Synthesis and Characterization of New Ruthenium Vinylidene Complexes

Araceli Martínez[a], Ricardo Clark-Tapia[a], Selena Gutiérrez[b] and Mikhail A. Tlenkopatchev[c*]

[a]*Instituto de Estudios Ambientales, Universidad de la Sierra Juárez, UNSIJ. Av. Universidad s/n, Ixtlán de Juárez, 68725 Oaxaca, México;* [b]*Centro de Investigaciones Biológicas del Noroeste, CIBNOR. Instituto Politécnico Nacional, No. 195, Playa Palo de Santa Rita Sur, 23096 B.C.S, México;* [c]*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacán, México, D.F. 04510, México*

Abstract: The synthesis of three new ruthenium vinylidene complexes **I-III** with general formula [RuCl$_2$(=C=CHR)(PCy$_3$)$_2$] (R= p-C$_6$H$_4$CF$_3$ (**I**), p-C$_6$H$_4$F (**II**) and C$_6$H$_9$ (**III**)) has been reported. The vinylidene complexes were isolated as crystalline solids and characterized by ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR, FT-IR spectroscopy, X-ray diffraction and elemental analyses. Due to the electronic repulsion between the chlorines and the steric repulsion between the cyclohexyl ring of PCy$_3$ and the substituent on the vinylidene ligand, the complexes **I-III** showed a distorted square-pyramidal structure. These complexes exhibited the high catalytic efficiency in the cross-metathesis degradation of challenging natural rubber (NR) in the presence of d-limonene and citrus oils as chain transfer agents.

Keywords: Metathesis activity, natural rubber, ruthenium vinylidene, synthesis.

1. INTRODUCTION

Transition metal vinylidene complexes are important intermediates for a large variety of catalytic reactions [1-4]. Alkyne dimerization, cyclotrimerization of conjugated enediynes, alkene and enyne metathesis and ring-opening metathesis polymerization (ROMP) are some of the examples of synthetic applications [5, 7]. Synthesis, structure and properties of many transition metal vinylidene complexes, in particular ruthenium vinylidene have been reviewed [8-12]. Ruthenium vinylidene complexes have attracted considerable attention because these catalysts can be easily prepared from commercially available simple ruthenium complexes and alkyne derivatives using appropriate experimental procedures [13]. This methodology is based on the application of inexpensive acetylenes, for example phenylacetylene and its derivatives instead of cyclopropenes or hazardous diazoalkanes which are used as a carbene source for the synthesis of well-defined ruthenium alkylidene complexes [14, 15]. In 1991, Wakatsuki and coworkers investigated the reaction of simple ruthenium complex [RuCl$_2$(PPh$_3$)$_3$] with *tert*-butylacetylene. It was shown that this reaction afforded a new ruthenium complex containing a vinylidene moiety [16]. The metathesis activity of ruthenium complexes prepared from [RuCl$_2$(PPh$_3$)$_3$] and phenylacetylene was observed by authors in 1997 [17]. It was reported that these complexes are good catalysts for the metathesis degradation of polyalkenamers [17]. Later, ruthenium vinylidene precatalysts have been tested for the ROMP of high functionalized norbornene derivatives [18, 19]. In 1998, Katayama and Ozawa

successfully used the ruthenium vinylidene complexes prepared from the arene ruthenium dimer [RuCl$_2$(p-cymene)]$_2$ and common terminal alkynes as catalysts for the ROMP of norbornenes and the ring-closing metathesis of α, ω dienes [20, 21]. The catalytic activity of the nonsubstitued vinylidene complex [RuCl$_2$(=C=CH$_2$)(PCy$_3$)$_2$] in the ROMP of cycloolefins has been reported by Grubbs in 1996 [22]. The synthesis and catalyst activity of other type of ruthenium precatalysts for example, pincer-type of ruthenium vinylidenes have been studied by authors [23-26].

The goal of this report is to study the synthesis, characterization and metathesis activity of new ruthenium vinylidene complexes [RuCl$_2$(=C=CH(p-C$_6$H$_4$CF$_3$))(PCy$_3$)$_2$] (**I**), [RuCl$_2$(=C=CH(p-C$_6$H$_4$F))(PCy$_3$)$_2$] (**II**) and [RuCl$_2$(=C=CH(C$_6$H$_9$)(PCy$_3$)$_2$] (**III**).

