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Synthesis of $[\text{TpRu}(\text{CO})(\text{PPh}_3)_2]_2(\mu\text{-CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CH}=\text{CH})$ from Wittig reactions

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Abstract

Treatment of $[\text{Ru}(\text{CH}=\text{CHCH}_2\text{PPh}_3)\text{X}(\text{CO})(\text{PPh}_3)_2]^+$ ($\text{X} = \text{Cl}, \text{Br}$) with KTp ($\text{Tp} = \text{hydridotris}(\text{pyrazolyl})\text{borate}$) and NaBPh_4 produced $[\text{TpRu}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)]\text{BPh}_4$. Reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with $\text{HC}\equiv\text{CCH}(\text{OEt})_2$ produced $\text{Ru}(\text{CH}=\text{CHCH}(\text{OEt})_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, which reacted with KTp to give $\text{TpRu}(\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)$. Treatment of $[\text{TpRu}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)]\text{BPh}_4$ with $\text{NaN}(\text{SiMe}_3)_2$ and benzaldehyde produced $\text{TpRu}(\text{CH}=\text{CHCH}=\text{CHPh})(\text{CO})(\text{PPh}_3)$. The later complex was also produced when $\text{TpRu}(\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)$ was treated with $\text{PhCH}_2\text{PPh}_3\text{Cl}/\text{NaN}(\text{SiMe}_3)_2$. The bimetallic complex $[\text{TpRu}(\text{CO})(\text{PPh}_3)_2]_2(\mu\text{-CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CH}=\text{CH})$ was obtained from the reaction of $[\text{TpRu}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)]\text{BPh}_4$ with $\text{NaN}(\text{SiMe}_3)_2$ and terephthalaldehyde.

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1. Introduction

Bimetallic complexes with conjugated hydrocarbon ligands bridging metal centers are attracting considerable interest for their structural and material properties [1]. In the past few years, many bimetallic complexes with M-alkynyl linkages have been synthesized [2]. In contrast, relatively few bimetallic complexes with M-alkenyl linkages are known. Reported bimetallic complexes with M-alkenyl linkages include those with $(\text{CH}=\text{CH})_n$ bridges ($n = 1$ [3], 2 [4–6], 3 [7], 4 [8]), C_2R_2 [9], $\text{PhC}=\text{CH}-\text{CH}=\text{CPh}$ [10], $\text{C}(\text{OR})=\text{CH}-\text{CH}=\text{CH}(\text{OR})$ [11], and $\text{CH}=\text{CH}-\text{Ar}-\text{CH}=\text{CH}$ [12,13]. The relatively little exploration on the latter complexes may be attributed, in part, to the lack of simple methods to synthesize such complexes. Previous common routes to prepare such bimetallic complexes involve the reactions of dialkynes with L_nMH , deprotonation of dicationic

biscarbene complexes (e.g. $\{[\text{CpFe}(\text{dppe})_2]_2(\mu\text{-C}(\text{OR})\text{CH}_2\text{CH}_2\text{C}(\text{OR}))\}^{2+}$), the reaction of $[\text{CpFe}(\text{CO})_2]^-$ with 3,4-dichlorocyclobutene, and ligand substitution reactions of preformed bimetallic alkenyl complexes. Wittig reactions have been proved to be one of the most efficient methods to synthesize olefins from phosphonium salts and aldehydes or ketones. The reactions have also been used recently in the synthesis of organometallic complexes. For example, reactions of $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{C}\equiv\text{CCH}_2\text{PPh}_3)(\text{PPh}_3)_2]\text{PF}_6$ with LiBu and appropriate aldehydes or ketones lead to $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{C}\equiv\text{CCH}=\text{CRR}')(\text{PPh}_3)_2$ [14]. Thus, one might expect that Wittig reactions could also be used for the synthesis of bimetallic complexes with M-alkenyl linkages starting from alkenyl phosphonio derivatives $[\text{L}_n\text{MCH}=\text{CHCH}_2\text{PR}_3]^+$ or alkenyl aldehydes $\text{L}_n\text{MCH}=\text{CHCHO}$. However, such a possibility has not been explored previously. In this paper, we wish to report the synthesis of a bimetallic alkenyl complex via Wittig reactions using $[\text{TpRu}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)]^+$ or $\text{TpRu}(\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)$ as the starting materials.

