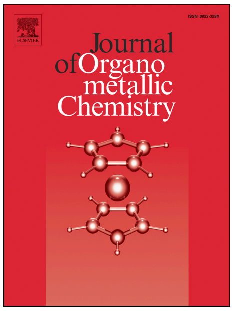


Isolation of ruthenium formyl complexes: Insight into the metal-mediated cleavage reaction of carbon-carbon triple bond

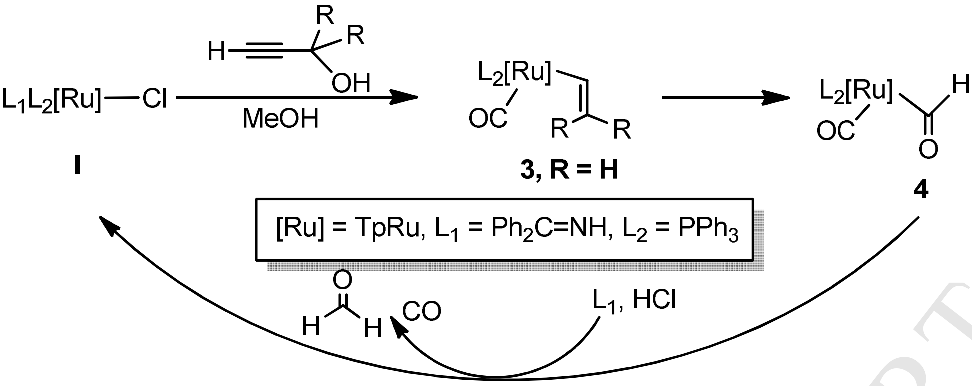
Yih-Hsing Lo, Ming-Che Li, Li-Yu Huang, Guan-Jie Hung

PII: S0022-328X(16)30566-6
DOI: 10.1016/j.jorganchem.2016.12.014
Reference: JOM 19737

To appear in: *Journal of Organometallic Chemistry*

Received Date: 5 August 2016
Revised Date: 19 November 2016
Accepted Date: 13 December 2016

Please cite this article as: Y.-H. Lo, M.-C. Li, L.-Y. Huang, G.-J. Hung, Isolation of ruthenium formyl complexes: Insight into the metal-mediated cleavage reaction of carbon-carbon triple bond, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2016.12.014.


H
R
R
OH
MeOH
L1L2[Ru]—Cl
I
L2[Ru]
OC
R
R
3, R = H
L2[Ru]
OC
H
O
4
[Ru] = TpRu, L1 = Ph2C=NH, L2 = PPh3
O
H
H
CO
L1, HCl

Isolation of Ruthenium Formyl Complexes: Insight into the Metal-mediated Cleavage Reaction of Carbon-Carbon Triple Bond

Yih-Hsing Lo*, Ming-Che Li, Li-Yu Huang and Guan-Jie Hung

Department of Applied Physics and Chemistry, University of Taipei, Taipei 10048, Taiwan, Republic of China. Corresponding author: E-Mail: yhlo@utaipei.edu.tw; Tel.: +886-2-2311-3040 Ext. 3111; Fax: +886-2-2389-7641

Abstract

We describe a simple and efficient ruthenium-catalyzed reaction in which propargylic alcohol $HC\equiv C\text{-}C(Ph)_2OH$ is split into carbon monoxide CO, formaldehyde $H_2C{=}O$ and ketone $(Ph)_2C{=}O$ *via* cleavage of carbon-carbon triple and single bonds. A plausible reaction mechanism is proposed on the basis of ruthenium vinyl and formyl intermediates.

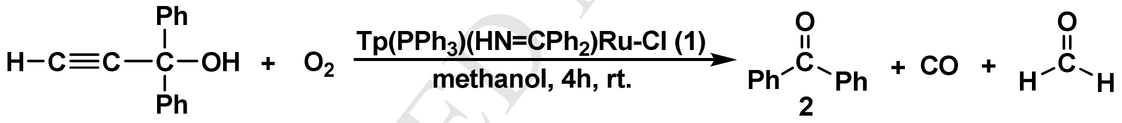
Keywords: Tris(pyrazolyl)borato; Ruthenium; Propargylic alcohol; Vinyl; Formyl

