COMMUNICATION

ChemComm
www.rsc.org/chemcomm

One-step synthesis of alkenyl ketone complexes from Cp*RhCl$_2$(PPh$_3$), alkyne and H$_2$O in the presence of KPF$_6$

Kenichi Ogata,[a] Katsuaki Kuge,[b] Kazuyuki Tatsumi[b] and Yasuhiro Yamamoto*[a]

[a] *Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan. E-mail: yamamoto@chem.sci.toho-u.ac.jp; Fax: (+81)47-475-1855*

[b] *Research Center for Materials Science and Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 454-8602, Japan*

Received (in Cambridge, UK) 2nd October 2001, Accepted 21st November 2001
First published as an Advance Article on the web 9th January 2002

The reaction of Cp*RhCl$_2$(PPh$_3$) 1 with 1-alkyne and H$_2$O in the presence of KPF$_6$ afforded the alkenyl ketone complex [Cp*Rh(PPh$_3$)(CPh=CHCOCH$_2$R)](PF$_6$) [R = *p*-tolyl (3a), R = Ph (3b)], whereas Cp*IrCl$_2$(PPh$_3$) 2 or [(η^6-C$_6$Me$_6$)-RuCl$_2$(PPh$_3$) gave the corresponding [Cp*IrCl-(CO)(PPh$_3$)](PF$_6$) 5a and [(η^6-C$_6$Me$_6$)RuCl-(CO)(PPh$_3$)](PF$_6$).

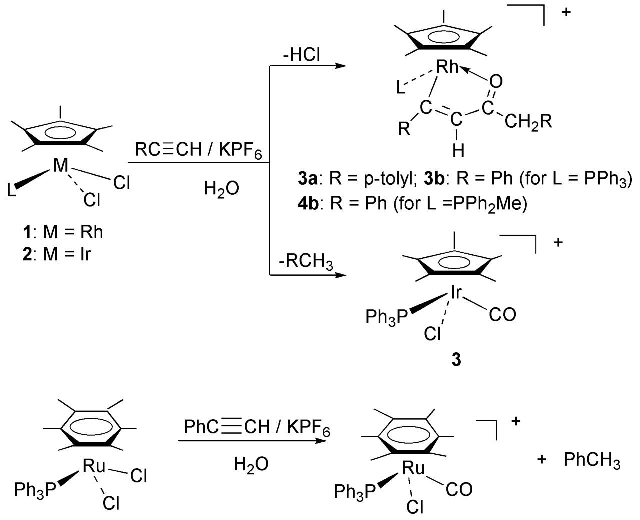
In metal-assisted organic syntheses the five-membered unsaturated γ-lactones are biologically important synthetic targets.[1] For example, the α,β-butenolide ring is present in a large number of biologically important natural products and certain butenolides exhibit antitumor, antifugal, and antibacterial 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 photo-induced 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*RhCl$_2$(PPh$_3$) **1** (Cp* = C$_5$Me$_5$) with 1-alkyne and water in the presence of KPF$_6$ led to the direct formation of alkenyl ketone complexes, whereas a similar reaction of Cp*IrCl$_2$(PPh$_3$) **2** cleaves a C–C triple bond of the alkyne to give [Cp*IrCl(PPh$_3$)(CO)](PF$_6$) 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 H$_2$O in the presence of KPF$_6$ in CH$_2$Cl$_2$ and acetone at rt, orange crystals formulated as [Cp*Rh(PPh$_3$)(C(*p*-tolyl)=CHCOCH$_2$(*p*-tolyl)](PF$_6$) **3a** (*p*-tolyl = 4-MeC$_6$H$_4$) from elementary analysis and FAB mass spectrometry were generated (Scheme 1).† The IR spectrum showed the presence of a PF$_6$ anion at *ca.* 840 cm^{-1}. The ^{1}H 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 ^{31}P{^{1}H} 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)°. 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(PPh$_3$)(CPh=CHCOCH$_2$Ph)](PF$_6$) having a similar structure was obtained in the reaction with phenylacetylene.† Diphenylphosphine complex Cp*RhCl$_2$(PPh$_2$Me) also gave [Cp*Rh(PPh$_2$Me)(CPh=CHCOCH$_2$Ph)](PF$_6$) **4b**.†

When **2** or (η^6-C$_6$Me$_6$)RuCl$_2$(PPh$_3$) were treated under similar conditions, [Cp*IrCl(CO)(PPh$_3$)](PF$_6$) **5a** or (η^6-C$_6$Me$_6$)RuCl(CO)(PPh$_3$)](PF$_6$), and toluene were generated.

