Reactions of RuHCl(CO)(PPh₃)₃ with 1-alkynols. Preparation and reactivity of hydroxyvinyl complexes

Guochen Jia *, Wan Fung Wu, Richard C.Y. Yeung, Haiping Xia

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Abstract

Reactions of $RuHCl(CO)(PPh_3)_3$ with $HC\equiv CC(OH)R_2$ (CR_2 = CPhMe, $cyclo$-C_6H_{10}, CH_2, CMe_2, CMeEt) produced the hydroxyvinyl complexes $RuCl(CH=CH-C(OH)R_2)(CO)(PPh_3)_2$. Treatment of the hydroxyvinyl complexes $RuCl(CH=CH-C(OH)PhMe)(CO)(PPh_3)_2$ and $RuCl(CH=CH-cyclo-C_6H_{10}(OH))(CO)(PPh_3)_2$ with alumina produced the dehydrated dienyl complexes $RuCl(CH=CH-CPh=CH_2)(CO)(PPh_3)_2$ and $RuCl(CH=CH-cyclo-C_6H_9)(CO)(PPh_3)_2$ respectively. The hydroxyvinyl complexes and the dienyl complexes reacted with L = 4-phenylpyridine to give six-coordinated complexes $RuCl(CH=CH-R)(CO)(PPh_3)_2(L)$ (R = C(OH)PhMe, $cyclo$-$C_6H_{10}(OH)$, CPh=CH₂, $cyclo$-C_6H_9). Treatment of the hydroxyvinyl complexes $RuCl(CH=CH-C(OH)PhMe)(CO)(PPh_3)_2$ and $RuCl(CH=CH-cyclo-C_6H_{10}(OH))(CO)(PPh_3)_2$ with HBF_4 or Ph_3CBF_4 produced the vinylcarbene complexes $[RuCl(=CH-CH=CPhMe)(CO)(PPh_3)_2]BF_4$ and $[RuCl(=CH-CH=C(CH_2)_5)(CO)(PPh_3)_2]BF_4$ respectively.

Keywords: Ruthenium hydride; Acetylenes; Insertion reaction

1. Introduction

1-alkynols $HC\equiv CC(OH)RR'$ 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 $[Cp^*Ru(PMe_2Ph)_2(=C=CHC(OH)RR')]^+$ and $RhCl(P(^iPr_3)_2(=C=CHC(OH)RR')$ could be obtained from the reactions of $HC\equiv CC(OH)RR'$ with $Cp^*RuCl(PMe_2Ph)_2$ [1] and $[RhCl(P(^iPr)_3)_2]_n$ [2] respectively. Allenylidene complexes $L_nM=C=C=CRR'$ could be isolated from the reactions of $HC\equiv CC(OH)RR'$ with complexes such as $CpRuCl(PMe_3)_2$ [3], $RuCl_2(dppm)_2$ [4], $RuCl_2(N(CH_2CH_2PPh_2)_3)$ [5], $RuCl_2(dppe)_2$ [6,7], $(\eta^5-C_9H_7)RuCl(PPh_3)_2$ [8,9], $Cp^*Ru(\mu-S^iPr)_3RuCp^*$ [10], $[CpFe(CO)(dppe)]^+$ [11], and $M(CO)_5(THF)$ [12]. Methoxyalkenylcarbene complexes such as $[(C_6Me_6)RuCl(=C(OMe)-CH=CRR')(PR_3)]^+$ were obtained from the reactions of $(C_6Me_6)RuCl_2(PR_3)$ with $HC\equiv CC(OH)RR'$ in methanol in the presence of $NaPF_6$ [13]. Reaction of

$CpRuCl(PMe_3)_2$ with 1-ethynylcyclohexanol led to the cationic cycloalkenyl vinylidene complex $[CpRu(=C=CH-cyclo-C_6H_9)(PMe_3)_2]^+$ [14]. Unusual coupling products were obtained from the reaction of $CpRuCl(PMe_3)_2$ with $HC\equiv CC(OH)Me_2$ [15], the reaction of $(\eta^5-C_9H_7)RuCl(PPh_3)_2$ with 1-ethynylcyclohexanol [16], and the reaction of $Cp^*Ru(\mu-S^iPr)_3RuCp^*$ with $HC\equiv CC(OH)R_2$ (R = Me, Ph, tol) [17]. The vinyl complex $Ir(CR=CR-CR=CR)(CO)(CH=CH_2)(PPh_3)_2$ (R = CO_2Me) was obtained from the reaction of $HC\equiv CCH_2OH$ with $IrCl(CR=CR-CR=CR)(PPh_3)_2$ [18]. γ-Hydroxyalkynyls of divalent palladium and platinum complexes $M(C\equiv CC(OH)R_2)_2L_2$ and $MX(C\equiv CC(OH)R_2)L_2$ (R = H, Me, Et, Ph, CF_3 or R_2 = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$; L = PPh_3, PMe_2Ph, $AsMe_2Ph$; X = 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 $HC\equiv CC(OH)(R)CHR'R''$ with metal hydride complexes L_nMH could produce hydroxyvinyl complexes L_nM-

* Corresponding author.