Introduction

Metal-catalyzed cleavage reactions of carbon-carbon bonds have been recognized as fascinating topics in organic reaction [1]. Recently, various unusual and helpful catalytic processes involving C-C and C=C bonds cleavage have been investigated [2]. What has remained unexplored is the cleavage of C≡C bond, which is a difficult target in organic chemistry [3]. Most previous studies on cleavage of C≡C bond have focused on stoichiometric organometallic reactions, such as alkyne-ligand scission on metal complexes [4], water-assisted splitting of alkyne into alkane and coordinated CO [5], as well as oxidative cleavage of alkynes to carboxylic acids [6]. Except for metathesis of alkynes, there have been very few reported examples for the metal-catalyzed organic alkyne cleavage reactions [7-13]. Because of the importance of carbon-carbon bond cleavage, we explored to identify a new pathway for the cleavage of alkyne. Recently, we report the novel one-step synthesis of alkenyl ketone complexes from $TpPPh_3(HN{=}CPh_2)RuCl$ (1, Tp = $HB(pz)_3$, pz = pyrazolyl) by incorporation of two H-C≡C-Ph and one H_2O molecule, through combination of insertion and hydration process [14]. Following a preliminary account of this work, we now disclose the results of detailed catalytic and structural investigations on the reaction of $H{-}C{\equiv}C{-}CPh_2OH$ with **1**. This reaction is mechanistically interesting because the mechanism is proposed to involve cleavage of C≡C and C-C bonds *via* ruthenium vinyl and formyl intermediates.

Results and Discussion

We first examined the effect of solvents and catalysts on catalytic reaction. Treatment of the 1,1-diphenylpropargyl alcohol with **1** (5.0 mol %) in MeOH at room temperature for 4 h gave benzophenone (**2**) in 83% yield (Scheme 1). Intriguingly, a small sharp peak of free formaldehyde at δ 9.61 was observable in ^{1}H NMR spectrum. GC-analysis of gaseous mixture of the reaction solution in a sealed tube showed the presence of carbon monoxide and formaldehyde. Ketone **2** was obtained in 25% yield in the absence of water. Under similar conditions, other solvents were less effective than methanol and gave 0-26% yields of **2**. MeCN showed a low activity to give 26% yield of **2**. The cationic complex [TpPPh$_3$(CH$_3$CN)$_2$Ru]Cl [15] could be isolated. In solvent with weaker coordinative ability, such as acetone or tetrahydrofuran (THF), the reaction also afforded **2** (12% yield), but the ruthenium portion decomposed. In chlorinated solvents, such as CH$_2$Cl$_2$ or CHCl$_3$, the reaction afforded a large amount of OPPh$_3$. No reaction was observed in H$_2$O, even under drastic, vigorous condition. Under the same conditions, Tp(PPh$_3$)$_2$RuCl [16] and other catalysts including TpPPh$_3$(MeCN)RuCl [15] and TpPPh$_3$(PhCN)RuCl [17] failed to give significant amounts of **2** but rather gave uncharacterized black tar.



Scheme 1 Reaction of the 1,1-diphenylpropargyl alcohol with **1** (5.0 mol %) in MeOH

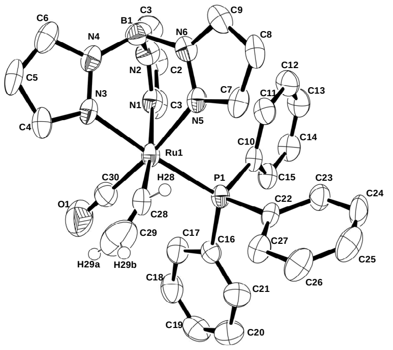


Fig. 1 The ORTEP drawing of **3** showing thermal ellipsoids at the 50% probability level. All hydrogen atoms, except H(28), H(29a) and H(29b), are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-N(1) 2.190(4), Ru(1)-N(3) 2.120(3), Ru(1)-N(5) 2.167(3), Ru(1)-C(28) 2.009(5), Ru(1)-C(30) 1.868(6), (28)-C(29) 1.148(6), C(30)-O(1) 1.069(5); Ru(1)-C(30)-O(1) 172.1(6), Ru(1)-C(28)-C(29) 142.6(5).