2. EXPERIMENTAL

2.1. Materials and Instrumentation

Dichloromethane solvent was distilled from a drying agent of calcium hydride. Toluene and methanol anhydrous, [RuCl$_2$(PPh$_3$)$_3$], [RuCl$_2$(p-cymene)]$_2$, tricyclohexylphosphine (PCy$_3$) and 4-ethynyl-α,α,α-trifluorotoluene, 1-ethynyl-4-fluorobenzene and 1-ethynylcyclohexene terminal alkynes were purchased from Aldrich. Solvents and terminal alkynes were degassed by freezing-pumping-thawing cycles prior to use. NMR spectra were recorded at 298 K with a Varian Unit Inova spectrometer at 300 MHz (^{1}H), 75 MHz (^{13}C), 121 MHz (^{31}P) or 282 MHz (^{19}F). The chemical shifts are provided in parts per million from SiMe$_4$ (^{1}H and ^{13}C{^{1}H}) as internal reference, 85% H$_3$PO$_4$ (^{31}P{^{1}H}) or C$_2$HF$_3$O$_2$ (^{19}F) as external reference. FT-IR spectra were recorded at room temperature on a Nicolet 6700 spectrometer. Elemental analyses were carried out with a Fisons A1108 instrument.

Address correspondence to this author at the Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacán, México, D, F. 04510, México;
Tel: 00(52)5556224586; Fax: 00(52)5556161201; E-mail: tma@unam.mx

Molecular weights and molecular weight distribution (MWD) were determined with reference to monodisperse polystyrene standards on a waters 2695 ALLIANCE Separation Module GPC at 30 °C in tetrahydrofuran (THF) using a universal column and a flow rate of 0.3 mL/min.

2.2. Synthesis of Vinylidene Complexes I-III, from [RuCl₂(PPh₃)₃]

Manipulations were performed under an atmosphere of dry nitrogen by using vacuum-line and standard Schlenk techniques. A solution of the [RuCl₂(PPh₃)₃] complex (0.5 g, 0.52 mmol) in toluene (10 mL) was added PCy₃ (0.32 g, 1.14 mmol) with stirring at room temperature. 4-ethynyl-α,α,α-trifluorotoluene for **I** (0.11 g, 0.62 mmol), 1-ethynyl-4-fluorobenzene for **II** (0.07 g, 0.62 mmol) or 1-ethynylcyclohexene for **III** (0.06 g, 0.62 mmol) was added to the solution. The reaction mixture was heated for 24 h at 70°C under stirring. The solution was concentrated and precipitated in *n*-hexane. Then the solid was purified using the liquid-liquid diffusion technique in CH₂Cl₂ solution into CH₃OH to obtained crystalline solids with yields over 43% (0.20 g) for **I**, 42% (0.19 g) for **II** and 40% for **III** (0.17 g) .

2.3. Synthesis of Vinylidene Complexes I-III, from [RuCl₂(*p*-cymene)]₂

A solution of the ruthenium dimer [RuCl₂(*p*-cymene)]₂ (0.5 g, 0.82 mmol) in toluene (27 mL) was added PCy₃ (0.92 g, 3.28 mmol) with stirring at room temperature. 4-ethynyl-α,α,α-trifluorotoluene for **I** (0.35 g, 1.97 mmol), 1-ethynyl-4-fluorobenzene for **II** (0.24 g, 1.97 mmol) or 1-ethynylcyclohexene for **III** (0.21 g, 1.97 mmol) was added to the solution. The reaction mixture was heated for 24 h at 80°C under stirring. The solution was concentrated and precipitated in CH₃OH. Then the solid was purified using the liquid-liquid diffusion technique in CH₂Cl₂ solution into CH₃OH. Red for **I**, purple for **II** and black for **III** crystalline solids were obtained with yields over 93% (0.34 g) for **I**, 93% (0.32 g) for **II** and 91% (0.31 g) for **III**.

[RuCl₂(=C=CH(*p*-C₆H₄CF₃))(PCy₃)₂], (I): m.p 207°C. ¹H NMR (300 MHz, CDCl₃, δ ppm): δ 7.34, 6.98 (d, 4H, Ph), 4.41(t, $^4J_{PH}$ = 3.1 Hz, 1H, =C=CH); 2.69-2.67, 2.06-1.55, 1.28-1.09 (each m, 66H, Cy) ppm. ¹³C NMR (75 MHz, CDCl₃, δ ppm): δ 339.58 (t, $^2J_{PC}$ = 13.9 Hz, Ru=C$_\alpha$=C), 138.38 (s, C¹ of Ph), 129.56, 125.95, 124.44 (each s, C^{2,6} of Ph), 107.54 (t, $^3J_{PC}$ = 4.1 Hz, Ru=C=C$_\beta$), 33.10 (t, *J* = 9.7 Hz, C¹ of Cy), 30.04 (s, C^{3,5} of Cy), 27.91 (t, *J* =4.8 Hz, C^{2,6} of Cy), 26.49 (s, C⁴ of Cy) ppm. ³¹P NMR (121 MHz, CDCl₃, δ ppm): δ20.58 (s) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ -61.17 (s) ppm. FT-IR (cm⁻¹): 2921 (C-H, asym str), 2847 (C-H, sym str), 1582 (C$_\alpha$=C$_\beta$, str.), 1565 (C=C, ar. str), 1446 (C-H, str), 1321 (C-F₃, str) cm⁻¹. Anal. Calcd. (%) for C₄₅H₇₁Cl₂F₃P₂Ru (902.93 g/mol): C, 59.86; H, 7.93. Found: C, 59.89; H, 7.90.

