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## Communications

# Reaction of the *in-Situ*-Generated Ruthenium−Acetylide Complex $C_5Me_5Ru(PPh_3)C\equiv CPh$ with Small Molecules

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*Summary: A coordinatively unsaturated acetylide species $C_5Me_5Ru(PPh_3)C\equiv CPh$ (**1**) was generated in situ from the reaction of ruthenium−vinylidene complex $C_5Me_5Ru(Cl)(PPh_3)=C=CHPh$ (**2**) with $Et_3N$. The vinylidene complex **2** was prepared from the substitution reaction of $C_5Me_5Ru(PPh_3)_2Cl$ with $PhC\equiv CH$. The in-situ-generated **1** was found to react readily with a variety of small molecules. For example, the reaction of **1** with CO produced the stable adduct $C_5Me_5Ru(CO)(PPh_3)C\equiv CPh$ (**3**) in 85% yield, the structure of which was established by X-ray crystallography. The similar reactions of **1** with $H_2$ and $PhC\equiv CPh$ also gave the hydride complex $C_5Me_5Ru(PPh_3)(H)(H_2C=CHPh)$ (**4**) (76% yield) and the alkyne complex $C_5Me_5Ru(PPh_3)(PhC\equiv CPh)C\equiv CPh$ (**5**) (85% yield), respectively. The reaction of **1** with $CO_2$ produced the carboxylate complex $C_5Me_5Ru(PPh_3)(\eta^2\text{-}O_2CC\equiv CPh)$ (**6**) from the insertion of $CO_2$ to the ruthenium−acetylide carbon bond.*

Transition metal $\sigma$-acetylide complexes are known to be involved in a number of catalytic and stoichiometric reactions of alkynes.[1] The copper−acetylide catalysts have been widely employed in industrial-scale alkyne coupling reactions, such as in the production of $H_2C=CHC\equiv CH$ from the linear dimerization of acetylene[1a] and in the synthesis of butyndiol from the coupling of acetylene with formaldehyde.[1b] A well-characterized rhodium−acetylide complex has recently been shown to promote the living polymerization of phenylacetylene.[1g] Interest in the metal-coordinated $\sigma$-acetylide complexes has also grown in recent years because such complexes have emerged as key components in generating nonlinear optical, molecular conducting and liquid crystalline materials.[2] While ligand-based reactions of coordinatively *saturated* metal−acetylide complexes have been well-established,[1e,3] the reactivity of *unsaturated* metal−acetylide complexes has not been thoroughly explored. In an attempt to extend the ruthenium-mediated dimerization of terminal alkynes[4] and $CO_2$ activation reactions,[5] we have begun searching for new ways to generate unsaturated ruthenium−acetylide complexes.

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

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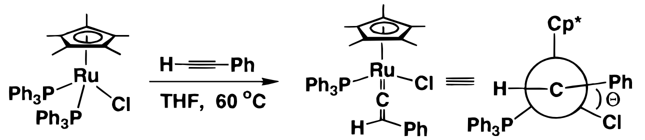
Herein, we report an *in situ* generation of a coordinatively unsaturated ruthenium acetylide species $C_5Me_5Ru(PPh_3)C{\equiv}CPh$ (**1**) and its reactions with small molecules.



**2**

Recent reports on the ruthenium−vinylidene complexes[1e,3] suggested that the coordinatively unsaturated ruthenium acetylide species **1** could be generated from the reaction of ruthenium−vinylidene complexes with a base. Following a literature procedure,[6] a chiral ruthenium−vinylidene precursor $C_5Me_5Ru(PPh_3)(Cl){=}C{=}CHPh$ (**2**) was readily prepared from the ligand substitution reaction of $C_5Me_5Ru(PPh_3)_2Cl$[7] with $PhC{\equiv}CH$ and a subsequent acetylene-to-vinylidene tautomerization reaction. Thus, treatment of $C_5Me_5Ru(PPh_3)_2Cl$ (1.0 g, 1.26 mmol) with excess $PhC{\equiv}CH$ (1.38 mL, 10 equiv) in THF at 60 °C for 12 h produced the vinylidene complex **2** (698 mg, 88% yield). The structure of **2** was completely established by both solution spectroscopic methods[8] and by single-crystal X-ray crystallography (Figure 1).[9] The X-ray crystal structure of **2** showed an antiperiplanar geometry between the $\beta$-vinylidene hydrogen and the chloride ligand, as indicated by the dihedral angle between the plane of the $\beta$-vinylidene carbon and the Ph group (C(12)−C(13)) and the plane containing the Ru and Cl atoms (Ru−Cl) ($\Theta = 20.0°$). The bond distance between Ru and the α-vinylidene carbon (Ru−C(11) = 1.817(3) Å) was typical for a ruthenium(II) complex.[1e] Recently, a crystal structure of a similar ruthenium−vinylidene complex, $TpRu(Cl)(PPh_3){=}C{=}CHPh$, has been reported.[10]