However, in the course of reaction no intermediate could be detected by NMR spectroscopy, but only the reaction product **2**. Fortunately, complex **1** was allowed to react with propargyl alcohol in methanol at 0 ^{0}C for 4h, isolated the ruthenium vinyl complex Tp(OC)(PPh_3)Ru-C(H)=CH_2 (**3**) (78% yield) and the ruthenium formyl complex Tp(OC)(PPh_3)Ru-C(O)H (**4**) (6% yield) after silica gel column separation using a CH_2Cl_2 eluent. When the reaction proceeded using 10 equiv of H_2O, the yield of **3** was increased (86% yield) in contrast to that of **4** (3% yield). The spectroscopic data were sufficient to unequivocally assign the structure of **3**. The IR spectrum of **3** in KBr contains very strong bands at 1951 cm^{-1} and a medium intensity absorption at 1587 cm^{-1}, which are assigned to ν(C≡O) and ν(C=C), respectively. With the help of 2D-NMR experiments, the signals of the three protons of the vinyl group are located in the ^{1}H NMR spectrum as two multiplets at δ 5.20-5.27 and 5.83-5.86. The ^{31}P{^{1}H} NMR spectrum displays a singlet at δ 50.6. An ORTEP view of complex **3** is shown in Figure 1. The coordination geometry around ruthenium in **3** can be viewed as a distorted octahedron with Tp, PPh_3, carbonyl (CO) and vinyl (HC=CH_2) ligands. The C(29)–C(28)–Ru(1) angle, 142.6(5)°, is surprisingly large for an sp^2-hybridized C atom

The complex **4** has been characterized by spectroscopic and elemental analysis. The IR spectrum contains two strong bands at 1952 cm^{-1} and 1609 cm^{-1}, corresponding to the characteristic stretching frequency of C≡O and C=O groups, respectively. In the ^{13}C{^{1}H} NMR spectrum, a strongly deshielded resonance as a doublet at δ 263.7 with J_{PC} = 16.3 Hz is assigned to formyl group and a doublet at δ 206.3 with J_{Cp} = 15.3 Hz is assigned to carbonyl group. The ^{1}H NMR spectrum shows a broad resonance centered at δ 9.61 assignable to C(O)*H* group. The ^{31}P{^{1}H} NMR spectrum displays a singlet resonance at δ 41.8. The X-ray analysis of the single crystals of **4** (Fig. 2) revealed the molecular structure of the complex with *cis*-orientation of the

Ru-CO and Ru-C(O)H moieties. Stable formyl complexes have been described for several group VIII and group IX late transition metals [18]. Hydride nucleophilic addition on coordinated carbon monoxide can lead to transition-metal formyl complexes [19], which have been proposed as intermediates in the Fischer-Tropsch reaction [20]. To the best of our knowledge, this is the first example that the ruthenium complex with alkynol yields a thermally stable and pure formyl product.

