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Metal-assisted preparation of the alkenyl ketone and carbonyl complexes from 1-alkyne and H_2O: C–C triple bond cleavage of terminal alkyne

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Abstract

Reactions of $Cp^*RhCl_2(PPh_3)$ (**1**) with 1-alkyne and H_2O in the presence of KPF_6 generated alkenyl ketone complexes $[Cp^*Rh(CR{=}CHCOCH_2R)(PPh_3)](PF_6)$ (**2**) (R = Ph (**a**), C_6H_4–*p*-Me (**b**), C_6H_4-*p*-COOMe (**c**), C_6H_4-*p*-NO_2 (**d**)). A similar complex $[Cp^*Rh(CPh{=}CHCOCH_2Ph)(PMePh_2)](PF_6)$ (**2e**) was obtained by use of $Cp^*RhCl_2(PMePh_2)$. It was revealed by X-ray analyses of **2b**, **2c** and **2e** that the complexes **2** consist of the five-membered ring structures bound by the carbon and oxygen atoms of the alkenyl ketone group. Similar reactions of $Cp^*IrCl_2(PPh_3)$ (**6**) or $(C_6Me_6)RuCl_2(PPh_3)$ (**7**) proceeded with a cleavage of C–C triple bond of 1-alkyne without formation of an alkenyl ketone complex, affording the corresponding carbonyl complexes, $[Cp^*IrCl(PPh_3)(CO)](PF_6)$ (**8**) or $[(C_6Me_6)RuCl(PPh_3)(CO)](PF_6)$ (**9**). The diphosphine complexes $[(Cp^*MCl_2)_2\{\mu\text{-diphos}\}]$ (**4**: M = Rh, diphos = dppm,; **12a**: M = Ir, diphos = dppm; **12b**: M = Ir, diphos = dppb) gave a Cl-bridged rhodium complex $[\{Cp^*Rh(\mu\text{-Cl})\}_2\{\mu\text{-dppm}\}](PF_6)_2$ (**5**), mono-carbonyl or dicarbonyl iridium complexes,$[(Cp^*IrCl_2)\{\mu\text{-dppm}\}\{Cp^*IrCl(CO)\}](PF_6)$(**13a**) or $[\{Cp^*IrCl(CO)\}_2\{\mu\text{-dppb}\}](PF_6)_2$ (**14b**), respectively.

Keywords: Rhodium complex; Iridium complex; Ruthenium complex; Alkenyl ketone complex; Alkyne; C–C triple bond-cleavage

1. Introduction

In metal-assisted organic syntheses the five-membered unsaturated γ-lactones are biologically important synthetic targets [1,2]. For example, the α,β-butenolide ring is present in a large number of biologically important natural products and certain butenolides indicate antitumor, antifungal and antibacterial activities. Carmona and his coworkers have reported that dimeric butenolides were generated by sequential insertion of phenylacetylene and carbon monoxide into nickel-acyl bonds, in which alkenyl ketone complexes are precursors of the butenolides [3]. The alkenyl ketone complexes have been usually generated by two or more steps: (1) an initial formation of acyl complexes and subsequent insertion of alkynes into metal-acyl bonds, and (2) an initial preparation of the metal carbonyl complexes and the photo-induced or thermal reactions of them with acetylenes. The acyl complexes *trans*-$NiCl(COR)(PMe_3)_2$ (R = Me, CH_2SiMe_3, CH_2CMe_3, $CH_2C_6H_4$-*o*-Me) reacted with phenylacetylene to give *trans*-$NiCl(PMe_3)_2\{CPh{=}CH(COR)\}$ [3]. The insertion of unsymmetrical alkynes into the M–C bonds of molybde-

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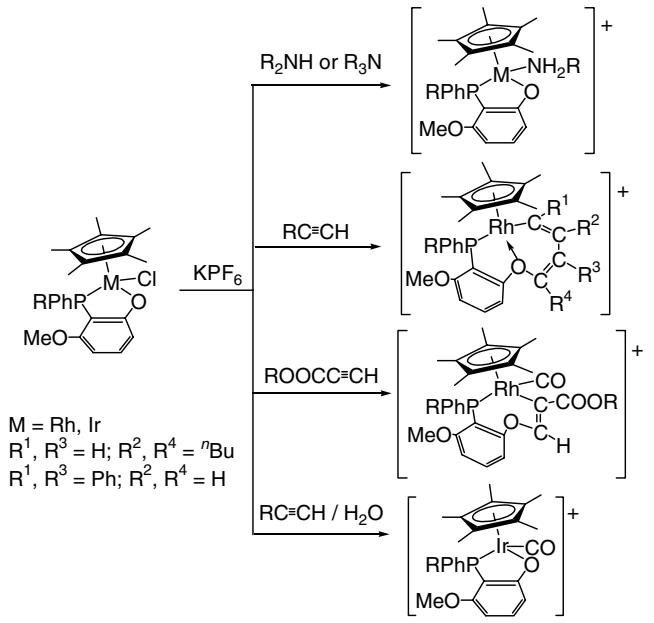
num and tungsten acyls has been reported to afford alkenyl ketone complexes [4]. The photo-induced reaction of $CpM(CO)_3R$ (M = Mo, W) with $R^1C{\equiv}CR^2$ generated alkenyl ketone complexes [4]. The formation of a dinuclear alkenyl ketone iron complex has also been reported which results from the reaction of acyl complex with η^2-alkyne intermediate complex [5].

Recently, we have provided the activation of small molecules by complexes, [Cp*MCl(MDMPP-*P*,*O*)] (M = Rh, Ir); Cp* = C_5Me_5; MDMPP-*P*,*O* = PPh_2(2-*O*-6-$MeOC_6H_3$), where one *ortho*-methoxy group in (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) was demethylated in the reactions with $[Cp^*MCl_2]_2$ (M = Rh, Ir) (Scheme 1).

For example, when they were treated with secondary or tertiary amines in the presence of KPF_6, the cleavage of the C–N bond of amines occurred readily, generating complexes, [Cp*M(MDMPP-*P*,*O*)(RNH_2)](PF_6) (R = Et, Pr, ^{i}Pr, etc.), bearing a corresponding primary amine [6]. They were also treated with 1-alkynes such as HC≡CCOOMe, PhC≡CH and ^{n}BuC≡CH, and disubstituted alkynes such as ROOCC≡CCOOR (R = Me, Et) in the presence of KPF_6, leading to unusual reactions; in the reaction with HC≡CCOOMe, an extraction of CO from an ester group and the insertion of another 1-alkyne into an Rh–O bond occurred, affording a seven-membered metallacycle, and reactions with HC≡CR (R = Ph, ^{n}Bu) led to the formation of complexes bearing five- and six-membered rings accompanying a double insertion of 1-alkynes into a Rh–O bond [7,8]. In a previous paper we have briefly described that the reaction of Cp*IrCl(MDMPP-*P*,*O*) with phenylacetylene and H_2O in the presence of KPF_6 led to a cleavage of the C–C triple bond, affording a carbonyl complex [Cp*Ir(MDMPP-*P*,*O*)(CO)](PF_6) [9].



Scheme 1. Activation of small molecules by [Cp*MCl(MDMPP-*P*,*O*)]. The PF_6 anions are omitted for clarity.

