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On the ROMP of 2-norbornene with an *in situ* ruthenium carbene complex: ESI-MS, NMR and DFT analyses

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ABSTRACT

During the reaction between $[\{RuCl(dppb)\}_2\text{-}(\mu\text{-}Cl)_2]$ and ethyldiazoacetate (EDA) a neutral carbene complex was observed *in situ* in a methylene chloride solution, with vigorous N_2 evolution. This reaction was investigated by ESI-MS analysis, which suggests the formation of a mononuclear carbene containing ruthenium complex as product, $[RuCl_2(dppb)({=}CHC(O)OCH_2CH_3]$. The carbene complex was also detected by proton NMR with δ 22.8 ppm for the heteronuclear coupling, $^3J_{HP} = 7$ Hz, and $^{31}P\{^1H\}$ NMR with a singlet signal at δ 30 ppm. The DFT calculation suggests a square pyramidal ruthenium structure for $[RuCl_2(dppb)({=}CHC(O)OCH_2CH_3]$ with 16 valence electrons and the carbene moiety *trans* to a vacant site. The carbene complex, generated *in situ*, was applied to the polymerization of 2-norbornene, achieving a wide range of turnover numbers and PDI values.

1. Introduction

Transition metal complexes that catalyze C–C bond formation via olefin metathesis are of considerable interest and synthetic utility, for instance in ring-opening metathesis polymerization (ROMP). The discovery, by Grubbs [1], that ruthenium carbene complexes of the general type $[RuCl_2(P)_2({=}CHR)]$ (where P = electron-rich monophosphine and R = phenyl, $CH{=}CH_2Ph_2$, etc) are highly active single component (pre)catalysts for all types of alkene metathesis reactions denoted a real breakthrough, which has triggered an avalanche of interest in such transformations [1]. In view of this, many ruthenium carbene complexes have been synthesized and successfully applied to metathesis reactions.

The generally accepted mechanism of metathesis reactions (Chauvin mechanism) consists of a sequence of formal [2 + 2] cycloadditions/cycloreversions, involving alkenes, metal carbenes, and metallacyclobutane intermediates [2]. Among the metal complexes used as catalysts or precatalysts (that convert into metal alkylidenes *in situ*), tungsten or molybdenum alkylidene complexes, developed by Schrock and co-workers [3–5], and ruthenium carbene complexes, introduced by Grubbs and co-workers [6–10], are undoubtedly the most popular and versatile.

Ruthenium complexes containing one chelating bis (tertiary phosphine) ligand per metal atom are key species for catalysis and are also precursors in the synthesis of new complex derivatives. Unsaturated complexes with 16 or 14 valence electrons with the general formula $[\{RuCl(P\text{–}P)\}_2\text{-}(\mu\text{-}Cl)_2]$ {P–P = chiral or achiral chelating diphosphines}, have been used to provide "Ru^{II}(P–P)" moieties as the active component of catalysts [11] and synthetic precursors [12,13].

The complex $[\{RuCl(dppb)\}_2\text{-}(\mu\text{-}Cl)_2]$ {dppb = 1,4-bis(diphenylphosphine)butane} can be achieved by H_2 reduction of mixed valence dinuclear complex (Ru^{II}/Ru^{III}) $[\{RuCl(dppb)\}_2\text{-}(\mu\text{-}Cl)_3]$ [12,14], or more appropriately by H_2 reduction of the aqua complex *mer*-$[RuCl_3(dppb)(H_2O)]$ [15] (Ru^{III}), as depicted in Scheme 1.

During the reaction between $[\{RuCl(dppb)\}_2\text{-}(\mu\text{-}Cl)_2]$ and ethyldiazoacetate (EDA), a neutral carbene complex was observed *in situ* in a methylene chloride solution, with vigorous N_2 evolution (see Scheme 2). It is interesting to mention that a similar carbene complex was described by Fogg and cvo-workers, [16, 17] with $[RuCl_2(P\text{–}P)(PPh_3)]$ as precursor {where P–P = aromatic and non-aromatic diphosphino ligand}, which was obtained *in situ* after reaction with phenyldiazomethane (PDM). The structure suggests was similar to the carbene complex described here, but the catalytic activity in the