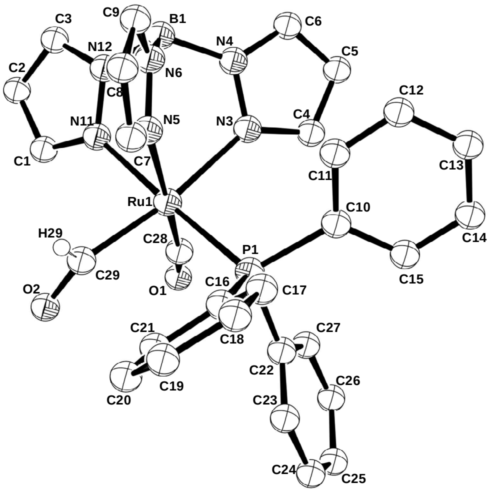
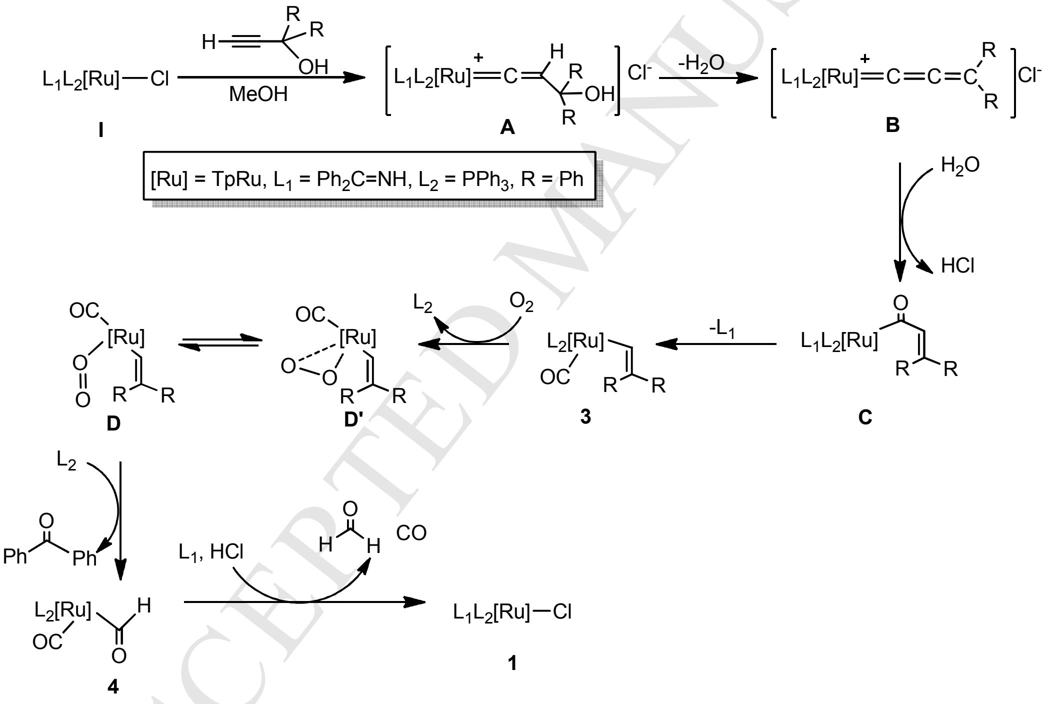


Fig. 2 The ORTEP drawing of **4** showing thermal ellipsoids at the 50% probability level. All hydrogen atoms, except C(28)–H, are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-N(1) 2.127(6), Ru(1)-N(3) 2.190(7), Ru(1)-N(5) 2.175(7), Ru(1)-C(28) 1.877(11), Ru(1)-C(29) 2.005(10), (29)-O(2) 1.230(14), C(28)-O(1) 1.083(12); O(1)-C(28)-Ru(1) 171.9(10), O(2)-C(29)-Ru(1) 140.8(10).

Interestingly, isolated complex **3** in methanol for 2 h gave rise to **4** and benzylphenone. To find the source of the oxygen atom, we carried out the reaction by adding $H_2{}^{18}O$ into a carefully dehydrated solvent in air. The mass spectrum of $Tp(OC)(PPh_3)Ru\text{-}C(O)H$, thus obtained, displayed the parent peak at m/z = 634.1, indicating no incorporation of ^{18}O. The oxygen atom was not from CH_3OH in the reaction because the reaction of **3** in dehydrated CH_2Cl_2 under nitrogen also gave formyl product **4**. Thus, the oxygen atom in formyl product was confirmed to come from oxygen in air, not from water or MeOH. Bubbling oxygen into the reaction could appreciably enhance the reaction rate. Therefore, along with the fact that a small amount of $OPPh_3$ was isolated from the reaction, dissociation of the phosphine ligand is considered to be a key step, possibly creating a vacant site for the coordination of an oxygen molecule. The reaction of **3** with oxygen in the presence of radical trap 2,2,6,6 tetramethylpiperidine-1-oxyl (TEMPO) and in MeOH in air nevertheless afforded **4**; this experiment suggested that the reaction does not proceed through a radical process.



Scheme 2 A plausible reaction mechanism is proposed on the basis of ruthenium vinyl and formyl intermediates.

