated with $[H(OEt_2)_2][BAr'_4]$ in THF-d_8, displaying a 2H signal at −9.4 ppm for $[Ru(2H)Cl(PPr^i{}_3)_2\{=C(Me)OEt\}]^+$, which also decomposes within an hour at 25 °C. The proton source $[H(OEt_2)_x][BF_4]$ may also be used to generate these cations with no apparent reduction in yield.

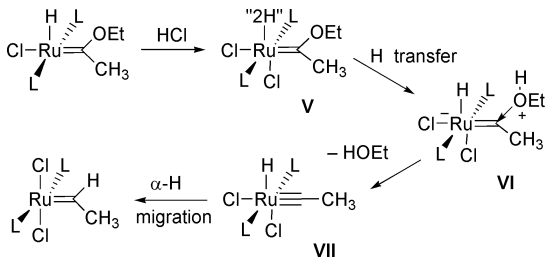


(9)

In contrast, when anhydrous HCl (1.0 M in ether) is used as the proton source toward acyclic carbene

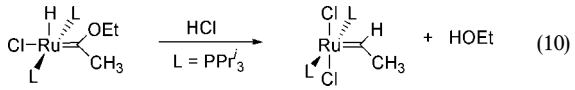
Table 1 ROMP of NBE with various initiators

Initiator	M_w/kg mol^{-1}	PDI	NBE : Ru
$RuHCl(PCy_3)_2(=COC_3H_6)$	110–200	4.20–6.25	500 : 1
$RuCl_2(PPh_3)_2$(=CHR′)[4]	32–42	1.04–1.10	100 : 1
$RuCl_2(Bu^t{}_2PCH_2PBu^t{}_2)$(=CHR′)[17]	5	2.75	120 : 1
$RuCl_2[R_2P(CH_2)_4PR_2]$(=CHR′)[1]	80–188	1.05–1.11	200 : 1
$Ru[R_2P(CH_2)_nPR_2]$(olefin)(=CHR′)[19]	210–381	1.8 : 2.9	150–250 : 1
Ru(COD)(olefin)(=CHR′)[19]	790	3.2	50 : 1



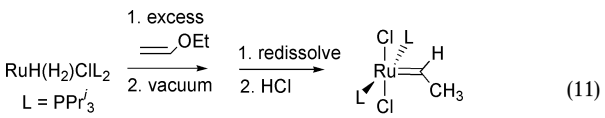
Scheme 1

$RuHCl(PPr^i_3)_2[=C(Me)OEt]$ in ether at −78 °C, the primary product is presumed to be the analogous species $Ru(2H)Cl_2(PPr^i_3)_2[=C(Me)OEt]$, **V** (Scheme 1), from the initial bleaching of the dark red–orange solutions (and precipitation of a pale orange solid). This bleaching was also observed in the protonation reactions above using $[H(OEt_2)_2][BAr'_4]$ and $[H(OEt_2)_x][BF_4]$. However, after slowly warming to room temperature and stirring overnight, this primary product evolves to a deep purple solution of dichloro carbene $RuCl_2(PPr^i_3)_2(=CHMe)$ with expulsion of HOEt, (observed by ^1H NMR when the reaction is performed in an NMR tube) [eqn. (10)]. Apparently the presence of a anionic chloride "support" ligand stabilizes the cations of eqn. (9) through coordination and allows the rearrangement to dichloro carbenes by the proposed mechanism shown in Scheme 1. Proton transfer from the Ru(2H) of $Ru(2H)Cl_2(PPr^i_3)_2[=C(Me)OEt]$, **V**, first forms **VI**, which contains the good leaving group HOEt; this H transfer to the oxygen lone pair is facilitated relative to the cationic complexes in eqn. (9) by the neutral nature of **V** and by the diminished OR → C(carbene) donation due to having Cl bound to Ru [more Ru → C(carbene) donation can occur]. Loss of HOEt then prompts, or is concurrent with, an α-H migration from Ru to the α-carbon in **VII** to form $RuCl_2(PPr^i_3)_2(=CHMe)$. The carbyne redox isomer $RuHCl_2L_2(\equiv CR)$, **VII**, has previously been shown to be less stable than carbene from $RuCl_2L_2(=CHR)$ by 28 kcal mol^{-1} ($L = PH_3$; $R = CH_3$).[21] A similar ethylidene species ($L = PCy_3$) has been shown to be a more active initiator for cross metathesis of terminal olefins than the analogous benzylidene,[6] and thus $RuCl_2(PPr^i_3)_2(=CHMe)$ might serve as an excellent substitute for the commercially available $RuCl_2(PCy_3)_2(=CHPh)$.