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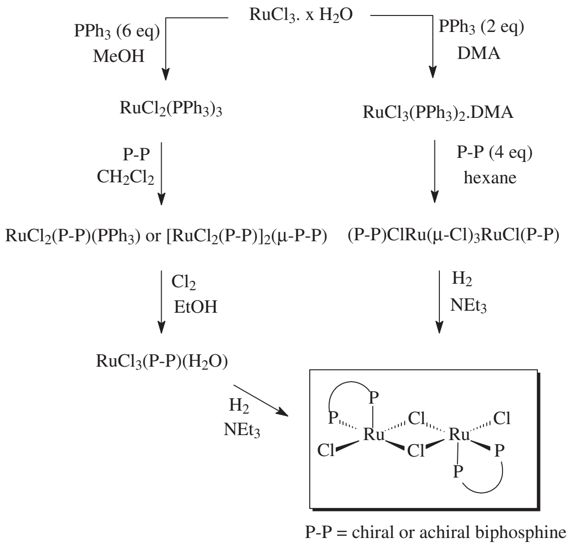


Scheme 1. Conventional routes to achieve "Ru^{II}(P—P)" moiety [15].

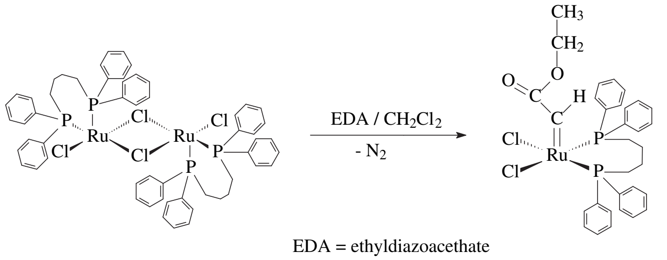
ROMP of 2-norbornene was quite different. The nucleophilic ligand (PPh_3) was displaced from the complexes of general formula [$RuCl_2(PPh_3)$(P—P)], during the reaction with the diazoalkane, poisoning the polymer assembly in the ROMP reaction [16].

Herein we report an *in situ* development of a new square-pyramidal ruthenium carbene complex, with diphosphino ligand but without the PPh_3, from [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] as precursor (Scheme 1). The carbene complex generated *in situ* was studied by NMR, mass spectrometry and DFT calculations.

2. Experimental section

2.1. Material and instrumentation

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. $RuCl_3.xH_2O$, triphenylphosphine (PPh_3), 1,4-bis(diphenylphosphine)butane (dppb) and ethyldiazoacetate (EDA) were purchased from Aldrich and used as received. Reagent grade solvents were distilled prior to use. The NMR spectra of the compounds were acquired with a Bruker ARX-200 spectrometer (4.7 T) equipped with a 5 mm inverse probe head. The ^1H NMR spectra were collected into 64 K computer data points with a spectral width of 5112.5 Hz. The 90 ° pulse width was 8.50 μs and the spectra were acquired by accumulating 64 scans. The summed FID data were first apodized with an exponential filter, corresponding to a line broadening of 0.3 Hz. Samples for ^{31}P {^1H} experiments were prepared under on inert atmosphere and measured at room temperature, with methylene chloride (CH_2Cl_2) as solvent and a D_2O capillary. Chemical shifts were reported with respect to the phosphorus signal in 85% phosphoric acid (H_3PO_4).



Scheme 2. *In situ* preparation of a neutral carbene complex: [$RuCl_2$(dppb)(=CHC(O)OCH_2CH_3)].

Gel permeation chromatography (GPC) was carried out in a Shimadzu CLASS-VPTM chromatograph equipped with LC-10 AD pump, Rheodyne 7725 I injector with 20 μL sample loop, and two columns of PL gel using $CHCl_3$ as eluent (0.5 mL min^{-1}). The molecular weight and PDI values were determined from a monodispersive polystyrene standard (Polymer Laboratories, $\overline{M}_W$ in the range 10–1.000 kDa).

Mass spectrometry analyses were carried out in a Quattro-LC APCI/ESI triple-quadrupole mass spectrometer (Waters, Manchester, UK), coupled to an Alliance 2695 HPLC (Waters, Manchester, UK). The mobile phase in the HPLC was composed of methylene chloride: methanol (99:1) (both HPLC grade, JT Baker, Ecatepec, Mexico), flowing at 120 μL min^{-1}. Samples were ionized in an electrospray ionization (ESI) source operating in positive mode. Temperatures of MS source block and probe were set at 85 and 300 °C, respectively. Flow rates of both nebulizer and desolvation gases (nitrogen) were set at 12 and 780 L h^{-1}, respectively. Ionization parameters, namely the capillary, cone, and extractor voltages, were set at 3.0 kV, 25V and 8V, respectively.