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2. Results and discussion

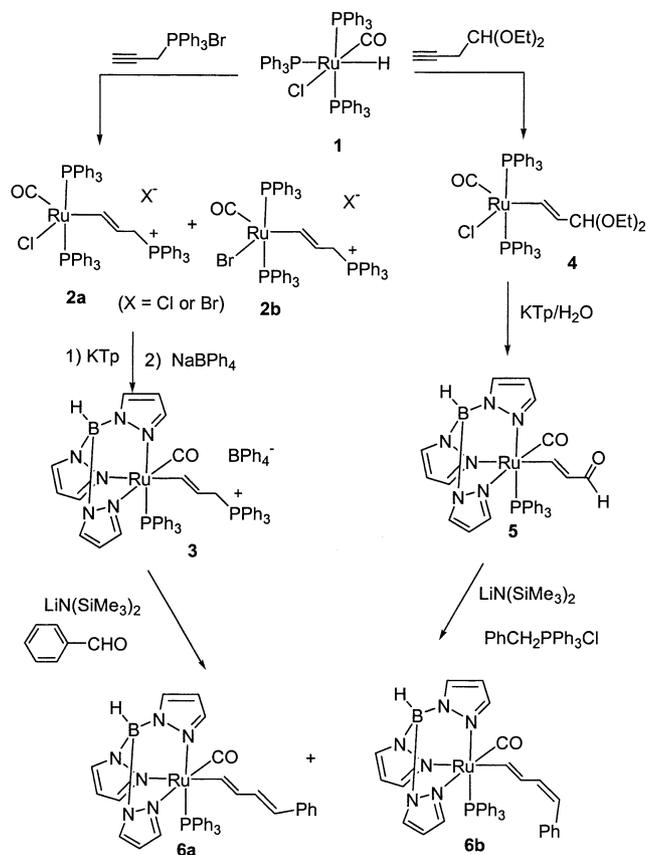
2.1. Synthesis of ruthenium vinyl complexes with phosphonium or aldehyde functional groups

In principle, bimetallic complexes $[L_nM]_2(\mu\text{-CH=CH-CH-R-CH=CH-CH})$ could be prepared from the Wittig reactions of $[L_nMCH=CHCH_2PR'_3]^+$ with $OCH-R-CHO$ or the reactions of $L_nMCH=CHCHO$ with $R'_3PCH_2-R-CH_2PR'_3$. Reactions of $RuHCl(CO)(PPh_3)_3$ (**1**) with $HC\equiv CR$ are known to give $Ru(CH=CHR)Cl(CO)(PPh_3)_2$ [15,16]. The reaction has been used to prepare bimetallic complexes such as $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-CH=CH-Ar-CH=CH})$ [12] and $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-(CH=CH)}_n)$ ($n = 2, 3, 4$) [6,7]. Thus, we have tried to prepare complexes $[L_nRuCH=CHCH_2PR'_3]^+$ and $L_nRu(CH=CHCHO)$ starting from the reactions of $RuHCl(CO)(PPh_3)_3$ with $HC\equiv CCH(OEt)_2$ and $HC\equiv CCH_2PPh_3Br$.