During our extended research on formation of carbonyl complexes, we found that simple complexes $Cp^*MCl_2(PPh_3)$ (M = Rh, Ir) led to a cleavage of the C–C triple bonds of 1-alkyne or a double insertion of alkynes in the presence of H_2O and KPF_6, affording carbonyl complexes or alkenyl ketone complexes, depending on metals. This paper reports the one-step synthesis of alkenyl ketone complexes and a facile C–C triple bond-cleavage of 1-alkyne. Part of this work has already been published [9].

2. Experimental

2.1. General procedures

All manipulations were carried out under a nitrogen atmosphere. Dichloromethane was distilled over CaH_2 and diethyl ether was distilled over $LiAlH_4$. $Cp^*RhCl_2(PPh_3)$ (**1**) [10], $Cp^*RhCl_2(PMePh_2)$ (**1e**) [10], $Cp^*IrCl_2(PPh_3)$ (**6**) [10], $(C_6Me_6)RuCl_2(PPh_3)$ (**7**) [11], [$(Cp^*MCl_2)_2$(μ-dppm)] (M = Rh (**4**), Ir (**12a**); dppm = $Ph_2PCH_2PPh_2$) [12] and [$(Cp^*IrCl_2)_2$(μ-dppb)] (**12b**) (dppb = $Ph_2P(CH_2)_4PPh_2$) [12] were prepared according to the literature methods. Other reagents employed in this research were commercially available and used without further purification. The infrared and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 instruments, respectively. The NMR spectra were recorded on a Bruker AC250 spectrometer. ^{1}H NMR spectra were measured at 250 MHz, and $^{31}P\{^1H\}$ NMR spectra were measured at 101 MHz using 85% H_3PO_4 as an external reference. All coupling constants were recorded in Hz. Fast atom bombardment (FAB) mass spectra were measured on a JMS-DX300 spectrometer. Elementary analyses were performed by Analytical Center, School of Pharmaceutical Science, Toho University.

2.2. Preparation of rhodium complexes

2.2.1. Preparation of [Cp*Rh(PPh3){CPh=CHC(O)CH2-Ph}](PF6) (2a)

To a solution of $[Cp^*RhCl_2(PPh_3)]$ (**1**) (97.6 mg, 0.171 mmol), H_2O (1.0 mL, 55 mmol) and KPF_6 (58.4 mg, 0.317 mmol) in CH_2Cl_2 (10 mL) and acetone (15 mL), phenylacetylene (0.2 mL, 1.8 mmol) was added at room temperature. After stirring for 24 h, the solvent was removed. The residue was washed with diethyl ether and recrystallized from CH_2Cl_2 and diethyl ether, giving a reddish brown complex (80.0 mg, 54.6%). FAB mass: *m*/*z* = 721 ($[M-1]^+$), 459 ($[M-PPh_3-1]^+$). IR(nujol): 1588, 1543 (C=C, C=O), 839 (PF_6) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ.19 (d, J_{HP} = 2.7 Hz, Cp*, 15H), 3.16 and 3.42 (AB system, J_{HH} = 16.0 Hz, CH_2, 2H) 6.73(s, =CH, 1H), 6.9–7.8 (m, Ph, 25H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.0 (d, J_{PRh} = 152 Hz), −143.7 (sep, J_{PF} = 712 Hz, PF_6). *Anal.* Calc. for $C_{44}H_{43}P_2F_6ORh$: C, 60.98; H, 5.00. Found: C, 61.03; H, 5.09%.

*2.2.2. Preparation of [Cp*Rh(PPh$_3$){C(C$_6$H$_4$-p-Me)=CHC(O)CH$_2$(C$_6$H$_4$-p-Me)}](PF$_6$) (**2b**)*

Reddish brown crystals of **2b** (41.4 mg, 42.9%) obtained from **1** (70.9 mg, 0.124 mmol), H_2O (1.0 mL, 55 mmol), *p*-tolylacetylene (0.1 mL, 0.8 mmol) and KPF_6 (46.7 mg, 0.254 mmol) according to a procedure similar to that of **2a**. FAB mass: *m/z*: 749 [M − 1$^+$]. IR(nujol): 1599, 1537 (C=O and C=C), 835 cm^{-1} (PF_6). ^{1}H NMR ($CDCl_3$): δ 1.20 (d, $J_{PH} = 2.6$ Hz, Cp*, 15H), 1.57 (s, *p*-Me, 3H), 2.34 (s, *p*-Me, 3H), 3.11, 3.29 (AB system, $J_{HH} = 16.0$ Hz, CH_2, 2H), 6.67 (s, CH, 1H), ca. 6.9–7.8 (c, ArH). ^{31}P{^{1}H} NMR($CDCl_3$): δ 38.0 (d, $J_{RhP} = 151$ Hz),−143.7 (sep. $J_{RhP} = 712$ Hz, PF_6). *Anal.* Calc. for $C_{46}H_{47}OF_6P_2Rh$: C, 61.75; H, 5.29. Found: C, 61.73; H, 5.22%.

*2.2.3. Preparation of [Cp*Rh(PPh$_3$){C(C$_6$H$_4$-p-COOMe)=CHC(O)CH$_2$(C$_6$H$_4$-p-COOMe)}](PF$_6$) (**2c**)*

Yellow crystals of **2c** (61.4 mg, 50.7%) were obtained from **1** (70.4 mg, 0.123 mmol), H_2O (1.0 mL, 55 mmol), HC≡CC$_6$H$_4$-*p*-COOMe (49.7 mg, 0.310 mmol) and KPF_6 (57.8 mg, 0.314 mmol) according to a procedure similar to that of **2a**. IR(nujol): 1717 (C=O), 1543 (C=O and C=C), 833 cm^{-1} (PF_6). ^{1}H NMR (CD_2Cl_2): δ 1.21 (d, $J_{PH} = 2.6$ Hz, Cp*), 3.25, 3.58 (AB system, $J_{HH} = 16.5$ Hz, CH_2, 2H),, 3.91 (s, Me, 3H), 3.93 (s, Me, 3H), 6.80 (s, CH, 1H), ca. 7.0–8.4 (c, ArH, 23H). ^{31}P{^{1}H} NMR(CD_2Cl_2): δ 37.2 (d, $J_{RhP} = 148$ Hz), −144.7 (sep. $J_{RhP} = 712$ Hz, PF_6). *Anal.* Calc. for $C_{48}H_{47}O_5F_6P_2Rh$: C, 58.66; H, 4.82. Found: C, 58.94; H, 4.80%.

