

Reactions of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with 1-alkynols. Preparation and reactivity of hydroxyvinyl complexes

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Abstract

Reactions of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with $\text{HC}\equiv\text{CC}(\text{OH})\text{R}_2$ ($\text{CR}_2 = \text{CPhMe}$, *cyclo*- C_6H_{10} , CH_2 , CMe_2 , CMeEt) produced the hydroxyvinyl complexes $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})\text{R}_2)(\text{CO})(\text{PPh}_3)_2$. Treatment of the hydroxyvinyl complexes $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})\text{PhMe})(\text{CO})(\text{PPh}_3)_2$ and $\text{RuCl}(\text{CH}=\text{CH}-\text{cyclo}-\text{C}_6\text{H}_{10}(\text{OH}))(\text{CO})(\text{PPh}_3)_2$ with alumina produced the dehydrated dienyl complexes $\text{RuCl}(\text{CH}=\text{CH}-\text{CPh}=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2$ and $\text{RuCl}(\text{CH}=\text{CH}-\text{cyclo}-\text{C}_6\text{H}_9)(\text{CO})(\text{PPh}_3)_2$ respectively. The hydroxyvinyl complexes and the dienyl complexes reacted with $\text{L} = 4\text{-phenylpyridine}$ to give six-coordinated complexes $\text{RuCl}(\text{CH}=\text{CH}-\text{R})(\text{CO})(\text{PPh}_3)_2(\text{L})$ ($\text{R} = \text{C}(\text{OH})\text{PhMe}$, *cyclo*- $\text{C}_6\text{H}_{10}(\text{OH})$, $\text{CPh}=\text{CH}_2$, *cyclo*- C_6H_9). Treatment of the hydroxyvinyl complexes $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})\text{PhMe})(\text{CO})(\text{PPh}_3)_2$ and $\text{RuCl}(\text{CH}=\text{CH}-\text{cyclo}-\text{C}_6\text{H}_{10}(\text{OH}))(\text{CO})(\text{PPh}_3)_2$ with HBF_4 or Ph_3CBF_4 produced the vinylcarbene complexes $[\text{RuCl}(\text{CH}=\text{CH}-\text{CPhMe})(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ and $[\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{CH}_2)_5)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ respectively.

Keywords: Ruthenium hydride; Acetylenes; Insertion reaction

1. Introduction

1-alkynols $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$ are interesting substrates in that a variety of metal complexes can be prepared from their interactions with organometallic compounds. For example, hydroxyvinylidene complexes such as $[\text{Cp}^*\text{Ru}(\text{PMe}_2\text{Ph})_2(=\text{C}=\text{CHC}(\text{OH})\text{RR}')^+]$ and $[\text{RhCl}(\text{P}^i\text{Pr}_3)_2(=\text{C}=\text{CHC}(\text{OH})\text{RR}')]$ could be obtained from the reactions of $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$ with $\text{Cp}^*\text{RuCl}(\text{PMe}_2\text{Ph})_2$ [1] and $[\text{RhCl}(\text{P}^i\text{Pr}_3)_2]_n$ [2] respectively. Allenylidene complexes $\text{L}_n\text{M}=\text{C}=\text{C}=\text{CRR}'$ could be isolated from the reactions of $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$ with complexes such as $\text{CpRuCl}(\text{PMe}_3)_2$ [3], $\text{RuCl}_2(\text{dppm})_2$ [4], $\text{RuCl}_2(\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3)$ [5], $\text{RuCl}_2(\text{dppe})_2$ [6,7], $(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{PPh}_3)_2$ [8,9], $\text{Cp}^*\text{Ru}(\mu\text{-Si}^i\text{Pr})_3\text{RuCp}^*$ [10], $[\text{CpFe}(\text{CO})(\text{dppe})]^+$ [11], and $\text{M}(\text{CO})_5(\text{THF})$ [12]. Methoxyalkenylcarbene complexes such as $[(\text{C}_6\text{Me}_6)\text{RuCl}(=\text{C}(\text{OMe})-\text{CH}=\text{CRR}')(\text{PR}_3)]^+$ were obtained from the reactions of $(\text{C}_6\text{Me}_6)\text{RuCl}_2(\text{PR}_3)$ with $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$ in methanol in the presence of NaPF_6 [13]. Reaction of

$\text{CpRuCl}(\text{PMe}_3)_2$ with 1-ethynylcyclohexanol led to the cationic cycloalkenyl vinylidene complex $[\text{CpRu}(=\text{C}=\text{CH}-\text{cyclo}-\text{C}_6\text{H}_9)(\text{PMe}_3)_2]^+$ [14]. Unusual coupling products were obtained from the reaction of $\text{CpRuCl}(\text{PMe}_3)_2$ with $\text{HC}\equiv\text{CC}(\text{OH})\text{Me}_2$ [15], the reaction of $(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{PPh}_3)_2$ with 1-ethynylcyclohexanol [16], and the reaction of $\text{Cp}^*\text{Ru}(\mu\text{-Si}^i\text{Pr})_3\text{RuCp}^*$ with $\text{HC}\equiv\text{CC}(\text{OH})\text{R}_2$ ($\text{R} = \text{Me}$, Ph , tol) [17]. The vinyl complex $\text{Ir}(\text{CR}=\text{CR}-\text{CR}=\text{CR})(\text{CO})(\text{CH}=\text{CH}_2)(\text{PPh}_3)_2$ ($\text{R} = \text{CO}_2\text{Me}$) was obtained from the reaction of $\text{HC}\equiv\text{CC}_2\text{OH}$ with $\text{IrCl}(\text{CR}=\text{CR}-\text{CR}=\text{CR})(\text{PPh}_3)_2$ [18]. γ -Hydroxyalkynyls of divalent palladium and platinum complexes $\text{M}(\text{C}\equiv\text{CC}(\text{OH})\text{R}_2)_2\text{L}_2$ and $\text{MX}(\text{C}\equiv\text{CC}(\text{OH})\text{R}_2)_2\text{L}_2$ ($\text{R} = \text{H}$, Me , Et , Ph , CF_3 or $\text{R}_2 = (\text{CH}_2)_4$, $(\text{CH}_2)_5$, $(\text{CH}_2)_6$; $\text{L} = \text{PPh}_3$, PMe_2Ph , AsMe_2Ph ; $\text{X} = \text{Cl}$, H) could be obtained from the reactions of 1-alkynols with appropriate palladium and platinum complexes [19,20]. Some of the acetylide complexes can be dehydrated to give enynyl complexes.