We propose a plausible mechanism (Scheme 2) that involves the formation of cationic ruthenium allenylidene species **B** *via* dehydration of the γ-OH group of cationic ruthenium vinylidene complex **A**.[24] Subsequent nucleophilic attack of a water molecule onto its α-carbon gives ruthenium-acyl species **C** derived from the elimination of HCl, followed by formation of **3** fron decarbonylation of species **C**. The oxygenation may proceed initially through dissociation of PPh_3, providing a vacant site. Then O_2 is activated, possibly either by an end-on coordination to the metal center to form **D** or by a side-on coordition mode generating **D**' [21]. Nevertheless, **D'** may be a more stable form [22], so that **D** is more reactive. Thereafter, coupling of oxo and vinyl ligands, assisted by incoming PPh_3, could yield **4** and benzophenone. Finally, reductive elimination regenerated active ruthenium catalyst **1** in addition to ketone and carbon monoxide. The preceding proposed mechanism involves cleavage of the carbon-carbon triple and single bonds of the propargylic alcohol. This reaction process is in sharp contrast to the ruthenium catalyzed transformation of ethynyl alcohol into alkene and carbon monoxide [12].

Concluding Remarks. In summary, we report the new ruthenium-catalyzed transformation of 1,1-diphenylpropargyl alcohol into benzylphenone, carbon monoxide and formaldehyde. A plausible mechanism is proposed on the basis of ruthenium vinyl and formyl intermediates. The development of new catalytic processes based on this principle is under investigation.

Experimental Procedures

General Procedure. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagents grade and were used without further purification. NMR spectra were recorded on a Bruker AC-300 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P), 267.45 MHz (^{11}B) or 75.4 MHz (^{13}C) using $SiMe_4$, $BF_3{\bullet}Et_2O$ or 85% H_3PO_4 as standard or on an Avance 500 FT-NMR spectrometer. FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at National Taiwan Normal University.

Procedure for Catalytic Reactions. In a 25 mL Schlenk tube equipped with a Teflon stopcock, the ruthenium catalyst Tp(PPh$_3$)(NH=CPh$_2$)Ru-Cl (**1**, 5 mol %) in 1 mL of methanol. Excess 1,1-diphenylpropargyl alcohol (0.80 mmol) was added to the solution, and the reaction mixture was stirred at room temperature for 4 h. Then the solution was evaporated under high vacuum. The residue was extracted with Et$_2$O, and the Et$_2$O solution was chromatographed on silica gel (*n*-hexane/Et$_2$O) in air. The rotary evaporation led to the ketone products.

Reaction of complex 1 with HC≡CCPh$_2$OH. To a distilled methanol (20 mL) solution of **1** (1.00 g, 1.3 mmol) was added propargyl alcohol (1 mL, 16.8 mmol) at room temperature. The reaction mixture was stirred at ^{0}C for 4 h. Then the resulting solution was dried *in vacuo*. The residue was extracted with hexane and the residual solid was further washed with diethyl ether to give the complex {Tp(PPh$_3$)(OC)Ru-(HC=CH$_2$)} (**3**) (0.6 g, 78% yield). The hexane extract was concentrated and was then eluted with CH$_2$Cl$_2$ on a silica gel packed column to give {Tp(PPh$_3$)(OC)Ru-(HC=O)} (**4**) (0.005 g, 6% yield). Spectroscopic data for **3**: IR (KBr, cm^{-1}): ν(B-H) 2451 (br), ν(C≡O) 1951 (vs), ν(C=C) 1587 (w). ^{1}H NMR (CDCl$_3$): δ 7.86 (d, J_{H-H} = 2.0 Hz, 1H, Tp), 7.74 (d, J_{H-H} = 2.0 Hz, 1H, Tp), 7.61 (d, J_{H-H} = 2.1 Hz, 1H, Tp), 7.53 (d, J_{H-H} = 2.1 Hz, 1H, Tp), 7.24-6.90 (m, Tp, Ph), 6.31 (d, J_{H-H} = 1.9 Hz, 1H, Tp), 6.11 (t, J_{H-H} = 2.0 Hz, 1H, Tp), 6.03 (t, J_{H-H} = 2.0 Hz, 1H, Tp), 5.20-5.27, 5.83-5.86 (mx2, 3 H, C*H*=C*H$_2$*). ^{13}C NMR (CDCl$_3$): δ 206.6 (d, $J_{P–C}$ = 15.9 Hz, CO), 153.1 (br, H*C*=), 144.3 - 111.5 (m, Tp, PPh$_3$), 107.1 (=*C*H$_2$). ^{31}P NMR (CDCl$_3$): δ 50.6. MS (FAB) m/z: 632.1 (M$^+$), 605.1 (M$^+$, HC=CH$_2$), 577.1 (M$^+$, HC=CH$_2$, CO). Anal. Calcd for $C_{30}H_{28}BN_6OPRu$ (632.12): C, 57.06; H, 4.47; N, 13.31. Found: C, 57.01; H, 4.39; N, 13.12.