All calculations were carried out using the Gaussian03 suite of programs [18]. The structures were optimized by the Density Functional Theory (DFT) method [19–21], employing the B3LYP hybrid functional, which three parameters non-local exchange term of Becke and the correlation term of Lee, Yang and Parr [22,23]. The basis set employed to build the molecular orbitals was 6-31G* for chlorine, phosphorus, and oxygen, and 6-31G for carbon and hydrogen [24,25]. The Los Alamos effective core potential (ECP) and double-zeta valence basis set (LanL2DZ) [26] were used to describe the ruthenium atom. The nature of the stationary state of the optimized structures was characterized at the same level of theory by analytical harmonic frequency calculations. All structures possessed positive definite Hessian matrices, indicating that they were located in a genuine minimum on the potential energy surface. The description of the molecular orbital composition was made by means of Mulliken population analysis [27], with the use of GaussSum program [28].

The [RuCl(dppb)]$_2$-(μ-Cl)$_2$ and *mer*-[$RuCl_3$(dppb)(H_2O)] complexes were synthesized as described previously [15,29].

2.2. *In situ preparation of [$RuCl_2$(dppb)(=CHC(O)OCH_2CH_3)]*

[{RuCl(dppb)}$_2$-(μ-Cl)$_2$] (2.0 mg, 1.7 μmol) were dissolved in CH_2Cl_2 (0.6 mL) in an NMR tube and ethyldiazoacetate was added (1.0 μL, 9.5 μmol), gas was evolved and a green blend formed, which was immediately analyzed by NMR: ^1H NMR (400 MHz $CDCl_3$): 22.8 ppm [t, $^3J_{PH}$ = 7Hz, Ru$C\underline{H}$(P—P)]; $^{31}P\{^1H\}$ NMR (81.0 MHz CH_2Cl_2/D_2O): 30.2 ppm (s, dppb).

3. Mass spectrometry analyses

A stock solution at 1.0 mg mL^{-1} of [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] was prepared by dissolving 2.0 mg in 2.0 mL of CH_2Cl_2. A 20 μL portion of this solution was diluted to 2.0 mL in CH_2Cl_2, to prepare a test solution of 10 μg mL^{-1} and 30 μL of this solution was injected into the ESI source. The product of reaction between [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] and ethyldiazoacetate was analyzed similarly. After the reaction in 2.0 mL of CH_2Cl_2, the sample was diluted as above and 30 μL were again injected into the ESI source. After many data acquisitions to test different sets of conditions, the best conditions were chosen and samples were injected in triplicate. The acquired mass spectra were compared with the theoretical ones (MassLynx 4.0, Waters, Manchester, UK).

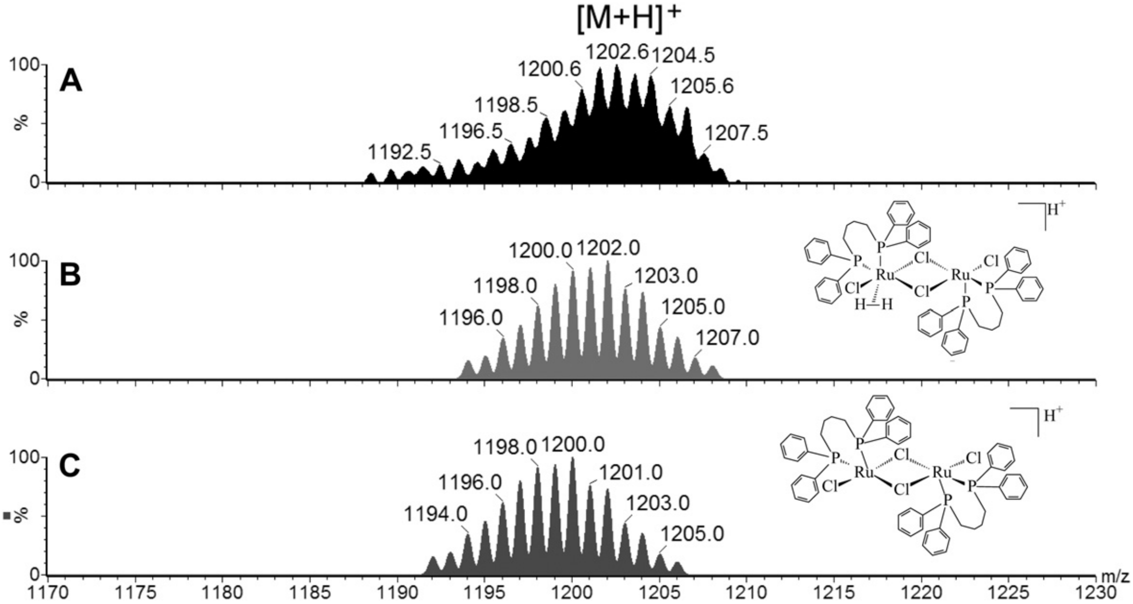


Fig. 1. Mass spectrum of protonated compound [{RuCl(dppb)}$_2$-(μ-Cl)$_2$]: A) experimental data generated by ESI ionization; B) simulated for protonated molecule complexed to H_2; C) simulated for molecule without H_2.