[RuCl₂(=C=CH(*p*-C₆H₄F))(PCy₃)₂], (II): m.p 195°C. ¹H NMR (300 MHz, CDCl₃, δ ppm): δ 6.85, 6.83 (d, 4H, Ph), 4.33 (t, $^4J_{PH}$ = 3.4 Hz, 1H, =C=CH); 2.65-2.55, 2.06-2.02, 1.70-1.51, 1.25-1.17 (each m, 66H, Cy) ppm. ¹³C NMR (75 MHz, CDCl₃, δ ppm): δ 342.41 (t, $^2J_{PC}$ = 13.8 Hz, Ru=C$_\alpha$=C), 161.37 (s, C¹ of Ph), 158.17, 128.87, 126.18,

114.91 (each s, C^{2,6} of Ph), 107.68 (t, $^3J_{PC}$ = 4.4 Hz, Ru=C=C$_\beta$), 33.16 (t, *J* = 8.6 Hz, C¹ of Cy), 30.16 (s, C^{3,5} of Cy), 27.99 (t, J= 4.9 Hz, C^{2,6} of Cy), 26.59 (s, C⁴ of Cy) ppm. ³¹P NMR (121 MHz, CDCl₃, δ ppm): δ21.36 (s) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ -119.35 (s) ppm. FT-IR (cm⁻¹): 2921 (C-H, asym str), 2847 (C-H, sym str); 1609 (C$_\alpha$=C$_\beta$, str.); 1585 (C=C, ar. str); 1502 (C-F, str); 1443 (C-H, str) cm⁻¹. Anal. Calcd. (%) for C₄₄H₇₁Cl₂FP₂Ru (852.96 g/mol): C, 61.96; H, 8.39. Found: C, 61.98; H, 8.41.

[RuCl₂(=C=CH(C₆H₉)(PCy₃)₂], (III): m.p 185°C. ¹H NMR (300 MHz, CDCl₃, δ ppm): δ 5.06 (s, 1H, =CH cyclohexene), 3.88 (t, $^4J_{PH}$ = 3.4 Hz, 1H, =C=CH); 2.64-2.56, 2.08-2.04 1.71-1.56, 1.27-1.22 (each m, 66H, Cy), 2.17, 1.71 (s, m, 8H, cyclohexene) ppm. ¹³C NMR (75 MHz, CDCl₃, δ ppm): δ 346.38 (t, $^2J_{PC}$ = 13.8 Hz, Ru=C$_\alpha$=C), 128.37 (s, C¹ cyclohexene), 115.88 (s, C⁶ cyclohexene), 111.07 (t, $^3J_{PC}$ = 4.5 Hz, Ru=C=C$_\beta$), 33.32 (t, J_{PC} = 8.5 Hz, C¹ of Cy), 30.17 (s, C^{3,5} of Cy), 28.04 (t, J$_{PC}$= 4.9 Hz, C^{2,6} of Cy), 26.69 (s, C⁴ of Cy), 25.70 (s, C² cyclohexene), 23.36 (s, C⁵ cyclohexene), 22.73 (s, C^{3,4} cyclohexene) ppm. ³¹P NMR (121 MHz, CDCl₃, δ ppm): δ19.38 (s) ppm. FT-IR (cm⁻¹): 2920 (C-H, asym str); 2848 (C-H, sym str), 1605 (C$_\alpha$=C$_\beta$, str.), 1442 (C-H, str) cm⁻¹. Anal. Calcd. (%) for C₄₄H₇₆Cl₂P₂Ru (839.38 g/mol): C, 63.21; H, 9.43. Found: C, 63.14; H, 9.40.

2.4. X-ray Crystallographic Studies

Red, purple and black prisms of **I**, **II**, and **III** complexes respectively were obtained by slow diffusion of CH₃OH into a concentrated solution of the complex in CH₂Cl₂ at 5°C within 24 h. The crystal data and the details of data collection and structure refinement are summarized in Table **1**. The X-ray diffraction of vinylidene complexes (**I-III**) was performed on a Brunker Smart Apex CCD diffractometer with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å) at 298 (2) °K a total of 18822 (**I**), 38512 (**II**) and 19526 (**III**) reflections were collected in the range 1.72° = θ = 25.38° (**I**), 1.61° = θ = 25.36° (**II**) and 1.74° = θ = 25.39° (**III**) of which 8252 (**I**), 8635 (**II**) and 8569 (**III**) were unique reflections with *I* > 2σ *(I)*, and were used for refinement. The final R and *Rw* were 0.0389 and 0.0813 (**I**); 0.0419 and 0.0784 (**I**); 0.0435 and 0.0961 (**III**), respectively. The structures were solved by the direct methods using the program SHELXTL.