DOI: 10.1039/b108953f



Scheme 1 Reactions of [Cp*MCl$_2$(L))] (M = Ir, Rh; L = PPh$_3$, PPh$_2$Me) or [(*p*-cymene)RuCl$_2$(PPh$_3$)] with 1-alkyne and H$_2$O in the presence of KPF$_6$. The PF$_6$ anion was omitted for clarity.

The reaction consists of initial formation of a vinylidene complex and subsequent addition of H$_2$O 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$_2$O to give [Cp*Rh(PPh$_3$)(*C*Ph=CHC*O*CDHPh)](PF$_6$) and the reaction of [Cp*RhCl(PPh$_3$){=C=CHPh}](PF$_6$) with phenylacetylene in the presence of H$_2$O 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

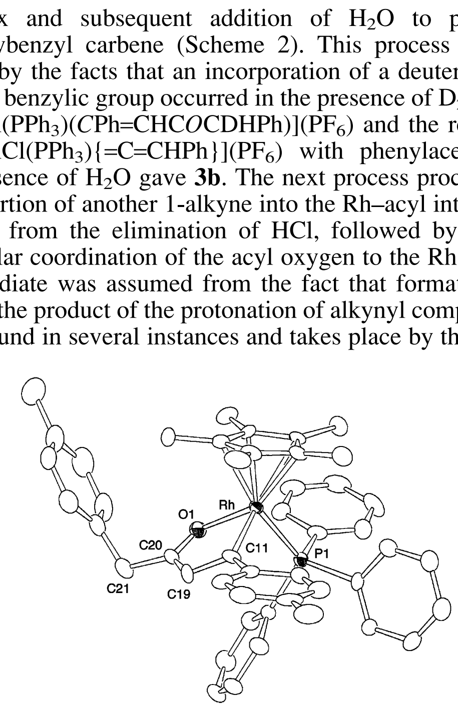
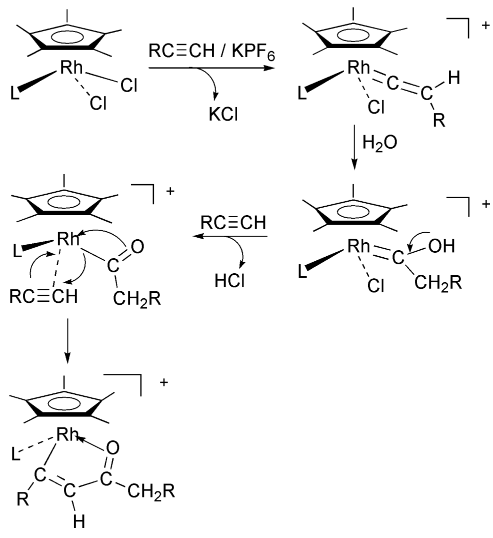


Fig. 1 Molecular structure of complex cation of [Cp*Rh(PPh$_3$){C(*p*-tolyl)=CHCOCH$_2$(*p*-tolyl)}](PF$_6$) **3a**. Selected bond lengths (Å) and angles (°): Rh–P(1) 2.339(3), Rh–O(1) 2.102(8), Rh–C(11) 2.01(1), O(1)–C(20) 1.26(1), C(11)–C(19) 1.42(2); P(1)–Rh–O(1) 86.4(2), P(1)–Rh–C(11) 93.5(4), O(1)–Rh–C(11) 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).



Scheme 2 Possible pathway for the formation of alkenyl ketone complexes. The PF_6 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 $^{18}OH_2$ in the presence of KPF_6 gave [Cp*Ir(MDMPP-*P,O*)($C^{18}O$)](PF_6) (MDMPP-*P,O* = *P*Ph_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.

