

Synthesis of monomeric and dendritic ruthenium benzylidene *cis*-bis-*tert*iobutyl phosphine complexes that catalyze the ROMP of norbornene under ambient conditions

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Abstract

The synthesis of monomeric and dendritic ruthenium benzylidene *cis*-bis-phosphine complexes that catalyze norbornene ROMP previously reported with dicyclohexyl bis-phosphines has now been extended to monomeric and dendritic bis-*tert*iobutyl phosphines. The reaction of Hoveyda's catalyst $[\text{RuCl}_2(\text{=CH-}o\text{-O-iPrC}_6\text{H}_4)\text{PPh}_3]$ (**1**) with the diphosphine $\text{PhCH}_2\text{N}(\text{CH}_2\text{P}t\text{Bu}_2)_2$ (**2**) gives the new air-stable green ruthenium carbene complex (**3**) in which (**2**) models a dendritic branch of poly(diphosphine) dendrimers $\text{DAB-dendr-}[\text{N}(\text{CH}_2\text{P}t\text{Bu}_2)_2]_n$ ($G_1, n = 4; G_2, n = 8; G_3, n = 16$). Metallodendrimers $\text{DAB-dendr-}[\text{N}(\text{CH}_2\text{P}t\text{Bu}_2)_2\text{Ru}(\text{=CHAr})(\text{Cl})_2]_n$ (**4**)–(**6**) derived from the three first generations of DAB polyamines containing, respectively, 4, 8 and 16 ruthenium branches have been synthesized. These dendritic ruthenium–benzylidene complexes initiate the ROMP of norbornene at room temperature to form star-shaped metallodendritic polymers slightly more rapidly than the analogues with bis-cyclohexyl phosphines. Interestingly, the metallodendrimers G_1 (**4**) initiates the ROMP of norbornene much faster than the model ruthenium complex (**3**) the overall rate order being $G_1 > G_2 > G_3 > \text{model}$, these positive and negative dendritic effects being comparable with those found for the dicyclohexyl bis-phosphine complexes.

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1. Introduction

Metallodendritic catalysts have started to emerge as a promising alternative to classic homogeneous and heterogeneous catalysts, because of their perfect molecular definition, solubility allowing mechanistic investigations and ease of recovery and re-use [1]. Among the metathesis reactions, ROMP is a popular one, among other techniques [2], leading to well-defined polymers [3]. We recently reported, in both a communication and a full publication [4], three generations of dendritic ruthenium benzylidene *cis*-bis-phosphine complexes that did not catalyse RCM reactions but were efficient ROMP catalysts under ambient conditions. Dendrimer-

cored polymer stars, an original form of polymers, could be synthesized in a living ROMP process by polymerization of norbornene. The chelating bis-phosphine used had the formula $\text{RN}(\text{CH}_2\text{PR}_2)_2$ in which $\text{R} = \text{Cy}$ [5]. Since Hofmann reported very efficient metathesis catalysts with *cis*-bis-phosphines in which the phosphorus atoms had *tert*-Bu substituents [6,7], we decided to investigate the $\text{RN}(\text{CH}_2\text{PR}_2)_2$ bis-phosphine with the *tert*-Bu substituents for the R groups and the resulting effect on the ROMP of norbornene. The increase of bulk on the metal center and increased electron density are supposed to favor metathesis activity in Grubbs' type catalysts, and this effect was indeed also positive on *cis*-phosphine ruthenium metathesis catalysts. Thus, we are reporting here the synthesis of ruthenium benzylidene complexes analogous to those previously reported with the Cy substituents with *cis*-bis-phosphine ligands $\text{RN}\{\text{CH}_2\text{P}(\text{tert-}$

