One-step synthesis of alkenyl ketone complexes from Cp*RhCl₂(PPh₃), alkyne and H₂O in the presence of KPF₆

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The reaction of Cp*RhCl₂(PPh₃) 1 with 1-alkyne and H₂O in the presence of KPF₆ afforded the alkenyl ketone complex [Cp*Rh(PPh₃)(CPh=CHCOCH₂R)](PF₆) [R = *p*-tolyl (3a), R = Ph (3b)], whereas Cp*IrCl₂(PPh₃) 2 or [(η^{6} -C₆Me₆)-RuCl₂(PPh₃) gave the corresponding [Cp*IrCl-(CO)(PPh₃)](PF₆) 5a and [(η^{6} -C₆Me₆)RuCl-(CO)(PPh₃)](PF₆).

In metal-assisted organic syntheses the five-membered unsaturated γ -lactones are biologically important synthetic targets.¹ For example, the α,β -butenolide ring is present in a large number of biologically important natural products and certain butenolides exhibit antitumor, antifugal, and antibacterial activities. Carmona *et al.* 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 butenolides.² The alkenyl ketone complexes have been usually generated by two or more steps: (1) an initial synthesis of acyl complexes and subsequent insertion of alkynes into metal–acyl bonds,³ and (2) an initial preparation of the metal carbonyl complexes and the photoinduced or thermal reactions of them with acetylenes.^{2,4}

During our research on the reactions of pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with 1-alkynes, we found that treatment of Cp*RhCl₂(PPh₃) **1** (Cp* = C₅Me₅) with 1-alkyne and water in the presence of KPF₆ led to the direct formation of alkenyl ketone complexes, whereas a similar reaction of Cp*IrCl₂(PPh₃) **2** cleaves a C–C triple bond of the alkyne to give [Cp*IrCl(PPh₃)(CO)](PF₆) and saturated hydrocarbon with one less carbon atom. In this article we report the novel one-step synthesis of alkenyl ketone complexes arising from two molecules of 1-alkyne and water.

When 1 was treated with a mixture of tolylacetylene and H₂O in the presence of KPF₆ in CH₂Cl₂ and acetone at rt, orange crystals formulated as [Cp*Rh(PPh3)(C(p-tolyl)=CHCOCH2(ptolyl)](PF₆) **3a** (*p*-tolyl = 4-MeC₆H₄) from elementary analysis and FAB mass spectrometry were generated (Scheme 1).† The IR spectrum showed the presence of a PF₆ anion at ca. 840 cm⁻¹. The ¹H NMR spectra showed a doublet at δ 1.20 due to Cp* protons, two singlets at δ 1.57 and 2.34 due to *p*-methyl protons, and an AB system with a center at δ 3.2 due to methylene protons. The ³¹P{¹H} NMR spectrum showed a doublet at δ 38.0 and a septet at δ -143.7. X-Ray analysis revealed that the rhodium atom was connected by triphenylphosphine, and the carbon and oxygen atoms of the alkenyl ketone moiety (Fig. 1).[‡] The O(1)-Rh-C(11) bite angle is $80.4(4)^\circ$. The Rh–C(11) and Rh–O(1) bond lengths are 2.01(1)and 2.102(8) Å, respectively. The C(11)–C(19) and C(20)–O(1) bond lengths are 1.42(2) and 1.26(1) Å, respectively, compared with those found for the C-C and C-O double bond lengths. Complex 3b, [Cp*Rh(PPh₃)(CPh=CHCOCH₂Ph)](PF₆) having a similar structure was obtained in the reaction with phenylacetylene.[†] Diphenylphosphine complex Cp*RhCl₂(PPh₂Me) also gave [Cp*Rh(PPh₂Me)(CPh=CHCOCH₂Ph)](PF₆) 4b.[†]



Scheme 1 Reactions of $[Cp^*MCl_2(L))]$ (M = Ir, Rh; L = PPh₃, PPh₂Me) or $[(p\text{-cymene})RuCl_2(PPh_3)]$ with 1-alkyne and H₂O in the presence of KPF₆. The PF₆ anion was omitted for clarity.

The reaction consists of initial formation of a vinylidene complex and subsequent addition of H_2O to produce a hydroxybenzyl carbene (Scheme 2). This process was confirmed by the facts that an incorporation of a deuterium atom into the benzylic group occurred in the presence of D_2O to give $[Cp*Rh(PPh_3)(CPh=CHCOCDHPh)](PF_6)$ and the reaction of $[Cp*RhCl(PPh_3){=C=CHPh}](PF_6)$ with phenylacetylene in the presence of H_2O gave **3b**. The next process proceeds with the insertion of another 1-alkyne into the Rh–acyl intermediate derived from the elimination of HCl, followed by an intramolecular coordination of the acyl oxygen to the Rh. The acyl intermediate was assumed from the fact that formation of an acyl as the product of the protonation of alkynyl complexes has been found in several instances and takes place by the reaction



Fig. 1 Molecular structure of complex cation of $[Cp*Rh(PPh_3){C(p-tolyl)=CHCOCH_2(p-tolyl)}](PF_6)$ 3a. Selected bond lengths (Å) and angles (°): Rh–P(1) 2.339(3), Rh–O(1) 2.102(8), Rh–C(11) 2.01(1), O(1)–C(20) 1.26(1), C(11)–C(19) 1.42(2); P(1)–Rh–O(1) 86.4(2), P(1)–Rh–C(11) 93.5(4), O(1)–Rh–C(11) 80.4(5), Rh–C(11)–C(19) 110.7(8), C(11)–C(19)–C(20) 116(1), O(1)–C(20)–C(19) 119(1).