4. Polymerization of 2-norbornene

In a Schlenk tube connected to an argon line 1–3 mmol of the substrate 2-norbornene was added to 1 mL of solvent [CH_2Cl_2, or $CHCl_3$ or $(CH_2)_2Cl_2$], when the substrate was completely dissolved the precursor [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] (2.0 mg, 1.7 μmol) and ethyldiazoacetate (1.0 μL, 9.5 μmol) were added, producing a white rubber which was characterized by ^{1}H NMR and GPC. The reactions were quenched with methanol (5 mL).

5. Results and discussion

5.1. Syntheses and characterization

The [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] and EDA reacted in CH_2Cl_2, with vigorous nitrogen evolution, to produce a neutral carbene complex that was active in the ROMP reaction of 2-norbornene. The $^{31}P\{^1H\}$-NMR data of [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] revealed two doublets at δ 55.3 and 63.3 ppm, $^2J_{PP} = 47$ Hz. In the presence of EDA (5 equivalents) the phosphorus signals changed from the two doublets to a singlet at 30 ppm, demonstrating the equivalence of the P-atoms in the phosphine ligand in the product, as depicted in Scheme 2. The reaction was carried out in the NMR tube with a Teflon cap under an argon atmosphere. With a great excess of EDA (50 equivalents), two new signals were observed, one singlet at δ 31.5 ppm due the dppb(O)$_2$ and an intense singlet around δ 24 ppm, attributed to the EDA/dppb adduct. These signals are in agreement with free dppb in the presence of EDA (50 equivalents) without the metal complex. A triplet signal was observed in the ^{1}H NMR data at δ 22.8 ppm for heteronuclear coupling ($^3J_{HP} = 7$ Hz) in the carbene complex generated *in situ*.

Analysis of NMR spectra allied to various kinds of mass spectrometry, has emerged as a good approach for the identification of

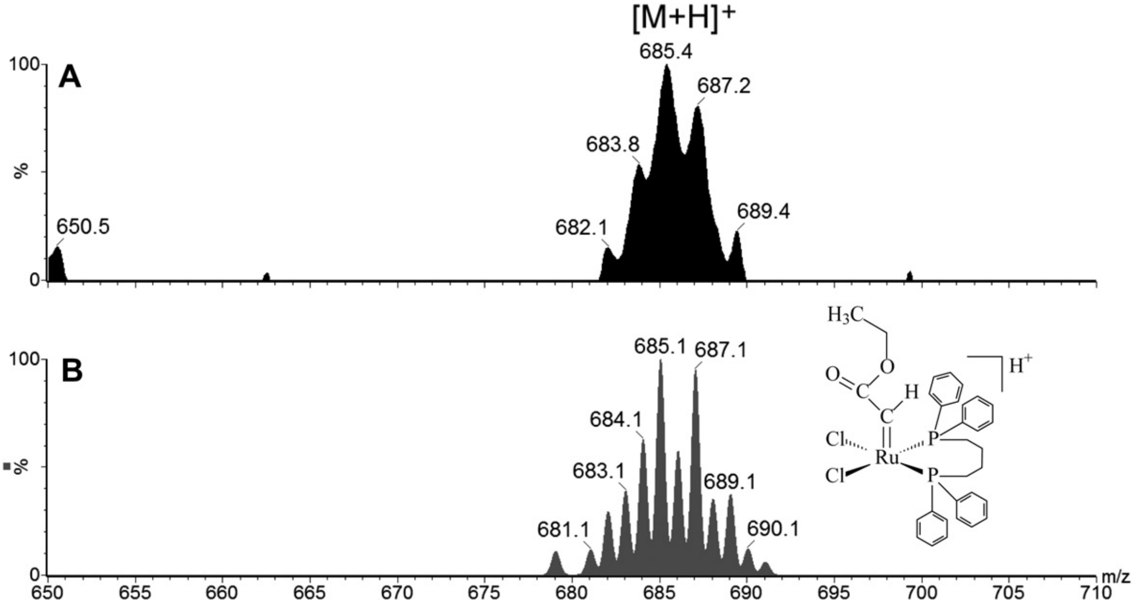


Fig. 2. Mass spectrum of the *in situ* ruthenium carbene complex: A) experimental data generated by ESI ionization; B) simulated for structural formula.