(10)

From these protonation studies, a simple one-pot preparation of useful dichloro carbenes using inexpensive and thermally stable ethyl vinyl ether as the source of the carbene carbon can be summarized in eqn. (11). This represents a marked improvement over a recently reported preparation,[22] which uses acetylene as the ethylidene source, due to the much lower light and heat sensitivity associated with vinyl ethers.

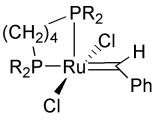


(11)

Overall yield = 80% (*in situ*)
45% (isolated)

Discussion

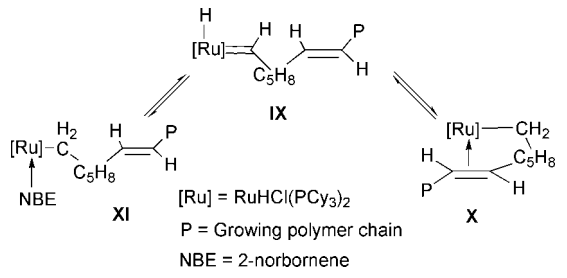
This work details how ROMP of 2-norbornene can be effectively initiated by heteroatom-substituted carbenes on a Ru hydrido-chloro framework, though previous studies on related dichloro species showed such carbenes to be inactive.[23] In addition, unlike the related dichloride, this initiation (and propagation) is unaffected by the presence of excess free phosphine. This lack of PR_3 dependence is likely due to the reorientation of the open site *cis* to the active carbene ligand in these hydrido-chloro species from the strong *trans* effect of the hydride ligand, so that no PR_3 dissociation is necessary.[10,14,15] In dichloride species containing monodentate phosphines, where PR_3 dependence is pronounced, and in a species supported by a small bite angle phosphine chelate (which shows low activity),[17] the open site is oriented *trans* to the carbene. A similar independence of polymerization rates on PR_3 concentration was recently established for a Ru dichloride bearing a wide bite angle chelating phosphine unit (**VIII**), where the open site is also oriented *cis* to the carbene ligand.[4] In addition, by orienting an open orbital (or one weakly stabilized by solvent) *cis* to the carbene as in cationic[24] $[RuCl(solvent)(Bu^t_2PCH_2PBu^t_2)(=CHR')]^+$ and in $[RuCl(solvent)(PR_3)_2(=CHMe)]^+$ [eqn. (7)],[20] metathesis activity is substantially increased.



R = Ph, Cy **VIII**

Though no phosphine dissociation is necessary for the ROMP of 2-norbornene by $RuHCl(PCy_3)_2(=COC_3H_6)$, polymerization rates are not especially high. This is likely due to two factors. First, as a result of the slow initiation rates of Ru=C(OR)R′ to generate a propagating species, very little catalyst precursor is actually activated toward propagation before all of the monomer is consumed, or until solution viscosity prevents effective mixing. This results in artificially low catalyst loadings for calculation of turnover rates. This slow initiation is also responsible for the very broad polydispersities seen for the isolated ROMP products of these hydridochloro species, although molecular weights are moderately high.