The reaction of $RuHCl(CO)(PPh_3)_3$ with $HC\equiv CCH_2PPh_3Br$ has previously been reported by Hill and coworkers [17]. Under mild conditions, the reaction produced a mixture of $[Ru(CH=CHCH_2PPh_3)Cl(CO)(PPh_3)_2]^+$ and $[Ru(CH=CHCH_2PPh_3)Br(CO)(PPh_3)_2]^+$; in refluxing ethanol, the reaction produced the bromide complex $[Ru(CH=CHCH_2PPh_3)Br(CO)(PPh_3)_2]^+$. Using the reported procedure, the complexes $[Ru(CH=CHCH_2PPh_3)Cl(CO)(PPh_3)_2]X$ (**2a**) and $[Ru(CH=CHCH_2PPh_3)Br(CO)(PPh_3)_2]X$ (**2b**) ($X = Cl$ or Br) were obtained from the one-pot reaction of $RuHCl(CO)(PPh_3)_3$ with $HC\equiv CCH_2PPh_3Br$. Attempts have been made to use **2** as the starting material to carry out Wittig reactions. However, complex **2** decomposed when treated with bases such as $NaOH$, $KO(t\text{-Bu})$, and $LiN(i\text{-Pr})_2$. The failure of performing Wittig reactions of **2** may be due to the complication that bases also attacked the halide ligand in complex **2**.

In order to avoid the side reactions, we have prepared the Tp complex $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]BPh_4$ (**3**) by treating **2** with KTp and $NaBPh_4$ (Scheme 1). Related complexes such as $TpRu(CH=CHPh)(CO)(PPh_3)$ and $TpRuPh(CO)(PPh_3)$ have been reported previously [18]. Complex **3** has been characterized by NMR spectroscopy and elemental analysis. In particular, the $^{31}P\{^1H\}$ -NMR spectrum showed two doublets at 15.8 and 48.6 ppm with $^5J(PP)$ of 2.5 Hz. The 1H -NMR spectrum showed the 1H signals of $CH=CHCH_2$ at 7.8 (Ru-CH), 4.8 (β -CH), and 3.6 (CH_2) ppm. The ^{13}C -NMR spectrum showed the ^{13}C signals of $CH=CHCH_2$ at 175.4 (Ru-CH), 125.5 (β -CH), and 32.3 (CH_2) ppm and that of CO at 206.0 ppm.

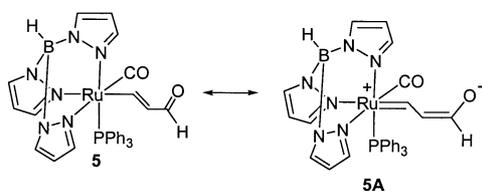
The alkenyl aldehyde complex $TpRu(CH=CHCHO)(CO)(PPh_3)$ (**5**) was prepared using similar methodology (Scheme 1). Addition of commercially available $HC\equiv CCH(OEt)_2$ to a suspension of



Scheme 1.

$RuHCl(CO)(PPh_3)_3$ (**1**) in dichloromethane produced the insertion product $Ru(CH=CHCH(OEt)_2)Cl(CO)(PPh_3)_2$ (**4**). The compound has been characterized by NMR and elemental analysis. The $^{31}P\{^1H\}$ -NMR spectrum showed a singlet at 29.8 ppm, which is typical for $RuCl((E)\text{-CH=CHR})(CO)(PPh_3)_2$. The 1H -NMR spectrum displayed the Ru-CH signal at 7.8 ppm, the β -CH signal at 5.1 ppm, and the δ -CH signal at 4.6 ppm. Monomeric complexes $Ru(RC=CHR')Cl(CO)(PPh_3)_2$ are known to adopt a distorted trigonal bipyramidal geometry around ruthenium with the two PPh_3 ligands in the apical positions [15]. Thus, it is reasonable to assume that complex **4** has a similar geometry around ruthenium.

Complex **4** reacted with KTp to give $TpRu(CH=CHCHO)(CO)(PPh_3)$ (**5**) which was isolated as a white solid after purification by column chromatography. Apparently, the $CH(OEt)_2$ group has been hydrolyzed to give the CHO group under the reaction conditions. The $^{31}P\{^1H\}$ -NMR spectrum showed a singlet at 46.9 ppm. The 1H -NMR spectrum displayed the Ru-CH signal at 9.9 ppm, the β -CH signal at 6.5 ppm, and the δ -CHO signal at 9.1 ppm. The relatively down-field chemical shift of the Ru-CH signal (9.9 ppm) may indicate that both forms **5** and **5A** have substantial contribution to the structure.