Table 1
Polymerization of 2-norbornene by *in situ* carbene complex obtained from [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] and EDA.

Trial	Time (min)	[norbornene] (mol L^{-1})	Solvent	Temperature (°C)	Yield (%)	Productivity (kg$_{pol}$ molRu^{-1} h^{-1})	TOF (h^{-1})	PDI[a]	Z/E[b]
1	3.5	1.06	$CHCl_3$	40	57	593	6294	–	–
2	3.5	1.09	$CHCl_3$	60	64	673	7152	–	–
3	7.0	1.08	$CHCl_3$	60	44	228	2420	–	–
4	15	1.06	$CHCl_3$	60	30	72.6	770	–	–
5	3.5	1.06	$(CH_2)_2Cl_2$	40	7	7.02	746	–	–
6	30	1.06	CH_2Cl_2	40	38	90.7	964	4.60	42/58
7	60	1.09	CH_2Cl_2	40	51	62.9	669	4.70	43/57
8	180	1.06	CH_2Cl_2	40	51	20.2	214	1.39	40/60
9	3.5	1.08	CH_2Cl_2	30	43	447	4748	3.39	10/90
10	3.5	0.55	CH_2Cl_2	40	36	189	2006	3.41	8/92
11	3.5	1.06	CH_2Cl_2	40	78	797	8471	3.21	13/87
12	3.5	2.15	CH_2Cl_2	40	78	1619	17 192	4.02	15/85
13	3.5	3.31	CH_2Cl_2	40	60	1889	20 059	5.36	15/85
14	7.0	1.07	CH_2Cl_2	40	86	394	4181	3.35	12/88
15	15	1.06	CH_2Cl_2	40	93	223	2368	3.09	11/89
16	30	1.08	CH_2Cl_2	40	95	116	1230	3.44	12/88

[a] PDI values were obtained by gel permeation chromatography (GPC), for example: number average molecular weight $M_n = 2.594$ and mass average $M_w = 3.614$. Therefore the polydispersity index M_w/M_n = PDI = 1.39. Standard deviation = $\sigma = M_n . (M_w/M_n - 1)^{1/2} = 1.63$.

[b] Polymer isomers estimed by ^{1}H-NMR in $CDCl_3$ solution. Amounts of ruthenium precursor and EDA in reaction: Trials 1–5 and 9–16 = 2 mg [{RuCl(dppb)}$_2$-μ-(Cl)$_2$], 1.0 μL de EDA; 6–8 = 1 mg of [{RuCl(dppb)}$_2$-μ-(Cl)$_2$], 5.0 μL of EDA.

metal complexes [30,31]. The mass spectral data confirmed the structures proposed for [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] and the carbene complex formed (Scheme 2). However, the [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] complex had a mass spectral profile that suggested the presence of a hydrogen molecule added to its structure. It is plausible a molecule of H_2 coordinated to Ru in [{RuCl(dppb)}$_2$-(μ-Cl)$_2$], comes from the H_2 used in its synthesis (see Scheme 1). Supporting evidence is found in the ^{1}H-NMR spectrum, as a broad signal at −8 ppm attributed to η^1- type coordination of H_2 to the metal centre. There is no evidence of hydride mode coordination at the ruthenium centre (Ru–H), which could produce a heteronuclear coupling between the hydride and phosphorus atoms in the ^{1}H NMR spectra. The Ru–H coordination mode could also change the oxidation state of the metal, producing a paramagnetic metal complex with Ru^{IV}. Since there is an excess of hydrogen molecules during the reaction to synthesize the binuclear ruthenium complex, the presence of H_2 occupying a vacant coordination site should be expected. The evidence for the Ru–H_2 coordination in the [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] was not detected in earlier work [15], since at that time the product of the reaction was obtained in the solid state, whereas here the Ru–H_2 species as detected *in situ*. In other words, the complex containing the Ru–H_2 bond is not stable enough to be isolated as a solid product.

The experimentally observed mass spectrum of the protonated binuclear complex is shown in Fig. 1A and may be compared with theoretical spectra in Fig. 1B, for the same molecule complexed to H_2 at Ru atom, and 1C, without any complexed H_2. Fig. 1B match perfectly, whereas 1C does not, providing evidence for the Ru–H_2 coordination. The formation of a molecular hydrogen complex in this kind of structure has previously been described in the literature [32].