CH=CHC(OH)(R)CHR'R" by insertion of acetylenes into M–H bonds. The hydroxyvinyl complexes L_nM–CH=CHC(OH)(R)CHR'R" can be used to prepare dienyl complexes L_nM–CH=CHC(R)=CR'R" upon dehydration or vinylcarbene complexes $[L_nM$=CH–CH=C(R)CHR'R"]$^+$ upon electrophilic abstraction of the OH group. Conjugated complexes with M–CH=CHC(R)=CR'R" linkage and M=CH–CH=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, $RuCl_2(PR_3)_2$=CH–CH=CPh$_2$ (R = Ph, Cy) are active catalysts for olefin metathesis, olefin polymerization (ROMP) [22–28] and ring forming reactions [29–32]. However, reactions of 1-alkynols HC≡CC(OH)(R)CHR'R" with metal hydride complexes L_nMH have received little attention. Harris and Hill [33] have reported reactions of $RuHCl(CO)(PPh_3)_2(BSD)$ (BSD = 2,1,3-benzoselenadiazole) with HC≡CC(OH)R$_2$ (CR$_2$ = CMe$_2$ and $cyclo$-C$_6$H$_{10}$) to give $RuCl(CH$=CHC(OH)R$_2)(CO)(PPh_3)_2(BSD)$. Either BSD or trifluoroacetic anhydride induced the dehydration of these complexes to give the dienyl complexes $RuCl(dienyl)(CO)(PPh_3)_2(BSD)$. Esteruelas et al. [34,35] have recently reported reactions of $MHCl(CO)(P(^iPr)_3)_2$ (M = Ru, Os) with HC≡CC(OH)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 $OsHCl(CO)(P(^iPr)_3)_2$ with HC≡CC(OH)HPh produced $OsCl_2(=CHCH$=CHPh)(CO)(P(^iPr)_3)_2$, whereas reaction of $RuHCl(CO)(P(^iPr)_3)_2$ with HC≡CC(OH)HPh produced $RuCl(CH$=CHC(OH)HPh)(CO)(P(^iPr)_3)_2$. Furlani et al. [36] reported that reactions of $PtHCl(PPh_3)_2$ with HC≡CC(OH)RR' in alcohols R"OH did not lead to the insertion products, but produced the acetylide complexes $PtCl(C≡CC(OR")RR')(PPh_3)_2$.

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 L_nM–CH=CHC(OH)RR', L_nM–CH = CHC(R)=CR'R" and L_nM = CH–CH=C(R)CHR'R" from alkynols and hydride complexes, we have investigated the reactions of $RuHCl(CO)(PPh_3)_3$ with alkynols. These reactions lead to the formation of ruthenium hydroxyvinyl complexes which can be readily converted into dienyl 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). ^{1}H, ^{31}P and ^{13}C NMR spectra were collected on a JEOL EX-400 spectrometer or a Bruker ARX-300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to TMS, and ^{31}P NMR chemical shifts relative to 85% H$_3$PO$_4$. IR spectra were collected on a Perkin–Elmer 1600 spectrometer (in Nujol mulls, or KBr disc). $RuHCl(CO)(PPh_3)_3$ [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 $RuHCl(CO)(PPh_3)_3$ with 2-phenyl-3-butyn-2-ol, preparation of $RuCl(CH = CH-C(OH)(CH_3)Ph)(CO)(PPh_3)_2$ (2)

2-phenyl-3-butyn-2-ol (73 mg, 0.50 mmol) was added to a suspension of $RuHCl(CO)(PPh_3)_3$ (428 mg, 0.45 mmol) in CH$_2$Cl$_2$ (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. C$_{47}$H$_{41}$ClO$_2$P$_2$Ru Calc.: C, 67.50; H, 4.94%. IR (Nujol, cm^{-1}): 3560 br [v(O–H)], 1932 vs [v(C≡O)], 1572 s [v(C=C)]. ^{1}H NMR (CDCl$_3$): δ 7.59–6.97 (m, 36H, Ru–CH, Ph, 2PPh$_3$), 5.02 (dt, J(HH) = 13.5 Hz, J(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(PC) = 14.7 Hz, Ru–CO), 147.5 (s, $ipso$-C of C$_6$H$_5$), 141.2 (t, J(PC) = 10.9 Hz, Ru–CH), 140.8 (t, J(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 $RuHCl(CO)(PPh_3)_3$ with propargyl alcohol, preparation of $RuCl(CH = CH-CH_2OH)(CO)(PPh_3)_2$ (3)

The experimental procedure was analogous to that described for 2; starting from $RuHCl(CO)(PPh_3)_3$ (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 [v(O–H)], 1922 vs [v(C≡O)], 1586 m, 1574 m [v(C=C)]. ^{1}H NMR (CDCl$_3$): δ 7.63–6.93 (m, 31H, Ru–CH=, 2PPh$_3$), 5.00–4.80 (dt, 1H, J(HH) = 14.1, 5.1 Hz, =CH–), 3.51 (dd, 2H, J(HH) = 5.1, 3.0 Hz, –CH$_2$–O), 1.27 (d, J(HH) = 3.0 Hz, OH). ^{31}P NMR (CDCl$_3$): δ 33.0 (s).