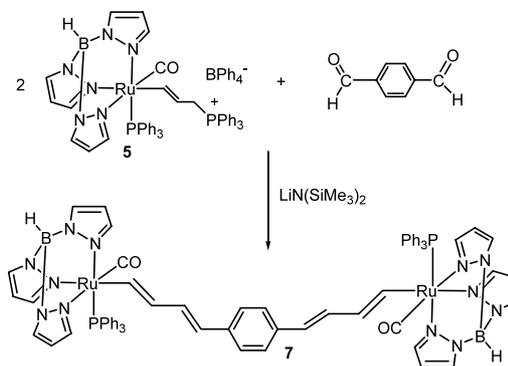
2.2. Wittig reactions of $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]BPh_4$ and $TpRu(CH=CHCHO)(CO)(PPh_3)$

To test the feasibility of using Wittig reactions to synthesize bimetallic complexes, the Wittig reactions using $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]BPh_4$ (**3**) and $TpRu(CH=CHCHO)(CO)(PPh_3)$ (**5**) as the starting materials have been carried out.

Treatment of **3** with $NaN(SiMe_3)_2$ produced a red solution, which readily reacted with benzaldehyde to give $TpRu(CH=CHCH=CHPh)(CO)(PPh_3)$ (**6**). The Wittig reaction appeared to be complete within 30 min and two isomers of (*EE*)- and (*EZ*)- $TpRu(CH=CHCH=CHPh)(CO)(PPh_3)$ were produced in a ratio of ca. 2:1. The presence of $CH=CHCH=CHPh$ in complex **6** is clearly indicated by the 1H -NMR spectroscopy. In the 1H -NMR spectrum, the 1H signals of $CH=CHCH=CHPh$ of **6a** were observed at 7.9 (Ru-CH), 6.4 (β -CH), 6.8 (γ -CH), and 6.0 (δ -CH) ppm, and those of **6b** were observed at 8.1 (Ru-CH), 6.9 (β -CH), 6.2 (γ -CH), and 5.7 (δ -CH) ppm. Complex **6** was also produced when the complex $TpRu(CH=CHCHO)(CO)(PPh_3)$ was treated with the ylide $PhCH=PPh_3$ (generated from the reaction of $PhCH_2PPh_3Cl$ with $NaN(SiMe_3)_2$). However, the reaction is slow. For example, only a small amount of the expected product was formed, after the reaction mixture was allowed to stand for 12 h at room temperature. The reaction proceeded slowly when the reaction mixture is heated at 50 °C. Under the reaction condition, the reaction is completed in 48 h to give two isomers of (*EE*)- and (*EZ*)- $TpRu(CO)(PPh_3)(CH=CH-CH=CH-Ph)$ in a ratio of ca. 2:1.

2.3. Synthesis of bimetallic complexes

We have tried to prepare bimetallic complexes from **3**. In THF, the ylide $TpRu(CH=CHCH=PPh_3)(CO)(PPh_3)$ (generated from reaction of $[TpRu(CH=CH-CH_2PPh_3)(CO)(PPh_3)]BPh_4$ with $NaN(SiMe_3)_2$) reacted with terephthalaldehyde to give a mixture of species, from which pure complex **7** can be isolated after purification by chromatography (Scheme 2). Complex **7** has been characterized by NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ -NMR spectrum showed a singlet at 48.8 ppm, the chemical shift of



Scheme 2.

which is similar to that of **6**. The presence of $CH=CHCH=CHAr$ group in complex **7** is indicated by 1H -NMR spectroscopy. In particular, the 1H -NMR spectrum showed the 1H signals of $CH=CHCH=CHAr$ at 7.82 (Ru-CH), 6.32 (β -CH), 6.70 (γ -CH), and 5.91 (δ -CH) ppm. Reported complexes related to **7** include bisalkenyl complexes $L_nM-CH=CH-Ar-CH=CH-ML_n$ [12,13] and biscarbene complexes $L_nM=C(OR)-CH=CH-Ar-CH=CH-C(OR)=ML_n$ [19].