In principle, reactions of 1-alkynols $\text{HC}\equiv\text{CC}(\text{OH})(\text{R})\text{CHR}'\text{R}''$ with metal hydride complexes L_nMH could produce hydroxyvinyl complexes $\text{L}_n\text{M}-$

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$\text{CH}=\text{CHC}(\text{OH})(\text{R})\text{CHR}'\text{R}''$ by insertion of acetylenes into M–H bonds. The hydroxyvinyl complexes $\text{L}_n\text{M}-\text{CH}=\text{CHC}(\text{OH})(\text{R})\text{CHR}'\text{R}''$ can be used to prepare dieny complexes $\text{L}_n\text{M}-\text{CH}=\text{CHC}(\text{R})=\text{CR}'\text{R}''$ upon dehydration or vinylcarbene complexes $[\text{L}_n\text{M}=\text{CH}-\text{CH}=\text{C}(\text{R})\text{CHR}'\text{R}'']^+$ upon electrophilic abstraction of the OH group. Conjugated complexes with $\text{M}-\text{CH}=\text{CHC}(\text{R})=\text{CR}'\text{R}''$ linkage and $\text{M}=\text{CH}-\text{CH}=\text{CRR}'$ linkage are interesting because they may exhibit interesting physical properties (for example, electrically conducting and non-linear optical) [21] and catalytic properties [22–32]. For example, $\text{RuCl}_2(\text{PR}_3)_2=\text{CH}-\text{CH}=\text{CPh}_2$ ($\text{R} = \text{Ph}, \text{Cy}$) are active catalysts for olefin metathesis, olefin polymerization (ROMP) [22–28] and ring forming reactions [29–32]. However, reactions of 1-alkynols $\text{HC}\equiv\text{CC}(\text{OH})(\text{R})\text{CHR}'\text{R}''$ with metal hydride complexes L_nMH have received little attention. Harris and Hill [33] have reported reactions of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_2(\text{BSD})$ ($\text{BSD} = 2,1,3$ -benzoselenadiazole) with $\text{HC}\equiv\text{CC}(\text{OH})\text{R}_2$ ($\text{CR}_2 = \text{CMe}_2$ and *cyclo*- C_6H_{10}) to give $\text{RuCl}(\text{CH}=\text{CHC}(\text{OH})\text{R}_2)(\text{CO})(\text{PPh}_3)_2(\text{BSD})$. Either BSD or trifluoroacetic anhydride induced the dehydration of these complexes to give the dieny complexes $\text{RuCl}(\text{dienyl})(\text{CO})(\text{PPh}_3)_2(\text{BSD})$. Esteruelas et al. [34,35] have recently reported reactions of $\text{MHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$) with $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$. The structures and properties of the products for these reactions are dependent on metals as well as the substituents on the alkynols. For example, reaction of $\text{OsHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ with $\text{HC}\equiv\text{CC}(\text{OH})\text{HPh}$ produced $\text{OsCl}_2(=\text{CHCH}=\text{CHPh})(\text{CO})(\text{P}^i\text{Pr}_3)_2$, whereas reaction of $\text{RuHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ with $\text{HC}\equiv\text{CC}(\text{OH})\text{HPh}$ produced $\text{RuCl}(\text{CH}=\text{CHC}(\text{OH})\text{HPh})(\text{CO})(\text{P}^i\text{Pr}_3)_2$. Furlani et al. [36] reported that reactions of $\text{PtHCl}(\text{PPh}_3)_2$ with $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$ in alcohols $\text{R}''\text{OH}$ did not lead to the insertion products, but produced the acetylide complexes $\text{PtCl}(\text{C}\equiv\text{CC}(\text{OR}'')\text{RR}')(\text{PPh}_3)_2$.

To investigate the effect of metallic centers and substituents on acetylenes on the nature of organometallic compounds obtained from reactions of alkynols and metal hydride complexes, and to explore the possibility of synthesizing $\text{L}_n\text{M}-\text{CH}=\text{CHC}(\text{OH})\text{RR}'$, $\text{L}_n\text{M}-\text{CH}=\text{CHC}(\text{R})=\text{CR}'\text{R}''$ and $\text{L}_n\text{M}=\text{CH}-\text{CH}=\text{C}(\text{R})\text{CHR}'\text{R}''$ from alkynols and hydride complexes, we have investigated the reactions of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with alkynols. These reactions lead to the formation of ruthenium hydroxyvinyl complexes which can be readily converted into dieny and vinylcarbene complexes.

2. Experimental section

All reactions were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents

were distilled under dinitrogen from sodium–benzophenone (hexane, diethyl ether, THF), calcium hydride (dichloromethane, CHCl_3). Microanalyses were performed by MEDAC Ltd. (Middlesex, UK) or MHW Lab (Phoenix, AZ). ^1H , ^{31}P and ^{13}C NMR spectra were collected on a JEOL EX-400 spectrometer or a Bruker ARX-300 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported relative to TMS, and ^{31}P NMR chemical shifts relative to 85% H_3PO_4 . IR spectra were collected on a Perkin–Elmer 1600 spectrometer (in Nujol mulls, or KBr disc). $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ [37] was prepared according to the literature method. Neutral alumina was used as purchased from BDH and all other reagents were used as purchased from Aldrich.

2.1. Reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with 2-phenyl-3-butyn-2-ol, preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})(\text{CH}_3)\text{Ph})(\text{CO})(\text{PPh}_3)_2$ (2)

2-phenyl-3-butyn-2-ol (73 mg, 0.50 mmol) was added to a suspension of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (428 mg, 0.45 mmol) in CH_2Cl_2 (10 ml). The reaction mixture was stirred for 15 min at room temperature and then concentrated until an orange solid began to form. Hexane (20 ml) was then added to complete precipitation. The solid was collected by filtration, washed with hexane and ether and dried in vacuo. Yield 305 mg, 81%. Anal. Found: C, 67.33; H, 5.04. $\text{C}_{47}\text{H}_{41}\text{ClO}_2\text{P}_2\text{Ru}$ Calc.: C, 67.50; H, 4.94%. IR (Nujol, cm^{-1}): 3560 br [$\nu(\text{O}-\text{H})$], 1932 vs [$\nu(\text{C}\equiv\text{O})$], 1572 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (CDCl_3): δ 7.59–6.97 (m, 36H, Ru–CH, Ph, 2 PPh_3), 5.02 (dt, $J(\text{HH}) = 13.5$ Hz, $J(\text{PH}) = 2.3$ Hz, 1H, =CH), 1.25 (s, 3H, CH_3), 1.02 (br, 1H, OH). ^{31}P NMR (CDCl_3): δ 30.35 (s), 30.30 (s). ^{13}C NMR (CDCl_3): δ 200.6 (t, $J(\text{PC}) = 14.7$ Hz, Ru–CO), 147.5 (s, *ipso*-C of C_6H_5), 141.2 (t, $J(\text{PC}) = 10.9$ Hz, Ru–CH), 140.8 (t, $J(\text{PC}) = 3.7$ Hz, Ru–CH=CH), 134.0 (m, *o*-PPh), 131.7 (m, *ipso*-PPh), 130.1 (s, *p*-PPh), 128.2 (m, *m*-PPh), 127.5 (s, Ph), 125.7 (s, Ph), 124.9 (s, Ph).

2.2. Reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with propargyl alcohol, preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{CH}_2\text{OH})(\text{CO})(\text{PPh}_3)_2$ (3)

The experimental procedure was analogous to that described for 2; starting from $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (428 mg, 0.45 mmol) and propargyl alcohol (28 mg, 0.50 mmol). The product is an orange solid. Yield 248 mg, 74%. IR (Nujol, cm^{-1}): 3579–3274 br [$\nu(\text{O}-\text{H})$], 1922 vs [$\nu(\text{C}\equiv\text{O})$], 1586 m, 1574 m [$\nu(\text{C}=\text{C})$]. ^1H NMR (CDCl_3): δ 7.63–6.93 (m, 31H, Ru–CH=, 2 PPh_3), 5.00–4.80 (dt, 1H, $J(\text{HH}) = 14.1$, 5.1 Hz, =CH–), 3.51 (dd, 2H, $J(\text{HH}) = 5.1$, 3.0 Hz, $-\text{CH}_2-\text{O}$), 1.27 (d, $J(\text{HH}) = 3.0$ Hz, OH). ^{31}P NMR (CDCl_3): δ 33.0 (s).

