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Ligand manipulation and design for ruthenium metathesis and tandem metathesis-hydrogenation catalysis

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Abstract

Results of investigations into tandem ring-opening metathesis polymerization (ROMP)-hydrogenation are reviewed, in which hydrogen and 3-chloro-3-methyl-1-butyne provide simple chemical toggles to switch between metathesis and hydrogenation chemistry, enabling multiple tandem catalysis in chlorocarbon solvent. In the presence of methanol, hydrogenation of metathesis polymers can be carried out under 1 atm H_2. Issues of ligand design are examined in developing new Ru-diphosphine catalysts with improved selectivity, and an important decomposition pathway is identified for $RuCl_2$(PP)(CHR) systems (PP = chelating diphosphine).

Keywords: Ruthenium; Metathesis; Hydrogenation; Selectivity; Diphosphines

1. Introduction

Metathesis chemistry has been one of the major success stories of homogeneous catalysis emerging over the last ten years, with important implications in both materials and organic chemistry [1–3]. Materials applications span the range from tough, insulating, optically clear plastics used primarily for structural and packaging applications (including microelectronics), to functionalized polymers relevant to fields as diverse as photonics and tissue engineering [2]. Developments in organic synthesis emerging from ring-closing metathesis and cross-metathesis reactions have likewise been spectacular, permitting construction of complex ring systems, with important consequences for natural products synthesis [3]. Despite these major advances, key areas remain underdeveloped. These include (a) development of *tandem* catalytic processes, and (b) design of catalysts that integrate robustness with high selectivity. This paper provides an overview of our progress toward these goals.

2. Results and discussion

2.1. Tandem ROMP-hydrogenation

Ruthenium has an exceptionally rich catalytic chemistry. Among the processes promoted by Ru complexes are C–C bond formation, including metathesis and Murai coupling; oxidation and isomerization reactions; nucleophilic addition to C–C and C–heteroatom multiple bonds; and H_2- and transfer hydrogenation [4]. This diversity holds great potential for development of tandem catalyses, in which one catalyst supports several functions, with two (or

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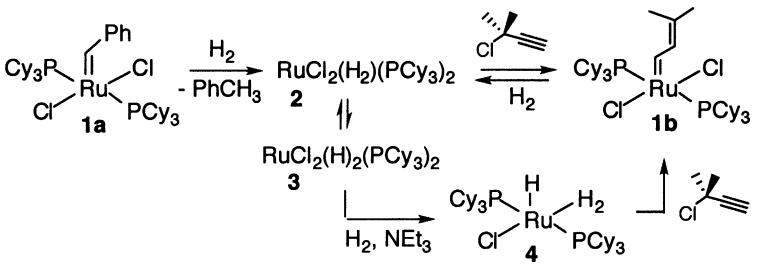
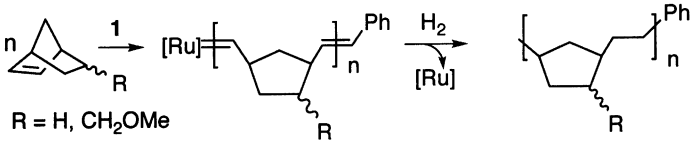


Scheme 1.

more) distinct catalytic processes being triggered for sequential modification of a substrate. In the case of metathesis, this may involve modification at a newly-formed olefin, or at a remote site. The ability to simply, controllably, and reversibly "turn on" different modes of catalysis is of keen interest for combinatorial and high-throughput organic synthesis [5], and holds important practical implications for applications ranging from natural products synthesis to polymer functionalization.