*2.2.4. Preparation of [Cp*Rh(PPh$_3$){CC$_6$H$_4$-p-NO$_2$=CHC(O)CH$_2$(C$_6$H$_4$-p-NO$_2$)}](PF$_6$) (**2d**)*

Dark-brown crystals of **2d** (33.2 mg, 24.2%) were obtained from **1** (81.9 mg, 0.143 mmol), H_2O (1.0 mL, 55 mmol), HC≡CC$_6$H$_4$-*p*-NO$_2$ (62.5 mg, 0.425 mmol) and KPF_6 (71.0 mg, 0.386 mmol) according to a procedure similar to that of **2a**. IR(nujol): 1510 (C=O and C=C), 843 cm^{-1} (PF_6). FAB mass: *m/z* 811 ([M − 1]$^+$). ^{1}H NMR (CD_2Cl_2): δ 1.23 (d, $J_{PH} = 2.6$ Hz, Cp*), 3.28, 3.82 (AB system, $J_{HH} = 16.5$ Hz, CH_2, 2H), 6.90 (d, $J_{RhH} = 2.0$ Hz, CH, 1H), ca. 7.0–8.4 (c, ArH, 23H). ^{31}P{^{1}H} NMR(CD_2Cl_2): δ 37.1 (d, $J_{RhP} = 148$ Hz), −144.6 (sep. $J_{RhP} = 712$ Hz, PF_6). *Anal.* Calc. for $C_{44}H_{41}N_2O_5F_6P_2Rh$: C, 55.24; H, 4.32; N, 2.93. Found: C, 55.02; H, 4.33; N, 3.12%.

*2.2.5. Preparation of [Cp*Rh(PMePh$_2$)-{CPh=CHC(O)CH$_2$ Ph}](PF$_6$) (**2e**)*

Yellow crystals of **2e** (54.1 mg, 61.5%) were obtained from Cp*RhCl$_2$(PMePh$_2$) (**1e**) (55.7 mg, 0.11 mmol), phenylacetylene (0.1 mL, 0.9 mmol), H_2O (1.0 mL, 55 mmol) and KPF_6 (43.6 mg, 0.237 mmol) according to a procedure similar to that of **2a**. IR(nujol): 1545 (C=O or C=C), 839 (PF_6) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.25 (d, $J_{PH} = 2.5$ Hz, Cp*, 15H), 2.07 (d, $J_{PH} = 9.0$ Hz, Me, 3H), 3.61, 3.72 (AB system, $J_{HH} = 15.5$ Hz, CH_2, 2H), 6.65 (d, $J_{RhH} = 2.0$ Hz, CH, 1H), 6.8–8.0 (c, ArH, 19H). ^{31}P{^{1}H} NMR($CDCl_3$): δ 17.9 (d, $J_{RhP} = 148$ Hz), −143.6 (sep. $J_{RhP} = 713$ Hz, PF_6). *Anal.* Calc. for $C_{39}H_{41}OF_6P_2Rh$: C, 58.22; H, 5.14. Found: C, 58.47; H, 5.44%.

*2.2.6. Preparation of [Cp*RhCl(PPh$_3$){CNC$_6$H$_4$-C≡CH}](PF$_6$) (**3**)*

A mixture of **1** (82.7 mg, 0.145 mmol), KPF_6 (88.9 mg, 0.483 mmol), H_2O (1.0 mL, 55 mmol) and HC≡CC$_6$H$_4$-4-(NC) (52.4 mg, 0.412 mmol) in CH_2Cl_2 (10 mL) and acetone (15 mL) was stirred at room temperature. The reddish brown solution changed to yellow. After 24 h, the solvent was removed and the residue was extracted with CH_2Cl_2. The solution was concentrated to 2 mL and diethyl ether was added, affording yellow complex of **3** (96.4 mg, 82.4%). IR(nujol): 3279 (C≡CH), 2174 (N≡C), 843 (PF_6) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.62 (d, $J_{PH} = 3.5$ Hz, Cp*), 3.20 (s, CH, 1H), 6.8-8.0 (c, ArH, 19H). ^{31}P{^{1}H} NMR(CD_2Cl_2): δ 32.3 (d, $J_{RhP} = 122$ Hz), −143.7 (sep. $J_{RhP} = 713$ Hz, PF_6). *Anal.* Calc. for $C_{37}H_{35}NClF_6P_2Rh$: C, 55.00; H, 4.37; N, 1.73. Found: C, 55.19; H, 4.12; N, 1.95%.

*2.2.7. Preparation of [Cp*Rh(PPh$_3$){CPh=CHC(O)-CHDPh}](PF$_6$)*

To a solution of **1** (88.7 mg, 0.155 mmol), D_2O (1.0 mL, 56 mmol) and KPF_6 (71.6 mg, 0.389 mmol) in CH_2Cl_2 (10 mL) and acetone (10 mL), phenylacetylene (0.1 mL, 1.8 mmol) was added at room temperature. After stirring for 6 h, the solvent was removed to dryness. The residue was washed with diethyl ether and was extracted with CH_2Cl_2. Removal of the solvent and the residue was recrystallized from CH_2Cl_2 and diethyl ether, giving reddish brown complex (69.7 mg, 51.7%). IR(nujol): 1543 (C=C, C=O), 839 (PF_6) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.22 (d, $J_{HP} = 2.5$ Hz, Cp*, 15H), 3.16 (br-s, CHD, 1H), 6.78 (s, H, 1H), 6.9–7.8 (m, Ph, 20H). ^{31}P{^{1}H} NMR($CDCl_3$): δ 38.0 (d, $J_{RhP} = 153$ Hz), −143.7 (sep. $J_{PF} = 713$ Hz, PF_6).

*2.2.8. Preparation of [{Cp*Rh(μ-Cl)}$_2$ (dppm)](PF$_6$)$_2$ (**5**)*

Orange crystals of **5** (20.8 mg. 44.8%) were obtained from [(Cp*RhCl$_2$)$_2$(μ-dppm)] (**4**) (38.1 mg, 0.038 mmol), KPF_6 (32.0 mg, 0.174 mmol), phenylacetylene (0.1 mL, 0.913 mol) and H_2O (0.1 mL, 5.6 mmol) according to a procedure similar to that of **2a**. FAB mass: *m/z* 1074 ([M + PF_6]$^+$), 931 ([M]$^+$). IR (nujol): 835 (PF_6) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 1.49 (d, $J_{HP} = 3.5$ Hz, Cp*, 30H), 4.30 (t, $J_{HP} = 12.0$ Hz, CH_2, 2H), 7.4–7.7 (m, Ph, 15H). ^{31}P{^{1}H} NMR(CD_3COCD_3): δ 25.4 (d, $J_{PRh} = 147.0$ Hz), −143.3 (sep. $J_{PF} = 712$ Hz, PF_6). *Anal.* Calc. for $C_{45}H_{52}P_4Cl_2F_{12}Rh_2$: C, 44.25; H, 4.29. Found: C, 44.53; H, 4.22%.

2.3. Preparation of iridium and ruthenium complexes

*2.3.1. Preparation of [Cp*IrCl(PPh$_3$)(CO)](PF$_6$) (**8**)*

To a solution of **6** (101 mg, 0.152 mmol) and $NaPF_6$ (96.5 mg, 0.575 mmol) in CH_2Cl_2 (15 mL) and acetone

(15 mL), phenylacetylene (0.5 mL, 4.6 mmol) and H_2O (0.5 mL, 28 mmol) were added at room temperature. After 20 h, the solvent was removed to dryness and the residue was extracted with CH_2Cl_2. The solvent was removed and the residue was recrystallized from CH_2Cl_2 and diethyl ether, affording yellow crystals of **8** (88.0 mg, 72.3%). FAB mass: *m/z* 653 ($[M]^+$), 625 ($[M - CO]^+$), 363 ($[M - CO - PPh_3]^+$). IR(nujol): 2049 (C≡O), 841 (PF_6) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.74 (d, $J_{HP} = 2.5$ Hz, Cp*, 15H), 7.3–7.8 (m, Ph, 15H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 1.51 (s, PPh_3), −144.1 (sep. $J_{PF} = 712$ Hz, PF_6). *Anal.* Calc. for $C_{29}H_{30}OClF_6P_2Ir$: C, 43.64; H, 3.79. Found: C, 43.77; H, 3.81%.