2.5. Procedure for the Metathesis Degradation of Natural Rubber (NR)

The reactions were carried out in glass vials under a dry nitrogen atmosphere at different temperatures. Metathesis degradation of NR (3.0g, 44 mmol) using *d*-limonene or mandarin oil as CTA was carried out at a molar ratio of [NR]/[CTA] = 1. **I**, **II** or **III** vinylidene catalyst was added in a molar ratio of [NR]/[Catalyst] = 250. After terminating the reaction by addition of a small amount of ethyl vinyl ether, the solution was poured into an excess of methanol. The products obtained were dried under a vacuum and characterized by ¹H, ¹³C NMR and GPC.

¹H NMR (300 MHz, CDCl₃, δ ppm): δ5.38 (br, CH=C) cyclic terpene), 5.13 (s, CH=C isoprene), 4.70-4.68 (d, CH₂=C terpene), 2.04 (s, CH₂), 1.68-1.59 (m, CH₃), 1.40-1.10 (m, terpene). ¹³C NMR (75 MHz, CDCl₃, δ ppm):

Table 1. Experimental crystallographic data and structure refinement for I, II and III.

| Empirical formula	$C_{45}H_{71}Cl_2F_3P_2Ru$, I	$C_{44}H_{71}Cl_2FP_2Ru$, II	$C_{44}H_{76}Cl_2P_2Ru$, III
Molecular weight	902.93	852.96	839.38
T(K)	298(2)	298(2)	298(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2$_1$/n	P-1
Lattice parameter (a, b, c), Å	a=13.2742(11) b=13.9647(11) c=15.1944(12)	a=14.6900(11) b=16.9582(12) c=20.0406(14)	a=13.1594(10) b=14.1514(11) c=14.5201(11)
(α,β,γ), deg	α=63.6920(10) β=71.3130(10) γ=64.8010(10)	α=90 β=109.1360(10) γ=90	α=76.9220(10) β=70.2080(10) γ=67.7810(10)
Volume (Å^3)	2254.3(3)	4716.6(6)	2340.3(3)
Z	2	4	2
$d_{calcd.}$ (mg/m^3)	1.330	1.321	1.311
μ (Mo K$_\alpha$), mm^{-1}	0.580	0.660	0.661
F(000)	952	1976	980
Crystal size (mm)/ color/shape	0.38x0.16x0.10 Red/ Prism	0.30x0.23x0.16 Purple/Prism	0.40x0.40x0.06 Black/ Prism
2θ range, (°)	1.72 to 25.38	1.61 to 25.36	1.74 to 25.39
Reflections collected	18822	38512	19526
Unique reflections (R$_{int}$)	8252 (0.0357)	8635 (0.0740)	8569 (0.0466)
R1, wR2	0.0389, 0.0813	0.0419, 0.0784	0.0435, 0.0961
$\Delta\rho$ (max, min) (e/Å)	0.550 y -0.313	0.512 y -0.465	0.643 y -0.549

δ 139.50 (s, C=C isoprene), 135.20, 133.60 (s, C=C terpene), 125.00 (s, CH isoprene), 120.90 (s, CH=C cyclic terpene), 109.80 (s, CH$_2$=C vinylic), 38.10 (s, CH terpene), 32.20 (s, CH$_2$ isoprene), 30.70, 29.10, 27.90 (s, CH$_2$ terpene), 26.40 (s, CH$_2$ isoprene), 23.80 (s, CH$_3$ aliphatic terpene), 23.40 (s, CH$_3$C=C isoprene), 22.50 (s, CH$_3$ aliphatic isoprene).

3. RESULTS AND DISCUSSION

The new ruthenium vinylidene catalysts **I-III** were synthesized using the [RuCl$_2$(PPh$_3$)$_3$] complex with PCy$_3$ and terminal alkynes (Scheme **1A**). [RuCl$_2$(PPh$_3$)$_3$] complex reacted in toluene with 2.2 equivalents of PCy$_3$ and 4-ethynyl-α,α,α-trifluorotoluene, 1-ethynyl-4-fluorobenzene or 1-ethynylcyclohexene (1.2 equiv/Ru) at 70°C for 24 hours, to give **I**, **II** and **III** complexes, respectively. The complexes were isolated as stable crystalline solids with yields ranging from 40-43%. The synthesis of these complexes was also carried out using the method reported by Ozawa [20], which involves the use of the ruthenium dimer [RuCl$_2$(*p*-cymene)]$_2$, PCy$_3$ (2 equiv/Ru) and the appropriate terminal alkynes (1 equiv/Ru) in toluene as solvent at 80°C

for 24 h to obtained crystalline solids with yields of 91-93% (Scheme **1B**).