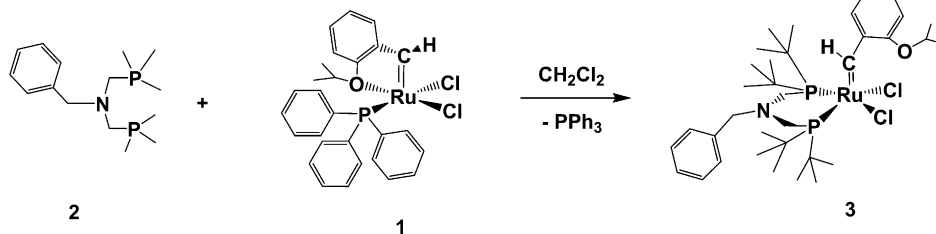
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$\text{Bu}_2\}_2$ including a monomeric model ($\text{R} = \text{PhCH}_2$) and three dendrimer generations and the ROMP of norbornene with these new monomeric and metallodendritic ROMP catalysts.

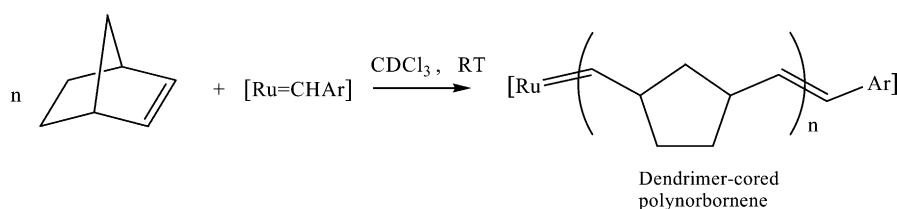
2. Results

2.1. Synthesis of the new ruthenium–benzylidene complex (3)

The reaction of Hoveyda's metathesis catalyst (**1**) [8] with the chelating bis-phosphine (**2**) bearing *tert*-Bu substituents in CH_2Cl_2 at 25°C gives the new ruthenium benzylidene [9] complex (**3**) (Eq. (1)) whose ^1H NMR spectrum shows the carbene proton at $\delta = 15.6$ ppm as a triplet indicating the coupling with two equivalent phosphorus atoms. The later give rise to a singlet at 41 ppm in the ^{31}P NMR spectrum confirming their equivalence. The triphenylphosphine signal have disappeared, indicating the substitution of this ligand and the ether oxygen atom by the chelating bis-phosphine (**2**). The presence of a deshielded signal at $\delta = 9.65$ ppm for an arene proton is characteristic of a non-coordinated oxygen atom. This complex was also characterized by a correct elemental analysis. It is thus analogous to the one previously obtained with the Cy substituent on the phosphorus atoms of the bis-phosphine, and serves as a model for the synthesis of the corresponding dendritic benzylidene complexes with dendritic bis-phosphines also bearing the *tert*-Bu substituents.



1



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2.2. Synthesis of the new dendritic ruthenium–benzylidene complexes (4)–(6)

Given the result for the synthesis of the model complex (**3**), we have extended the synthetic procedure under ambient con-

Table 1
Comparison of the reaction times required for 99% conversion for ROMP reactions catalyzed by the ruthenium–benzylidene complexes (**3**)–(**6**)