3. Summary and conclusion

The functionalized ruthenium complexes $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]BPh_4$ and $TpRu(CH=CHCHO)(CO)(PPh_3)$ have been prepared. These complexes can be used as starting materials for Wittig reactions. The bimetallic complex $[TpRu(CO)(PPh_3)]_2(\mu-CH=CH-CH=CH-C_6H_4-CH=CH-CH=CH)$ was obtained from the reaction of $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]BPh_4$ with $NaN(SiMe_3)_2$ and terephthalaldehyde.

4. Experimental

All manipulations were carried out at room temperature (r.t.) under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, $CHCl_3$). The starting materials KTp [20] and $RuHCl(CO)(PPh_3)_3$ [21] were prepared according to literature methods. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). 1H -, $^{13}C\{^1H\}$ -, and $^{31}P\{^1H\}$ -NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). 1H - and ^{13}C -NMR chemical shifts are relative to TMS, and ^{31}P -NMR chemical shifts are relative to 85% H_3PO_4 .

4.1. $[Ru(CH=CHCH_2PPh_3)Cl(CO)(PPh_3)_2]X$ (**2a**)
and $[Ru(CH=CHCH_2PPh_3)Br(CO)(PPh_3)_2]X$ (**2b**)
($X = Cl$ or Br)

To a suspension of $RuHCl(CO)(PPh_3)_3$ (**1**) (2.5 g, 2.6 mmol) in dichloromethane (20 ml) was added $HC\equiv CCH_2PPh_3Br$ (1.05 g, 2.75 mmol). The reaction mixture was stirred at r.t. for 20 min to give a yellow suspension. The volume of the reaction mixture was then reduced to ca. 5 ml under vacuum. Addition of ether (50 ml) to the reaction mixture produced a yellow solid, which was collected by filtration, washed with chloroform (2 \times 5 ml) and diethyl ether (3 \times 30 ml), and dried under vacuum. Yield: 2.8 g, 98%. The NMR spectra of the solid show that it is a mixture of $[Ru(CH=CHCH_2PPh_3)Cl(CO)(PPh_3)_2]X$ (**2a**, major) and $[Ru(CH=CHCH_2PPh_3)Br(CO)(PPh_3)_2]X$ (**2b**, minor) ($X = Cl$ or Br) in a ratio of ca. 3:1. $^{31}P\{^1H\}$ -NMR (121.50 MHz, CD_2Cl_2): δ 16.7 (s, CH_2PPh_3), 25.3 (s, $RuPPh_3$) (major); 16.9 (s, CH_2PPh_3), 26.3 (s, $RuPPh_3$) (minor). The compounds have been previously reported by Hill and coworkers [17].

4.2. $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]BPh_4$ (**3**)