2.3. Reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with 2-methyl-3-butyn-2-ol, preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})(\text{CH}_3)_2)(\text{CO})(\text{PPh}_3)_2$ (4)

The experimental procedure was analogous to that described for **2**; starting from $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (428 mg, 0.45 mmol) and 2-methyl-3-butyn-2-ol (42 mg, 0.50 mmol). The product is an orange solid. Yield 305 mg, 81%. IR (Nujol, cm^{-1}): 3448 m [$\nu(\text{O}-\text{H})$], 1924 vs [$\nu(\text{C}\equiv\text{O})$], 1586 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (CDCl_3): δ 7.66–7.40 (m, 30H, 2 PPh_3), 7.15 (dt, $J(\text{HH}) = 14.5$ Hz, $J(\text{PH}) = 1.9$ Hz, 1H, Ru–CH), 4.93 (dt, $J(\text{HH}) = 14.5$ Hz, $J(\text{PH}) = 1.7$ Hz, 1H, =CH–), 0.85 (s, 6H, 2 CH_3), 0.52 (s, 1H, OH). ^{31}P NMR (CDCl_3): δ 32.6 (s). ^{13}C NMR (CDCl_3): δ 203.9 (t, $J(\text{PC}) = 14.4$ Hz, Ru–CO), 140.1 (m, Ru–CH=CH), 134.1 (t, $J(\text{PC}) = 5.6$ Hz, *o*-Ph), 131.8 (t, $J(\text{PC}) = 21.7$ Hz, *ipso*-Ph), 129.9 (s, *p*-Ph), 128.1 (t, $J(\text{PC}) = 4.7$ Hz, *m*-Ph), 71.5 (s, C(OH)), 28.9 (s, CH_3).

2.4. Reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with 3-methyl-1-pentyn-3-ol, preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})(\text{CH}_3)(\text{CH}_2\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$ (5)

The experimental procedure was analogous to that described for **2**; starting from $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (428 mg, 0.45 mmol) and 3-methyl-1-pentyn-3-ol (49 mg, 0.50 mmol). The product is an orange solid. Yield 238 mg, 67%. Anal. Found: C, 63.91; H, 5.09. $\text{C}_{43}\text{H}_{41}\text{ClO}_2\text{P}_2\text{Ru} \cdot \text{H}_2\text{O}$ Calc.: C, 64.13; H, 5.26%. IR (Nujol, cm^{-1}): 3452 br [$\nu(\text{O}-\text{H})$], 1916 vs [$\nu(\text{C}\equiv\text{O})$], 1584 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (C_6D_6): δ 7.94–7.10 (m, 31H, 2 PPh_3 , Ru–CH=), 5.38 (d, $J(\text{HH}) = 13.2$ Hz, 1H, =CH–), 1.54 (q, $J(\text{HH}) = 7.2$ Hz, 2H, CH_2), 1.17 (s, 3H, CH_3), 0.86 (t, 3H, CH_3). ^{31}P NMR (C_6D_6): δ 31.1 (s).

2.5. Reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with 1-ethynylcyclohexanol, preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{cyclo-C}_6\text{H}_9(\text{OH}))(\text{CO})(\text{PPh}_3)_2$ (6)

1-ethynylcyclohexanol (62 mg, 0.5 mmol) was added to a suspension of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (428 mg, 0.45 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 15 min at room temperature and then concentrated until an orange solid began to form. Hexane (20 ml) was then added to complete precipitation. The solid was collected by filtration, washed with hexane and ether and dried in vacuo. Yield 275 mg, 75%. Anal. Found: C, 66.42; H, 5.18. $\text{C}_{45}\text{H}_{43}\text{ClO}_2\text{P}_2\text{Ru}$ Calc.: C, 66.38; H, 5.32%. IR (Nujol, cm^{-1}): 3566 s [$\nu(\text{O}-\text{H})$], 1932 vs [$\nu(\text{C}\equiv\text{O})$], 1589 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (CDCl_3): δ 7.62–7.26 (m, 31H, Ru–CH, 2 PPh_3), 4.94 (dt, $J(\text{HH}) = 13.1$ Hz, $J(\text{PH}) = 1.5$ Hz, 1H, =CH), 1.45–1.11 (m, 10H, 5 CH_2), 0.48 (s, OH). ^{13}C NMR (CDCl_3): δ 202.3

(t, $J(\text{PC}) = 5.8$ Hz, Ru–CO), 141.5 (s, =CH), 139.5 (t, $J(\text{PC}) = 10.3$ Hz, RuCH), 134.1 (t, $J(\text{PC}) = 5.6$ Hz, *o*-Ph), 131.8 (t, $J(\text{PC}) = 8.7$ Hz, *ipso*-Ph), 130.1 (s, *p*-Ph), 128.2 (t, $J(\text{PC}) = 5.0$ Hz, *m*-Ph), 72.2 (s, C(OH)), 38.0 (s, CH_2), 25.6 (s, CH_2), 22.5 (s, CH_2). ^{31}P NMR (CDCl_3): δ 30.5 (s).

2.6. Reaction of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with 4-pentyn-2-ol, preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$ (7)

The experimental procedure was analogous to that described for **2**; starting from $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (428 mg, 0.45 mmol) and 4-pentyn-2-ol (42 mg, 0.50 mmol). The product is an orange solid. Yield 272 mg, 78%. Anal. Found: C, 65.20; H, 5.33. $\text{C}_{42}\text{H}_{39}\text{ClO}_2\text{P}_2\text{Ru}$ Calc.: C, 65.16; H, 5.08%. IR (Nujol, cm^{-1}): 3550 br [$\nu(\text{O}-\text{H})$], 1932 vs [$\nu(\text{C}\equiv\text{O})$], 1586 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (C_6D_6): δ 7.67–7.00 (m, 31H, 2 PPh_3 , Ru–CH), 5.14 (m, 1H, =CH–), 3.50 (m, 1H, –CH(OH)), 2.14 (m, 2H, – CH_2 –), 1.16 (br, OH), 1.04 (d, $J(\text{HH}) = 6.0$ Hz, 3H, CH_3). ^{31}P NMR (C_6D_6): δ 31.4 (s).

2.7. Preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{Ph})=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2$ (8)

A solution of **2** (209 mg, 0.25 mmol) in CH_2Cl_2 (30 ml) was stirred with 5 g of neutral Al_2O_3 for 1 h. Al_2O_3 was removed by filtration to give an orange–red solution. The orange–red solution was concentrated to ca. 2 ml. Hexane (20 ml) was then added to precipitate the product. The orange solid was collected by filtration, washed with hexane (20 ml) and dried in vacuo. Yield 119 mg, 58%. Anal. Found: C, 68.87; H, 5.04. $\text{C}_{47}\text{H}_{39}\text{ClO}_2\text{P}_2\text{Ru}$ Calc.: C, 68.99; H, 4.80%. IR (Nujol, cm^{-1}): 1920 vs [$\nu(\text{C}\equiv\text{O})$], 1590 s, 1552 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (CDCl_3): δ 7.75 (d, 1H, $J(\text{HH}) = 13.8$ Hz, Ru–CH=), 7.60–7.15 (m, 35H, 2 PPh_3 , Ph), 5.60 (d, $J(\text{HH}) = 13.8$ Hz, 1H, =CH–), 4.39 (s, 2H, = CH_2). ^{31}P NMR (CDCl_3): δ 30.3 (s).