2.3.2. Preparation of [(C6Me6)RuCl(PPh3)(CO)](PF6) (9)

Yellow crystals of **9** (69.6 mg, 46.7%) were obtained from $(C_6Me_6)RuCl_2(PPh_3)$ (**7**) (121 mg, 0.20 mmol), $NaPF_6$ (146 mg, 0.87 mmol), phenylacetylene (0.3 mL, 2.7 mmol) and H_2O (1.5 mL, 83 mmol) according to a procedure similar to that of **8**. FAB mass: *m/z* 590 ($[M - 1]^+$), 562 ($[M - CO - 1]^+$). IR(nujol): 1985 (C≡O), 837 (PF_6) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 2.05 (s, C_6Me_6, 18H), 7.4–7.7 (m, Ph, 15H). $^{31}P\{^1H\}$ NMR(CD_3COCD_3): δ 42.1 (s, PPh_3), −143.3 (sep. $J_{PF} = 712$ Hz, PF_6). *Anal.* Calc. for $C_{31}H_{33}OClF_6P_2Ru$: C, 50.72; H, 4.53. Found: C, 50.29; H, 4.53%.

2.3.3. Preparation of [{Cp*IrCl(CO)}{Cp*IrCl2}-(dppm)](PF6) (13a)

Yellow crystals of **13a** (26.8 mg, 47.3%) were obtained from [$(Cp^*IrCl_2)_2$(μ-dppm)] (**12a**) (51.2 mg, 0.043 mmol), KPF_6 (43.0 mg, 0.219 mmol), phenylacetylene (0.1 mL, 0.913 mmol) and H_2O (0.1 mL, 5.6 mmol) according to a procedure similar to that of **8**. FAB mass: *m/z* 1172 ($[M - 1]^+$), 775 ($[M - Cp^*IrCl_2]^+$). IR(nujol): 2046 (CO), 841 (PF_6) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.27 (d, $J_{PH} = 2.5$ Hz, Cp*, 15H), 1.68 (d, $J_{PH} = 2.5$ Hz, Cp*, 15H), 4.60 (m, CH_2, 1H), 5.11 (m, CH_2, 1H), 6.9–7.7 (m, Ph, 20H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ −1.62 (d, $J_{PP} = 52.0$ Hz), −11.2 (d, $J_{PP} = 52.0$ Hz), −144.0 (sep. $J_{PF} = 707$ Hz, PF_6). *Anal.* Calc. for $C_{46}H_{52}OCl_3F_6P_3Ir_2$: C, 40.56; H, 3.95. Found: C, 40.59; H, 3.95%.

2.3.4. Preparation of [{Cp*IrCl(CO)2}2(dppb)](PF6) (14b)

Yellow complex of **14b** (53.0%) was obtained from [$(Cp^*IrCl_2)_2$(μ-dppb)] (**12b**) (50.4 mg 0.041 mmol), phenylacetylene (0.1 mL, 0.913 mmol), H_2O (0.1 mL, 55 mmol) and KPF_6 (43.0 mg, 0.219 mmol) according to a procedure similar to that of **8**. The recrystallization was carried out from CH_2Cl_2, methanol and diethyl ether. FAB mass: *m/z* 1353 ($[M + PF_6]^+$). IR(nujol): 2052 (CO), 835 (PF_6) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.29 (br, CH_2, 4H), 1.67 (d, $J_{PH} = 2.5$ Hz, Cp*, 30H), 2.55 (m, CH_2, 4H), 2.65 (m, CH_2, 4H), 7.4–7.7 (m, Ph, 20H). $^{31}P\{^1H\}$ NMR(CD_2Cl_2): δ −1.92 (s), −144.1 (sep. $J_{PF} = 707$ Hz, PF_6). *Anal.* Calc. for $C_{50}H_{58}O_2Cl_2F_{12}P_4Ir_2$: C, 38.05; H, 3.78. Found: C, 38.06; H, 3.85%.

2.4. Reaction of 2a with HBF4

A mixture of **2a** (43.4 mg, 0.05 mmol) and HBF_4 (0.1 mL, 48 wt.% aq., 0.76 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature. After 12 h, the solvent was removed and the residue was extracted with CH_2Cl_2. The solution was concentrated and diethyl ether was added, recovering orange crystals of **2a** (13.9 mg, 32.0%). The work-up of the mother liquor gave a yellow solid of the BF_4 compound (15.6 mg, 38.7%). The structure was determined in comparison with the spectroscopic data of **2a**.

2.5. X-ray crystallography – data collection

All complexes were recrystallized from CH_2Cl_2/diethyl ether. Cell constants of **2b** and **2e** · Et_2O were determined from 20 reflections on a Rigaku AFC5S diffractometer. Data collections were carried out on a Rigaku AFC5S diffractometer. Intensities were measured by the $2\theta - \omega$ scan method using Mo Kα radiation ($\lambda = 0.71069$ Å) at 24°. Throughout the data collection the intensities of the three standard reflections were measured every 200 reflections as a check of the stability of the crystals and no decay was observed. Absorption corrections were made with ψ scans. Crystal of **2c** was mounted at the top of quartz fiber using perfluoro(polyoxopropylene ethylether), which was set on a MSC/ADSC Quantum CCD/Rigaku AFC8 (ultraX 18) diffractometer. The measurement was made by using Mo Kα radiation ($\lambda = 0.71069$ Å) at 0 °C under a cold nitrogen stream. Four preliminary data frames were measured at 0.5° increments of ω, in order to assess the crystal quality and preliminary unit cell parameters were calculated. The cell parameters were refined using all the reflections measured in the range $2.8° < 2\theta < 55.1°$. The intensity images were measured at 0.5° intervals of ω or a duration of 20 s. The frame data were integrated using a d*TREK program package and the data sets were corrected for absorption using a REQAB program. The crystal parameters along with data collections are summarized in Table 1.

Intensities were collected for Lorenz and polarization effects. Atomic scattering factors were taken from the usual tabulation of Cromer and Waber [13]. Anomalous dispersion effects were included in F_{calc} [14]; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [15]. All calculations were performed using the TEXSAN crystallographic software package [16].