Spectroscopic data for **4**: IR (KBr, cm^{-1}): ν(B-H) 2449 (br), ν(C≡O) 1952 (vs), ν(C=O) 1609 (vs). ^{1}H NMR (CDCl$_3$): δ 9.81 (br, 1H, C(O)*H*), 7.81 (d, J_{H-H} = 1.9 Hz, 1H, Tp), 7.61 (d, J_{H-H} = 2.0 Hz, 1H, Tp), 7.52 (d, $J_{H\text{-}H}$ = 1.9 Hz, 1H, Tp), 7.41 -7.10 (m, Ph, Tp), 6.85 (1H, Tp), 6.71 (1H, Tp), 6.61 (1H, Tp), 6.42 (t, $J_{H\text{-}H}$ = 2.1 Hz, 1H, Tp), 5.92 (t, $J_{H\text{-}H}$ =2.1 Hz, 1H, Tp), 5.82 (t, $J_{H\text{-}H}$ =2.1 Hz, 1H, Tp). ^{13}C NMR ($CDCl_3$): δ 263.7 (d, $J_{P\text{-}C}$ = 16.3 Hz, Ru-*C*(O)H), 206.3 (d, $J_{P\text{-}C}$ = 15.3 Hz, Ru-*C*O), 146.9 -105.6 (m, Ph, PPh_3, Tp). ^{31}P NMR ($CDCl_3$): δ 41.8. MS (FAB) m/z:634.1 (M^+), 605.1 (M^+, HCO), 577.1 (M^+, HCO, PPh_3). Anal. Calcd for $C_{29}H_{26}B\ N_6O_2PRu$: C, 54.99; H, 4.14; N, 13.27. Found: C, 54.81; H, 4.09; N, 13.08.

Structure Determination of Complexes 3 and **4**. Single crystal X-ray diffraction data were measured on a Bruker SMART Apex CCD diffractometer using μ(Mo Kα) radiation (λ= 0.71073 Å). The data collection was executed using the SMART program; cell refinement and data reduction were performed with the SAINT program. The structure was determined using the SHELXTL/PC program and refined using full-matrix least-squares [23]. Crystallographic refinement parameters [24] of complexes **3** and **4** selected bond distances and angles are listed in the Supporting Information.

Acknowledgment. We gratefully acknowledge the financial support in part from the Ministry of Science and Technology, Taiwan (MOST 104-2113-M-845-001). We also thank Mr. Ting Shen Kuo (Department of Chemistry, National Taiwan Normal University, Taiwan) for his assistance in X-ray single crystal structure analysis

Supporting Information Available: Complete crystallographic data for **3** and **4** (CIF).

References

[1] B. Rybchinski and D. Milstein, Angew. Chem., Int. Ed. 38 (1999) 870.

[2] (a) T. Takemori, A. Inagaki and H. Suzuki, J. Am. Chem. Soc. 123 (2001) 1762; (b) B. R. Travis, R. S. Narayan and B. Borhan, J. Am. Chem. Soc. 124 (2002) 3824; (c) V. Kogan, M. M. Quintal and R. Neumann, R. Org. Lett. 7 (2005) 5039; (d) K. Miyamoto, N. Tada and M.

Ochiai, J. Am. Chem. Soc. 129 (2007) 2772. and references therein.

[3] P. W. Jennings and L. L. Johnson, Chem. Rev. 94 (1994) 2241.

[4] R. L. M. Chamberlin, D. C. Rosenfeld, P. T. Wolczanski and E. B. Lobkovsky, Organometallics 21 (2002) 2724.

[5] C. S. Chin, D. Chong, B. Maeng, J. Ryu, H. Kim, M. Kim and H. Lee, Organometallics 21 (2002) 1739.

[6] R. M. Moriarty, R. Penmasta, A. K. Awasthi and I. Prakash, J. Org. Chem. 53 (1998) 6124.

[7] (a) A. Furstner and C. Mathes, Org. Lett. 2001, 3, 221; (b) G. Brizius and U. H. F. Bunz, Org. Lett. 4 (2002) 2829.