Catalyst	Time (h)	Conversion (%)
3	168	99
4	15	99
5	22	99
6	24	99

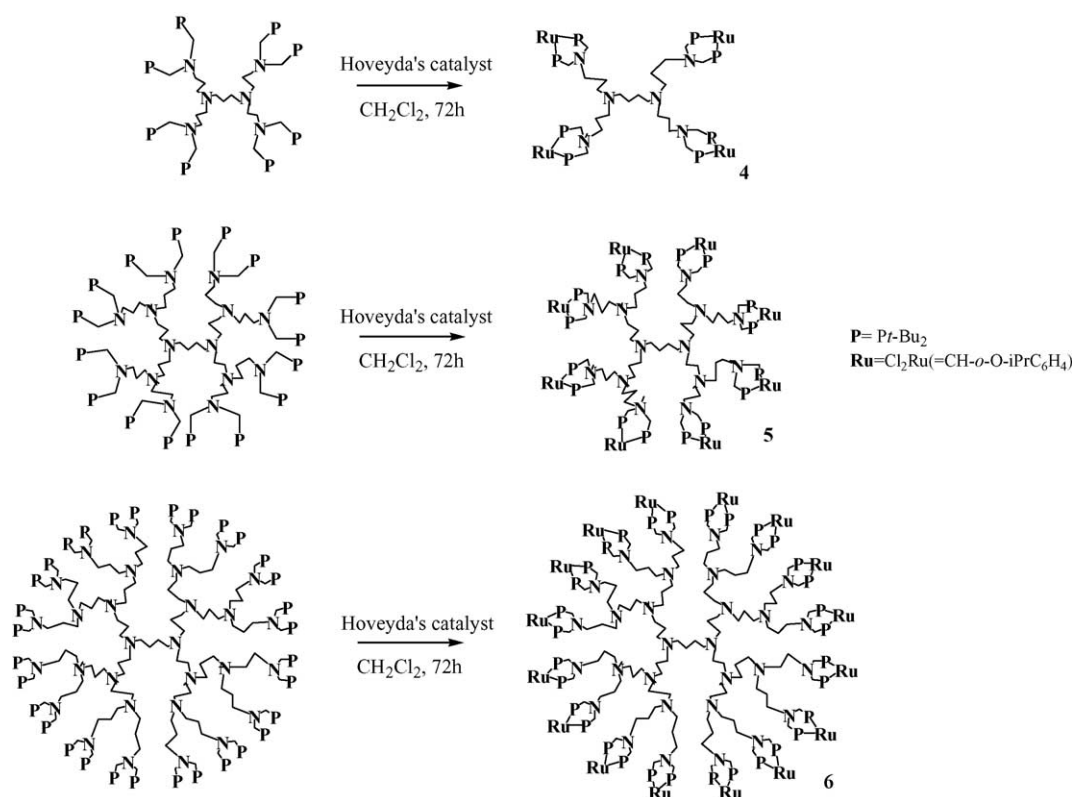
These reaction times were obtained upon following the ROMP reactions by ^1H NMR *cis/trans* ratio: 30/70.

ditions to the three first generations of dendritic phosphines. These reactions yielded the corresponding dendritic ruthenium benzylidene complexes (**4**)–(**6**) that also showed the dowfield triplet for the carbene proton and the singlet in ^{31}P NMR. Besides satisfactory spectroscopic data for these three metallodendrimers (**4**)–(**6**), the first-generation metallodendrimer (G_1), namely (**4**) was also characterized by elemental analysis (Scheme 1).

2.3. ROMP of norbornene to form metallodendritic stars

The ROMP reaction of norbornene catalyzed by the model complex (**3**) and by the dendritic ruthenium benzylidene complexes (**4**)–(**6**) was carried out at 25°C under an inert atmosphere (Eq. (2)). The model complex yielded a linear polymer, and the metallodendritic complexes gave dendrimer-cored polynorbornene stars analogous to those previously obtained with Cy phosphine substituents. The kinetics of the ROMP reactions was followed by ^1H NMR, and the data are gathered in Table 1).

Table 1 clearly shows that the reaction time required for 99% conversion is considerably longer (of the order of 10 times) for the model complex (**3**) than for the dendrimers (**4**)–(**6**). It also shows a negative dendritic effect on the catalytic efficiency, i.e. the reaction times slightly increases as the dendrimer generation also increases.



Scheme 1. Synthesis of the three first generations of dendritic ruthenium–benzylidene complexes (4)–(6) with $\text{P} = \text{P}(\text{tert-Bu})_2$. The *tert-Bu* substituents on phosphorus atoms the chloride ligands and the benzylidene ligand on Ru atoms are omitted for clarity.