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Scheme 2 Possible pathway for the formation of alkenyl ketone complexes. The PF₆ anion was omitted for clarity.

of a highly reactive vinylidene intermediate with traces of water.⁵ Formation of the acyl complex of ruthenium has been reported by Bianchini et al.⁶ In the iridium complex the C-C bond cleavage from the hydroxycarbene complex occurred to form the carbonyl complex and toluene. It was confirmed by the following separate experiment that the oxygen atom of the carbonyl ligand was generated from water; the reaction of $Cp*Ir(MDMPP-P,O)Cl_2$ with ¹⁸OH₂ in the presence of KPF₆ gave $[Cp*Ir(MDMPP-P,O)(C^{18}O)](PF_6)$ (MDMPP-P,O $PPh_2(C_6H_3-2-MeO-6-O))$.⁷ The metal-assisted cleavage of the C-C triple bond with formation of the carbonyl complex and the saturated hydrocarbon with one less carbon atom has been known in ruthenium, platinum or iridium complexes.^{6,8}

The present reactions provide a convenient one-pot synthesis of alkenyl ketone complexes from metal halide bearing pentamethylcyclopentadienyl group, alkynes and water. We are currently investigating application of the reaction to the synthesis of lactone and vinylketone using a catalytic amount of a rhodium complex.

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Notes and references

† Satisfactory analytical data were obtained for new complexes: Preparation of 3b: A solution of 1 (97.6 mg, 0.171 mmol), phenylacetylene (0.2 mL, 18 mmol) and H₂O (1.5 mL, 83 mmol) in CH₂Cl₂ (10 mL) and acetone (15 mL) was stirred at rt. After 24 h, the solvent was removed, and the residue was extracted with CH2Cl2. The CH2Cl2 was concentrated, and diethyl ether was added to give reddish brown crystals of 3b (80.0 mg, 54.6%). IR (Nujol): 1588, 1547 (C=O and C=C), 839 cm⁻¹ (PF₆); UV (CH₂Cl₂): λ_{rr} \approx 302 nm. $\delta_{\rm H}$ (CDCl₃): 1.19 (d, $J_{\rm PH}$ = 2.7 Hz, Cp*, 15H), 3.16 and 3.32

(AB system, J = 16.0 Hz, CH₂, 2H), 6.73 (s, CH, 1H), ca. 6.9–7.8 (c, ArH, 25H). ³¹P{¹H}NMR (CDCl₃) δ 38.0 (d, J_{Rh-P} = 152 Hz), -143.7 (sep. $J_{\text{Rh-P}} = 710 \text{ Hz}, \text{PF}$). FAB MS (m/z of cation part (M)): found: 721 (M⁺ – 1).

3a (reddish brown, 42.9%): IR (Nujol) 1599, 1537 (C=O and C=C), 835 cm⁻¹ (PF₆). UV (CH₂Cl₂) $\lambda_{mas} \approx 298$ nm. $\delta_{\rm H}$ (CDCl₃) 1.20 (d, $J_{P-\rm H} = 2.6$ Hz, Cp*, 15H), 1.57 (s, *p*-Me 3H), 2.34 (s, *p*-Me, 3H), 3.11 and 3.29 (AB type system, J = 16.5 Hz, 2H), 6.67 (s, CH, 1H), ca. 6.9–7.8 (c, ArH, 23H). ${}^{31}P{}^{1}H{}NMR (CDCl_3) \delta 38.0 (d, J_{Rh-P} = 151 Hz), -143.7 (sep. J_{P-F} = 151 Hz)$ 712 Hz, PF). FAB MS (*m.z* of cation part, M) found 749 (M⁺ - 1).

4b (yellow, 61.5%): IR (Nujol) 1545 (C=O and C=C), 839 cm⁻¹ (PF₆). UV (CH₂Cl₂) $\lambda_{\text{max}} \approx 268(\text{sh}), 400(\text{sh}) \text{ nm. } \delta_{\text{H}} \text{ (CDCl}_3) 1.25 \text{ (d, } J_{\text{P-H}} = 2.7$ Hz, Cp*, 15H), 2.07 (d, J_{P-H} = 9.2 Hz, Me 3H), 3.61 and 3.72 (AB type system, J = 15.5 Hz, 2H), 6.65 (d, $J_{P-H} = 2.2$ Hz, 1H), ca. 6.8–7.9 (c, ArH, 20H). ³¹P{¹H}NMR (CDCl₃) δ 17.9 (d, J_{Rh-P} = 148 Hz), -143.7 (sep. J_{P-F} = 712 Hz, PF). Anal. Found: C 58.47, H 5.44%. Calcd. for $C_{39}H_{41}OF_6P_2Rh$: C 58.22, H 5.14%.

 $\ddagger Crystal data$ for 3a: M = monoclinic, space group Pn (No. 7), Z = 2, a = 11.363(8), b = 9.32(1), c = 20.289(7) Å, $\beta = 103.06(4)^\circ$, U = 2093(2)Å³. The structure was solved by Patterson methods and refined by fullmatrix least-squares techniques for all unique reflections (3676) to R =0.121 and $Rw = 0.180 [w = 1/\sigma^2(Fo^2)]$ and R1 = 0.060 (for 3285) reflections ($I > 2.0\sigma(I)$)), GOF = 2.34. CCDC 163783. See http:// www.rsc.org/suppdata/cc/b1/b108953f/ for crystallographic files in .cif format

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