Second, the nature of the propagating species is undefined since it is never observed in the ROMP mixtures monitored *in situ* by ^1H NMR, even though Ru carbenes Ru=C*H*(P) show diagnostic signals in the unobscured region between 15–20 ppm. This could be due to spectroscopically unobservable concentrations of such species due to the slow initiation rates. More likely, however, is the presence of an alternate resting state for such a propagating species (**IX**; Scheme 2) since $MH(=CH_2)$ compounds can rearrange to a more stable $M(CH_3)$ (M = Ru, Os) unit.[25–27] Though such rearrangement lowers the valence electron count by two, this can be compensated for by intramolecular stabilization of the resulting 14-electron species by coordination to a pendant olefin of the growing polymer chain (**X**), or through coordination of the incoming NBE substrate (**XI**), as shown in Scheme 2. If involved as a rate-limiting step, the added activation barrier for returning from **X** or **XI** to hydrido carbene (**IX**) could substantially slow the propagation rates. These resting states would also likely have their ^1H spectroscopic signatures buried under the signals for the parent (and >90% unactivated) carbene $RuHCl(PCy_3)_2(=COC_3H_6)$, the unreacted 2-norbornene and the product polynorbornene, thus



[Ru] = $RuHCl(PCy_3)_2$
P = Growing polymer chain
NBE = 2-norbornene

Scheme 2

offering an explanation for the lack of a spectroscopically defined chain carrier.

This report also details the simple one-pot synthesis of dichloro carbene $RuCl_2(PPr^i_3)_2(=CHMe)$, a member of a class of compounds whose use in a wide variety of metathesis reactions is extensive.[1,2] This novel route uses commercially available, inexpensive ethyl vinyl ether as the carbene source, an improvement over those that currently use alkynes[22] and diazoalkanes[3] to form Ru=CHR. Eqn. (10) takes advantage of electrophilic removal of OEt from the carbene intermediate, but by the intermediacy of protonation of a hydride on Ru.

Experimental

General considerations

All manipulations were performed using standard Schlenk techniques or in an argon-filled glovebox, unless otherwise noted. Solvents were distilled from Na, Na–benzophenone, P_2O_5 or CaH_2, degassed prior to use, and stored over 4 Å molecular sieves in air-tight vessels. 2,3-Dihydrofuran and ethyl vinyl ether were dried over Na–benzophenone and vacuum transferred before use. $RuH(H_2)Cl(PPr^i_3)_2$,[11] $RuHCl(PPr^i_3)_2(=COC_3H_6)$,[9,10] $RuHCl(PPr^i_3)_2[=CN(H)C_3H_6]$[12] and $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$[28,29] were prepared as described in the literature. ^1H NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. ^{31}P NMR spectra are referenced to an external standard of 85% H_3PO_4 (0 ppm). NMR spectra were recorded on Varian Gemini 2000 (300 MHz ^1H; 121 MHz ^{31}P; 75 MHz ^{13}C; 282 MHz ^{19}F) and Varian Unity INOVA (400 MHz ^1H; 162 MHz ^{31}P; 101 MHz ^{13}C; 376 MHz ^{19}F and 500 MHz ^1H; 126 MHz ^{13}C) instruments. The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, q = quartet, vt = virtual triplet, dvt = doublet of virtual triplets, m = multiplet, br = broad, ap = apparent. Infrared spectra were recorded using a Nicolet 510P FTIR spectrometer.

ROMP of 2-norbornene

Bulk polymer isolation. The percent *cis* and *trans* polymer was determined by ^1H NMR from comparison to literature data.[30] Bulk polymer isolation for GPC analysis was performed as follows. Under argon, 1.00 g (10.62 mmol) 2-norbornene was dissolved in 49 mL fluorobenzene and brought to the appropriate run temperature in an oil bath. A solution of 16.3 mg (0.021 mmol) of $RuHCl(PCy_3)_2(=COC_3H_6)$ in 1.0 mL toluene was added *via* syringe. After 4 h, the reaction was quenched by pouring the viscous mixture into 500 mL of stirred MeOH. The precipitated polymer was collected, washed with fresh MeOH (2 × 100 mL) and dried *in vacuo* to give an off-white rubbery material. Yields are reported below.