The composition of new vinylidenes was fully characterized by various analytical techniques. The FT-IR spectra of **I-III** catalysts exhibited a strong absorption peak at 2921 and 2847 cm^{-1} assigned to the aliphatic C-H stretching vibration band, and the absorption peak ranging from 1582 to 1605 cm^{-1} was attributed to the vinylidene C=C bond stretching. ^{1}H NMR analysis confirmed that the exchange of *p*-cymene to PCy$_3$ ligand showed signals of the aliphatic protons at ranging from 2.67-1.09 ppm. The vinylidene ligand coordinated to ruthenium was confirmed showing the vinylidene proton which resonated as a triplet at 4.41 ppm for **I**, 4.33 ppm for **II** and 3.88 ppm for **III**, respectively (Fig. **1**). In analogy to the structurally characterized vinylidene **I-III**, these resonances appear as triplets due to $^4J_{PH}$ coupling with the phosphorus atom. The most interesting signals were observed in the downfield for C$_\beta$ and upfield for C$_\alpha$ regions of ^{13}C NMR spectra. C$_\alpha$ and C$_\beta$ signals appear at 339.58 and 107.54 ppm for **I**, 342.41 and 107.68 ppm for **II** and 346.31
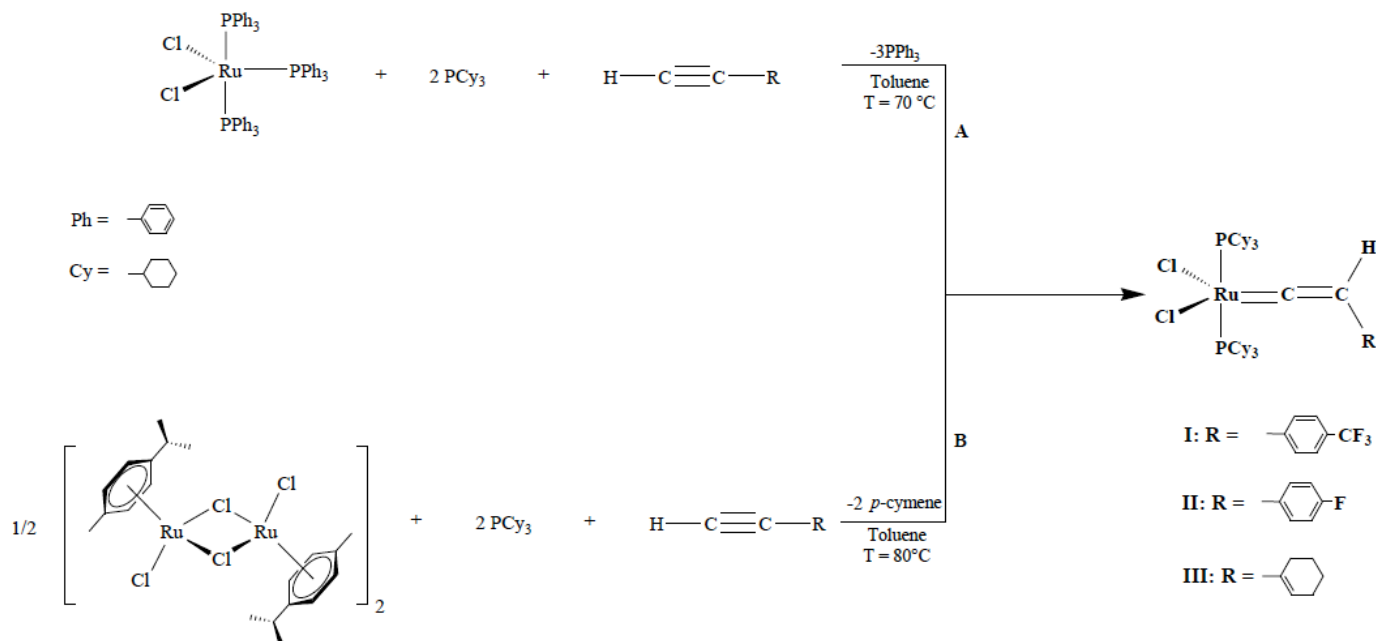
Scheme 1. Synthesis of ruthenium vinylidenes **I-III** using the simple ruthenium complexes and terminal alkynes.
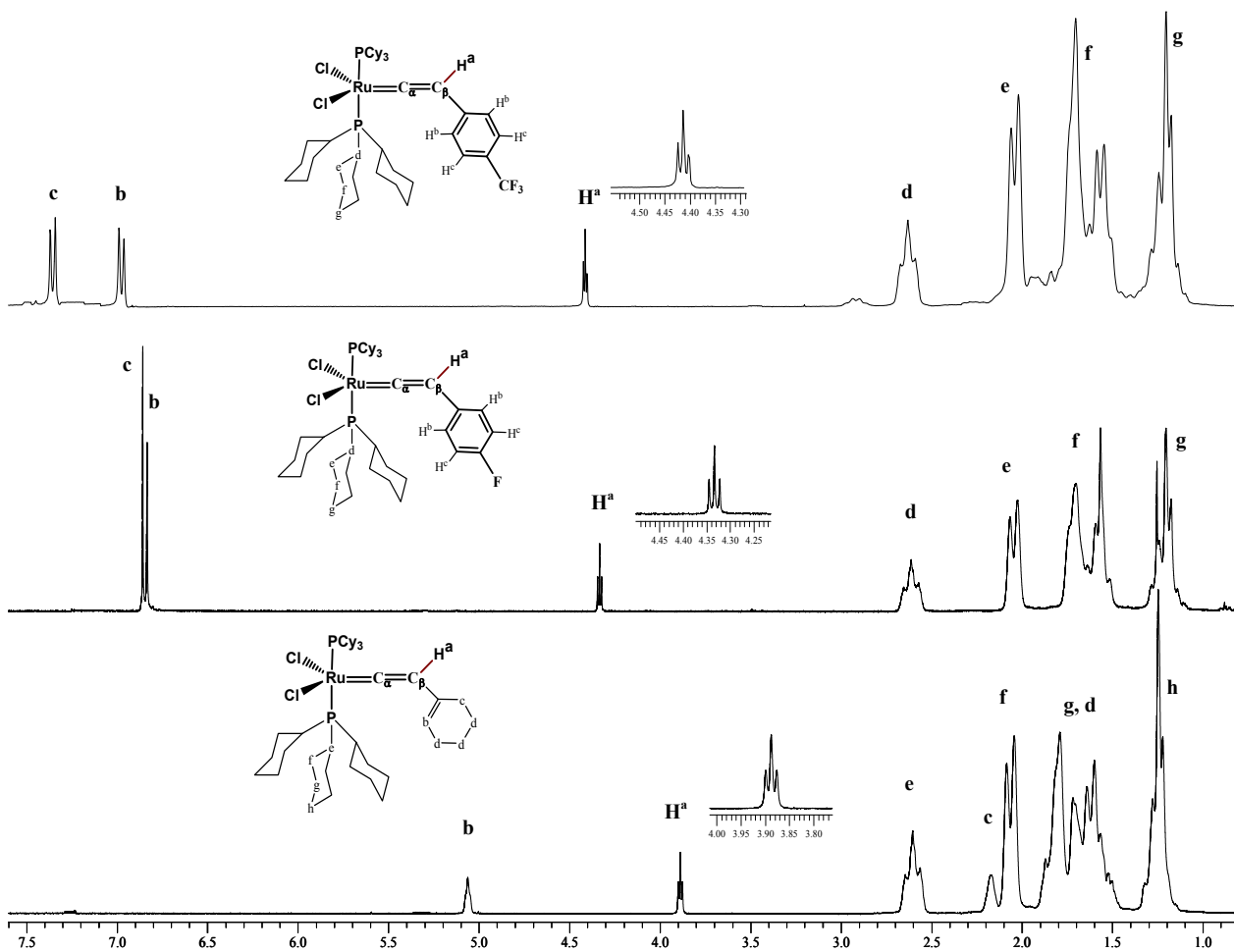
Fig. (1). ^{1}H-NMR spectra of **I**, **II** and **III** complexes.