2.8. Preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{cyclo-C}_6\text{H}_9)(\text{CO})(\text{PPh}_3)_2$ (9)

A solution of **6** (200 mg, 0.24 mmol) in CH_2Cl_2 (30 ml) was stirred with 5 g of neutral Al_2O_3 for 1 h. Al_2O_3 was removed by filtration to give an orange–red solution. The orange–red solution was concentrated to ca. 2 ml. Hexane (20 ml) was then added to precipitate the product. The red solid was collected by filtration, washed with hexane (20 ml) and dried in vacuo. Yield 155 mg, 76%. Anal. Found: C, 67.59; H, 5.22. $\text{C}_{45}\text{H}_{41}\text{ClO}_2\text{P}_2\text{Ru}$ Calc.: C, 67.88; H, 5.19%. IR (Nujol, cm^{-1}): 1936 vs [$\nu(\text{C}\equiv\text{O})$], 1640 s, 1584 w [$\nu(\text{C}=\text{C})$].

^1H NMR (CDCl_3): δ 7.59–6.99 (m, 31H, 2PPh_3 , Ru–CH=), 5.34 (d, $J(\text{HH}) = 13.5$ Hz, 1H, Ru–CH=CH), 4.95 (m, 1H, =CH–CH₂–), 2.17–1.46 (m, 8H, 4CH_2). ^{31}P NMR (CDCl_3): δ 29.5 (s).

2.9. Preparation of $[\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{Ph})\text{CH}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (**10**)

A solution of **2** (209 mg, 0.25 mmol) in CHCl_3 (10 ml) was treated with $\text{HBF}_4 \cdot \text{OEt}_2$ (54%; 40 μl , 0.30 mmol). The red solution was concentrated to 2 ml and then Et_2O (10 ml) was added to precipitate the product. The red solid formed was collected by filtration, washed repeatedly with Et_2O and hexane, and then dried in vacuo. The product is a red solid. Yield 134 mg, 59%. Anal. Found: C, 62.50; H, 4.27. $\text{C}_{47}\text{H}_{40}\text{BClF}_4\text{OP}_2\text{Ru}$ Calc.: C, 62.30; H, 4.45%. IR (KBr, cm^{-1}): 1964 vs [$\nu(\text{C}\equiv\text{O})$], 1630 w, 1528 s [$\nu(\text{C}=\text{C})$], 1090 s br [$\nu(\text{BF}_4^-)$]. ^1H NMR (CDCl_3): δ 15.98 (d, $J(\text{HH}) = 12.9$ Hz, Ru=CH), 15.65 (br, Ru=CH), 7.98–7.29 (m, 2PPh_3 , –CH=, =CPh), 1.99 (s, CH_3), 1.68 (s, CH_3). ^{31}P NMR (CDCl_3): δ 25.8 (s), 23.7 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 305.3 (brt, $J(\text{PC}) = 8.5$ Hz, Ru=CH), 301.6 (brt, $J(\text{PC}) = 10.2$ Hz, Ru=CH), 201.9 (br, CO), 200.0 (t, $J(\text{PC}) = 13.6$ Hz, CO), 164.2 (s, =CH), 161.6 (s, =CH), 145.8–124.3 (m, other Ph, =C), 18.5 (s, CH_3), 17.9 (s, CH_3).

2.10. Preparation of $[\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{CH}_2)_5)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (**11**)

A solution of **6** (203 mg, 0.25 mmol) in CHCl_3 (10 ml) was treated with $\text{HBF}_4 \cdot \text{OEt}_2$ (54%; 40 μl , 0.30 mmol). The yellow green solution was concentrated to 2 ml and Et_2O (10 ml) was then added to precipitate the product. The yellow solid formed was collected by filtration, washed repeatedly with Et_2O and hexane, and then dried in vacuo. Yield 124 mg, 56%. Anal. Found: C, 61.17; H, 4.78. $\text{C}_{45}\text{H}_{42}\text{ClF}_4\text{BOP}_2\text{Ru}$ Calc.: C, 61.14; H, 4.79%. IR (Nujol, cm^{-1}): 1970 vs [$\nu(\text{C}\equiv\text{O})$], 1544 s [$\nu(\text{C}=\text{C})$], 1092 s br [$\nu(\text{BF}_4^-)$]. ^1H NMR (acetone- d_6): δ 16.2 (br, 1H, Ru=CH), 7.79–7.04 (m, 31H, =CH, 2PPh_3), 1.85–1.13 (m, 10H, 5CH_2). ^{31}P NMR (acetone- d_6): δ 21.7 (s).

2.11. Preparation of $[\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{CH}_3)_2)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (**12**)

The experimental procedure was analogous to that described for **10**; starting from **4** (193 mg, 0.25 mmol) and $\text{HBF}_4 \cdot \text{OEt}_2$ (54%; 40 μl , 0.30 mmol). The product is a yellow solid. Yield 135 mg, 61%. IR (Nujol, cm^{-1}): 1960 vs [$\nu(\text{C}\equiv\text{O})$], 1556 s [$\nu(\text{C}=\text{C})$], 1094 s br [$\nu(\text{BF}_4^-)$]. ^1H NMR (acetone- d_6): δ 15.6 (br, 1H,

Ru=CH), 7.87–7.05 (m, 31H, =CH, 2PPh_3), 1.55 (s, 6H, 2CH_3). ^{31}P NMR (acetone- d_6): δ 20.8 (s). Anal. Found: C, 60.78; H, 5.06. $\text{C}_{42}\text{H}_{38}\text{BClF}_4\text{OP}_2\text{Ru}$ Calc.: C, 59.01; H, 4.48%.

2.12. Preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})(\text{CH}_3)\text{Ph})(\text{CO})(\text{PPh}_3)_2(\text{NC}_5\text{H}_4-\text{C}_6\text{H}_5)$ (**13**)

4-phenylpyridine (42 mg, 0.27 mmol) was added to a solution of **2** (209 mg, 0.25 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 15 min at room temperature and it was then concentrated until solid began to form. Hexane (20 ml) was then added to complete precipitation. The solid was collected by filtration, washed with hexane, and dried in vacuo to give a gray solid. Yield 216 mg, 87%. Anal. Found: C, 69.95; H, 4.86, N, 1.16. $\text{C}_{58}\text{H}_{50}\text{ClNO}_2\text{P}_2\text{Ru}$ Calc.: C, 70.26; H, 5.08; N, 1.41%. IR (Nujol, cm^{-1}): 3510–3220 br [$\nu(\text{O}-\text{H})$], 1916 vs [$\nu(\text{C}\equiv\text{O})$], 1612 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (CDCl_3): δ 8.47 (m, 2H, N=CH), 7.83 (d, $J(\text{HH}) = 16.5$ Hz, 1H, Ru–CH=), 7.48–6.84 (m, 40H, 2PPh_3 , 2Ph), 6.83 (m, 2H, N=CH–CH), 5.26 (d, $J(\text{HH}) = 16.5$ Hz, =CH–), 1.26 (s, 3H, CH_3). ^{31}P NMR (CDCl_3): δ 24.1 (s).

2.13. Preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{cyclo-C}_6\text{H}_{10}(\text{OH}))(\text{CO})(\text{PPh}_3)_2(\text{NC}_5\text{H}_4-\text{C}_6\text{H}_5)$ (**14**)

4-Phenylpyridine (42 mg, 0.27 mmol) was added to a solution of **6** (203 mg, 0.25 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 15 min at room temperature and it was then concentrated until solid began to form. Hexane (20 ml) was then added to complete precipitation. The solid was collected by filtration, washed with hexane, and dried in vacuo. Yield 206 mg, 85%. Anal. Found: C, 69.52; H, 5.65; N, 1.44. $\text{C}_{56}\text{H}_{52}\text{ClNO}_2\text{P}_2\text{Ru}$ Calc.: C, 69.38; H, 5.41; N, 1.45%. IR (Nujol, cm^{-1}): 3510–3250 br [$\nu(\text{O}-\text{H})$], 1914 vs [$\nu(\text{C}\equiv\text{O})$], 1612 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (CDCl_3): δ 8.45 (m, 2H, N=CH), 7.82 (d, 1H, $J(\text{HH}) = 16.8$ Hz, Ru–CH=), 7.60–7.05 (m, 35H, 2PPh_3 , Ph), 6.82 (m, 2H, N=CH–CH), 5.22 (d, $J(\text{HH}) = 16.8$ Hz, =CH–), 1.47–1.06 (m, 10H, 5CH_2). ^{31}P NMR (CDCl_3): δ 24.1 (s).