Fundamental to this goal is the ability to exchange an alkylidene ligand for other chemically or catalytically reactive entities. We recently described H_2-hydrogenolysis of $RuCl_2(PCy_3)_2(CHR)$ (**1a**, R = Ph) to afford tautomers $RuCl_2(H_2)(PCy_3)_2$ **2** and $RuH_2Cl_2(PCy_3)_2$ **3**, with evolution of toluene (Scheme 1) [6]. In the presence of base, **2**/**3** are transformed cleanly into hydrogenation-active $RuHCl(H_2)(PCy_3)_2$ **4**. Dihydrogen thus functions as a simple chemical trigger to enable a switch from metathesis to hydrogenation catalysis, permitting hydrogenation of unsaturated, metathesis-derived small molecules or polymers. Reduction of metathesis polymers is fundamental to expanding the range of applications in which such materials can be deployed, via elimination of olefinic sites susceptible to oxidative and thermal unsaturation [7]. Interest in reduction of ring-opening metathesis polymerization (ROMP) polymers is driven by industrial demand for lightweight, moldable polymers with desirable optical characteristics [8,9]. Amorphous thermoplastic resins prepared from cycloolefin polymers are attractive for their high transparency and low birefringence, good processability, high impact strength, and high resistance to heat and humidity. Hydrogenated poly(norbornene), commercialized by Nippon Zeon under the trade name of Zeonex, offers superior humidity resistance over the widely-used optical plastics polymethylmethacrylate (PMMA) and polycarbonate, owing to the absence of polar functionalities. Absorption of water associated with polar groups can lead to deformation of optical devices, leading to disk tracking errors or spherical aberrations in lenses or prisms [8,9].

Hydrogenation of internal olefins is a challenging problem, exacerbated in the case of polymer substrates by the bulk of the substituents, as well as perturbations on solvent parameters by the polymer itself. Recent procedures described in the patent literature for hydrogenation of ROMP polymers include a "one-pot" process of Mo-catalyzed ROMP, followed by homogeneous hydrogenation via $RuCl_2(PPh_3)_4$ under forcing conditions (165 °C, >1000 psi H_2) [10]. Variable success has been reported on use of palladium and nickel catalysts [11,12]. Of particular interest is the catalytic utility of $RuHCl(CO)(PCy_3)_2$ **5**, which McManus and Rempel [7] have identified as the most active of a series of Ru catalysts evaluated for reduction of structurally related polybutadiene rubbers. The presence of an electron-rich alkylphosphine ligand in **5** is responsible for the increase in activity relative to arylphosphine catalysts; the correlation between phosphine basicity and hydrogenation activity has been noted [13]. Reduction of poly(norbornene) via added **5** has been achieved under reaction conditions comparable to those noted above [14], but our own results indicate that much milder conditions can suffice [15] (vide infra). Stoichiometric techniques such as diimide reduction, which lift the requirement for specialized hydrogenation equipment, are common in benchtop practice [11], but the susceptibility to side reactions (previously noted [16] with diene polymers) limits the utility of this approach.



Scheme 2.

Table 1
ROMP-hydrogenation of cyclooctene[a]

Entry	Solvent	Additive[b]	Time (h)	T (°C)	pH_2 (psi)	Conversion (%)[c]
1	CH_2Cl_2		24	22	1000	32
2	3:1 THF-CH_2Cl_2		24	22	1000	100
3	3:1 THF-CH_2Cl_2		24	22	100	9
4	CH_2Cl_2	NEt_3	24	22	100	85
5	CH_2Cl_2	NEt_3	24	50	100	100
6	3:1 THF-CH_2Cl_2	NEt_3	24	22	100	55
7	4:1 CH_2Cl_2-MeOH	NEt_3	24	60	14.6	100
8	4:1 CH_2Cl_2-MeOH		4	22	100	83
9	9:1 CH_2Cl_2-MeOH		4	22	100	51

[a] General conditions: ROMP at RT under N_2 in CH_2Cl_2 (2 ml); 1.5 h, 1.2 mM **1a**, 204 eq. cyclooctene. Hydrogenation carried out for 24 h, following dilution with THF, CH_2Cl_2, and/or MeOH (to total volume of 10 ml). Dilution must precede addition of MeOH, to prevent polymer precipitation.

[b] NEt_3 if applicable, prior to MeOH.

[c] Determined by ^1H NMR; average of 3 trials (± 3%).