3. Discussion

The synthesis and chemistry of the new ruthenium benzylidene complex (3) and of the new dendritic benzylidene complexes (4)–(6) is analogous to that of the complexes in which the bis-phosphine bears Cy groups instead of *tert-Bu* groups. In synthesizing the *tert-Bu* series, we were hoping that these ruthenium benzylidene complexes would be more efficient as metathesis catalysts than the Cy analogues. In fact, the ROMP reaction of norbornene catalyzed by the *tert-Bu* series of complexes is only slightly faster than that using the Cy series. With the most efficient catalyst that is the first-generation dendrimer (4), the 99% conversion is reached after 15 h whereas the corresponding first-generation dendrimer with Cy substituents required 25 h to reach 99% conversion. Thus, it can be concluded that the *tert-Bu* group is slightly more favorable than the Cy group. No RCM metathesis was obtained with catalyst (4)–(6) which was already the case for the Cy series. We speculated, in the Cy series, that the initial step for metathesis was the decoordination of a phosphine ligand on the basis of the much slower catalytic activity compared to Grubbs catalysts. DTF calculation, increased reactivity of dendrimer compared to the monomer and air sensitivity of the metallodendrimers whereas the monomer was air stable, were in agreement with this proposal. The same trend is found here, confirming this hypothesis.

4. Concluding remarks

1. A new family of thermally stable monomeric and dendrimeric ruthenium benzylidene complexes (including three dendrimer generations) with bis-phosphines bearing *tert-Bu* substituents has been synthesized and characterized. The monomer is moderately air stable and the metallodendrimers are air sensitive as in the Cy series. These new compounds are analogous to those previously reported in the Cy series.
2. The new complexes are only slightly more active catalysts for the ROMP of norbornene than their analogues of the Cy series. The metallodendrimers catalyze the ROMP of norbornene much more rapidly than the monomer (positive dendritic effect probably due to the easier decoordination of a phosphine in the dendrimers than in the monomer), but the catalytic efficiency decreases upon increasing the dendrimer generation (negative dendritic effect probably due to increased steric inhibition upon increasing the generation). These effects are analogous to those already found in the Cy series.
3. Neither series is active for RCM metathesis. Other synthetic strategies are now clearly called for in order to reach dendritic ruthenium carbene complexes active in RCM and cross metathesis that is most useful in organic chemistry.

5. Experimental

5.1. General data

All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere drylab. Solvents were freshly distilled under nitrogen. Reagent-grade CH_2Cl_2 and pentane were predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. All other chemicals were used as received. ^1H NMR spectra were recorded at 25 °C with a Bruker AC 300 (300 MHz) spectrometer. ^{13}C NMR spectra were obtained in the pulsed FT mode at 75 MHz with a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million (δ , ppm) with reference to Me_4Si (TMS). Elemental analyses were carried out at the Vernaison CNRS Center.

5.2. Synthesis of ruthenium–benzylidene complexes (3)–(6)

The mixture of the diphosphine or dendritic phosphine DAB–*dendr*- $\text{N}(\text{CH}_2\text{-PrBu}_2)_n$ and Hoveyda's catalyst, $[\text{RuCl}_2(\text{=CH-}o\text{-O-iPrC}_6\text{H}_4\text{PPh}_3)]$ (**1**) was stirred at room temperature in CH_2Cl_2 under nitrogen for 72 h. The reaction mixture was concentrated under reduced pressure to about 2 mL, and pentane (20 mL) was added. The product precipitated in the form of green powder.

Monomer (**3**). Yield: 90%. ^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 1.32 (s, *t*Bu), 1.36 (s, *t*Bu), 1.41 (d, $\text{OCH}(\text{CH}_3)_2$), 2.74 (m, NCH_2P), 3.60 (m, NCH_2Ph), 4.80 (m, $\text{OCH}(\text{CH}_3)_2$), 6.71–7.62 (m, H_{Ar}), 9.65 (m, H_{Ar}), 15.60 (t, $\text{Ru}=\text{CH}$). ^{31}P NMR (CDCl_3 , 81.03 MHz), δ_{ppm} : 40.8 (*PrBu*₂). ^{13}C NMR (62.9 MHz, CDCl_3): δ 135.9–127.4 (C_{Ar}), 70.1 (OCH), 68.3 (CH_2N), 55.9 (PCH_2N), 33.2 (*t*Bu), 32.8 (*t*Bu), 31.8 ($\text{OCH}(\text{CH}_3)_2$). Anal. calcd for $\text{C}_{35}\text{H}_{59}\text{Cl}_2\text{NOP}_2\text{Ru}$: C, 56.52; H, 8.00. Found: C, 56.23; H, 7.89.