Concerning the differences between the mass spectra of the compound [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] and the product of the reaction with EDA, the two exhibit different isotopic cluster profiles, having different molecular masses. The compound [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] has two ruthenium atoms as central metals and thus shows isotopologue ions for protonated molecule [M + H$^+$] varying from *m/z* 1192 to *m/z* 1206 (Fig. 1A). Such isotopic variation is in agreement with the molecular formula proposed for this compound ($C_{56}H_{58}P_4Ru_2Cl_4$).

The mass spectrum of the carbene ruthenium complex generated *in situ* was consistent with that of its binuclear precursor. However, it has only one ruthenium atom, so the isotopic cluster profile is quite different from that of [{RuCl(dppb)}$_2$-(μ-Cl)$_2$]. Isotopologue ions for [M + H$^+$] varied from *m/z* 680 to *m/z* 692 (Fig. 2) as predicted from the molecular formula $C_{32}H_{34}O_2P_2RuCl_2$ and the feature of the observed mass spectrum agree with the theoretical data, confirming the molecular formula (Fig. 2). Therefore, the mass spectral data obtained for both [{RuCl(dppb)}$_2$-(μ-Cl)$_2$] and the carbene complex do indicate the occurrence of the proposed reaction and confirm the chemical structures of precursor and product even though they cannot provide stereochemical information.

5.2. Polymerization of norbornene with [RuCl$_2$(dppb)(=CHR)]

The binuclear complex {[RuCl(dppb)]$_2$-(μ-Cl)$_2$} affords a 14 valence electron complex when the chloride bridge is broken and this can be used to produce an active carbene complex with 16 valence electrons in the presence of EDA. The complex arising from that reaction is able to polymerize 2-norbornene with a high turnover frequency, as shown in Table 1, which gives details of the performance achieved under various sets of conditions.

In the presence of chloroform ($CHCl_3$) as solvent, the yield of unsaturated polymer fell as the reaction time rose from 3.5 to 15.0 min (trials 1–4), suggesting a bite polymerization. The precatalyst is quite insoluble in dichloroethane ($(CH_2)_2Cl_2$) which

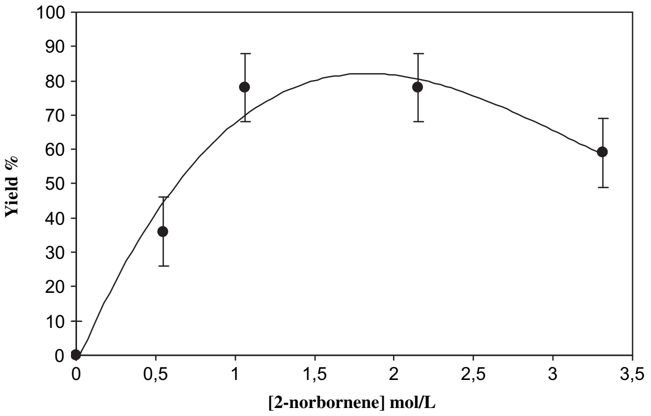


Fig. 3. Influence of 2-norbornene concentration on the activity of the [{RuCl(dppb)}$_2$-(μ-Cl)$_2$]/EDA system.

greatly reduced the catalyst performance (trial 5) even at 40 °C. The results improved in the solvent of methylene chloride (CH_2Cl_2), and a screening was conducted to investigate the $[\{RuCl(dppb)\}_2\text{-}(\mu\text{-}Cl)_2]$/EDA system for the polymerization of 2-norbornene. With CH_2Cl_2 as solvent, the Z/E mixture was predominantly E, with yields up to 90% for the E isomer. The isomer Z/E relation for each polymer was obtained by direct integration of the vinyl hydrogen signals in ^1H-NMR data of the isolated polymer in a $CDCl_3$ solution. The catalyst activity initially increases with 2-norbornene concentration and then drops after reaching a maximum, as shown in(Fig. 3)

Phosphine loss is require in the kinetically dominant pathway in metathesis where monodentate ligands are used in ROMP via Ru-phosphine [17,33]. Thus, coordination of the substrate *trans* to the apical alkylidene in Grubb's catalyst means that productive