2.3. Reaction of RuHCl(CO)(PPh₃)₃ with 2-methyl-3-butyn-2-ol, preparation of RuCl(CH = CH−C(OH)(CH₃)₂)(CO)(PPh₃)₂ (4)

The experimental procedure was analogous to that described for **2**; starting from RuHCl(CO)(PPh₃)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 [v(O–H)], 1924 vs [v(C≡O)], 1586 s [v(C=C)]. ¹H NMR (CDCl₃): δ 7.66–7.40 (m, 30H, 2PPh₃), 7.15 (dt, J(HH) = 14.5 Hz, J(PH) = 1.9 Hz, 1H, Ru–CH), 4.93 (dt, J(HH) = 14.5 Hz, J(PH) = 1.7 Hz, 1H, =CH–), 0.85 (s, 6H, 2CH₃), 0.52 (s, 1H, OH). ³¹P NMR (CDCl₃): δ 32.6 (s). ¹³C NMR (CDCl₃): δ 203.9 (t, J(PC) = 14.4 Hz, Ru–CO), 140.1 (m, Ru–CH=CH), 134.1 (t, J(PC) = 5.6 Hz, o-Ph), 131.8 (t, J(PC) = 21.7 Hz, ipso-Ph), 129.9 (s, p-Ph), 128.1 (t, J(PC) = 4.7 Hz, m-Ph), 71.5 (s, C(OH)), 28.9 (s, CH₃).

2.4. Reaction of RuHCl(CO)(PPh₃)₃ with 3-methyl-1-pentyn-3-ol, preparation of RuCl(CH = CH−C(OH)(CH₃)(CH₂CH₃)(CO)(PPh₃)₂ (5)

The experimental procedure was analogous to that described for **2**; starting from RuHCl(CO)(PPh₃)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. C₄₃H₄₁ClO₂P₂Ru · H₂O Calc.: C, 64.13; H, 5.26%. IR (Nujol, cm⁻¹): 3452 br [v(O–H)], 1916 vs [v(C≡O)], 1584 s [v(C=C)]. ¹H NMR (C₆D₆): δ 7.94–7.10 (m, 31H, 2PPh₃, Ru–CH=), 5.38 (d, J(HH) = 13.2 Hz, 1H, =CH–), 1.54 (q, J(HH) = 7.2 Hz, 2H, CH₂), 1.17 (s, 3H, CH₃), 0.86 (t, 3H, CH₃). ³¹P NMR (C₆D₆): δ 31.1 (s).

2.5. Reaction of RuHCl(CO)(PPh₃)₃ with 1-ethynyl-cyclohexanol, preparation of RuCl(CH = CH−cyclo-C₆H₁₀(OH))(CO)(PPh₃)₂ (6)

1-ethynylcyclohexanol (62 mg, 0.5 mmol) was added to a suspension of RuHCl(CO)(PPh₃)₃ (428 mg, 0.45 mmol) in CH₂Cl₂ (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. C₄₅H₄₃ClO₂P₂Ru Calc.: C, 66.38; H, 5.32%. IR (Nujol, cm⁻¹): 3566 s [v(O–H)], 1932 vs [v(C≡O)], 1589 s [v(C=C)]. ¹H NMR (CDCl₃): δ 7.62–7.26 (m, 31H, Ru–CH, 2PPh₃), 4.94 (dt, J(HH) = 13.1 Hz, J(PH) = 1.5 Hz, 1H, =CH), 1.45–1.11 (m, 10H, 5CH₂), 0.48 (s, OH). ¹³C NMR (CDCl₃): δ 202.3

(t, J(PC) = 5.8 Hz, Ru–CO), 141.5 (s, =CH), 139.5 (t, J(PC) = 10.3 Hz, RuCH), 134.1 (t, J(PC) = 5.6 Hz, o-Ph), 131.8 (t, J(PC) = 8.7 Hz, ipso-Ph), 130.1 (s, p-Ph), 128.2 (t, J(PC) = 5.0 Hz, m-Ph), 72.2 (s, C(OH)), 38.0 (s, CH₂), 25.6 (s, CH₂), 22.5 (s, CH₂). ³¹P NMR (CDCl₃): δ 30.5 (s).

2.6. Reaction of RuHCl(CO)(PPh₃)₃ with 4-pentyn-2-ol, preparation of RuCl(CH = CH−CH₂CH(OH)CH₃)(CO)(PPh₃)₂ (7)

The experimental procedure was analogous to that described for **2**; starting from RuHCl(CO)(PPh₃)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. C₄₂H₃₉ClO₂P₂Ru Calc.: C, 65.16; H, 5.08%. IR (Nujol, cm⁻¹): 3550 br [v(O–H)], 1932 vs [v(C≡O)], 1586 s [v(C=C)]. ¹H NMR (C₆D₆): δ 7.67–7.00 (m, 31H, 2PPh₃, Ru–CH), 5.14 (m, 1H, =CH–), 3.50 (m, 1H, –CH(OH)), 2.14 (m, 2H, –CH₂–), 1.16 (br, OH), 1.04 (d, J(HH) = 6.0 Hz, 3H, CH₃). ³¹P NMR (C₆D₆): δ 31.4 (s).