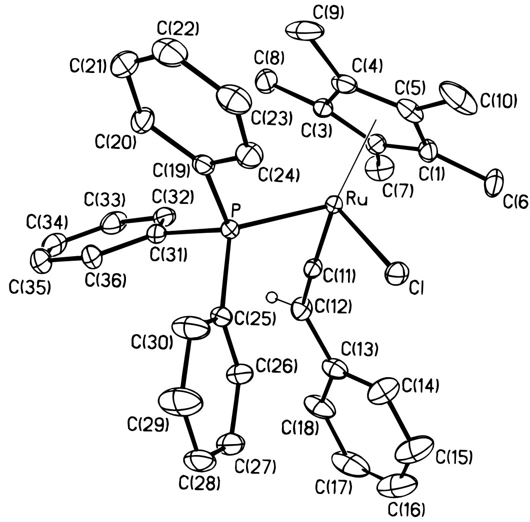


**Figure 1.** Molecular structure of **2** drawn with 30% thermal ellipsoids. Selected bond lengths (Å) and bond angles (deg): Ru−C(11), 1.817(3); C(11)−C(12), 1.315(4); Ru−Cl, 2.4018(7); Ru−P, 2.3099(7); Ru−Cp* (cent), 1.936(3); Cl−Ru−P, 89.17(3); C(11)−Ru−P, 88.03(9); Ru−C(11)−C(12), 175.3(3); C(11)−C(12)−C(13), 123.6(3).

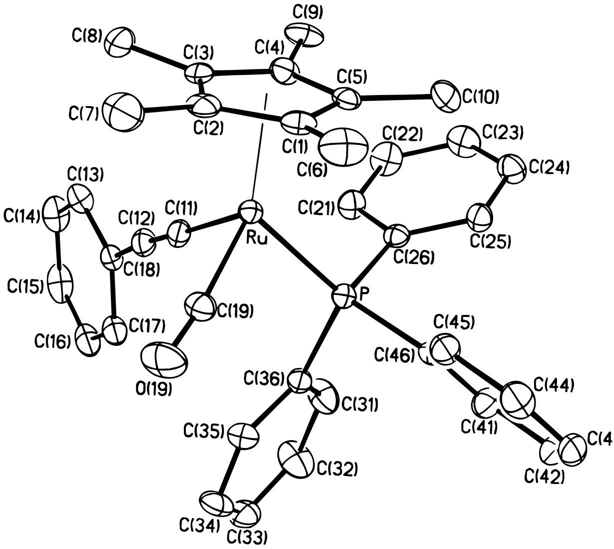


**Figure 2.** Molecular structure of **3** drawn with 30% thermal ellipsoids. Selected bond lengths (Å) and bond angles (deg): Ru−C(11), 2.030(4); C(11)−C(12), 1.203(5); Ru−C(19), 1.850(4); Ru−P, 2.3144(10); Ru−Cp* (cent), 1.902(4); C(11)−Ru−P, 82.52(10); C(11)−Ru−C(19), 93.5(2); C(11)−C(12)−C(18), 173.7(4).