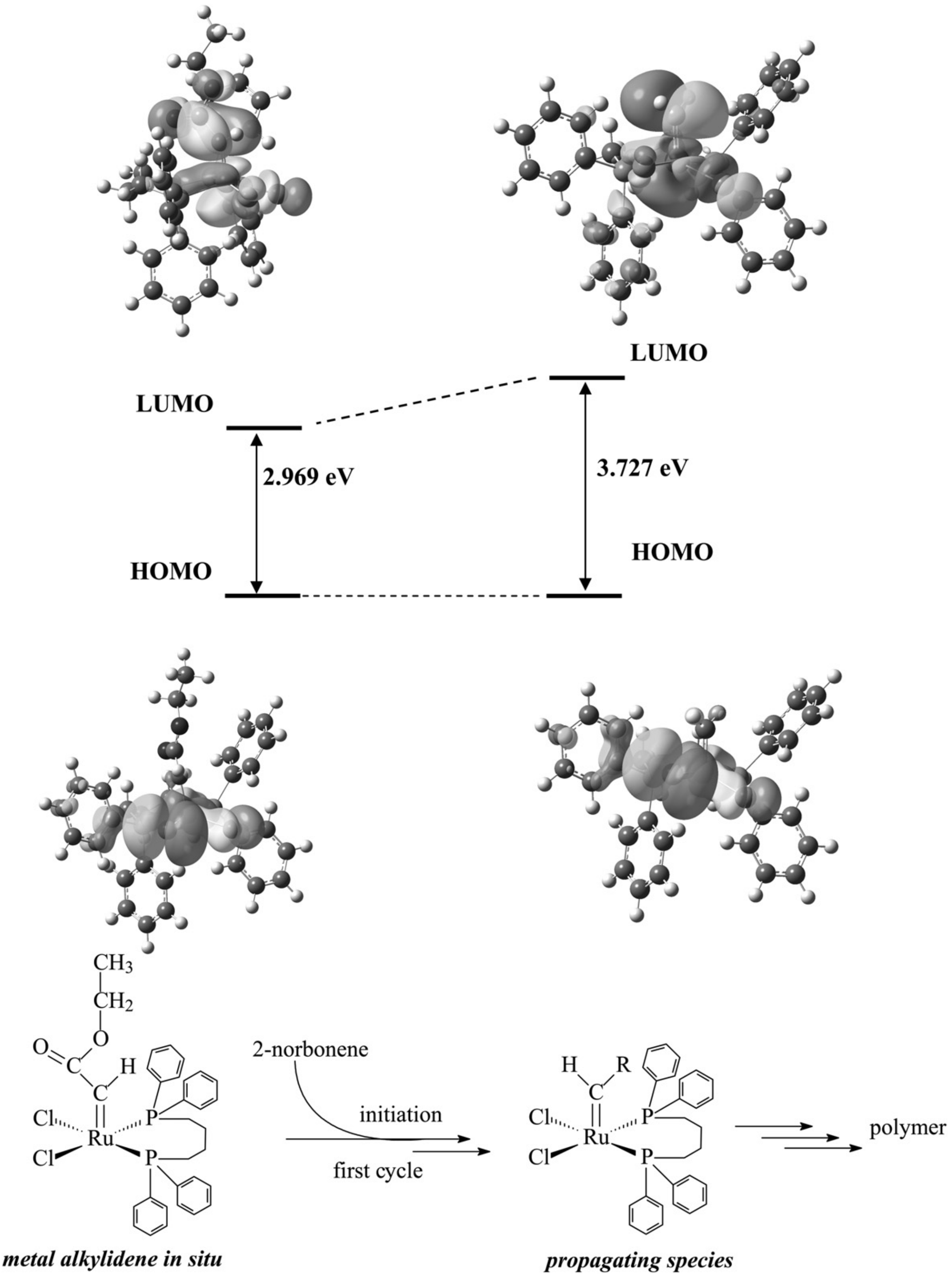


Fig. 4. Orbital character of the *in situ* carbene complex as the catalyst precursor and the propagating species.

metathesis can occur only following isomerization (swing-through propagation mechanism of the metallacyclobutane) [34] or (more favorably) phosphine loss [33], after which olefin is coordinated *cis* to alkylidene.

In complexes containing a chelating *cis*-diphosphine ligand, obtained in the same circumstances the alkylidene occupies the apical site as previously published by Fogg and co-workers [17] and in this case three possibilities can occur. 1) the alkylidene can be placed at a basal site and ligand loss is not required. 2) the ligand set can be designed to bias the geometric preference in favor of a trigonal bipyramidal structure, the requirement for ligand loss may also be lifted. 3) abstraction of halide, which carries a lower steric penalty in terms of defining the active site than does loss of a bulky phosphine ligand [35]. It may be noted that catalysts like the one described here may yet afford metathesis-active species.