2.7. Preparation of RuCl(CH = CH−C(Ph)= CH₂)(CO)(PPh₃)₂ (8)

A solution of **2** (209 mg, 0.25 mmol) in CH₂Cl₂ (30 ml) was stirred with 5 g of neutral Al₂O₃ for 1 h. Al₂O₃ 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. C₄₇H₃₉ClOP₂Ru Calc.: C, 68.99; H, 4.80%. IR (Nujol, cm⁻¹): 1920 vs [v(C≡O)], 1590 s, 1552 s [v(C=C)]. ¹H NMR (CDCl₃): δ 7.75 (d, 1H, J(HH) = 13.8 Hz, Ru–CH=), 7.60–7.15 (m, 35H, 2PPh₃, Ph), 5.60 (d, J(HH) = 13.8 Hz, 1H, =CH–), 4.39 (s, 2H, =CH₂). ³¹P NMR (CDCl₃): δ 30.3 (s).

2.8. Preparation of RuCl(CH = CH−cyclo-C₆H₉)(CO)(PPh₃)₂ (9)

A solution of **6** (200 mg, 0.24 mmol) in CH₂Cl₂ (30 ml) was stirred with 5 g of neutral Al₂O₃ for 1 h. Al₂O₃ 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. C₄₅H₄₁ClOP₂Ru Calc.: C, 67.88; H, 5.19%. IR (Nujol, cm⁻¹): 1936 vs [v(C≡O)], 1640 s, 1584 w [v(C=C)].

^{1}H NMR (CDCl$_3$): δ 7.59–6.99 (m, 31H, 2PPh$_3$, Ru–CH=), 5.34 (d, J(HH) = 13.5 Hz, 1H, Ru–CH=CH), 4.95 (m, 1H, =CH–CH$_2$–), 2.17–1.46 (m, 8H, 4CH$_2$). ^{31}P NMR (CDCl$_3$): δ 29.5 (s).

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

A solution of 2 (209 mg, 0.25 mmol) in CHCl$_3$ (10 ml) was treated with HBF$_4$ · OEt$_2$ (54%; 40 µl, 0.30 mmol). The red solution was concentrated to 2 ml and then Et$_2$O (10 ml) was added to precipitate the product. The red solid formed was collected by filtration, washed repeatedly with Et$_2$O 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. C$_{47}$H$_{40}$BClF$_4$OP$_2$Ru Calc.: C, 62.30; H, 4.45%. IR (KBr, cm^{-1}): 1964 vs [v(C≡O)], 1630 w, 1528 s [v(C=C)], 1090 s br [v(BF$_4^-$)]. ^{1}H NMR (CDCl$_3$): δ 15.98 (d, J(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}C{^{1}H} NMR (CDCl$_3$): 305.3 (brt, J(PC) = 8.5 Hz, Ru=CH), 301.6 (brt, J(PC) = 10.2 Hz, Ru=CH), 201.9 (br, CO), 200.0 (t, J(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 [RuCl{=CH–CH=C(CH$_2$)$_5$}(CO)(PPh$_3$)$_2$]BF$_4$ (11)

A solution of 6 (203 mg, 0.25 mmol) in CHCl$_3$ (10 ml) was treated with HBF$_4$ · OEt$_2$ (54%; 40 µl, 0.30 mmol). The yellow green solution was concentrated to 2 ml and Et$_2$O (10 ml) was then added to precipitate the product. The yellow solid formed was collected by filtration, washed repeatedly with Et$_2$O and hexane, and then dried in vacuo. Yield 124 mg, 56%. Anal. Found: C, 61.17; H, 4.78. C$_{45}$H$_{42}$ClF$_4$BOP$_2$Ru Calc.: C, 61.14; H, 4.79%. IR (Nujol, cm^{-1}): 1970 vs [v(C≡O)], 1544 s [v(C=C)], 1092 s br [v(BF$_4^-$)]. ^{1}H 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 [RuCl{=CH–CH=C(CH$_3$)$_2$}(CO)(PPh$_3$)$_2$]BF$_4$ (12)

The experimental procedure was analogous to that described for 10; starting from 4 (193 mg, 0.25 mmol) and HBF$_4$ · OEt$_2$ (54%; 40 µl, 0.30 mmol). The product is a yellow solid. Yield 135 mg, 61%. IR (Nujol, cm^{-1}): 1960 vs [v(C≡O)], 1556 s [v(C=C)], 1094 s br [v(BF$_4^-$)]. ^{1}H 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. C$_{42}$H$_{38}$BClF$_4$OP$_2$Ru Calc.: C, 59.01; H, 4.48%.

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

4-phenylpyridine (42 mg, 0.27 mmol) was added to a solution of 2 (209 mg, 0.25 mmol) in CH$_2$Cl$_2$ (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. C$_{58}$H$_{50}$ClNO$_2$P$_2$Ru Calc.: C, 70.26; H, 5.08; N, 1.41%. IR (Nujol, cm^{-1}): 3510–3220 br [v(O–H)], 1916 vs [v(C≡O)], 1612 s [v(C=C)]. ^{1}H NMR (CDCl$_3$): δ 8.47 (m, 2H, N=CH), 7.83 (d, J(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(HH) = 16.5 Hz, =CH–), 1.26 (s, 3H, CH$_3$). ^{31}P NMR (CDCl$_3$): δ 24.1 (s).