2.14. Preparation of $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{Ph})=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2(\text{NC}_5\text{H}_4-\text{C}_6\text{H}_5)$ (**15**)

The experimental procedure was analogous to that described for **13**; starting from **8** (205 mg, 0.25 mmol) and 4-phenylpyridine (42 mg, 0.27 mmol). The product is a pale green solid. Yield 214 mg, 88%. Anal. Found: C, 71.46; H, 5.00; N, 1.43. $\text{C}_{58}\text{H}_{48}\text{ClNOP}_2\text{Ru}$ Calc.: C, 71.56; H, 4.97; N, 1.44%. IR (Nujol, cm^{-1}): 1918 vs [$\nu(\text{C}\equiv\text{O})$], 1610 s, 1588 s [$\nu(\text{C}=\text{C})$]. ^1H NMR (CDCl_3): δ 8.45 (br, 2H, N=CH), 8.26 (d, 1H, $J(\text{HH}) = 16.8$ Hz,

Ru–CH=), 7.54–6.85 (m, 40H, 2PPh₃, 2Ph), 6.74 (br, 2H, N=CH–CH), 5.88 (d, $J(\text{HH}) = J(\text{HH}) = 16.8$ Hz, 1H, =CH–), 4.39 (s, 1H, =CH₂), 4.35 (s, 1H, =CH₂). ³¹P NMR (CDCl₃): δ 25.1 (s).

2.15. Preparation of RuCl(CH=CH–cyclo-C₆H₉)(CO)(PPh₃)₂(NC₅H₄–C₆H₅) (16)

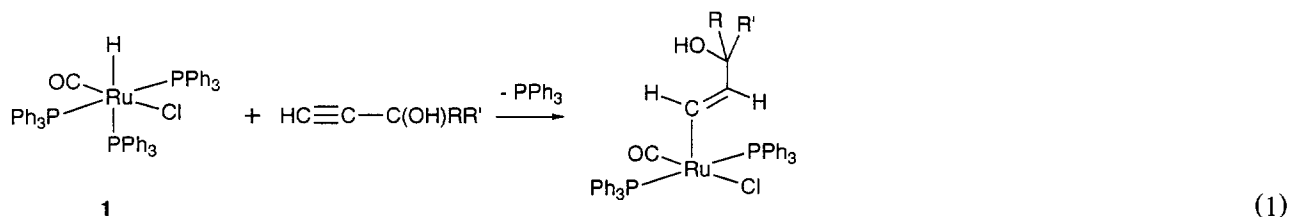
The experimental procedure was analogous to that described for **13**; starting from **9** (199 mg, 0.25 mmol) and 4-phenylpyridine (42 mg, 0.27 mmol). The product is a pale green solid. Yield 199 mg, 84%. Anal. Found: C, 70.48; H, 5.11; N, 1.44. C₅₆H₅₀ClN₂O₂P₂Ru. Calc.: C, 70.69; H, 5.30; N, 1.47%. IR (Nujol, cm^{−1}): 1912 vs [$\nu(\text{C}\equiv\text{O})$], 1612 s, 1550s [$\nu(\text{C}=\text{C})$]. ¹H NMR (CDCl₃): δ 8.47 (m, 2H, $J(\text{HH}) = 5.7$ Hz, N=CH), 7.86 (d, 1H, $J(\text{HH}) = 16.5$ Hz, Ru–CH=), 7.55–7.13 (m, 35H, 2PPh₃, Ph), 6.76 (m, 2H, N=CH–CH), 5.53 (d, $J(\text{HH})$

= 16.5 Hz, 1H, Ru–CH=CH), 4.86 (m, 1H, C=CH), 1.99–1.48 (m, 8H, 4CH₂). ³¹P NMR (CDCl₃): δ 24.9 (s).

3. Results and discussion

3.1. Insertion reactions of RuHCl(CO)(PPh₃)₃ with alkynols

Treatment of CH₂Cl₂ solutions of the carbonyl hydrido complex RuHCl(CO)(PPh₃)₃ (**1**) with 1-alkynols such as 2-phenyl-3-butyn-2-ol, propargyl alcohol, 2-methyl-3-butyn-2-ol, 3-methyl-1-pentyn-3-ol, and 1-ethynylcyclohexanol resulted in the formation of the five-coordinated hydroxyvinyl compounds RuCl((E)-CH=CHC(OH)RR')(CO)(PPh₃)₂ (**2–6**) in 67–81% yield (Eqs. (1) and (2)).

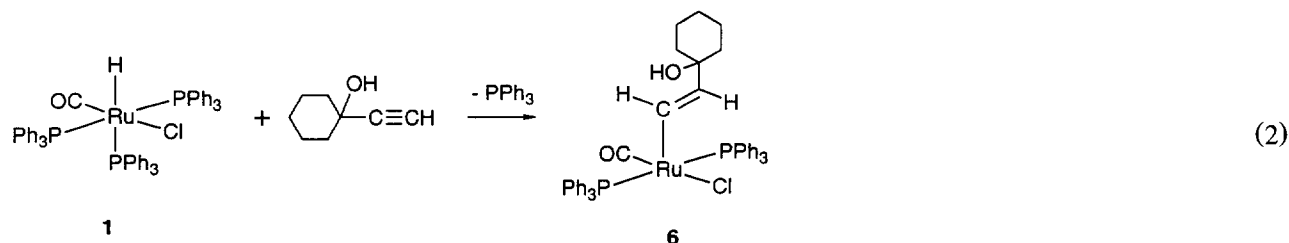


2, R = Ph, R' = Me

3, R = R' = H

4, R = R' = Me

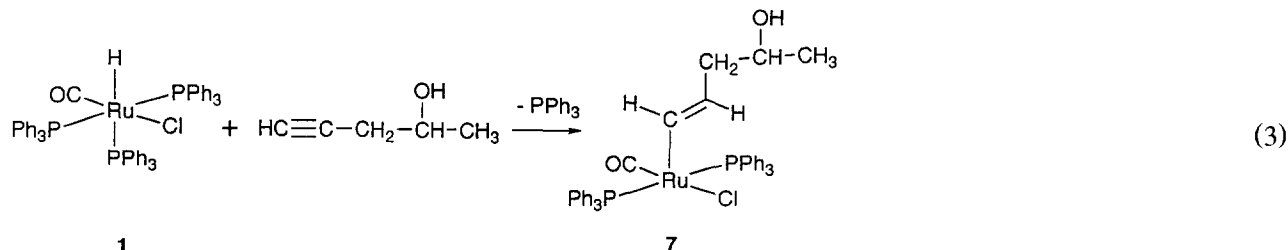
5, R = Me, R' = Et



The elemental analysis and spectroscopic data of the products are consistent with the square pyramidal structures shown in Eqs. (1) and (2). The alternative trigonal bipyramidal structures are also consistent with the spectroscopic data and thus cannot be excluded. Analogous five-coordinate ruthenium vinyl complexes such as RuCl(CH=CH–R)(CO)(PPh₃)₂ and RuCl(CH=CH–R)(CO)(P(ⁱPr)₃)₂ have been reported previously [38,39]. The ³¹P NMR spectra of complexes **2–6** in CDCl₃ displayed singlets in the region 30–33 ppm, indicating that the two phosphine ligands are equivalent and *trans* to each other. In the IR spectra broad bands at ca. 3400 cm^{−1}, characteristic of $\nu(\text{OH})$ absorption, were