5.3. DFT calculation

In a d^6 transition metal pentacoordination complex, Rossi and Hoffmann [36] suggest an equilibrium between a low-spin square pyramid and a high-spin trigonal bipyramid structure. This situation is analogous to the low-spin square-planar and high-spin tetrahedral equilibrium in Ni(II) and other d^8 systems. The formation of a ruthenium carbene complex (low-spin d^6-species) with a bidentate diphosphine ligand coordinated to the Ru, observed by mass spectrometry (Fig. 2) and NMR spectroscopy, is described in this study. In view of this, a square pyramid with the carbene moiety *trans* to the vacant site, as suggested by Rossi and Hoffmann [36], was used as a starting point for DFT calculations.

Owing to the *trans* effect, the strongest donor ligand normally occupies the apical position in the complex, *trans* to the vacant site, in a pyramidal structure. Caulton [37] prepared mixed hydride chloride carbene complexes, in which the hydride ligand also occupied the apical position. The reason for this geometry is the stability of the strong σ-donor hydride *trans* to an empty site. However, the *trans* effect may be modulated by geometric factors. Esteruelas and co-workers [38] reported an osmium carbonyl complex in which alkylidene, rather than CO, occupied the apical site.

As suggested by the DFT calculation (Fig. 4), the HOMO orbital is predominantly metal-chlorine while the LUMO orbital is delocalized among Ru═CH–C(═O)O– bonds. The LUMO orbital suggests an appropriate moiety for nucleophilic attack from the substrate towards the polymer assembly. After the first catalytic cycle, the $[RuCl_2(dppb)({=}CHC(O)OCH_2CH_3]$ complex must generate an alkylidene complex with the ═CHR group, $[RuCl_2(dppb)({=}CHR)]$, where R is an alkyl group. When R═H, the propagating species has 92% of the HOMO orbital localized between the Ru–Cl bonds and 49% of the LUMO orbital restricted to the $Ru{=}CH_2$ bond, with a HOMO–LUMO energy gap of 3.727 eV. In the previous complex, $[RuCl_2(dppb)({=}CHC(O)OCH_2CH_3]$ the HOMO orbital has the same composition (92% at Ru–Cl bonds), but the LUMO orbital is 58% delocalized over Ru═CH–C(═O)O– bonds, with an energy gap of 2969 eV. The ester group included in the alkylidene moiety increases the participation of several atoms in the delocalized LUMO orbital.

6. Conclusion

The reaction between $[\{RuCl(dppb)\}_2\text{-}\mu\text{-}(Cl)_2]$ and ethyldiazoacetate affords a neutral carbene containing ruthenium complex, $[RuCl_2(dppb)({=}CHC(O)OCH_2CH_3]$. This reaction was investigated by ESI-MS and NMR analysis, and DFT calculation. The information obtained in this way confirmed the proposed structures for $[\{RuCl(dppb)\}_2\text{-}(\mu\text{-}Cl)_2]$ and the carbene complex derived from this complex and EDA, $[RuCl_2(dppb)({=}CHC(O)OCH_2CH_3]$. The precursor compound $[\{RuCl(dppb)\}_2\text{-}(\mu\text{-}Cl)_2]$ has two ruthenium atoms as central metals, and thus consistently shows isotopologue ions for the protonated molecule $[M+H^+]$ varying from *m/z* 1192 to *m/z* 1206, with a H_2 molecule coordinated at a vacant site of the binuclear complex. This coordination produced a broad signal at −8 ppm at ^{1}H-NMR spectrum. Isotopologue ions for $[M+H^+]$ in the carbene complex varied from *m/z* 680 to *m/z* 692. This outcome confirms the molecular formula $C_{32}H_{34}O_2P_2RuCl_2$. The carbene complex was also observed by NMR techniques: ^{1}H with δ 22.8 ppm for the heteronuclear coupling $^3J_{HP} = 7$ Hz and $^{31}P\{^1H\}$ NMR with a singlet signal at 30.2 ppm. DFT calculation suggests a 16 valence eletron, square pyramidal ruthenium structure for $[RuCl_2(dppb)({=}CHC(O)OCH_2CH_3]$, with the carbene moiety *trans* to the vacant site. The catalyst activity initially increases with 2-norbornene concentration and then drops after reaching maximum activity at around 1.5 mol L^{-1} norbornene. The Z/E relation in the polynorbornene was dominated by isomer E, with yields higher than 90% of the polymer.

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