We [15,17] and others [18–21] have focused on development of *tandem* metathesis-hydrogenation (Scheme 2), utilizing the hydrogenation activity of dihydrogen complex **3** to effect polymer hydrogenation under moderate conditions (50–135 °C, 100–300 psi H_2, or RT, 1000 psi) in chlorocarbon and/or THF solvent. Activity is higher in the presence of THF, unless base is added to promote formation of **4**, in which case THF is detrimental to catalyst activity (Table 1) [15]. Elegant recent work by Grubbs and coworkers [18] on double-tandem ROMP-ATRP-hydrogenation describes reduction of diblock acrylate-containing copolymers at 65 °C and 150 psi H_2.[1] An ingenious alternative approach involving sequential hydrogenolysis and immobilization of the catalyst has been developed by Wagener's group: the simple expedient of introducing H_2 and Si gel following Ru-catalyzed ADMET polymerization generates a heterogeneous catalyst system that effects polymer reduction under ca. 120 psi H_2 [19]. While the necessity for separation of reduced polymer from the silica support limits this methodology to readily-soluble polyolefins, the facile removal of residual Ru [23] is an attractive feature.

Regeneration of a ROMP-active alkylidene (**1b**, R=CHC=CMe_2) can be effected following hydrogenation, by addition of 3-chloro-3-methyl-1-butyne to **4** [24], **2**/**3**, or any of **2–4** (Scheme 1) [15]. The reaction can be carried out in CH_2Cl_2 or THF; the presence of NEt_3 has no effect. Regeneration of alkylidene under catalytically-relevant conditions affords access to multiple-tandem processes involving repeated cycles of metathesis and hydrogenation. We have used this approach to prepare well-defined poly(norbornene) and polyethylene blends, via sequential processes of ROMP and hydrogenation, ROMP-hydrogenation-ROMP, or (in neat CH_2Cl_2 in the absence of base) ROMP-hydrogenolysis-ROMP. Gel permeation chromatographs of polymers derived from 5-norbornene-2-methoxyether exhibit two distinct, narrow-polydispersity molecular-weight fractions. Such blends are of value for their ability to improve the processability of narrow-polydispersity

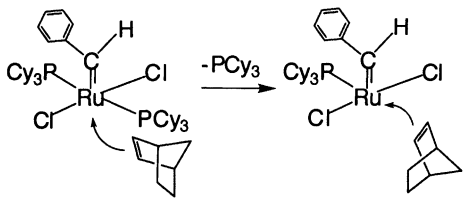
[1] Very recently, Grubbs and coworkers also reported an example of ROMP followed by transfer hydrogenation of a remote ketone functionality [22].

polymers, via the plasticizing effect of a lower-molecular-weight fraction [25].

We recently described the activating effect of methanol cosolvent, arising in part from transformation of **4** into the potent hydrogenation catalyst [26] $RuHCl(CO)(PCy_3)_2$ **5** [15]. Polymer hydrogenation via **5** is effected under unprecedentedly mild reaction conditions;[2] exceptionally, the activity of the new catalyst system is comparable to Rh catalysis [27]. Thus, tandem ROMP-hydrogenation of cyclooctene via precursor **1a** is carried out under 1 atm of hydrogen by adding methanol, as well as base, after metathesis is complete [15]. Reaction rates increase in proportion to the methanol concentration (Table 1, Entries 8, 9). Solubility considerations limit the proportion of methanol that can be tolerated in reduction of hydrocarbon polymers such as poly(norbornene) or poly(octene) to 10–20%; at higher MeOH concentrations, incompletely-reduced polymer precipitates from solution. Even greater hydrogenation efficiency is thus anticipated for more soluble substrates (polar polymers or small molecules derived from RCM) that tolerate a higher proportion of methanol.

2.2. Catalyst selectivity

Molybdenum catalysts have demonstrated extraordinary selectivity in ROMP [28], as well as, more recently, asymmetric ring-closing and ring-opening metathesis [29,30]. Despite the fundamental importance of these advances, however, the Mo systems are limited in some applications by their inherent air- and water sensitivity, and the affinity of the metal for polar functional groups. The tremendous impact of Ru initiators of type **1** (and the second-generation Grubbs catalyst, $RuCl_2(PCy_3)(IMes)(CHR)$, IMes = 1,3-dimesityl-imidazol-2-ylidene) is due to an unprecedented stability toward electrophilic and nucleophilic attack, which permits metathesis of an unusually wide range of substrates under less stringent reaction conditions than required in the Mo systems [1]. Offsetting this robustness, however, is the low selectivity which to date remains characteristic of Ru



Scheme 3.