Kinetic runs (phosphine dependence). Under argon, a solution of 2.0 mg (2.6 μmol) of $RuHCl(PCy_3)_2(=COC_3H_6)$ and the appropriate molar amount of free PCy_3 in 0.50 mL of C_6D_6 was added to an NMR tube charged with 12.3 mg (0.130 mmol) of 2-norbornene. 1.0 μL of hexamethyldisiloxane was added as an internal standard *via* syringe, the tube was sealed, and immediately placed in a pre-heated NMR probe (50 °C). ^1H NMR spectra were taken in 5 min intervals for 6 h, with a pulse delay of 5 s to ensure accurate integrations. Reaction rates are based on decay of the monomer peak relative to the internal standard.

GPC analysis. The samples were prepared by the addition of 10 ml of THF to approximately 25.0 mg of each sample. The solutions were filtered using a 0.2 micron PTFE syringe filter. 150 μL of each solution was injected into a two column set (Jordi Associates mixed bed and 500A columns) by a Waters 2690 separation module. The 2690 operated at room temperature, using THF as the eluent, flowing at a rate of 1.0 ml min^{-1}. Changes in concentration were detected by an HP 1047A refractive index detector. The molecular weight calculations were based upon a calibration made of narrow dispersity polystyrenes ranging in molecular weight from 6.30×10^6 to 266. The actual calculations were completed with Caliber software from Polymer Labs (Amherst, MA, USA).

Preparations

$RuH(H_2)Cl(PCy_3)_2$. The method used was adapted from a previously reported *in situ* preparation.[31] Under argon, 4.00 g (14.28 mmol) $[(cod)RuCl_2]_x$ (cod = cycloocta-1,5-diene) and 8.08 g (28.56 mmol) PCy_3 were slurried in 125 mL of Pr^iOH. 4.27 mL (28.56 mmol) of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was added *via* syringe. The mixture was refluxed under an argon atmosphere for 12 h and the volatiles were removed to a liquid N_2 trap after cooling to room temperature. The red–orange residue was washed with MeOH (2 × 50 mL), then pentane (1 × 50 mL), and dried *in vacuo* to yield 8.50 g (85%) of the title compound as an orange powder. ^1H and ^{31}P NMR spectra were identical to those previously reported.[32,33]

$RuHCl(PCy_3)_2(=COC_3H_6)$. Under argon, 1.00 g (1.43 mmol) $RuH(H_2)Cl(PCy_3)_2$ was stirred for 30 min at room temperature in 10 mL of 2,3-dihydrofuran (neat). The volatiles were removed to a liquid N_2 trap and the yellow–orange residue was washed with pentane (1 × 20 mL) before drying *in vacuo*. Yield: 0.850 g (92%). Note that the starting $RuH(H_2)Cl(PCy_3)_2$ must be completely free of the alcohols used as solvent or as a wash medium in its preparation to avoid contamination of the product by $RuHCl(CO)(PCy_3)_2$. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ −19.27 (t, $^2J_{P-H} = 22$, 1H, RuH), 1.30, 1.68, 1.80, 2.04, 2.26 [m, 66H, $P(C_6H_{11})_3$], 1.40 (ap quintet, $^3J_{H-H} = 8$, 2H, $Ru{=}COC_3H_6$), 3.13 (t, $^3J_{H-H} = 8$, 2H, $Ru{=}COC_3H_6$), 3.92 (t, $^3J_{H-H} = 7$ Hz, 2H, $Ru{=}COC_3H_6$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): δ 47.5 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 20 °C): δ 23.8 (s, $Ru{=}CO\mathit{C}_3H_6$), 27.1 [s, $P(C_6H_{11})_3$], 28.2 [vt, $J_{P-C} = 4$, $P(C_6H_{11})_3$], 28.3 [vt, $J_{P-C} = 5$, $P(C_6H_{11})_3$], 30.3 [s, $P(C_6H_{11})_3$], 30.7 [s, $P(C_6H_{11})_3$], 35.8 [vt, $J_{P-C} = 9$, $P(C_6H_{11})_3$], 51.1 (s, $Ru{=}CO\mathit{C}_3H_6$), 75.6 (s, $Ru{=}CO\mathit{C}_3H_6$), 286.1 (t, $^2J_{P-C} = 10$ Hz, $Ru{=}\mathit{C}OC_3H_6$).