Table 2. Selected angles (deg) derived from the crystal structures of complexes I-III.

	I	II	III
Cl1-Ru-Cl2	156.88(3)	157.85(4)	157.40(3)
P1-Ru-P2	170.30(3)	169.91(3)	170.99(3)
Cl1-Ru-P1	90.14(3)	89.35(3)	87.60(3)
Cl1-Ru-P2	88.29(3)	85.71(3)	88.89(3)
Cl2-Ru-P1	89.54(3)	88.69(3)	90.64(3)
Cl2-Ru-P2	88.16(3)	92.56(4)	89.42(3)
Cl1-Ru-C1	102.40(9)	102.44(11)	103.28(10)
Cl2-Ru-C1	100.69(9)	99.71(11)	99.33(10)
P1-Ru-C1	93.53(10)	94.04(12)	94.86(10)
P2-Ru-C1	96.15(10)	95.62(12)	94.02(10)
Ru-C1-C2	177.60(3)	178.10(3)	176.50(3)
C1-C2-C3	128.80(3)	129.90(4)	128.80(3)

Table 3. Selected bond lengths (Å) derived from the crystal structure of complexes I-III.

	I	II	III
Ru-Cl1	2.356(8)	2.337(10)	2.357(9)
Ru-Cl2	2.339(8)	2.351(10)	2.352(8)
Ru-P1	2.414(8)	2.434(10)	2.422(8)
Ru-P2	2.439(8)	2.419(10)	2.416(9)
Ru-C1	1.747(3)	1.754(4)	1.763(3)
C1-C2	1.316(4)	1.324(4)	1.325(4)
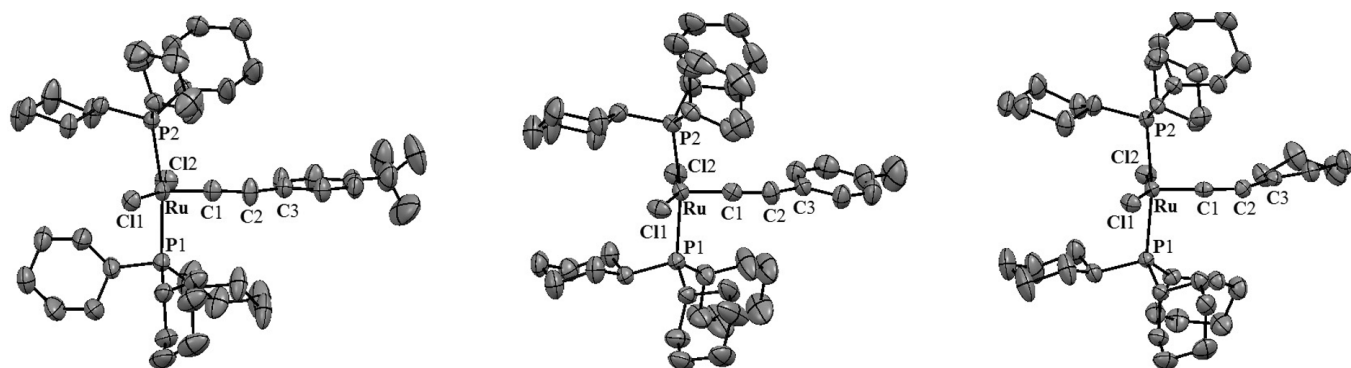
Fig. (2). ORTEP diagram of new ruthenium vinylidene complexes of the form [RuCl$_2$(=C=CHR)(PCy$_3$)$_2$] (R= *p*-C$_6$H$_4$CF$_3$ (**I**), *p*-C$_6$H$_4$F (**II**) and C$_6$H$_9$ (**III**)). Thermal ellipsoids were drawn at the 50% probability level.

and 111.07 ppm for **III**, respectively. In the same way these signals appear as triplets due to ^{31}P coupling. The ^{31}P NMR spectra displayed an absorption in 20.58 ppm, 21.36 ppm and 19.38 ppm for **I**, **II** and **III**, respectively. The chemical shift of this signal is due to the substituent on the vinylidene ligand in the complexes.

On the other hand the solid-state structures of vinylidene complexes **I**, **II** and **III** were determined by single-crystal X-ray diffraction (XRD) studies. Single crystals of all three complexes were obtained by liquid-liquid diffusion technique using methanol into a dichloromethane solution. Experimental crystallographic data are given in Table **1** and
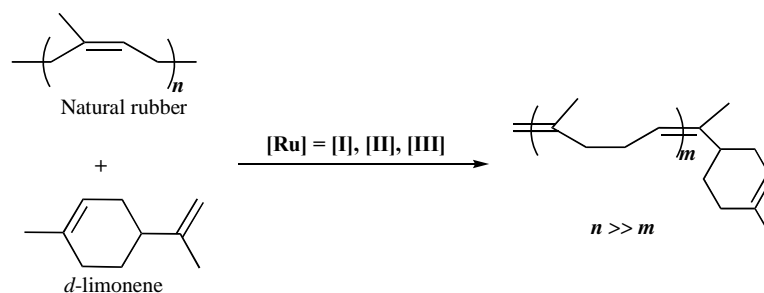
Scheme 2. Metathesis degradation of NR using *d*-limonene as a CTA.

Table 4. Degradation of NR with *d*-limonene and essential oils using vinylidene complexes (I-III).

Entry	Catalyst	CTA	Temp °C	Yield[b] (%)	M_n[c] (^{1}H RMN)	M_n[d] (GPC)	MWD[d] (GPC)
Natural Rubber[a]						1,700,000	1.50
1	**I**	*d*-limonene	50	64	17,536	18,185	1.90
2	**I**	Mandarin oil	50	67	18,300	18,710	2.00
3	**I**	*d*-limonene	80	96	8,401	8,593	1.80
4	**I**	Mandarin oil	80	94	8,232	8,488	2.00
5	**I**	Lemon oil	80	95	8,700	8,802	2.00
6	**II**	Mandarin oil	80	94	9,298	9,941	2.20
7	**III**	Mandarin oil	80	96	9,577	9,693	2.10

[a] Guatemala natural rubber; [b] Isolated yield of products; [c] M_n determined by ^{1}H-NMR end groups analysis, where one unit of *d*-limonene is attached to the end group of the isoprene oligomeric chain; [d] Number-average (M_n) molecular weights and molecular weight distribution (MWD) were calculated by gel permeation chromatography (GPC) with THF as the eluent, values are reported relative to PS standards.

selected angles and bond distances are listed in Tables **2** and **3**, respectively. As seen from the ORTEP in Fig. **2** these complexes have a distorted square-pyramidal structure. **P**1 and **P**2 phosphines and **Cl**1 and **Cl**2 chlorine atoms construct the square-based pyramid having the vinylidene ligand and apical position.