A mixture of **2** (1.72 g, 1.61 mmol) and KTp (0.65 g, 2.58 mmol) in dichloromethane (60 ml) was stirred for 1 h to give a red solution and a white precipitate. The volume of the reaction mixture was reduced to ca. 40 ml under vacuum. Diethyl ether (30 ml) was then added. The resulting mixture was stirred for 30 min and then filtered through a column of Celite to remove the KCl and KBr salts. The volume of the filtrate was reduced to ca. 5 ml under vacuum. Addition of diethyl ether (60 ml) to the residue produced a pale orange solid, which was collected by filtration, washed by ether (2 \times 30 ml), and dried under vacuum to give 1.29 g (yield: 81%) of a white solid of $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]X$ ($X = Br, Cl$). $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]BPh_4$ was obtained from $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]X$ ($X = Cl, Br$) as follows: a mixture of $[TpRu(CH=CHCH_2PPh_3)(CO)(PPh_3)]X$ ($X = Cl, Br$) (1.85 g, 1.88 mmol) and $NaBPh_4$ (1.6 g, 4.7 mmol) in methanol (40 ml) was stirred for 15 min to give a white solid, which was collected by filtration, washed by methanol–water (1:1 mixture) followed with methanol and diethyl ether, and dried under vacuum. Yield: 1.77 g, 89.6%. Anal. Calc. for $C_{73}H_{64}B_2N_6OP_2Ru$: C, 71.43; H, 5.26; N, 6.85. Found: C, 71.38; H, 5.40; N, 6.66%. 1H -NMR (300.13 MHz, acetone- d_6): δ 3.6 (m, 2H, CH_2), 4.8 (m, 1H, $Ru-CH=CH$), 5.7–7.7 (m, 60H, Tp, PPh_3, BPh_4), 7.8 (m, 1H, $Ru-CH$). $^{31}P\{^1H\}$ -NMR (121.50 MHz, acetone- d_6): δ 15.8 (d, $^5J(PP) = 2.5$ Hz, CH_2PPh_3), 48.6 (d, $^5J(PP) = 2.5$ Hz, $RuPPh_3$). $^{13}C\{^1H\}$ -NMR (75.47 MHz,

$CDCl_3$): δ 32.3 (d, $^1J(PC) = 45.1$ Hz, CH_2), 125.5 (m, $Ru-CH=CH$), 175.4 (t, $^2J(PC) = 12.7$ Hz, $Ru-CH$), 206.0 (d, $^2J(PC) = 16.0$ Hz, $Ru-CO$), 105.2–164.9 (m, Tp, PPh_3, BPh_4). IR (KBr, cm^{-1}): $\nu_{CO} = 1936$ s.

4.3. $Ru(CH=CHCH(OEt)_2)Cl(CO)(PPh_3)_2$ (**4**)

$HC\equiv CCH(OEt)_2$ (0.30 ml, 1.8 mmol) was slowly added to a suspension of $RuHCl(CO)(PPh_3)_3$ (**1**) (1.00 g, 1.05 mmol) in dichloromethane (20 ml). The mixture was stirred at r.t. for 5 min to give a red solution. The volume of the reaction mixture was reduced to ca. 5 ml under vacuum. *n*-Hexane (30 ml) was added to the reaction mixture to give a yellow solid, which was collected by filtration, washed with *n*-hexane (3 \times 30 ml), and dried under vacuum. Yield: 0.50 g, 58%. Anal. Calc. for $C_{44}H_{43}ClO_3P_2Ru$: C, 64.54; H, 5.3. Found: C, 64.6; H, 5.16%. 1H -NMR (300.13 MHz, $CDCl_3$): δ 1.1 (t, $^3J(HH) = 7.0$ Hz, 6H, OCH_2CH_3), 3.1 (dq, $^2J(HH) = 9.3$ Hz, $^3J(HH) = 7.0$ Hz, 2H, $OCHHCH_3$), 3.3 (dq, $^2J(HH) = 9.3$ Hz, $^3J(HH) = 7.0$ Hz, 2H, $OCHHCH_3$), 4.6 (d, $^3J(HH) = 6.5$ Hz, 1H, $\gamma-CH$), 5.1 (ddt, $^3J(HH) = 13.2$, 6.5 Hz, $^4J(PH) = 2.0$ Hz, 1H, $Ru-CH=CH$), 7.4–7.7 (m, 30H, PPh_3), 7.8 (d, $^3J(HH) = 13.2$ Hz, 1H, $Ru-CH$). $^{31}P\{^1H\}$ -NMR (121.50 MHz, $CDCl_3$): δ 29.8 (s, PPh_3). $^{13}C\{^1H\}$ -NMR (75.47 MHz, $CDCl_3$): δ 15.1 (OCH_2CH_3), 60.4 (s, OCH_2CH_3), 103.1 (s, $CH(OEt)_2$), 127.6–134.4 (m, $Ru-CH=CH, PPh_3$), 146.4 (t, $^2J(PC) = 11.2$ Hz, $Ru-CH$), 201.2 (t, $^2J(PC) = 14.9$ Hz, $Ru-CO$). IR (KBr, cm^{-1}): $\nu_{CO} = 1940$ s.