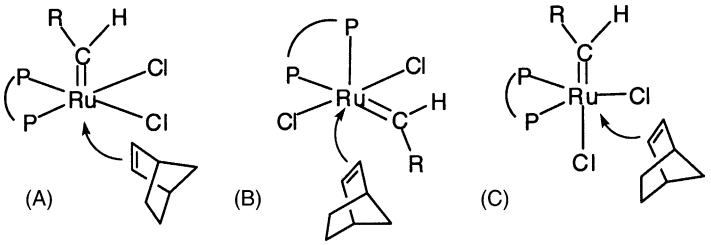
metathesis. In ROMP, for example, *cis*/*trans* olefin mixtures are invariably obtained, and issues of tacticity remain unaddressed. Development of a new generation of Ru catalysts integrating high reactivity, functional-group tolerance, and structural control holds great promise for powerful, general routes to both chiral molecules and structurally defined, functionally diverse polymers.

We [31,32] and others [33,34] have recently described Ru metathesis catalysts containing chelating diphosphine ligands. Our own motivation stems from the very high selectivities attainable in asymmetric catalysis via Ru complexes of chiral diphosphines [35], which we ultimately seek to incorporate into Ru-catalyzed metathesis. The otherwise exclusive use of monodentate ligands in ROMP via Ru-phosphine complexes arises from the well-established requirement for phosphine loss in the kinetically dominant pathway in metathesis [1]. The resulting loss in steric definition of the active site is manifested in the low structural selectivity of these catalyst systems. We considered that ligand loss is necessitated by the specific geometric features of these square pyramidal species, rather than an inherent property of Ru-alkylidene systems. Thus, coordination of substrate *trans* to apical alkylidene in **1** means that productive metathesis can occur only following isomerization or (more favorably) phosphine loss, followed by coordination of olefin *cis* to alkylidene (Scheme 3) [1].

In complexes containing a chelating *cis*-diphosphine ligand, precisely the same circumstances obtain, *if* alkylidene occupies the apical site (**A**, Scheme 4).[3] If

[2] Rigorous air-exclusion is observed. Following ROMP in an N_2-filled drybox, the solution is transferred to an autoclave in the box. Initial hydrogen pressures of 1 atm increase on heating in the sealed vessel.

[3] The strongest *trans*-effect ligand normally occupies the apical position (i.e. *trans* to the vacant site), though this may be modulated by geometric factors. That the *trans* effect of alkylidene is rather high, however, is suggested by Esteruelas' report of an osmium carbonyl complex in which alkylidene, rather than CO, occupies the apical site [36].



Scheme 4.

alkylidene can be placed in a basal site, ligand loss is no longer required, olefin then being constrained to *cis*-entry (**B**). Likewise, where the ligand set can be designed to bias the geometric preference in favor of a trigonal bipyramidal structure (**C**), the requirement for ligand loss may be lifted. It may be noted that catalysts of type **A** may yet afford metathesis-active species with some stereocontrol, via abstraction of halide, which carries a lower steric penalty in terms of defining the active site than does loss of a bulky phosphine ligand.

Fig. 1 summarizes the ligand sets studied in our group to date. The remainder of this paper focuses largely on the *cis*-chelating diphosphine derivatives $RuX_2(PP)_2(CHR)$ (X = Cl, **6**) and in particular the dcypb derivative **6b** (dcypb = 1,4-bis(dicyclohexyl) phosphinobutane). The coordination and catalytic chemistry of bulky, basic diphosphines with chelate ring sizes greater than 5 is virtually unexplored, despite the established correlation between ligand