According to Table **2** molecular structure of the **I-III** complexes showed a large deviation to linearity of the **Cl**1-**Ru**-**Cl**2 angle (156.88(3)°, **I**; 157.85(4)°, **II** and 157.40(3)°, **III**). The structures are distorted due to the electronic repulsion between the chlorines, and the steric repulsion between the cyclohexyl rings of PCy_3 and the substituent on the vinylidene ligand (C_α=C_β-R) with **P**1-**Ru**-**P**2 angle of: 170.30(3)°, **I**; 169.91(3)°, **II**; and 170.99(3)°, **III**. The **Ru**-**C**1-**C**2 angles were almost linear (177.60(3)°, **I**; 178.10(3)°, **II** and 176.50(3)°, **III**).

The **Ru**-**C**1 bond distances for **I-III** vinylidene complexes (Table **3**) were comparable to each other 1.747(3) Å (**I**), 1.754(4) Å (**II**) and 1.763(3) Å (**III**) and to those of [$RuCl_2$(=C=CH(Ph))(PPr^i_3)$_2$] (1.750(4) Å), [$RuCl_2$(=C=CH(Ph))(PCy_3)$_2$] (1.761(2) Å) and [$RuBr_2$(=C=CH(Bu^t))(PPh_3)$_2$] (1.768(17) Å) vinylidene complexes [20, 27, 28]. The **C**1-**C**2 bond distances 1.324(4) Å, 1.325 Å for **II** and **III** complexes, respectively were similar to each other and slightly longer than that of **I** complex (1.316(4) Å). This may be explained by the presence of the strongly electron-withdrawing *p*-CF_3 group in **I**.

The catalytic activity of the synthesized **I-III** vinylidene complexes was tested in the cross-metathesis degradation of NR with *d*-limonene and citrus oils. It is important to note that metathesis of NR is challenging due to the presence of a methyl group substituent at a double bond of the main chain [29-31]. (Scheme **2**) depicts the degradation of NR in the presence of *d*-limonene as a chain transfer agent (CTA).

Table **4** shows the results of NR degradation *via* cross-metathesis with *d*-limonene, mandarin and lemon oils by ruthenium vinylidene complexes **I**, **II** and **III**. These complexes exhibited high activity toward metathesis degradation of NR with *d*-limonene and citrus oils as CTAs. For example, the products had molecular weights giving values around M_n x 10^4 and yields around 64% and 67% for *entries 1* and *2*, respectively when the reaction was carried out at 50°C. A further experiment performed at 80°C led to an increase in activity, giving products with molecular weight values around M_n x 10^3 and yields ranging from 94 to 96% (*entries 3-7*).

The ^{1}H NMR spectrum after the degradation *via* cross-metathesis with *d*-limonene showed signals of C=CH_2 protons of the terpene group at 4.68 and 4.70 ppm. It also showed the signals of C=CH isoprene protons at 5.13 ppm, and signals of C=CH protons of the monocyclic terpene at 5.38 ppm. The signals of the aliphatic protons of *d*-limonene are observed at 1.1-1.4 ppm.

4. CONCLUSION

Three new ruthenium vinylidene complexes **I**, **II** and **III** were synthesized and characterized. The experimental crystallographic data showed that the **Ru**-**C**1 bond distances for **I**-**III** vinylidene complexes were comparable to each other 1.747(3) Å (**I**), 1.754(4) Å (**II**) and 1.763(3) Å (**III**). The **C**1-**C**2 bond distances 1.324(4) Å, 1.325 Å for **II** and **III** complexes, respectively were similar to each other and slightly longer than that of **I** complex (1.316(4) Å). This was explained by the presence of the strongly electron-withdrawing *p*-CF$_3$ group in **I**. The catalytic activity of **I**-**III** complexes was tested in the cross-metathesis degradation of NR in the presence of *d*-limonene and citrus oils as CTAs. This reaction was investigated at temperatures ranging from 50 to 80°C. In all cases the degradation of challenging NR by **I**-**III** complexes was observed. When the cross-metathesis of NR with *d*-limonene, mandarin and lemon oils was performed at 80°C only the low molecular weight terpene terminated polyisoprene was obtained quantitatively within 24h.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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