4.4. $TpRu(CH=CHCHO)Cl(CO)(PPh_3)_2$ (**5**)

A mixture of complex **4** (1.00 g, 1.22 mmol) and KTp (0.36 g, 1.43 mmol) in dichloromethane (30 ml) was stirred for 2 h. Then diethyl ether (30 ml) was added and the reaction mixture was stirred for additional 30 min. The reaction mixture was then filtered through a column of Celite to obtain a greenish filtrate. The filtrate was passed through a silica gel column under a N_2 atmosphere with the following eluents: *n*-hexane (80 ml), dichloromethane (100 ml), and methanol (80 ml). The methanol eluent was collected and concentrated to obtain a white solid, which was collected and dried under vacuum. Yield: 0.25 g, 32%. Anal. Calc. for $C_{31}H_{28}BN_6O_2PRu$: C, 56.35; H, 4.28; N, 12.73. Found: C, 56.36; H, 4.43; N, 12.86%. 1H -NMR (300.13 MHz, CD_2Cl_2): δ 6.5 (dd, $^3J(HH) = 16.4$ Hz, 8.0 Hz, 1H, $Ru-CH=CH$), 5.9–7.7 (m, 25H, PPh_3, Tp), 9.1 (d, $^3J(HH) = 8.0$ Hz, 1H, CHO), 9.9 (d, $^3J(HH) = 16.4$ Hz, 1H, $Ru-CH$). $^{31}P\{^1H\}$ -NMR (121.50 MHz, acetone- d_6): δ 46.9 (s, PPh_3). IR (KBr, cm^{-1}): $\nu_{CO} = 1944.9$ s, $\nu_{CHO} = 1650$ s.

4.5. $TpRu(CH=CHCH=CHPh)(CO)(PPh_3)$ (**6**)

4.5.1. Method A

A THF solution of $NaN(SiMe_3)_2$ (1 M, 1 ml, 1 mmol) was added dropwise to a Schlenk flask containing complex $[TpRu-CH=CHCH_2PPh_3](CO)(PPh_3)BPh_4$ (0.60 g, 0.49 mmol) and THF (30 ml). The reaction mixture was stirred for 10 min and then benzaldehyde (200 μ l, 1.96 mmol) was added to give a yellow solution with a white precipitate. After the reaction mixture was stirred for 20 min, it was filtered through a column of Celite. The solvent of the filtrate was completely removed under vacuum to give a yellow solid. The solid was redissolved in ca. 3 ml of benzene and *n*-hexane (60 ml) was added to generate an orange precipitate. The solid was separated by filtration and the yellow filtrate was collected. The solvent of the yellow filtrate was completely removed under vacuum to give a yellow solid, which was washed with hexane and dried under vacuum. Yield: 0.17 g, 47%. 1H - and $^{31}P\{^1H\}$ -NMR spectra show that both (*EE*)- and (*EZ*)-isomers of $TpRu(CH=CHCH=CHPh)(CO)(PPh_3)$ are present ((*EE*)-isomer:(*EZ*)-isomer = 2:1). Anal. Calc. for $C_{38}H_{34}BN_6OPRu$: C, 62.11; H, 4.67; N, 11.44. Found: C, 61.81; H, 4.90; N, 11.27%. IR (KBr, cm^{-1}): ν_{CO} = 1936 s .