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

4-Phenylpyridine (42 mg, 0.27 mmol) was added to a solution of 6 (203 mg, 0.25 mmol) in CH$_2$Cl$_2$ (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. C$_{56}$H$_{52}$ClNO$_2$P$_2$Ru Calc.: C, 69.38; H, 5.41; N, 1.45%. IR (Nujol, cm^{-1}): 3510–3250 br [v(O–H)], 1914 vs [v(C≡O)], 1612 s [v(C=C)]. ^{1}H NMR (CDCl$_3$): δ 8.45 (m, 2H, N=CH), 7.82 (d, 1H, J(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(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 RuCl(CH = CH–C(Ph)= CH$_2$)(CO)(PPh$_3$)$_2$(NC$_5$H$_4$-C$_6$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. C$_{58}$H$_{48}$ClNOP$_2$Ru Calc.: C, 71.56; H, 4.97; N, 1.44%. IR (Nujol, cm^{-1}): 1918 vs [v(C≡O)], 1610 s, 1588 s [v(C=C)]. ^{1}H NMR (CDCl$_3$): δ 8.45 (br, 2H, N=CH), 8.26 (d, 1H, J(HH) = 16.8 Hz,

Ru–CH=), 7.54–6.85 (m, 40H, 2PPh₃, 2Ph), 6.74 (br, 2H, N=CH–C*H*), 5.88 (d, *J*(HH) = *J*(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. C₅₆H₅₀ClNOP₂Ru Calc.: C, 70.69; H, 5.30; N, 1.47%. IR (Nujol, cm⁻¹): 1912 vs [υ(C≡O)], 1612 s, 1550s [υ(C=C)]. ¹H NMR (CDCl₃): δ 8.47 (m, 2H, *J*(HH) = 5.7 Hz, N=CH), 7.86 (d, 1H, *J*(HH) = 16.5 Hz, Ru–CH=), 7.55–7.13 (m, 35H, 2PPh₃, Ph), 6.76 (m, 2H, N=CH–C*H*), 5.53 (d, *J*(HH)

= 16.5 Hz, 1H, Ru–CH=C*H*), 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)).
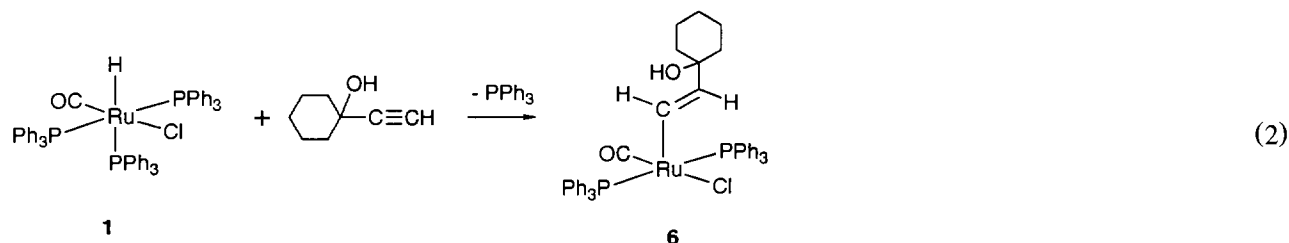

                                                                    (1)
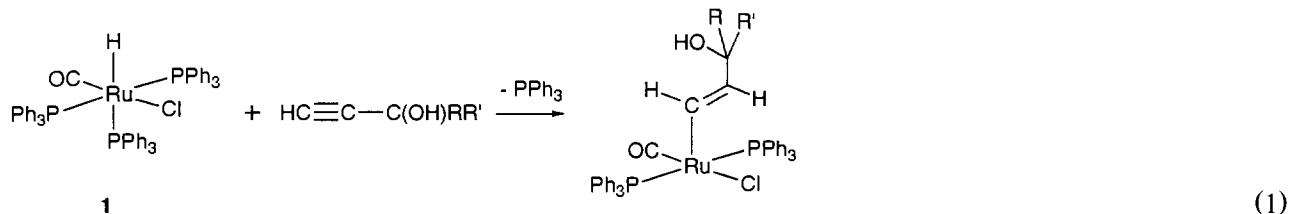
2, R = Ph, R' = Me

3, R = R' = H

4, R = R' = Me

5, R = Me, R' = Et
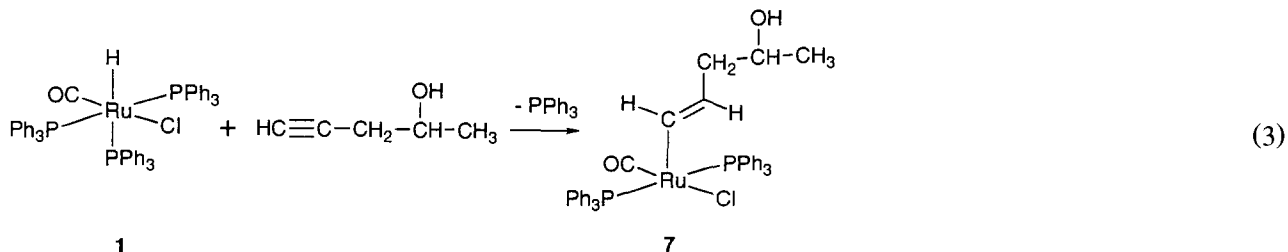

                                                                    (2)