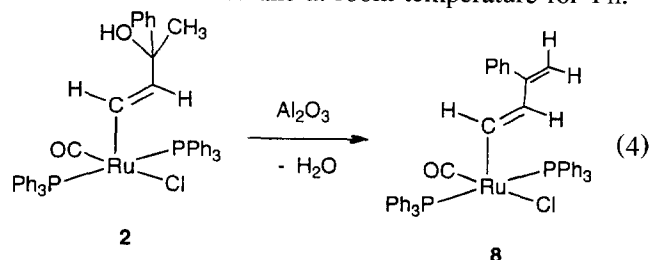
observed. The ¹H NMR spectra showed resonances for the two vinylic hydrogen atoms near 7.6 and 5 ppm with $J(\text{HH}) = 13$ –15 Hz. The magnitude of the coupling constants indicates that the two vinylic protons are *trans* to each other and that the acetylenes are *cis* inserted into the Ru–H bond [38,39]. *Cis* insertions of acetylenes into Ru–H bonds have been reported for complexes such as RuHCl(CO)(PPh₃)₃ [38], RuH(CO)(P(ⁱPr)₃)₂ [39], RuHCl(CO)₂(L)₂ (L = PMe₂Ph, AsMe₂Ph) [40], RuHCl(CO)(PPh₃)₂(L) (L = Py [41,42], Me₂Hpz [41,42], BSD [33]), and [RuH(CO)(L)₂(PPh₃)₂]⁺ (L = Py, CH₃CN) [43].

Treatment of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with 4-pentyn-2-ol gave the five-coordinated hydroxyvinyl complex $\text{RuCl}(\text{E})\text{--CH=CHCH}_2\text{C}(\text{OH})\text{HMe}(\text{CO})(\text{PPh}_3)_2$ (**7**)



3.2. Dehydration reactions

During the attempts to purify the simple insertion products using column chromatography, it was found that the hydroxyvinyl complexes could be easily dehydrated. For example, if a solution of **2** in CH_2Cl_2 was passed through a column of neutral alumina, an orange fraction could be obtained. Analytical and spectroscopic data of the orange compound suggest that the dehydrated compound $\text{RuCl}(\text{CH=CH--C}(\text{Ph})=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2$ (**8**) was produced when compound **2** was treated with alumina (Eq. (4)). The dehydrated product can be best obtained by stirring solutions of the simple insertion product in the presence of alumina in dichloromethane at room temperature for 1 h.

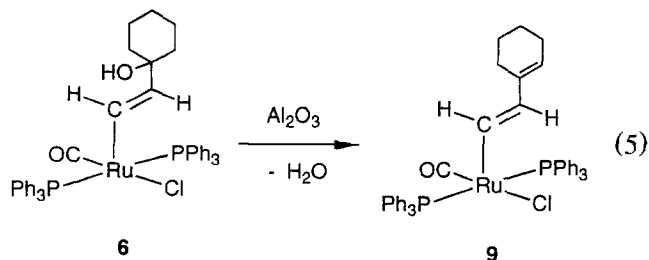


Compared with the IR spectrum of the non-dehydrated complex **2**, it was noted that the broad band near 3560 cm^{-1} due to $\nu(\text{OH})$ disappeared and that the $\nu(\text{CO})$ band shifted to 1920 cm^{-1} for the dehydrated product **8** from 1932 cm^{-1} for the non-dehydrated product **2**. In the ^1H NMR spectrum of the dehydrated product **8** in CDCl_3 , the signals for Ru--CH and Ru--CH=CH were observed at 7.75 (d, $J(\text{HH}) = 13.8\text{ Hz}$) and 5.60 ppm (d, $J(\text{HH}) = 13.8\text{ Hz}$) respectively. The signals of the two $=\text{CH}_2$ protons were observed as a singlet at 4.39 ppm, although they are magnetically inequivalent. In the ^{31}P NMR spectrum (in CDCl_3), a singlet at 30.3 ppm assignable to the PPh_3 ligand was observed. The chemical shift of 30.3 ppm is almost identical to those of the non-dehydrated complex **2**. The similarity in ^{31}P and IR data for complexes **2** and **8** indicates that the two compounds have similar geometry around ruthenium.

When complex **6** was treated with neutral alumina,

which has the OH group on the δ carbon atom (Eq. (3)). The spectroscopic data of **7** are very similar to those of compounds **2--6**.

an analogous dehydration reaction also occurred to give the dehydrated product $\text{RuCl}(\text{CH=CH--cyclo-C}_6\text{H}_9)(\text{CO})(\text{PPh}_3)_2$ (**9**) as confirmed by the elemental analysis, IR, ^1H and ^{31}P NMR spectroscopic data (Eq. (5)). In the ^1H NMR spectrum of the dehydrated product **9** in CDCl_3 , a doublet at 5.34 ppm ($J(\text{HH}) = 13.8\text{ Hz}$) assignable to an RuCH=CH proton and a multiplet at 4.95 ppm assignable to a $=\text{CH--CH}_2$ proton were observed. The ^1H NMR data are similar to those [34] observed for $\text{RuCl}(\text{CH=CH--cyclo-C}_6\text{H}_9)(\text{CO})(\text{P}^i\text{Pr})_2$. The ^{31}P NMR spectrum in CDCl_3 exhibited a singlet at 29.5 ppm, which is very similar to that of the corresponding non-dehydrated product **6** ($\delta(\text{P}) = 30.5\text{ ppm}$).



Dehydration reactions of complexes **3--5** were also attempted under similar conditions. These reactions usually led to a mixture of products and separation and characterization of these species were not successful. The use of alumina to dehydrate hydroxyl-containing hydrocarbons is previously known. For example, Werner et al. [2] have observed that rhodium hydroxyvinylidene complexes $\text{RhCl}(\text{P}^i\text{Pr})_3)_2(=\text{C=CHC}(\text{OH})\text{RR}')$ reacted with neutral alumina to give either vinylvinylidene complexes or allenylidene complexes.

There are a few reported examples of dehydrating hydroxyvinyl complexes. Esteruelas et al. [34] recently reported that reaction of $\text{RuHCl}(\text{CO})(\text{P}^i\text{Pr})_3)_2$ with 1-ethynylcyclohexanol in toluene at 60°C for 4 days could produce the dehydrated product $\text{RuCl}(\text{CH=CH--cyclo-C}_6\text{H}_9)(\text{CO})(\text{P}^i\text{Pr})_2$ in moderate yield (51%). Similarly, Harris and Hill [33] noted that prolonged storage (1 week) of solutions of $\text{RuCl}(\text{CH=CH--C}(\text{OH})\text{Me}_2)(\text{PPh}_3)_2(\text{BSD})$ in chloroform produced the