The antiperiplanar geometry between the $\beta$-vinylidene proton and the chloride ligand of complex **2** is nicely set up for the elimination of HCl. The treatment of complex **2** (200 mg, 0.31 mmol) with $Et_3N$ (0.22 mL, 5 equiv) in the presence of CO (1 atm) at room temperature cleanly gave the stable acetylide complex $C_5Me_5Ru(CO)(PPh_3)C{\equiv}CPh$ (**3**) in an 85% isolated yield (Scheme 1). The structure of **3** was established by both spectroscopic methods[8] and by X-ray crystallography (Figure 2).[11] Bond lengths of the acetylide ligand (Ru−C(11) = 2.030(4) Å, C(11)−C(12) = 1.203(5) Å, and

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[3] For a recent review on Ru−acetylide complexes, see: (a) Hill, A. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1994; Vol. 7. (b) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1. Other recent selected examples: (c) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466. (d) Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293. (e) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735. (f) Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (g) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276. (h) Matsuzaka, H.; Hirayama, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. *Organometallics* **1993**, *12*, 36. (i) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804. (j) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922. (k) Weng, W.; Bartik, T.; Johnson, M. T.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1995**, *14*, 889. (l) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775. (m) Kawata, Y.; Sato, M. *Organometallics* **1997**, *16*, 1093. (n) Field, L. D.; George, A. V.; Malouf, E. Y.; Hambley, T. W.; Turner, P. *J. Chem. Soc., Chem. Commun.* **1997**, 133. (o) Whiteford, J. A.; Lu, C. V.; Stang, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 2524.

[4] Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968.

[5] Yi, C. S.; Liu, N. *Organometallics* **1995**, *14*, 2616.

[6] (a) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585. (b) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272.

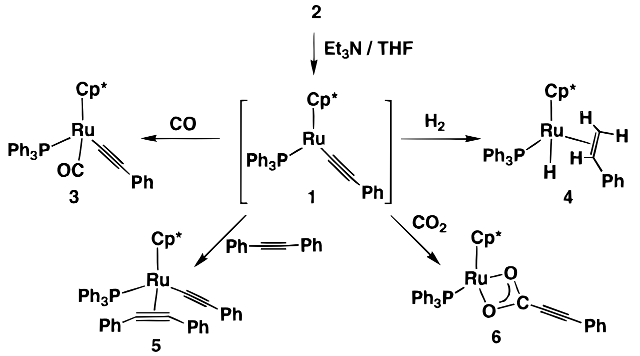
[7] (a) Serron, S. A.; Luo, L.; Li, C.; Cucullu, M. E.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1995**, *14*, 5290. (b) Luo, L.; Nolan, S. P.; Fagan, P. J. *Organometallics* **1993**, *12*, 4305. (c) Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1987**, *322*, 221.

[8] See the Supporting Information for the spectroscopic data of the complexes **2**−**6**.

[9] Crystal data for **2**: $C_{36}H_{36}ClPRu$, orthorhombic, $P2_12_12_1$, $a$ = 9.2332(2) Å, $b$ = 16.27470(10) Å, $c$ = 20.35730(10) Å, $V$ = 3059.04(7) Å$^3$, $Z$ = 4, $T$ = 222 K, $D_{calcd}$ = 1.381 g cm$^{-1}$, $R(F)$ = 2.81% for 6240 observed independent reflections (3.20° ≤ $2\theta$ ≤ 56.80°).

[10] Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.

**Scheme 1**



C(12)−C(18) = 1.446(5) Å) indicate a minimal $\pi$-delocalization between the acetylide ligand and the metal center.

The formation of **3** was consistent with the generation of an unsaturated acetylide species **1**. In an attempt to directly detect the acetylide **1** in the reaction mixture, the reaction of **2** with $Et_3N$ in THF-$d_8$ was monitored by $^1$H NMR spectroscopy. No detectable intermediates were detected with or without CO in the temperature range of 25−60 °C, and the reaction did not proceed in the absence of CO at room temperature. The relatively long reaction time (~24 h) for the formation of complex **3** suggested that the concentration of **1** was too low to be detected by NMR with the weak base $NEt_3$. The reaction of complex **2** (10 mg, 0.016 mmol) with the strong base LiOMe (6 mg, 10 equiv) in THF-$d_8$ (0.5 mL) was monitored by $^1$H NMR at room temperature. The initially red-colored solution turned to brownish-yellow after 5 h, and a set of new peaks gradually appeared at the expense of those due to **2**. The spectral data of the new species was consistent with the solvent-coordinated form of the acetylide complex **1**·THF,[12] but several attempts to isolate the complex were not successful as it decomposed during evaporation of the solvent. Treatment of this solution with CO (1 atm) led to the formation of the same adduct **3**.