2.6. Determination of the structure

The structures of **2b**, **2c** and **2e** · Et_2O were solved by Patterson methods (DIRDIF92 PATTY) and refined on F^2 values for **2b** and **2c**, and on F values for **2e** · Et_2O. The positions of all non-hydrogen atoms were refined with

Table 1
Crystal data for [Cp*Rh(*P*Ph$_3$){*C*(C$_6$H$_4$-*4*-Me)=CHC*O*CH$_2$(C$_6$H$_4$-*4*-Me)}](PF$_6$) **2b**, [Cp*Rh(*P*Ph$_3$){*C*(C$_6$H$_4$-*4*-CO$_2$Me)=CHC*O*CH$_2$(C$_6$H$_4$-*4*-CO$_2$Me)}](PF$_6$) **2c** and [Cp*Rh(*P*MePh$_2$) {*C*(Ph)=CHC*O*CH$_2$Ph}](PF$_6$) **2e** · Et$_2$O

Compound	**2b**	**2c**	**2e** · Et$_2$O
Formula	$C_{46}H_{47}OP_2F_6Rh$	$C_{48}H_{47}O_5P_2F_6Rh$	$C_{43}H_{51}O_2P_2F_6Rh$
Molecular weight	894.72	982.74	878.72
Crystal system	monoclinic	triclinic	monoclinic
Space group	*Pn* (No. 7)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	11.363(8)	9.530(2)	10.840(2)
b (Å)	9.32(1)	11.592(3)	20.653(5)
c (Å)	20.289(7)	20.716(4)	18.956(3)
α (°)	90.0	75.12(1)	90.0
β (°)	103.06(4)	83.834(2)	95.38(2)
γ (°)	90.0	88.685(2)	90.0
V (Å)	2093(2)	2198.8(8)	4225(1)
Z	2	2	4
D_c (g cm^{-3})	1.419	1.484	1.381
μ (Mo Kα) (cm^{-1})	5.45	5.32	5.40
Number of reflections	3690	9975	7428
(2*θ*) (°)	(50.0)	(55.1)	(50.0)
Number of data used	3676 ($I > 3.0\sigma(I)$)	5192 ($I > 3.0\sigma(I)$)	4331 ($I > 2.5\sigma(I)$)
Number of variables	476	559	487
R:R_W[a,b]	0.121; 0.180[b]	0.069; 0.081[a]	0.088; 0.175[b]
R_1 (reflections)	0.060(3285)		0.055(4331)
Goodness-of-fit (GOF)[c]	2.34	2.52	0.86

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$).

[b] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$ and $R_W = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$); $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ for $I > 2.0\sigma(I)$.

[c] GOF $= [\sum w(|F_o| - |F_c|^2)/(N_o - N_p)]^{1/2}$.

anisotropic thermal parameters by using full-matrix least-squares methods. All hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å.

3. Results and discussion

3.1. Alkenyl ketone complexes of rhodium(III)

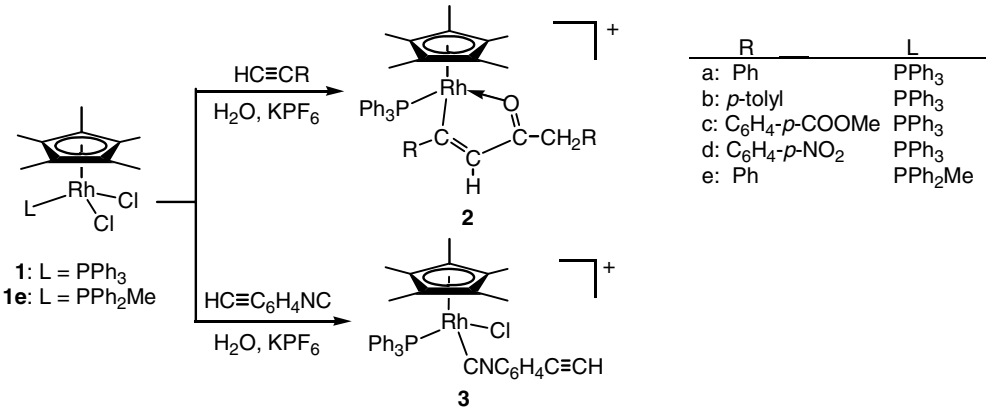
On the treatment of Cp*RhCl$_2$(PPh$_3$) (**1**) with phenylacetylene and H$_2$O in the presence of KPF$_6$ in CH$_2$Cl$_2$ and acetone at room temperature, orange crystals **2a** were obtained (Scheme 2).

Molecular peak of $m/z = 721$ in the FAB mass spectrometry and elementary analysis corresponded to the formula of [Cp*Rh(PPh$_3$)(PhC≡CH)$_2$(OH)](PF$_6$). The characteristic bands in the IR spectrum appeared at 1588 and 1547 cm^{-1} due to a conjugated double bond in addition to a PF$_6$ anion at 839 cm^{-1}. The ^{1}H NMR spectrum showed a doublet at 1.19 ppm due to Cp* protons and an AB system centered at 3.25 ppm due to methylene protons. The ^{31}P{^{1}H} NMR spectrum showed a doublet at 38.0 ppm and a septet at −143.6 ppm assignable to PPh$_3$ and PF$_6$, respectively. Instead of KPF$_6$, use of NaPF$_6$ or NH$_4$PF$_6$ also gave **2a**. Other terminal alkynes such as *p*-tolyl, *4*-methoxycarbonylphenyl or *4*-nitrophenyl acetylene also generated the corresponding alkenyl ketone complexes [Cp*Rh(PPh$_3$){*C*R=CHC*O*CH$_2$R}](PF$_6$) (**2 b**: R = C$_6$H$_4$-*p*-Me; **2c**: R = C$_6$H$_4$-*p*-COOMe; **2d**: R = C$_6$H$_4$-*p*-NO$_2$). Similar spectroscopic data were observed for the **2b**, **2c** and **2d** in the IR and ^{1}H NMR measurements. It was determined by the X-ray analyses of **2b** and **2c** that the rhodium atom is connected by triphenylphosphine, and the carbon and carbonyl-oxygen atoms of the alkenyl ketone moiety (Figs. 1, 2).

Reaction of **1** with *4*-isocyanophenylacetylene afforded yellow complex **3** formulated as [Cp*RhCl(PPh$_3$)-(CNC$_6$H$_4$C≡CH)](PF$_6$) in high yield. The IR spectrum showed characteristic bands at 3279 and 2174 cm^{-1} in addition to the presence of a PF$_6$ anion at 843 cm^{-1}. The former was assigned to an ethynyl moiety and the latter to a terminal isocyanide. This spectral data suggested the structure that a terminal carbon atom of isocyanide coordinated the Rh metal, indicating strong coordination ability of isocyanide.

Diphenylmethylphosphine complex **1e**, Cp*RhCl$_2$-(PMePh$_2$) reacted readily with phenylacetylene and H$_2$O in the presence of KPF$_6$ to afford the alkenyl ketone complex **2e** in 61.5% yield, in which the structure was confirmed by X-ray analysis (Fig. 3). A similar reaction with a binuclear dppm complex, [{Cp*RhCl$_2$}$_2$(μ-dppm)] (**4**), generated a Cl-bridged complex [{Cp*Rh(μ-Cl)}$_2$(μ-dppm)](PF$_6$)$_2$(**5**) without forming the corresponding alkenyl ketone complex (Scheme 3).

In some attempts to substitute the coordinated carbonyl-oxygen of alkenyl ketone or the coordinated triphenylphosphine of **2a**, the reactions with xylyl isocyanide, P(OMe)$_3$ or P(*p*-tolyl)$_3$ were carried out and recovered the starting complex of 80–91%. Complex **2a** was treated



Scheme 2. Reactions of $Cp^*RhCl_2(PPh_3)$ with 1-alkynes and H_2O in the presence of KPF_6. The PF_6 anions are omitted for clarity.