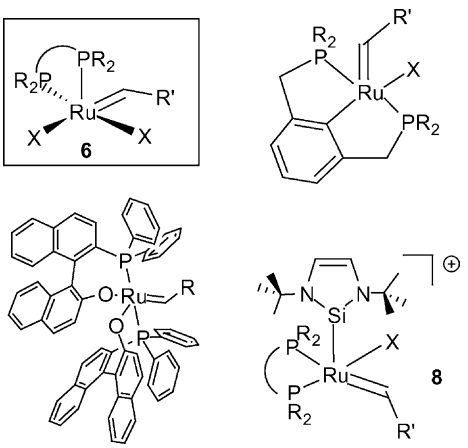
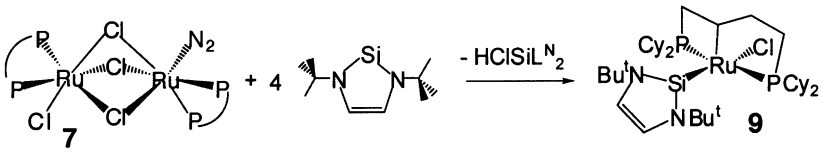


Fig. 1.

basicity and metathesis [1] or hydrogenation [13] activity, as well as the potential of larger ring sizes for extending ligand-based steric control over the active site. We have developed a route into the formerly elusive dcypb complexes via the N_2-stabilized dimer $RuCl(dcypb)(\mu\text{-}Cl)_3Ru(dcypb)(N_2)$ **7** [32]. The achiral systems are explored to establish the ground rules of this chemistry, with introduction of chirality being deferred for subsequent optimization. Of the remaining structures in Fig. 1, the pincer derivatives will be described in a subsequent publication [37]. Alkylidene derivatives of the chelating, heterobifunctional phosphine-phenoxide ligand proved unattainable: instead, π-bound binaphtholates were obtained, recognized by their characteristic upfield aromatic signals in ^{1}H NMR spectra [38].

Cationic catalysts of type $[RuX(PP)(L)(CHR')]^+$ (**8**, Fig. 1) represent a potentially attractive variant on **6**, in which the steric effects of the diphosphine ligand are amplified by the presence of a bulky donor. In the structure shown, this ligand is the stable silylene 1,3-di-*tert*-butyl-1,3,2-diazasilol-2-ylidene (SiL_2^N), a silicon analog of the *N*-heterocyclic "Arduengo" carbenes [39]. Reaction of **7** with 4 eq. of SiL_2^N did not result in simple adduct formation, however, instead giving $RuCl(\eta^3\text{-dcypb})(SiL_2^N)$ **9**, in which the novel tridentate, *trans*-PP geometry results from an unprecedented attack of the metal on the tetramethylene ligand backbone (Scheme 5) [40]. While this does not preclude introduction of alkylidene to generate a novel pincer alkylidene species, reactivity studies carried out on **9** indicated that the silylene does not function as a phosphine mimic in these coordinatively unsaturated systems, but is rather easily displaced by small molecules such as carbon monoxide (RT, minutes). The Ru–Si bond is also susceptible to hydrolysis: exposure to trace water and H_2 liberates the silylene as

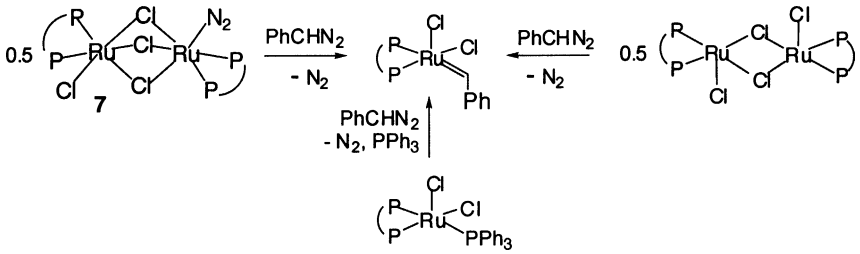


Scheme 5.

a siloxane dimer. Given that the key advantage of Ru metathesis lies in its robustness, we chose not to pursue the silylene chemistry further.