4.5.2. Method B

To an NMR tube charged with $PhCH_2PPh_3Cl$ (39 mg, 0.10 mmol) and THF (0.5 ml) was added $NaN(SiMe_3)_2$ (0.05 ml, 2 M in THF, 0.1 mmol). After the mixture was stood for 30 min, a solution of $TpRu(CH=CHCHO)(CO)(PPh_3)$ (33 mg, 0.05 mmol) in THF- d_8 (0.2 ml) was added. The reaction mixture was then monitored by NMR spectroscopy. As indicated by NMR, very little olefin was formed after the reaction mixture was allowed to stand for 12 h at r.t. After standing for 48 h at 50 °C, the solvents were removed, then the residue was redissolved in CD_2Cl_2 . 1H - and $^{31}P\{^1H\}$ -NMR spectra show that (*EE*)- and (*EZ*)-isomers of $TpRu(CH=CHCHO)(CO)(PPh_3)$ were produced in a ratio of ca. 2:1.

Selected NMR data for **6a** ((*EE*)-isomer) are as follows. $^{31}P\{^1H\}$ -NMR (121.50 MHz, $CDCl_3$): δ 48.8 (s, PPh_3). 1H -NMR (300.13 MHz, $CDCl_3$): δ 6.0 (d, $^3J(HH)$ = 15.3 Hz, 1H, =*CHPh*), 6.4 (m, 1H, Ru-CH=CH), 6.8 (m, 1H, γ -CH), 5.8–7.7 (m, 30H, Tp, PPh_3 , Ph), 7.9 (d, $^3J(HH)$ = 16.0 Hz, 1H, Ru-CH). Selected NMR data for **6b** ((*EZ*)-isomer) are as follows. $^{31}P\{^1H\}$ -NMR (121.50 MHz, $CDCl_3$): 49.0 (s, PPh_3). 1H -NMR (300.13 MHz, 298 K, $CDCl_3$): δ 5.7 (d, $^3J(HH)$ = 11.4 Hz, 1H, =*CHPh*), 6.2 (m, 1H, γ -CH), 6.9 (m, 1H, Ru-CH=CH), 5.8–7.7 (m, 30H, Tp, PPh_3 , Ph), 8.1 (d, $^3J(HH)$ = 16.4 Hz, 1H, Ru-CH).

4.6. $[TpRu(CO)(PPh_3)]_2(\mu-CH=CH-CH=CH-C_6H_4-CH=CH-CH=CH)$ (**7**)

To a solution of $[TpRu(CH=CH-CH_2PPh_3)(CO)(PPh_3)]BPh_4$ (1.00 g, 0.82 mmol) in THF (30 ml) was added $NaN(SiMe_3)_2$ (0.5 ml, 1 mmol, 2 M in THF). The reaction mixture was stirred for 30 min to give a red solution. Then, terephthalaldehyde (0.054 g, 0.40 mmol) in THF (20 ml) was slowly added to the reaction mixture over a period of 2 h. The reaction mixture was stirred for additional 2 h and then quenched with water (0.3 ml). The solvents were then removed completely. The ^{31}P -NMR spectrum of the residue showed two peaks at 48.8 and 49.1 ppm in about 9:2 ratio, indicating the formation of isomers. The major isomer was obtained in pure form by column chromatography (silica gel, eluent: CH_2Cl_2) and was identified to be the (*EE*)-isomer. Anal. Calc. for $C_{70}H_{62}B_2N_{12}O_2P_2Ru_2$: C, 60.53; H, 4.50; N, 12.10. Found: C, 60.35; H, 4.70; N, 11.94%. 1H -NMR (300.13 MHz, $CDCl_3$): δ 5.91 (d, 2H, $^3J(HH)$ = 15.0 Hz, δ -CH), 6.32 (dd, $^3J(HH)$ = 15.9, 10.2 Hz, 2H, β -CH), 6.70 (dd, $^3J(HH)$ = 15.0, 10.2 Hz, 2H, γ -CH), 5.85–7.64 (m, 54H, Tp, Ph), 7.82 (dd, $^3J(HH)$ = 15.9 Hz, $^3J(PH)$ = 1.8 Hz, 2H, Ru-CH). $^{31}P\{^1H\}$ -NMR (121.50 MHz, $CDCl_3$): δ 48.8 (s).

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