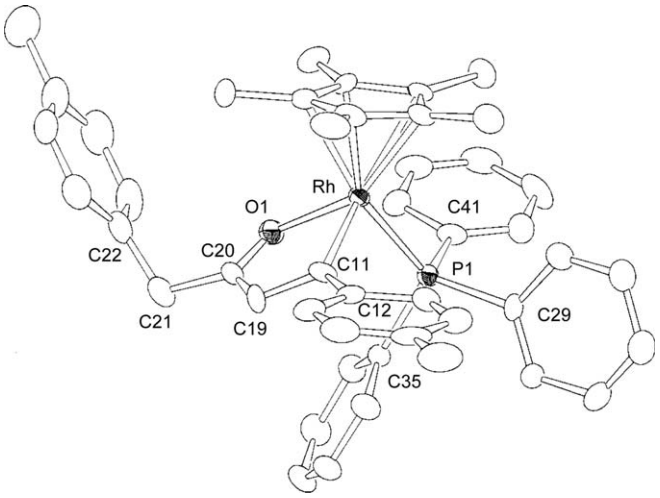


Fig. 1. ORTEP drawings for the complex cation of **2b**; the PF_6 anion and hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

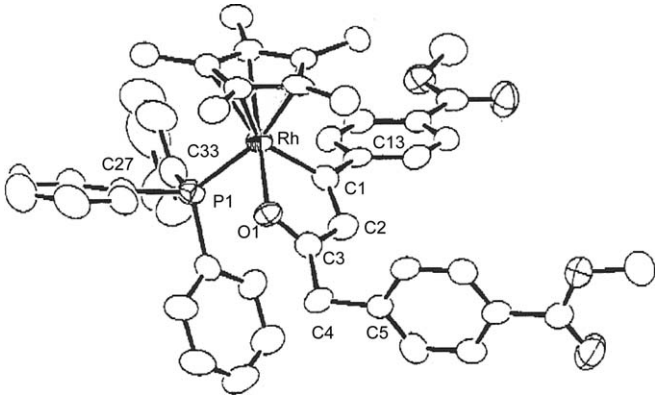


Fig. 2. ORTEP drawings for the complex cation of **2c**; the PF_6 anion and hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

with HBF_4 at room temperature, generating $[Cp^*Rh(PPh_3)\{CPh{=}CHCOCH_2Ph\}](BF_4)$ by occurrence of an anion-exchange. These reactions showed a high stability of the five-membered ring structure and of the Rh–P bond.

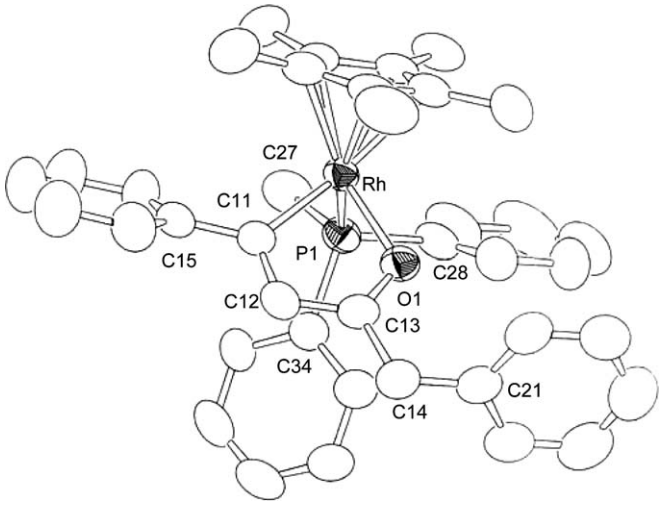
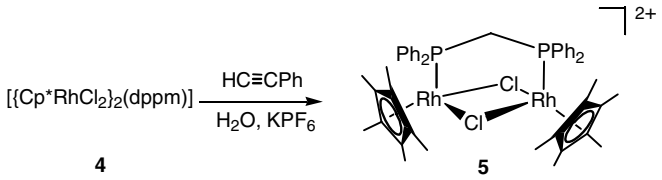


Fig. 3. ORTEP drawings for the complex cation of **2e**; the PF_6 anion, Et_2O and hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.



Scheme 3. Reactions of $[\{Cp^*RhCl_2\}_2(dppm)]$ with phenylacetylene and H_2O in the presence of KPF_6. The PF_6 anions are omitted for clarity.

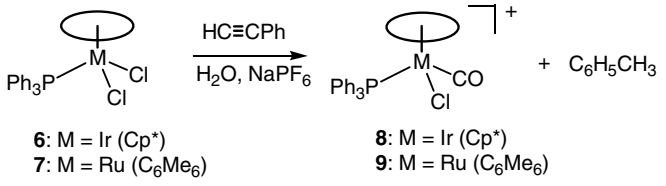
3.2. The C–C triple bond-cleavage by iridium and ruthenium complexes

In some attempts to investigate whether the aforementioned reaction can be applicable for similar type of other metal complexes, isoelectronic complexes such as $Cp^*IrCl_2(PPh_3)$ (**6**) and $(C_6Me_6)RuCl_2(PPh_3)$ (**7**) were used. When **6** was treated with phenylacetylene, H_2O and KPF_6 (or $NaPF_6$), carbonyl complex **8** formulated as $[Cp^*IrCl(PPh_3)(CO)](PF_6)$ from FAB mass spectrometry

and elemental analysis, was obtained in 72.3% yield as a yellow solid (Scheme 4).

The IR spectrum showed a band at 2049 cm^{-1} due to a terminal carbonyl group together with a band at 841 cm^{-1} due to a PF_6 anion. Similar reaction also occurred in ruthenium complex **7**, giving the corresponding carbonyl complex $[(C_6Me_6)RuCl(PPh_3)(CO)](PF_6)$ (**9**), whereas $CpRuCl(PPh_3)_2$ afforded a vinylidene complex $[CpRu(=C=CHPh)(PPh_3)_2](PF_6)$ [17]. An origin of the oxygen atom of carbonyl ligand had been confirmed to be responsible for water. Thus, the reaction of Cp*IrCl(MDMPP-*P*,*O*) with phenylacetylene was carried out in the presence of H_2 ^{18}O and gave [Cp*Ir(MDMPP-*P*,*O*)($C^{18}O$)](PF_6) in high yield [9]. The carbonyl stretching frequency shifted from 2051 to 2004 cm^{-1} in the IR spectrum. This shift was in good agreement with the calculated value. In these reactions, saturated hydrocarbon with one less carbon atom derived from cleavage of the C–C triple bond of the terminal alkyne was detected by gas chromatogram and ^1H NMR spectrum. For example, toluene was detected in case of the reaction of iridium complex **6** with phenylacetylene, H_2O and KPF_6.