Several examples now exist of ruthenium alkylidenes of type **6**. Hofman and coworkers [33] have explored small chelate ring sizes, of four or five members, while we have chosen to focus on seven-membered chelates, containing dppb (**6a**, dppb = 1,4-bis(diphenylphosphino)butane), dcypb (**6b**), or binap (**6c**, binap = 2,2′-bis(diphenylphosphino) 1,1′-binaphthyl) [31,32]. Routes to **6a–c** are summarized in Scheme 6. Complexes **6a** and **b** can be generated via addition of phenyldiazomethane to the chloride-bridged dimers $[RuCl_2(dcypb)]_2(N_2)$ **7** or $[RuCl_2(dppb)]_2$. An alternative route to **6a–c** via mixed-phosphine precursors $RuCl_2(PP)(PPh_3)$ is undermined by the coproduction of PPh_3, a potent catalyst poison. While molecular modeling and reactivity data (vide infra) for **6a–c** suggest that alkylidene occupies the basal site of a square pyramidal structure, these species are highly reactive. This instability precludes crystallographic confirmation of the structure, and necessitates generation and use of these catalyst systems in situ. In contrast, the dtbpm derivative **6d** (dtbpm = bis(di-*tert*-butylphosphino)methane) is quite stable, and X-ray analysis revealed a square pyramid with apical alkylidene [33]. Consistent with our analysis above, **6d** exhibits very low metathesis activity prior to abstraction of a basal chloride ligand. In the solid state, the dicationic product exists as a dichloro-bridged dimer, but high activity results from the lability [41] of the dative chloride bonds.

Catalysts **6a–c** are the first Ru-phosphine catalysts to exhibit high metathesis activity without ligand abstraction [31,32], consistent with placement of alkylidene in the basal plane. These systems exhibit the correlation between phosphine basicity and metathesis activity previously noted in monodentate **1** [1]. Dcypb system **6b** is particularly active, effecting complete ROMP of 200 eq. of NBE before the first NMR measurement could be made (5 min, $CDCl_3$, minimum TOF = 2400 h^{-1}; Fig. 2). While, in principle, the active catalyst could be generated via dechelation of one end of the phosphine, no "dangling" phosphine is spectroscopically observable, no induction period is evident (Fig. 2), and the exceptionally narrow polydispersities of the poly(norbornene) obtained (1.05–1.16) clearly indicate that rates of initiation exceed rates of propagation. Addition of halide or phosphine scavengers is detrimental to catalyst activity, in contrast to the behavior of **1** [1] and **6d** [33]. This evidence is difficult to reconcile with a dechelated intermediate, which should furthermore reproduce the broader polydispersities (PDIs) found with **1**. PDIs found for the neutral dtbpm catalyst are still higher (Table 2, Entry 4). The relatively high *cis* content associated with



Scheme 6.

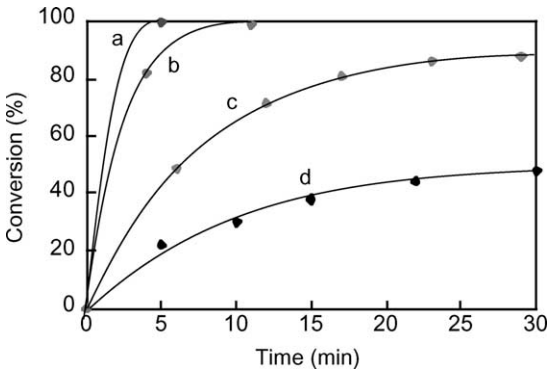


Fig. 2. ROMP of norbornene (NBE; 200 eq.) via $RuCl_2(PP)(CHPh)$ **6** (1.5 mM in $CDCl_3$, RT). Catalyst generated in situ via (a) $[RuCl_2(dcypb)]_2(N_2) + 2\ PhCHN_2$; (b) $[RuCl_2(dppb)]_2 + 2\ PhCHN_2$; (c) $RuCl_2(dppb)(PPh_3) + 1\ PhCHN_2$; (d) $[RuCl_2(dppb)]_2 + 10\ PhCHN_2$.