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 bipyramid 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 υ(OH) absorption, were

observed. The ¹H NMR spectra showed resonances for the two vinylic hydrogen atoms near 7.6 and 5 ppm with *J*(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(L₂) (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 $RuHCl(CO)(PPh_3)_3$ with 4-pentyn-2-ol gave the five-coordinated hydroxyvinyl complex $RuCl((E)-CH=CHCH_2C(OH)HMe)(CO)(PPh_3)_2$ (7)

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.

$$(3)$$

1   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 $RuCl(CH=CH-C(Ph)=CH_2)(CO)(PPh_3)_2$ (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.

$$(4)$$

2   8
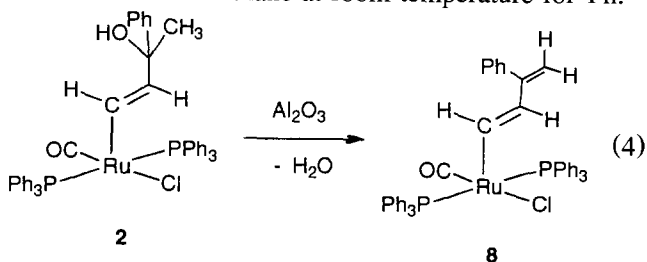
Compared with the IR spectrum of the non-dehydrated complex 2, it was noted that the broad band near $3560\,cm^{-1}$ due to $v(OH)$ disappeared and that the $v(CO)$ band shifted to $1920\,cm^{-1}$ for the dehydrated product 8 from $1932\,cm^{-1}$ for the non-dehydrated product 2. In the ^1H NMR spectrum of the dehydrated product 8 in $CDCl_3$, the signals for Ru–CH and Ru–CH=CH were observed at 7.75 (d, $J(HH) = 13.8\,Hz$) and 5.60 ppm (d, $J(HH) = 13.8\,Hz$) respectively. The signals of the two $=CH_2$ 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,

an analogous dehydration reaction also occurred to give the dehydrated product $RuCl(CH=CH-cyclo-C_6H_9)(CO)(PPh_3)_2$ (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 ($J(HH) = 13.8\,Hz$) assignable to an RuCH=CH proton and a multiplet at 4.95 ppm assignable to a $=CH-CH_2$ proton were observed. The ^1H NMR data are similar to those [34] observed for $RuCl(CH=CH-cyclo-C_6H_9)(CO)(P(^iPr)_3)_2$. 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 ($\delta(P) = 30.5\,ppm$).

$$(5)$$

6   9
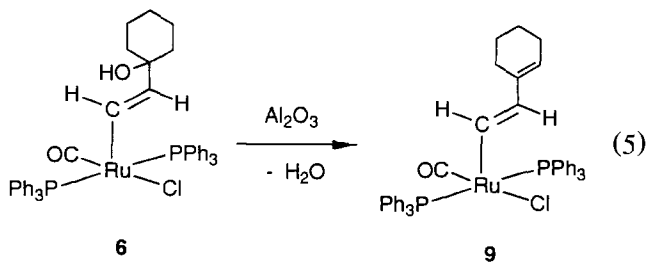
Dehydration reactions of complexes 3–5 were also attempted under similar conditions. These reactions usually led to a mixture of products and separation and characterization of these species were not successful. The use of alumina to dehydrate hydroxyl-containing hydrocarbons is previously known. For example, Werner et al. [2] have observed that rhodium hydroxyvinylidene complexes $RhCl(P(^iPr)_3)_2(=C=CHC(OH)RR')$ 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 $RuHCl(CO)(P(^iPr)_3)_2$ with 1-ethynylcyclohexanol in toluene at 60°C for 4 days could produce the dehydrated product $RuCl(CH=CH-cyclo-C_6H_9)(CO)(P(^iPr))_2$ in moderate yield (51%). Similarly, Harris and Hill [33] noted that prolonged storage (1 week) of solutions of $RuCl(CH=CH-C(OH)Me_2)(PPh_3)_2(BSD)$ in chloroform produced the

dehydrated product RuCl(CH = CH – CMe(=CH₂)(PPh₃)₂(BSD). They also noted that addition of trifluoacetic anhydride or excess BSD accelerated the dehydration of RuCl(CH = CH – C(OH)R₂)(PPh₃)₂(BSD) (CR₂ = CMe₂, cyclo-C₆H₁₀) to give the corresponding dienyl complexes.

There are many examples of dehydration of other unsaturated hydroxyhydrocarbon ligands. For example, reactions of HC≡CC(OH)RR′ with transition metal complexes such as CpRuCl(PMe₃)₂ [3], RuCl₂(dppm)₂ [4], RuCl₂(N(CH₂CH₂PPh₂)₃) [5], and RuCl₂(dppe)₂ [6,7] produced allenylidene complexes LₙM=C=C=CRR′ via spontaneous dehydration of hydroxyvinylidene intermediates LₙM=C=CH–C(OH)RR′. Reaction of CpRuCl(PMe₃)₂ with 1-ethynylcyclohexanol yielded the cationic cycloalkenyl vinylidene complexes [CpRu(=C=CH–cyclo-C₆H₉)(PMe₃)₂]⁺ [14]. γ-Hydroxyalkynyls of divalent platinum complexes such as Pt(C≡CC(OH)Me₂)₂(PMe₂Ph)₂ could be dehydrated to give enynyl complexes in refluxing acetic anhydride containing a small amount of pyridine [19].