Reactions of binuclear iridium diphosphine complexes $[(Cp^*IrCl_2)_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$ (**12**) (**a**: $n = 1$; **b**: $n = 4$) under similar condition were carried out (Scheme 5). The dppm complex **12a** gave yellow crystals formulated as $[\{Cp^*IrCl(CO)\}(Cp^*IrCl_2)(\mu\text{-dppm})](PF_6)$ (**13a**) from FAB mass spectrometry. The IR spectrum showed a strong band at 2046 cm^{-1}. The ^1H NMR spectrum showed two doublets at 1.27 and 1.68 ppm consisting of a 1:1 ratio for Cp* protons. The $^{31}P\{^1H\}$ NMR spectrum indicated two doublets at −1.62 and −11.2 ppm with the coupling constant $^2J_{PP} = 52.0$ Hz in addition to a resonance at −144.0 ppm due to the PF_6 anions. These ^1H and ^{31}P NMR data indicate the unsymmetrical structure of **13a**. In order to prepare a dicarbonyl complex of dppm, a further reaction of **13a** with phenyl acetylene and H_2O was carried out in the presence of KPF_6, and **13a** was recovered quantitatively. No isolation of the dicarbonyl complex of dppm is considered to result in electronic demand rather than steric one, because carbonyl complex has been isolated for the triphenylphosphine complex. The dppb complex **12b** afforded a pale yellow compound **14b**. The IR spectrum of **14b** showed a CO stretching band at 2052 cm^{-1}. In the FAB mass spectrometry, the highest value is *m*/*z* 1353, corresponding to the fragment of $[\{Cp^*IrCl(CO)\}_2(\mu\text{-dppb}) + PF_6]^+$. The Cp* protons appeared at 1.67 ppm as a doublet in the ^1H NMR spectrum and the P nuclei of dppb appeared at −1.92 ppm as a singlet in the $^{31}P\{^1H\}$ NMR spectrum. These data suggested that **14b** is a symmetrical dicarbonyl complex $[\{Cp^*IrCl(CO)\}_2(\mu\text{-dppb})](PF_6)_2$.

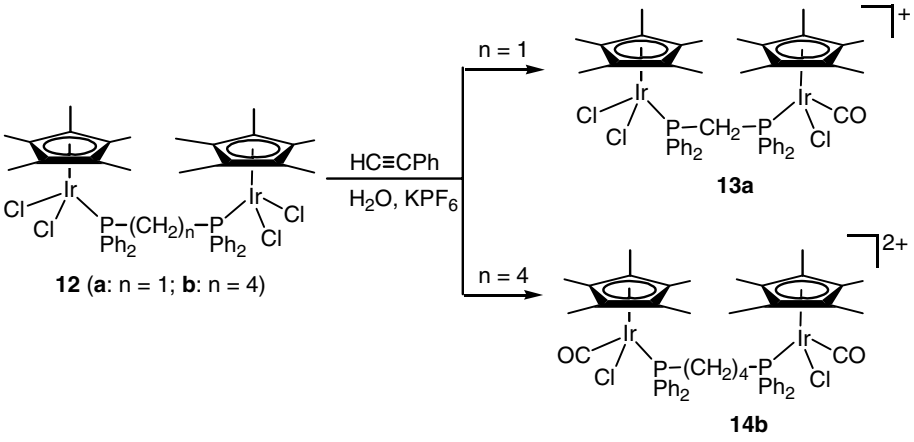


Scheme 4. Reactions of $Cp^*IrCl_2(PPh_3)$ or $(C_6Me_6)RuCl_2(PPh_3)$ with phenylacetylene and H_2O in the presence of $NaPF_6$. The PF_6 anions are omitted for clarity.

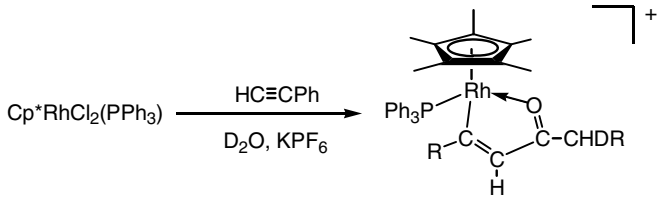
3.3. Reaction pathway

In order to examine an origin of methylene protons in the alkenyl ketone complexes, the reaction of **1** with phenylacetylene and D_2O took place in the presence of KPF_6. In the ^1H NMR spectrum, the methylene protons appeared at 3.16 ppm as a broad signal, suggesting that one of the methylene protons was incorporated from water (Scheme 6).

The reaction consists of an initial formation of a vinylidene complex and a subsequent addition of H_2O to produce a hydroxybenzyl carbene (Scheme 7). This process was confirmed by the fact that in a separate experiment, the tube reaction of a vinylidene complex $[Cp^*RhCl(PPh_3)\{=C=CHPh\}](PF_6)$ with phenylacetylene in the presence of H_2O gave **2a**. The next process proceeds with



Scheme 5. Reactions of $[\{Cp^*IrCl_2\}(diphos)]$ with phenylacetylene and H_2O in the presence of KPF_6. The PF_6 anions are omitted for clarity.



Scheme 6. Reactions of $Cp^*RhCl_2(PPh_3)$ with phenylacetylene and D_2O in the presence of KPF_6. The PF_6 anions are omitted for clarity.

the insertion of another alkyne into the acyl-Rh intermediate derived from the elimination of an H^+ ion, followed by an intramolecular coordination of the acyl oxygen atom to the Rh metal. The acyl intermediate was assumed from the fact that transformation of a hydroxycarbene complex to an acyl one has been cited in several instances [18]. An insertion of 1-alkyne into an acyl complex has also been documented [4].

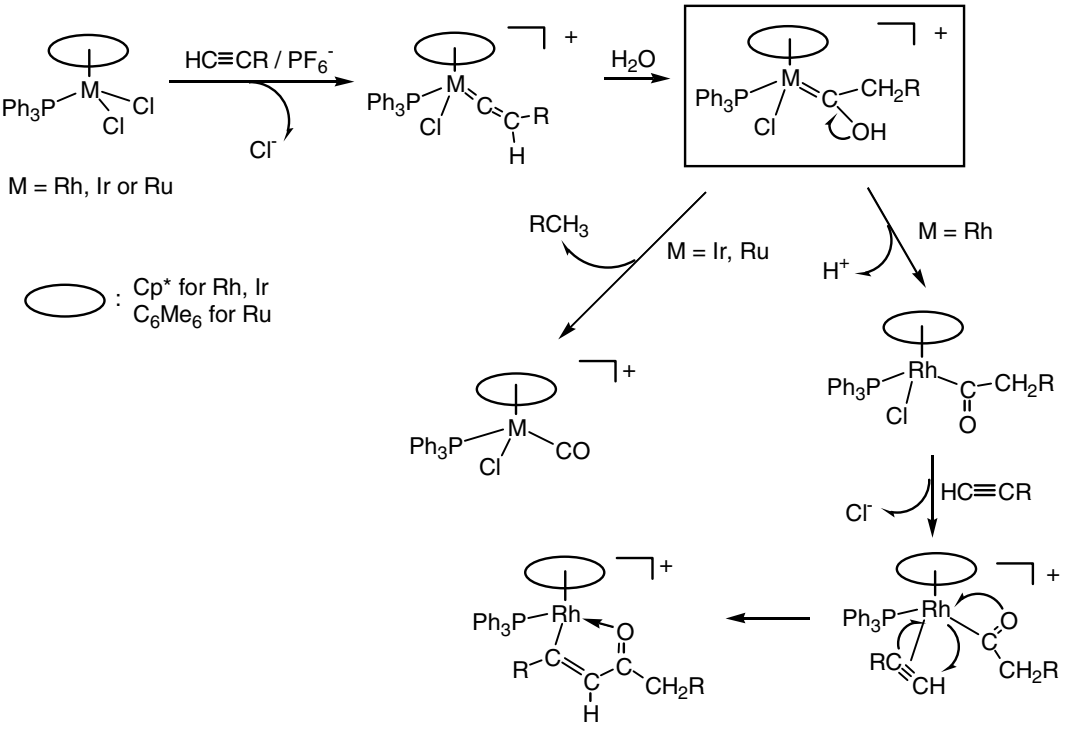
In the iridium and ruthenium complexes the C–C bond-cleavage from the hydroxycarbene complex occurred to form the carbonyl complex and toluene derivative. The toluene derivative was detected by ^1H NMR and GC analysis. The oxygen atom of the carbonyl ligand was confirmed to be generated from water by the separate experiment using $H_2\,{}^{18}O$ as mentioned above.