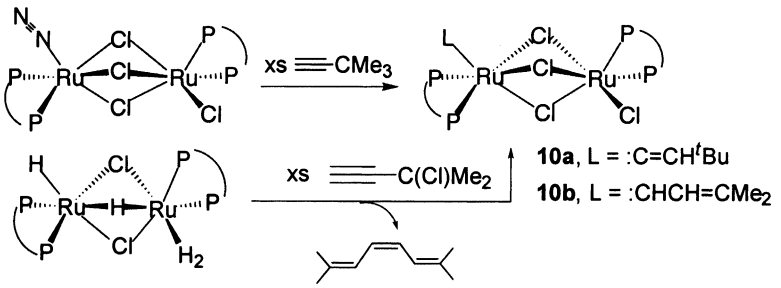
use of binap also argues for retention of the chelate during polymerization, presenting the first "proof-of principle" for increased structural definition of the active site in the diphosphine systems. Increased *cis* content is a benchmark for increased structural definition of the active site: even such structurally ill-defined catalysts as $RuCl_3$ give 80–90% *trans*-olefinic linkages on ROMP of norbornene.

The activity of these systems is promising, as is the observation of some preliminary steric control evidenced by the binap result. Replacement of the benzylidene functionality with less reactive vinylidene and alkylidene functionalities (R =:CHCH = CMe_2) was undertaken with the hope of arresting decomposition, and evaluating structure/activity and structure/selectivity correlations. Unexpectedly, treatment

Table 2
Properties of poly(norbornene) produced by Ru-phosphine catalysts **6** and **1**

Entry	Catalyst (PP)	PDI	% *trans*
1	**6a** (dppb)	1.05	81
2	**6b** (dcypb)	1.16	83
3	**6c** (binap)	1.06	68
4	**6d** (dtbpm)	2.75	80
5	**1a** $(PCy_3)_2$	1.2–2	90

of $Ru(Cl)(dcypb)(\mu\text{-}Cl)_3Ru(dcypb)(N_2)$ with excess *t*-butylacetylene gave dinuclear, monovinylidene **10a** as the sole product (Scheme 7) [42]. While this may indicate facile dimerization of an initially-formed mononuclear vinylidene analogous to **6**, the alternative possibility of reaction of intact dimer **7** could not be ruled out, especially in view of the very low solubility of both starting material and product. We undertook the corresponding reaction of $Ru(H)(dcypb)(\mu\text{-}Cl)_3Ru(dcypb)(H_2)$ with excess 3-chloro-3-methyl-1-butyne in order to dispel the ambiguity about the number of Ru centers involved. Dinuclear monoalkylidene **10b** was formed as one of two principal products; the second was tentatively identified as an isomeric species. Also observed by ^1H NMR was the triene resulting from alkylidene displacement and coupling. The identity of **10b** was confirmed by X-ray diffraction [42]. Rapid formation of this perchloro product confirms facile homodimerization of an initially-formed, mononuclear species. This evidence, along with the low ROMP activity of the monoalkylidene species (1 h for 80% ROMP of norbornene under the conditions of Fig. 2), reveals a major deactivation pathway for catalysts of type **6**.



Scheme 7.

3. Conclusions

We have demonstrated that tandem ROMP-hydrogenation via Grubbs' catalyst in the presence of methanol can afford saturated polymers under 1 atm H_2. In chlorocarbon solvents, multiple tandem catalysis can be effected. We have also described the first examples of ROMP via Ru-phosphine systems in which high activity is achieved without any need for ligand abstraction, through use of diphosphines that afford seven-membered chelate rings. These findings validate the feasibility of deploying RuX_2(PP)(CHR) systems for metathesis chemistry, opening the way for systems with more sterically defined active sites. Chloride-bridged dimers are atom-efficient precursors to vinylidene and alkylidene derivatives, but these synthetic routes are undermined by facile dimerization to yield stable face-bridged dimers that exhibit low metathesis activity. Replacement of the chloride ligands in **6** (PP = chiral and achiral diphosphines) with alternative anionic donors is thus attractive as a means of both increasing definition of the active site, and arresting decomposition via dimerization pathways. This is the avenue that we are currently pursuing, in conjunction with development of chiral versions applicable to stereoselective Ru metathesis. This line of investigation provides a potentially important adjunct to our tandem metathesis-hydrogenation processes, and tandem metathesis-asymmetric hydrogenation will also be explored.

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