$[Ru(2H)Cl(PPr^i_3)_2(=COC_3H_6)][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$. Under argon, 10.0 mg (0.019 mmol) of $RuHCl(PPr^i_3)_2(=COC_3H_6)$ and 19.2 mg (0.019 mmol) of $[H(OEt_2)_2][B\{(CF_3)_2C_6H_3\}_4]$ were combined in THF-d_8 and added to an NMR tube. ^1H and ^{31}P NMR spectra taken immediately showed >90% conversion to the title compound. The signal for the central CH_2 of the carbene ring is obscured by the resonances from the PPr^i_3 ligands. ^1H NMR (400 MHz, THF-d_8, 20 °C): δ −8.62 [br s, 2H, Ru(2H)], 1.29 [dvt, $J_{P-H} = {}^3J_{H-H} = 7$, 18H, $P(CH\mathit{Me}_2)_3$], 1.32 [dvt, $J_{P-H} = {}^3J_{H-H} = 7$, 18H, $P(CH\mathit{Me}_2)_3$], 2.02 [t, $^3J_{H-H} = 8$, 2H, OC_3H_6], 2.70 [m, 6H, $P(C\mathit{H}Me_2)_3$], 4.65 [t, $^3J_{H-H} = 8$ Hz, 2H, OC_3H_6], 7.60 {s, 4H, $B[(CF_3)_2C_6H_3]_4$}, 7.81 {s, 8H, $B[(CF_3)_2C_6H_3]_4$}. $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20 °C): δ 52.5 (s).

$[Ru(2H)Cl(PPr^i_3)_2(=CN(H)C_3H_6)][BF_4]$. Under argon, 10.0 mg (0.019 mmol) of $RuHCl(PPr^i_3)_2[=CN(H)C_3H_6]$ was dissolved in 0.5 mL of THF-d_8 and added to an NMR tube equipped with a Teflon seal. 2.6 μL (0.019 mmol) of HBF_4

(54% in Et_2O) was added *via* syringe, the tube was sealed and then agitated to give a yellow solution. ^1H and ^{31}P NMR spectra taken immediately showed >90% conversion to the title compound. ^1H NMR (400 MHz, THF-d_8, 20 °C): δ −9.81 [br s, 2H, Ru(2H)], 1.21 [dvt, $J_{P-H} = {}^3J_{H-H} = 7$, 18H, $P(CHMe_2)_3$], 1.30 [dvt, $J_{P-H} = {}^3J_{H-H} = 7$, 18H, $P(CHMe_2)_3$], 1.87 [ap quintet, $^3J_{H-H} = 8$, 2H, $N(H)C_3H_6$], 2.73 [m, 6H, $P(CHMe_2)_3$], 3.32 [br s, $^3J_{H-H}$ not resolved, 2H, $N(H)C_3H_6$], 3.41 [br t, $^3J_{H-H} = 8$ Hz, 2H, $N(H)C_3H_6$], 9.72 [s, 1H, $N(H)C_3H_6$]. $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20 °C): δ 47.6 (s).