$\text{G}_1\text{-Ru}_4\text{P}_8$ (**4**). Yield: 63%. ^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 1.24 (m, CH_2CH_2), 1.29 (s, *t*Bu), 1.33 (s, *t*Bu), 1.40 (d, $\text{OCH}(\text{CH}_3)_2$), 2.70 (m, NCH_2), 3.54 (m, NCH_2Ph), 4.72 (m, $\text{OCH}(\text{CH}_3)_2$), 7.01–7.83 (m, H_{Ar}), 9.55 (m, H_{Ar}), 15.51 (t, $\text{Ru}=\text{CH}$). ^{31}P NMR (CDCl_3 , 81.03 MHz), δ_{ppm} : 40.8 (*PrBu*₂). ^{13}C NMR (62.9 MHz, CDCl_3): δ 134.9–126.5 (C_{Ar}), 70.1 (OCH), 59.4 (CH_2N), 55.9 (PCH_2N), 33.1 (*t*Bu), 32.7 (*t*Bu), 31.8 ($\text{OCH}(\text{CH}_3)_2$). Anal. calcd for $\text{C}_{128}\text{H}_{240}\text{Cl}_8\text{N}_6\text{O}_4\text{P}_8\text{Ru}_4$: C, 56.52; H, 8.00. Found: C, 56.23; H, 7.89.

$\text{G}_2\text{-Ru}_8\text{P}_{16}$ (**5**). Yield: 65%. ^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 1.23 (m, CH_2CH_2), 1.30 (s, *t*Bu), 1.36 (s, *t*Bu), 1.39 (d, $\text{OCH}(\text{CH}_3)_2$), 2.72 (m, NCH_2), 3.57 (m, NCH_2Ph), 4.75 (m, $\text{OCH}(\text{CH}_3)_2$), 6.99–7.79 (m, H_{Ar}), 9.54 (m, H_{Ar}), 15.51 (t, $\text{Ru}=\text{CH}$). ^{31}P NMR (CDCl_3 , 81.03 MHz), δ_{ppm} : 40.8 (*PrBu*₂). ^{13}C NMR (62.9 MHz, CDCl_3): δ 134.3–126.9 (C_{Ar}), 69.9 (OCH), 59.3 (CH_2N), 55.6 (PCH_2N), 33.1 (*t*Bu), 32.9 (*t*Bu), 31.8 ($\text{OCH}(\text{CH}_3)_2$).

$\text{G}_3\text{-Ru}_{16}\text{P}_{32}$ (**6**). Yield: 64%. ^1H NMR (CDCl_3 , 300 MHz), δ_{ppm} : 1.20 (m, CH_2CH_2), 1.33 (s, *t*Bu), 1.39

(s, *t*Bu), 1.42 (d, $\text{OCH}(\text{CH}_3)_2$), 2.74 (m, NCH_2), 3.59 (m, NCH_2Ph), 4.72 (m, $\text{OCH}(\text{CH}_3)_2$), 6.87–7.42 (m, H_{Ar}), 9.49 (m, H_{Ar}), 15.49 (t, $\text{Ru}=\text{CH}$). ^{31}P NMR (CDCl_3 , 81.03 MHz), δ_{ppm} : 40.8 (*PrBu*₂). ^{13}C NMR (62.9 MHz, CDCl_3): δ 135.1–127.0 (C_{Ar}), 70.1 (OCH), 59.5 (CH_2N), 55.8 (PCH_2N), 33.2 (*t*Bu), 32.8 (*t*Bu), 31.9 ($\text{OCH}(\text{CH}_3)_2$).

5.3. Polymerization of norbornene by monomeric and dendrimeric ruthenium complexes

Norbornene and the ruthenium–benzylidene catalyst (0.003 mmol) were introduced in a dry Schlenk tube under an inert atmosphere in 2 mL of CDCl_3 , and the reaction was followed at 25 °C by ^1H NMR (see data in Table 1 and characterizations in Ref. [4]).

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