We thank Professor Shigetoshi Takahashi and Dr Fumie Takei for measurements of FAB mass spectroscopy. This work was partially supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

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 H_2O (1.5 mL, 83 mmol) in CH_2Cl_2 (10 mL) and acetone (15 mL) was stirred at rt. After 24 h, the solvent was removed, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 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} (PF_6); UV (CH_2Cl_2): λ_{max} ≈ 302 nm. δ_H ($CDCl_3$): 1.19 (d, J_{PH} = 2.7 Hz, Cp*, 15H), 3.16 and 3.32 (AB system, J = 16.0 Hz, CH_2, 2H), 6.73 (s, CH, 1H), *ca.* 6.9–7.8 (c, ArH, 25H). $^{31}P\{^1H\}$NMR ($CDCl_3$) δ 38.0 (d, J_{Rh-P} = 152 Hz), −143.7 (sep. J_{Rh-P} = 710 Hz, 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} (PF_6). UV (CH_2Cl_2) λ_{mas} ≈ 298 nm. δ_H ($CDCl_3$) 1.20 (d, J_{P-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). $^{31}P\{^1H\}$NMR ($CDCl_3$) δ 38.0 (d, J_{Rh-P} = 151 Hz), −143.7 (sep. J_{P-F} = 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} (PF_6). UV (CH_2Cl_2) λ_{max} ≈ 268(sh), 400(sh) nm. δ_H ($CDCl_3$) 1.25 (d, J_{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). $^{31}P\{^1H\}$NMR ($CDCl_3$) 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%.

‡ *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, $\beta = 103.06(4)°$, $U = 2093(2)$ Å^3. The structure was solved by Patterson methods and refined by full-matrix 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.

1 M. Ryang, Y. Sawa, S. N. Somasundaram, S. Murai and S. Tsutumi, *J. Organomet. Chem.*, 1972, **46**, 375; P. Deshong, D. R. Sidler, P. J. Rybcznski, G. A. Slough and A. L. Rheingold, *J. Am. Chem. Soc.*, 1988, **110**, 2575; A. B. Smith, P. A. Levenberg, P. J. Jerris, R. M. Scarborough, Jr. and P. M. Wovkulich, *J. Am. Chem. Soc.*, 1981, **103**, 1501; C. Bianchini, P. Innocenti, A. Melli and M. Sabat, *Organometallics*, 1986, **5**, 72.

2 E. Carmona, E. G. Puebla, A. Monge, J. M. Marín, M. Paneque and M. L. Poveda, *Organometallics*, 1989, **8**, 976.

3 H. G. Alt and M. E. Jansen, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 861; H. G. Alt and U. Thewalt, *J. Organomet. Chem.*, 1984, **368**, 235; H. G. Alt, *J. Organomet. Chem.*, 1985, **288**, 149; H. G. Alt, H. E. Engelhardt, U. Thewalt and J. Riede, *J. Organomet. Chem.*, 1985, **288**, 165; H. G. Alt and H. I. Hayen, *J. Organomet. Chem.*, 1986, **315**, 337; Y. Kataoka, Y. Iwato, A. Shibahara, T. Yamagata and K. Tani, *Chem. Commun.*, 2000, 841.

4 D. L. Reger and D. G. Garza, *Organometallics*, 1993, **12**, 554.

5 M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197; M. I. Bruce, *Chem. Rev.*, 1998, **98**, 2797; C. Bruneau and P. H. Dixneuf, *Acc. Chem. Res.*, 1999, **32**, 311; F. A. Hill, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, UK, 1995, vol. 7, p. 351; C. Menéndez, D. Morales, J. Pérez, V. Fiera and D. Miguel, *Organometallics*, 2001, **20**, 2775.

6 C. Bianchini, J. A. Casares, M. Peruzzini, A. Romerosa and F. Zanobini, *J. Am. Chem. Soc.*, 1996, **118**, 4585; W. Knaup and H. Werner, *J. Organomet. Chem.*, 1991, **411**, 471.

7 K. Sugawara and Y. Yamamoto, unpublished results.

8 M. I. Bruce and A. G. Swincer, *Aust. J. Chem.*, 1980, **33**, 1471; O. M. Abu Sala and M. I. Bruce, *J. Chem. Soc., Dalton Trans.*, 1974, 2302; B. P. Sullivan, R. S. Smythe, E. M. Kober and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4701; C. Mountassir, T. B. Hadada and H. Le Bozec, *J. Organomet. Chem.*, 1990, **388**, C13; M. I. Bruce, *Pure Appl. Chem.*, 1986, **58**, 553; S. Davies, J. P. McNally and A. J. Smallridge, *Adv. Organomet. Chem.*, 1990, **30**, 30; C. Bianchini, M. A. Peruzzini, F. Zanobini, C. E. Lopez, I. de los Rios and A. Romerosa, *J. Chem. Soc., Chem. Commun.*, 1999, 443; U. Belluco, R. Bertani, F. Meneghetti, R. A. Michelin and M. Mozzon, *J. Organomet. Chem.*, 1999, **583**, 131.