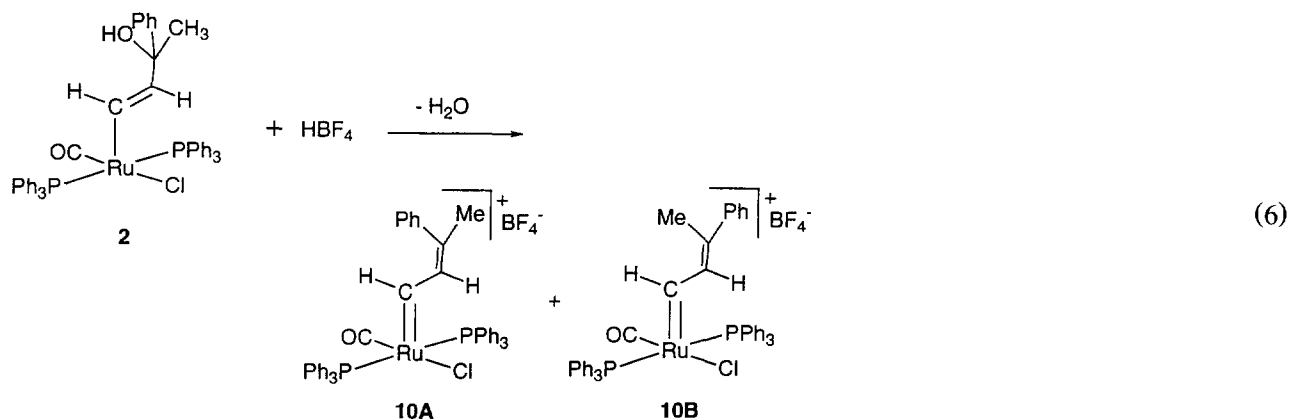
dehydrated product $\text{RuCl}(\text{CH}=\text{CH}-\text{CMe}(\text{=CH}_2)(\text{PPh}_3)_2)(\text{BSD})$. They also noted that addition of trifluoroacetic anhydride or excess BSD accelerated the dehydration of $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})\text{R}_2)(\text{PPh}_3)_2(\text{BSD})$ ($\text{CR}_2 = \text{CMe}_2$, *cyclo*- C_6H_{10}) to give the corresponding dienyl complexes.

There are many examples of dehydration of other unsaturated hydroxyhydrocarbon ligands. For example, reactions of $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$ with transition metal complexes such as $\text{CpRuCl}(\text{PMe}_3)_2$ [3], $\text{RuCl}_2(\text{dppm})_2$ [4], $\text{RuCl}_2(\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3)$ [5], and $\text{RuCl}_2(\text{dppe})_2$ [6,7] produced allenylidene complexes $\text{L}_n\text{M}=\text{C}=\text{C}=\text{CRR}'$ via spontaneous dehydration of hydroxyvinylidene intermediates $\text{L}_n\text{M}=\text{C}=\text{CH}-\text{C}(\text{OH})\text{RR}'$. Reaction of $\text{CpRuCl}(\text{PMe}_3)_2$ with 1-ethynylcyclohexanol yielded the cationic cycloalkenyl vinylidene complexes $[\text{CpRu}(\text{=C}=\text{CH}-\text{cyclo}-\text{C}_6\text{H}_9)(\text{PMe}_3)_2]^+$ [14]. γ -Hydroxyalkynyls of divalent platinum complexes such as $\text{Pt}(\text{C}\equiv\text{CC}(\text{OH})\text{Me}_2)_2(\text{PMe}_2\text{Ph})_2$ could be dehydrated to give enynyl complexes in refluxing acetic anhydride containing a small amount of pyridine [19].

3.3. Formation of vinylcarbene complexes

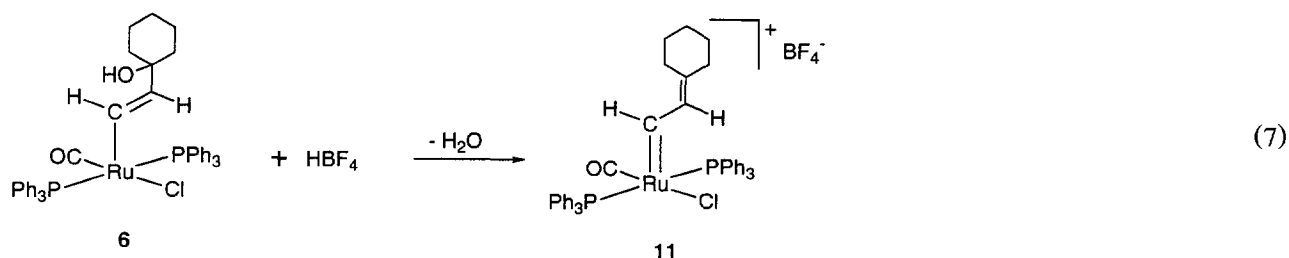
Complex **2** reacted with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ or Ph_3CBF_4 in CH_2Cl_2 to afford the cationic five-coordinated vinylcarbene compound $[\text{RuCl}(\text{=CH}-\text{CH}=\text{C}(\text{Ph})\text{CH}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (**10**, Eq. (6)). The analogous complex $[\text{RuCl}(\text{=CH}-\text{CH}=\text{C}(\text{Ph})\text{CH}_3)(\text{CO})(\text{P}^i\text{Pr})_2]\text{BF}_4$ has recently been char-

acterized by an X-ray diffraction study [34]. As expected, two isomers were observed for **10**. However, the relative amounts of the two isomers appear dependent on the conditions used for its isolation. When ether was used as the precipitating solvent, we could sometimes obtain samples with only one isomer. The presence of an $\text{Ru}=\text{CH}$ functionality in complex **10** is supported by its ^1H and ^{13}C NMR. In the ^1H NMR in CDCl_3 at room temperature, the $\text{Ru}=\text{CH}$ signals for the two isomers were observed at 15.98 (br d, $J(\text{HH}) = 12.9$ Hz) and 15.65 ppm (br). The carbene proton signals were even broader when the ^1H NMR spectrum was collected in acetone- d_6 . The carbene signals appeared as sharp doublets ($J(\text{HH}) = 12.9$ and 13.8 Hz respectively) when the ^1H NMR spectrum was collected at -40°C in acetone- d_6 . In the room temperature ^{13}C NMR spectrum (in CDCl_3), the $\text{Ru}=\text{CH}$ signals for the two isomers were observed at 305.3 and 301.6 ppm as broad triplets. The origin of the broadness of the carbene signals in the ^1H and ^{13}C NMR spectra of complex **10** is not clear. Broad carbene proton signals were also observed in the room temperature ^1H NMR spectra of $[\text{RuCl}(\text{=CH}-\text{R})(\text{CO})(\text{P}^i\text{Pr})_3]\text{BF}_4$ ($\text{R} = \text{CH}=\text{CHPh}$, $\text{CH}=\text{CPh}_2$, *cyclo*- C_6H_9) [34]. The broadness of the carbene signals in the ^1H and ^{13}C NMR spectra of complex **10** could be due to the formation of solvated complexes such as $[\text{RuCl}(\text{=CH}-\text{CH}=\text{C}(\text{Ph})\text{CH}_3)(\text{CO})(\text{PPh}_3)_2(\text{H}_2\text{O})]\text{BF}_4$, or $[\text{RuCl}(\text{=CH}-\text{CH}=\text{C}(\text{Ph})\text{CH}_3)(\text{CO})(\text{PPh}_3)_2(\text{acetone})]\text{BF}_4$. Exchange of coordinated and non-coordinated H_2O or acetone in solutions would give broad carbene signals.



Reaction of **6** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ or Ph_3CBF_4 in CH_2Cl_2 gave the corresponding vinylcarbene complex $[\text{RuCl}(\text{=CH}-\text{C}(\text{CH}_2)_5)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (**11**, Eq. (7)). Complex **11** also exhibited in its ^1H NMR spectrum (in acetone- d_6) a broad signal at 16.2 ppm characteristic of carbene proton resonance. Unfortunately, we could not

obtain a good ^{13}C NMR due to its poor solubility. The ^{31}P NMR spectrum is similar to that of complex **10** and displayed a singlet at 21.7 ppm suggesting that phosphine ligands are equivalent and are mutually *trans* disposed.