[8] C.-H. Jun, H. Lee, C.-W. Moon and H.-S. Hong, J. Am. Chem. Soc. 123 (2001) 8600.

[9] T. Shimada and Y. Yamamoto, J. Am. Chem. Soc. 125 (2003) 6646.

[10] Y.-H. Liu, F.-J. Song and S.-H. Guo, J. Am. Chem. Soc. 128 (2006) 11332.

[11] A. Wang and H. Jiang, J. Am. Chem. Soc. 130 (2008) 5030.

[12] S. Datta, C.-L. Chang, K.-L. Yeh and R.-S.Liu, J. Am. Chem. Soc. 125 (2003)9294.

[13] H.-C. Shen, H.-L. Su, Y.-C. Hsueh and R.-S. Liu, Organometallics 23 (2004) 4332.

[14] C.-J. Cheng, H.-C. Tong, Y.-H. Fong, P.-Y. Wang, Y.-L. Kuo, Y.-H. Lo and C.-H. Lin, Dalton Trans., (2009) 4435.

[15] B. Buriez, I. D. Burns, A. F. Hill, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, Organometallics 18 (1999) 1504.

[16] W. Nathaniel, N. W. Alock, I. D. Burns, K. S. Claire and A. F. Hill, Inorg. Chem. 31 (1992) 2906.

[17] Y.-H. Lo, H.-G. Chen and T.-S. Kuo, Dalton Trans., 40 (2001) 2711.

[18] (a) S. Reinartz, M. Brookhart and J. L. Templeton, Organometallics 21 (2002) 247; (b) S.

Crementieri, P. Leoni, F. Marchetti, L. Marchetti and M. Pasquali, Organometallics 21 (2002) 2575.

[19] (a) W. Tam, G. Y. Lin, W. K. Wong, W. A. Kiel, V. K. Wong and J. A. Gladysz, J. Am. Chem. Soc. 104 (1982) 141; (b) J. R. Sweet, and W. A. G. Graham, J. Am. Chem. Soc. 104 (1982) 2811.

[20] For reviews of the Fischer-Tropsch reaction see: (a) H. H. Storch, N. Golumbic and R. B. Anderson, The Fischer-Tropsch and Related Synthesis; Wiley: New York, NY, 1951; (b) P. H. Ed. Emmett, Catalysis, Vol. 4; Reinhold: New York, NY, 1956.

[21] (a) V. L. Pecoraro, M. J. Baldwin and A. Gelasco, Chem. Rev. 94 (1994) 807; (b) E. A. Lewis and W. B. Tolman, Chem. Rev. 104 (2004) 1047; (c) M. Costas, M. P. Mehn, M. P. Jensen and J. Lawrence Que, Chem. Rev. 104 (2004) 939; (d) S. S. Stahl, Angew. Chem. 116 (2004) 3480; Angew. Chem. Int. Ed. 2004, 43, 3400; (e) M. Suzuki, Acc. Chem. Res. 40 (2007) 609.

[22] G. Jia, W. S. Ng, H. S. Chu, W.-T. Wong, N.-T. Yu and I. D. Williams, Organometallics 18 (1998) 3597.

[23] (a) The SADABS program is based on the method of Blessing; see: R. H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33. (b) SHELXTL: Structure Analysis Program, version 5.04; Siemens Industrial Automation Inc.: Madison, WI, 1995.

[24] GOF = $[\Sigma[w(F^2o - F^2c)^2]/(n - p)]^{1/2}$, where n and p denote the number of data and parameters. R1= $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, wR2 = $[\Sigma- [w(F_o^2 - F_c^2)_2]/å[w(Fo^2)^2]]^{1/2}$ where w = $1/[\sigma^2(F^2{}_o) + (aP)^2 + bP]$ and P = $[(max; 0, F^2{}_o) + 2Fc^2]/3$.

- W disclose the results of detailed catalytic and structural investigations on the reaction of H-C≡C-CH_2OH with $TpPPh_3(HN{=}CPh_2)RuCl$.
- A number of new ruthenium complexes have been prepared.
- A plausible reaction mechanism is proposed on the basis of ruthenium vinyl and formyl intermediates.
- Their structures are elucidated by IR, NMR and X-ray crystallography.