$[Ru(2H)Cl(PPr^i_3)_2\{=C(Me)OEt\}][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$. $RuHCl(PPr^i_3)_2[=C(Me)OEt]$ was generated as follows. Under argon, 10.0 mg (0.022 mmol) of $RuH(H_2)Cl(PPr^i_3)_2$ was dissolved in 0.5 mL of benzene and added to an NMR tube equipped with a Teflon seal. 10.4 μL (0.109 mmol) of ethyl vinyl ether was added *via* syringe, the tube was sealed, and then tumbled for 60 min at 25 °C; at this time ^{31}P NMR showed complete conversion to $RuHCl(PPr^i_3)_2[=C(Me)OEt]$. The volatiles were removed *in vacuo*, then 22.1 mg (0.022 mmol) of $[H(OEt_2)_2][B\{(CF_3)_2C_6H_3\}_4]$ and 0.5 mL of THF-d_8 were added to the tube. ^1H and ^{31}P NMR spectra taken immediately showed 60% conversion to the title compound, with the balance of the material as unidentified products. Selected NMR data follows. ^1H NMR (400 MHz, THF-d_8, 20 °C): δ −9.41 [br s, 2H, Ru(2H)], 2.74 [s, 3H, $Ru{=}CCH_3(OR)$], 4.42 [q, $^3J_{H-H} = 7$ Hz, 2H, OCH_2CH_3], 7.58 {s, 4H, $B[(CF_3)_2C_6H_3]_4$}, 7.80 {s, 8H, $B[(CF_3)_2C_6H_3]_4$}. $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 20 °C): δ 54.1 (s).

$RuCl_2(PPr^i_3)_2$(=CHMe). Under argon, 2.08 mL (21.7 mmol) of ethyl vinyl ether was added *via* syringe to a solution of 1.00 g (2.17 mmol) of $RuH(H_2)Cl(PPr^i_3)_2$ in 20 mL of toluene. The reaction was stirred for 2 h at room temperature before removal of the volatiles *in vacuo*. The red residue was dissolved in 50 mL of ether, cooled to −78 °C, and 2.17 mL of a 1.0 M HCl solution (in ether) was added dropwise *via* syringe to give a pale solution with a light orange precipitate. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The resulting purple solution was filtered, reduced to 15 mL *in vacuo*, then cooled to −78 °C for 2 days to precipitate the title compound as purple microcrystals. The isolated yield, after decanting the supernatant *via* cannula and drying the product *in vacuo*, was 0.510 g (45%). The yield of this reaction when performed in an NMR tube in THF-d_8 was 80%, as determined *in situ* by ^{31}P NMR integration. Full NMR data has been reported previously.[34]

Acknowledgements

This work was supported by the donors of the Petroleum Research Foundation, administered by the American Chemical Society. The GPC analyses were performed at the 3M Corporation analytical laboratories with the cooperation of Dr Allen Siedle. His generosity is greatly appreciated.