Reaction of $\text{RuCl}(\text{CH}=\text{CHC}(\text{OH})\text{Me}_2)(\text{CO})(\text{PPh}_3)_2$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 produced the corresponding vinylcarbene complex $[\text{RuCl}(\text{CH}=\text{CH}=\text{CMe}_2)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (**12**) which exhibited in its ^1H NMR spectrum a broad signal at 15.6 ppm assignable to the $\text{Ru}=\text{CH}$ proton, and a singlet at 1.55 ppm assignable to the CH_3 group. Complex **12** appears unstable in solution. Thus we could not collect ^{13}C NMR as it decomposed to an uncharacterized mixture during data collection. When compounds **3** and **5** were treated with HBF_4 under similar conditions, carbene compounds were also formed as indicated by the presence of the carbene signals at about 16 ppm in the ^1H NMR spectrum. However, the carbene complexes were usually contaminated with other unidentified species. Purification of these species was not attempted.

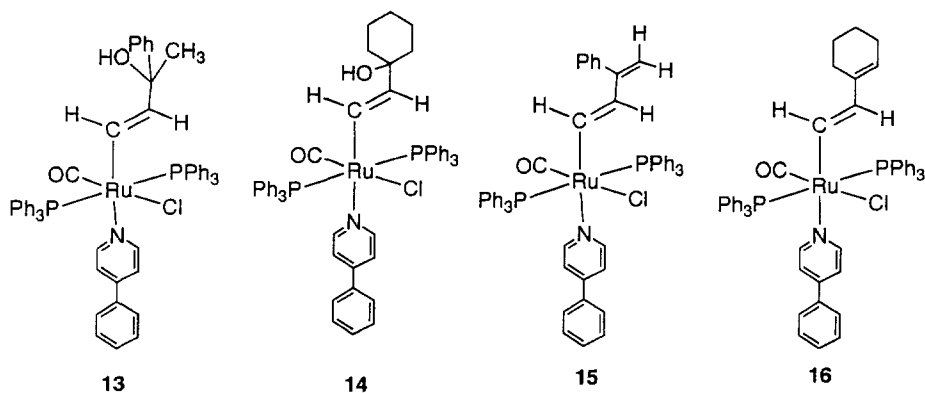
Esteruelas et al. [34] recently reported similar reactions which involve the electrophilic abstraction of the OH group from the hydroxyvinyl complexes $\text{RuCl}(\text{CH}=\text{CHC}(\text{OH})\text{RR}')(\text{CO})(\text{P}(\text{iPr})_3)_2$ ($\text{CRR}' = \text{CHPh}$, CPh_2 and $\text{cyclo-C}_6\text{H}_{10}$) with HBF_4 to give the corresponding vinylcarbene complexes $[\text{RuCl}(\text{CH}=\text{CH}=\text{CRR}')(\text{CO})(\text{P}(\text{iPr})_3)_2]\text{BF}_4$. There are also other examples of electrophilic abstraction of OR groups using H^+ or Ph_3C^+ . For example, reaction of $\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{C}-\text{C}\equiv\text{CCPh}_2\text{OSiMe}_3)$ with Ph_3CPF_6 produced $[\text{RuCl}(\text{dppe})_2(\text{C}=\text{C}=\text{C}=\text{C}=\text{CPh}_2)]\text{PF}_6$ [6], reaction of $(\eta^5\text{-C}_9\text{H}_8)\text{Ru}(\text{LL})(\text{C}\equiv\text{C}-\text{CPh}_2\text{OMe})$ ($\text{LL} =$

dppe , dppm) with HBF_4 produced $(\eta^5\text{-C}_9\text{H}_8)\text{Ru}(\text{LL})(\text{C}=\text{C}=\text{C}=\text{CPh}_2)]\text{BF}_4$ [9].

Reactions of vinyl compounds with electrophiles could lead to carbene complexes by electrophilic attack at the β -carbon atoms [44]. We found that protonation of the dienyl complex **8** and **9** with HBF_4 led to the formation of the vinylcarbene complexes **10** and **11** respectively. Thus electrophilic attack of a proton at the δ -carbon atoms of the dienyl ligands occurred. This observation is in agreement with the recently reported reaction of $\text{RuCl}(\text{CH}=\text{CH}-\text{cyclo-C}_6\text{H}_9)(\text{CO})(\text{P}(\text{iPr})_3)_2$ with HBF_4 [34].

3.4. Formation of six-coordinated complexes

Complexes **1–12** are coordinatively unsaturated, thus one might expect that six-coordinated adducts would be formed when they are treated with small ligands. When compounds **2**, **6**, **8** and **9** were allowed to react with 4-phenylpyridine in CH_2Cl_2 , the six-coordinate adducts **13–16** were obtained. These complexes were fully characterized by elemental analysis and spectroscopic methods. The ^{31}P NMR spectra exhibited singlets around 25 ppm, indicating that the two phosphine ligands are equivalent and are mutually *trans* disposed. The ^1H NMR spectra showed characteristic resonances for the PPh_3 , and 4-phenylpyridine ligands and the vinyl groups. The IR spectra showed $\nu(\text{CO})$ in the region of 1912–1918 cm^{-1} .



The geometry of the adducts around ruthenium is assigned by analogy to those of similar six-coordinated complexes. Complexes $\text{RuCl}(\text{CH}=\text{CHR})(\text{CO})(\text{PPh}_3)_2$ are known to react with heterocycles *L* such as Me_2Hpz [45], BSD [33] to give the six-coordinated compounds $\text{RuCl}(\text{CH}=\text{CHR})(\text{CO})(\text{PPh}_3)_2(\text{L})$ with two mutually *trans* PPh_3 ligands and the vinyl group *cis* to the carbonyl ligand. Insertion reactions of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_2(\text{Py})$ with $\text{HC}\equiv\text{CR}$ produced similar complexes $\text{RuCl}(\text{CH}=\text{CHR})(\text{CO})(\text{PPh}_3)_2(\text{Py})$ [41].

Reactions between cationic vinylcarbene complexes **10** and **11** with 4-phenylpyridine did not produce the

cationic six-coordinate adducts of vinylcarbene complexes, but gave the corresponding neutral dienyl complexes **15** and **16** respectively. Thus deprotonation of the δ proton by the pyridine base occurred.

4. Conclusion

This study showed that the reactivity of alkynols towards $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ is similar to that of non-functionalized acetylenes. Thus $\text{HC}\equiv\text{CC}(\text{OH})\text{R}_2$ ($\text{CR}_2 = \text{CPhMe}$, $\text{cyclo-C}_6\text{H}_{10}$, CH_2 , CMe_2 , and CMeEt) were

cis inserted into the Ru–H bond of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ to give the five-coordinated hydroxyvinyl complexes $\text{RuCl}(\text{CH}=\text{CH}-\text{C}(\text{OH})\text{R}_2)(\text{CO})(\text{PPh}_3)_2$. Treatment of the hydroxyvinyl complexes with alumina produced the dehydrated dienyl complexes and with HBF_4 or Ph_3CBF_4 produced the vinylcarbene complexes. The ready availability of alkynols [46] and the simplicity of the reactions described here suggest that such reactions may be useful in the preparation of new conjugated organometallic complexes or materials containing $\text{M}-\text{CH}=\text{CH}-\text{CH}=\text{CRR}'$ or $\text{M}=\text{CH}-\text{CH}=\text{CRR}'$ linkages.

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