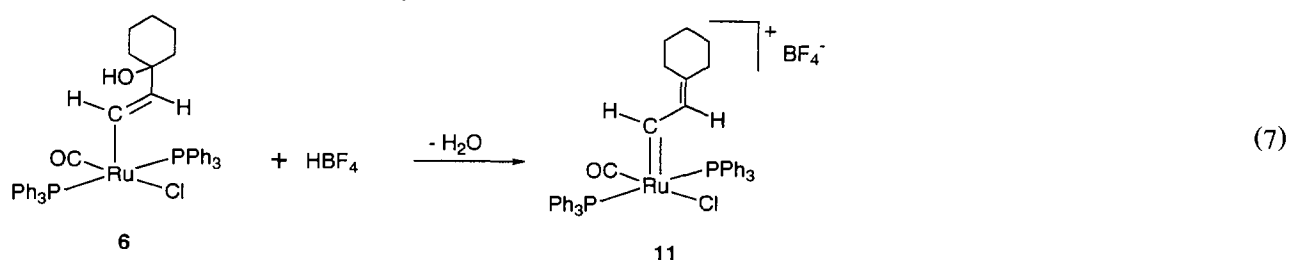### 3.3. Formation of vinylcarbene complexes

Complex **2** reacted with HBF₄ · Et₂O or Ph₃CBF₄ in CH₂Cl₂ to afford the cationic five-coordinated vinylcarbene compound [RuCl(= CH – CH=C(Ph)CH₃)(CO)(PPh₃)₂]BF₄ (**10**, Eq. (6)). The analogous complex [RuCl(= CH – CH=CPh₂)(CO)(P(ᶦPr)₃)₂]BF₄ 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 Ru=CH functionality in complex **10** is supported by its ¹H and ¹³C NMR. In the ¹H NMR in CDCl₃ at room temperature, the Ru=CH signals for the two isomers were observed at 15.98 (br d, J(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-d₆. The carbene signals appeared as sharp doublets (J(HH) = 12.9 and 13.8 Hz respectively) when the ¹H NMR spectrum was collected at −40 °C in acetone-d₆. In the room temperature ¹³C NMR spectrum (in CDCl₃), the Ru=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 ¹³C NMR spectra of complex **10** is not clear. Broad carbene proton signals were also observed in the room temperature ¹H NMR spectra of [RuCl(=CH–R)(CO)(P(ᶦPr)₃)₂]BF₄ (R = CH=CHPh, CH=CPh₂, cyclo-C₆H₉) [34]. The broadness of the carbene signals in the ¹H and ¹³C NMR spectra of complex **10** could be due to the formation of solvated complexes such as [RuCl(=CH–CH=C(Ph)CH₃)(CO)(PPh₃)₂(H₂O)]BF₄, or [RuCl(= CH – CH=C(Ph)CH₃)(CO)(PPh₃)₂(acetone)]BF₄. Exchange of coordinated and non-coordinated H₂O or acetone in solutions would give broad carbene signals.

$$(6)$$
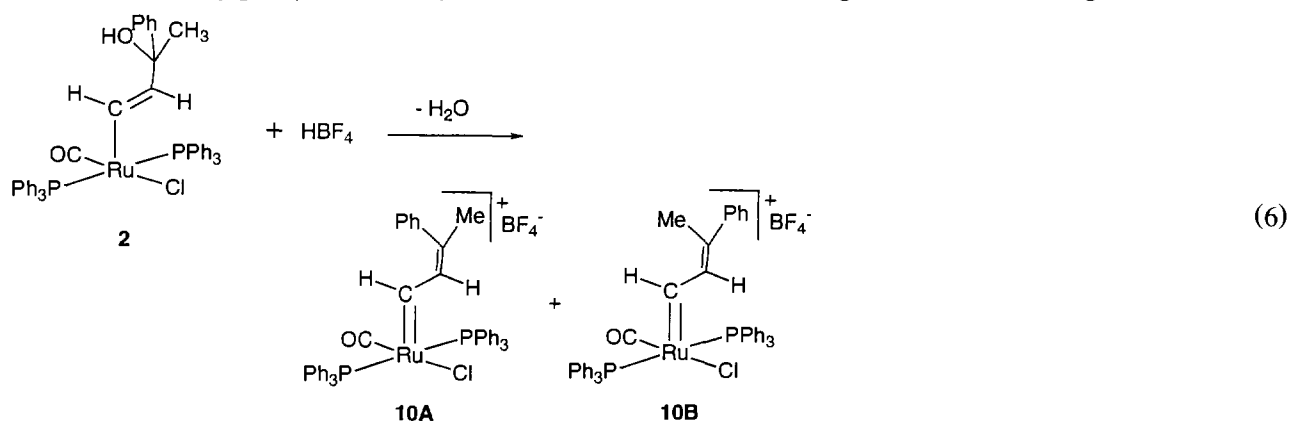
Reaction of **6** with HBF₄ · Et₂O or Ph₃CBF₄ in CH₂Cl₂ gave the corresponding vinylcarbene complex [RuCl(=CH–C(CH₂)₅)(CO)(PPh₃)₂]BF₄ (**11**, Eq. (7)). Complex **11** also exhibited in its ¹H NMR spectrum (in acetone-d₆) a broad signal at 16.2 ppm characteristic of carbene proton resonance. Unfortunately, we could not

obtain a good ¹³C NMR due to its poor solubility. The ³¹P 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.