References and notes

1 M. R. Buchmeiser, *Chem. Rev.*, 2000, **100**, 1565 and references therein.
2 T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18.
3 P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100.
4 D. Amoroso and D. E. Fogg, *Macromolecules*, 2000, **33**, 2815.
5 M. Ulman and R. H. Grubbs, *J. Org. Chem.*, 1999, **64**, 7202.
6 M. Ulman and R. H. Grubbs, *Organometallics*, 1998, **17**, 2484.
7 While Ru systems consistently yield predominantly *trans* polymer, systems based on early metals or Mo often favor the *cis* polymer, see ref. 1 and K. Mashima, M. Kaidzu, Y. Tanaka, Y. Nakayama, A. Nakamura, J. G. Hamilton and J. J. Rooney, *Organolmetallics*, 1998, **17**, 4183.
8 Recently, it has been established that the ratio of *trans* : *cis* polymer in Ru systems can be systematically modulated to a slight degree by ligand environment, see: C. Six, K. Beck, A. Wegner and W. Leitner, *Organometallics*, 2000, **19**, 4639.
9 J. N. Coalter III, G. J. Spivak, H. Gerard, E. Clot, E. R. Davidson, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1998, **120**, 9388.
10 J. N. Coalter III, J. C. Bollinger, J. C. Huffman, U. Werner-Zwanziger, K. G. Caulton, E. R. Davidson, H. Gérard, E. Clot and O. Eisenstein, *New J. Chem.*, 2000, **24**, 9.
11 J. N. Coalter III, G. F. Ferrando and K. G. Caulton, *New J. Chem.*, 2000, **24**, 835.
12 G. F. Ferrando, J. N. Coalter III, H. Gérard, J. C. Huffman, O. Eisenstein and K. G. Caulton, submitted.
13 Estimated materials cost for $RuHCl(PCy_3)_2(=COC_3H_6)$ are less than $10 per gram. In contrast, commercially available $RuCl_2(PCy_3)_2(=CHPh)$ costs $35 per gram in bulk (Strem).
14 The quoted propagation rate suppression is for the related process of RCM of diethyl diallylmalonate, see: E. L. Dias, S. T. Nguyen and R. H. Grubbs, *J. Am. Chem. Soc.*, 1997, **19**, 3887.
15 Dramatic rate *enhancements* for ROMP have also been seen with the use of the phosphine scavengers CuCl, $[(C_6R_6)MCl_2]_2$ (M = Ru, Os) and $[(C_5R_5)RhCl_2]_2$, see: E. L. Dias and R. H. Grubbs, *Organometallics*, 1998, **17**, 2758 and ref. 4.
16 A dramatic solvent dependence on ROMP rates has been reported before, see: S. T. Nguyen and R. H. Grubbs, *J. Am. Chem. Soc.*, 1993, **115**, 9858.
17 S. M. Hansen, F. Rominger, M. Metz and P. Hofmann, *Chem. Eur. J.*, 1999, **5**, 557.
18 The actual catalysis precursors in these halide-free systems are diallyl species. It is proposed that these two allyl ligands undergo a coupling reaction to form a metallocyclobutane, followed by cycloreversion to generate an olefin and an active carbene ligand, see ref. 8.
19 K. Matyjaszewski, *Macromolecules*, 1993, **26**, 1787.
20 W. Stüer, J. Wolf, H. Werner, P. Schwab and M. Schulz, *Angew. Chem., Int. Ed.*, 1998, **37**, 3421.
21 G. J. Spivak, J. N. Coalter III, M. Olivan, O. Eisenstein and K. G. Caulton, *Organometallics*, 1998, **17**, 999.
22 J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab and M. Schultz, *Angew. Chem., Int. Ed.*, 1998, **37**, 1124.
23 See, however: H. Katayama, H. Urushima and F. Ozawa, *J. Organomet. Chem.*, 2000, **606**, 16.
24 M. S. Hansen, A. O. Martin, F. R. Volland, F. Eisenträger and P. Hofmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 1273.
25 H. Gérard, E. Clot and O. Eisenstein, *New J. Chem.*, 1999, **23**, 495.
26 D. H. Huang, G. J. Spivak and K. G. Caulton, *New J. Chem.*, 1998, **22**, 1023.
27 H. Werner, W. Stuer, M. Laubender, C. Lehmann and R. Herbst-Irmer, *Organometallics*, 1997, **16**, 2236.
28 K. Abdur-Rashid, T. P. Fong, B. Greaves, D. G. Gusev, J. G. Hinman, S. E. Landau, A. J. Lough and R. H. Morris, *J. Am. Chem. Soc.*, 2000, **122**, 9155.
29 M. Brookhart, B. Grant and A. F. Volkpe, Jr., *Organometallics*, 1992, **11**, 3920.
30 L. Bencze, G. Szala, J. G. Hamilton and J. J. Rooney, *J. Mol. Catal. A*, 1997, **115**, 193.
31 P. A. van der Schaaf, R. Kolly and A. Hafner, *Chem. Commun.*, 2000, 1045.
32 M. Christ, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1994, **13**, 3800.
33 T. Burrow, S. Sabo-Etienne and B. Chaudret, *Inorg. Chem.*, 1995, **34**, 2470.
34 C. Grünwald, O. Gevert, J. Wolf, P. González-Herrero and H. Werner, *Organometallics*, 1996, **15**, 1960.