It is a well-known reaction that the binary combination of the 1-alkynes and water by iron-group metal complexes lead to the cleavage of the C–C triple bond with formation of CO and saturated hydrocarbon with one less carbon atom [19]. Recently platinum- and iridium-assisted cleavage of the C–C triple bond by water has been documented [20].

3.4. Molecular structures

Crystal structures of ***2b***, ***2c*** and ***2e***: Perspective drawings of **2b**, **2c** and **2e** with the atomic numbering scheme are given in Figs. 1–3 and selected bond lengths and angles are listed in Tables 2–4.

The molecules have the piano-stool structures. The rhodium atom is surrounded by tertiary phosphine and a five-membered ring derived from coordination of the carbon and carbonyl-oxygen atoms of the alkenyl ketone moiety. The average C–Rh–O bite angle and P–Rh–C bond angle are 79.1° and 93.1°, respectively. The P–Rh–O angles are



Scheme 7. Possible pathway for the formation of the alkenyl ketone and carbonyl complexes. The PF_6 anions are omitted for clarity.

Table 2
Selected bond lengths and angles for $[Cp^*Rh(PPh_3)\{C(C_6H_4\text{-}4\text{-}Me)=CHCOCH_2(C_6H_4\text{-}4\text{-}Me)\}](PF_6)$ (**2b**)

Rh(1)–P(1)	2.339(3)	Rh(1)–O(1)	2.102(8)	Rh(1)–C(11)	2.01(1)
C(11)–C(19)	1.42(2)	C(19)–C(20)	1.39(2)	O(1)–C(20)	1.26(1)
P(1)–Rh(1)–C(11)	93.5(4)	O(1)–Rh(1)–C(11)	80.4(4)	P(1)–Rh(1)–O(1)	86.4(2)
Rh(1)–C(11)–C(19)	110.7(8)	C(11)–C(19)–C(20)	116(1)	Rh(1)–O(1)–C(20)	111.6(8)
O(1)–C(20)–C(19)	119(1)	O(1)–C(20)–C(21)	115(1)		

Table 3
Selected bond lengths and angles for [Cp*Rh(PPh$_3$){C(C$_6$H$_4$-*4*-COOMe)=CHCOCH$_2$(C$_6$H$_4$−4-COOMe)}](PF$_6$) (**2c**)

Rh(1)–P(1)	2.355(2)	Rh(1)–O(1)	2.113(5)	Rh(1)–C(1)	2.016(6)
O(1)–C(3)	1.251(9)	C(1)–C(2)	1.37(1)	C(2)–C(3)	1.43(1)
P(1)–Rh(1)–C(1)	93.3(2)	O(1)–Rh(1)–C(1)	79.0(3)	P(1)–Rh(1)–O(1)	85.0(1)
Rh(1)–C(1)–C(2)	113.5(6)	C(1)–C(2)–C(3)	115.4(7)	Rh(1)–O(1)–C(3)	113.0(5)
O(1)–C(3)–C(2)	119.0(7)	O(1)–C(3)–C(4)	119.4(7)		

Table 4
Selected bond lengths and angles for [Cp*Rh(PPh$_2$Me){C(Ph)=CHCOCH$_2$Ph}](PF$_6$) (**2e**)

Rh(1)–P(1)	2.314(2)	Rh(1)–O(1)	2.091(4)	Rh(1)–C(11)	2.027(6)
O(1)–C(13)	1.274(7)	C(11)–C(12)	1.370(9)	C(12)–C(13)	1.399(9)
P(1)–Rh(1)–C(11)	92.6(2)	O(1)–Rh(1)–C(11)	78.6(2)	P(1)–Rh(1)–O(1)	89.0(1)
Rh(1)–C(11)–C(12)	113.5(5)	C(11)–C(12)–C(13)	115.8(5)	Rh(1)–O(1)–C(13)	113.5(4)
O(1)–C(13)–C(12)	118.6(5)	O(1)–C(13)–C(14)	116.9(6)		

89.0(1)°, 86.4(2)° and 85.0(1)° for **2e**, **2b** and **2c**, respectively. This trend was traced back to a decrease of the Rh–P bond lengths: 2.313(2), 2.339(3) and 2.355(2) Å for **2e**, **2b** and **2c**, respectively, resulting in release of steric interaction of tertiary phosphine ligand. The C–O and C–C double bond lengths are 1.26 and 1.38 Å, respectively, not significantly different from the corresponding usual values.

The Rh–O coordinated bond lengths are in the range from 2.091 to 2.113 Å, longer than those (2.050–2.08 Å) found in the Rh–O σ-bond lengths of the neutral or ionic complexes such as Cp*RhCl(MDMPP-*P*,*O*) [21], Cp*RhCl(BDMPP-*P*,*O*) [8] and [Cp*Rh(BDMPP-*P*,*O*)(CO)](PF$_6$) (BDMPP-*P*,*O* = PPh{C$_6$H$_3$-2,6-(MeO)$_2$}(C$_6$H$_3$-2-*O*-6-MeO)) [21]. This trend results in the difference of the bonding modes.

4. Conclusion

This paper provides difference on reactivity between rhodium and iridium complexes. Thus it reports a convenient one-pot synthesis of alkenyl ketone complexes from simple pentamethylcyclopentadienyl rhodium(III) complex, 1-alkyne and H_2O in the presence of KPF_6. In iridium(III) and ruthenium(II) complexes, a C–C triple bond-cleavage of the 1-alkyne occurred readily, generating carbonyl complex and saturated hydrocarbon with one less carbon atom. Since double insertion of 1-alkyne into the Rh–O bonds has been documented [7,8], rhodium complexes may be expected as the precursors for metal-assisted multiple insertion of 1-alkynes. The C–C triple bond-cleavage reactions have been well-known in ruthenium complexes [19]. Iridium complexes may be candidates for a catalyst of the C–C multiple bond-cleavage. There is no evidence to explain the different reactivities between rhodium and iridium complexes, but tendency for the C–C triple bond-cleavage assisted by the rhodium complexes is more effective than that by the iridium complexes. The similar trend has been observed in the reactions of the P,O-chelate complexes with 1-alkyne as shown in Scheme 1.

5. Supplementary material

CCDC numbers: 163783 for **2b**, 211504 for **2c** and 211505 for **2e**. Copies of this information can be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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