$$(7)$$

Reaction of RuCl(CH=CHC(OH)Me₂)(CO)(PPh₃)₂ with HBF₄ · Et₂O in CH₂Cl₂ produced the corresponding vinylcarbene complex [RuCl(=CH–CH=CMe₂)(CO)(PPh₃)₂]BF₄ (12) which exhibited in its ¹H NMR spectrum a broad signal at 15.6 ppm assignable to the Ru=CH proton, and a singlet at 1.55 ppm assignable to the CH₃ group. Complex 12 appears unstable in solution. Thus we could not collect ¹³C NMR as it decomposed to an uncharacterized mixture during data collection. When compounds 3 and 5 were treated with HBF₄ 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 RuCl(CH=CHC(OH)RR')(CO)(P(ⁱPr)₃)₂ (CRR' = CHPh, CPh₂ and cyclo-C₆H₁₀) with HBF₄ to give the corresponding vinylcarbene complexes [RuCl(=CH–CH=CRR')(CO)(P(ⁱPr)₃)₂]BF₄. There are also other examples of electrophilic abstraction of OR groups using H⁺ or Ph₃C⁺. For example, reaction of RuCl(dppe)₂(C≡C–C≡CCPh₂OSiMe₃) with Ph₃CPF₆ produced [RuCl(dppe)₂(=C=C=C=C=CPh₂)]PF₆ [6], reaction of (η⁵-C₉H₈)Ru(LL)(C≡C-CPh₂OMe) (LL =

dppe, dppm) with HBF₄ produced (η⁵-C₉H₈)Ru(LL)(=C=C=CPh₂)]BF₄ [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 HBF₄ 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 RuCl(CH=CH–cyclo-C₆H₉)(CO)(P(ⁱPr)₃)₂ with HBF₄ [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 CH₂Cl₂, the six-coordinate adducts 13–16 were obtained. These complexes were fully characterized by elemental analysis and spectroscopic methods. The ³¹P 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 PPh₃, and 4-phenylpyridine ligands and the vinyl groups. The IR spectra showed ν(CO) in the region of 1912–1918 cm⁻¹.

13   14   15   16
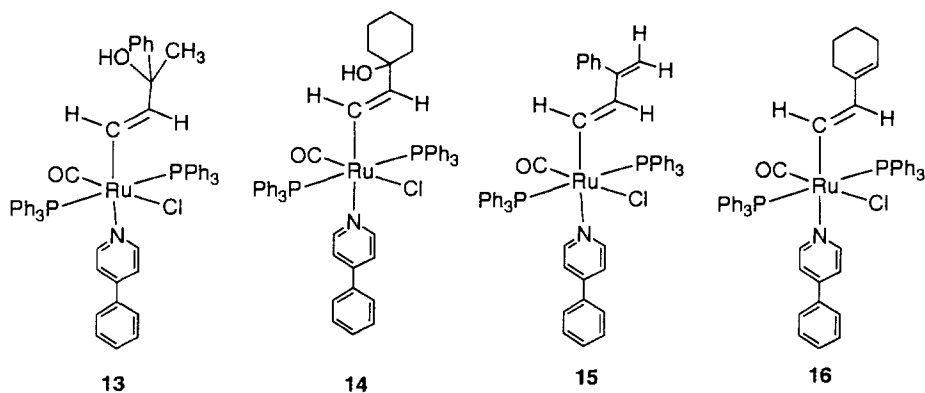
The geometry of the adducts around ruthenium is assigned by analogy to those of similar six-coordinated complexes. Complexes RuCl(CH=CHR)(CO)(PPh₃)₂ are known to react with heterocycles L such as Me₂Hpz [45], BSD [33] to give the six-coordinated compounds RuCl(CH=CHR)(CO)(PPh₃)₂(L) with two mutually trans PPh₃ ligands and the vinyl group cis to the carbonyl ligand. Insertion reactions of RuHCl(CO)(PPh₃)₂(Py) with HC≡CR produced similar complexes RuCl(CH=CHR)(CO)(PPh₃)₂(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 RuHCl(CO)(PPh₃)₃ is similar to that of non-functionalized acetylenes. Thus HC≡CC(OH)R₂ (CR₂ = CPhMe, cyclo-C₆H₁₀, CH₂, CMe₂, and CMeEt) were

cis inserted into the Ru–H bond of RuHCl(CO)(PPh$_3$)$_3$ to give the five-coordinated hydroxyvinyl complexes RuCl(CH=CH–C(OH)R$_2$)(CO)(PPh$_3$)$_2$. Treatment of the hydroxyvinyl complexes with alumina produced the dehydrated dienyl complexes and with HBF$_4$ or Ph$_3$CBF$_4$ 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 M–CH=CH–CH=CRR' or M=CH–CH=CRR' linkages.

Acknowledgements

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