The *in-situ*-generated acetylide species **1** was found to react with small molecules, such as $H_2$, PhC≡CPh, and $CO_2$, under mild reaction conditions. For example, the reaction of *in-situ*-generated **1** with $H_2$ at room temperature cleanly produced the hydride−alkene complex **4**. In a typical reaction, $H_2$ (1 atm) was transferred *via* a vacuum line to a THF solution containing complex **2** (200 mg, 0.31 mmol) and $Et_3N$ (0.44 mL, 10 equiv) and the reaction mixture was stirred at room temperature for 24 h. Analytically pure ruthenium product **4** was obtained after a recrystallization in $Et_2O$/hexanes (144 mg, 76% yield). The $^1$H NMR of **4** exhibited a single ruthenium−hydride resonance at $\delta$ −10.20 (d, $J_{PH}$ = 36.8 Hz), along with the coordinated alkene resonances.[8] The similar reaction of **1** with PhC≡CPh produced the alkyne adduct **5** in 85% yield.[8] The addition of $Et_3N$ was found to be essential in initiating these reactions since the vinylidene complex **2** alone did not produce **4** or **5** in its absence.

The addition of $CO_2$ (2−3 atm) to a $C_6D_6$ solution of *in-situ*-generated **1** at 60 °C resulted in the formation of the carboxylate complex **6**. Complex **6** was cleanly formed in a sealed NMR tube (>90%) but decomposed to uncharacterizable products upon evaporation of the solvent. The $\eta^2$-carboxylate geometry of **6** was established from the observations of a carbonyl carbon at $\delta$ 168.2 (d, $J_{PC}$ = 8.6 Hz) in the $^{13}$C NMR and two carbonyl stretching modes ($\nu_{CO_2}$ (sym) = 1452, $\nu_{CO_2}$ (asym) = 1618 cm$^{-1}$) in the IR spectrum, which are similar to the previously characterized formate complex $C_5Me_5Ru(PCy_3)(\eta^2\text{-}O_2CH)$.[5] The formation of **6** can be explained by migratory insertion of the nucleophilic acetylide ligand to a weakly coordinated carbonyl carbon of $CO_2$. The insertion of $CO_2$ to metal−carbon and −hydrogen bonds has been commonly observed in other organometallic $CO_2$ reactions.[13] The addition of $CO_2$ to a saturated metal−acetylide complex is usually known to occur at the $\beta$-acetylide carbon to produce a carboxylate-substituted vinylidene complex.[14] Related $CS_2$ insertion to a ruthenium−acetylide complex has also been documented.[3a,b]

In summary, the unsaturated ruthenium−acetylide complex **1** was cleanly generated *in situ* from the reaction of ruthenium−vinylidene complex **2** with a base. Complex **1** was shown to react with a variety of small molecules, such as CO, $H_2$, PhC≡CPh, and $CO_2$. Recent preliminary results indicate that complex **1** is an effective catalyst for the dimerization of terminal alkynes.[15] Studies directed toward the reactions of **1** with alkenes and alkynes are currently underway.

**Acknowledgment.** Financial support from Marquette University, Committee-on-Research, is gratefully acknowledged.

**Supporting Information Available:** Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and H-atom coordinates for **2** and **3** and spectroscopic data for the ruthenium complexes **2**−**6** (14 pages). Ordering information is given on any current masthead page.

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[11] Crystal data for **3**: $C_{37}H_{35}OPRu$: monoclinic, $P2_1/n$, $a$ = 8.7254(2) Å, $b$ = 17.8548(5) Å, $c$ = 19.5265(5) Å, $\beta$ = 98.9732(3)°, $V$ = 3004.81(13) Å$^3$, $Z$ = 4, $T$ = 223(2) K, $D_{calcd}$ = 1.388 g cm$^{-1}$, $R(F)$ = 4.90% for 4588 observed independent reflections (3.10° ≤ 2$\theta$ ≤ 56.54°).

[12] Selected spectroscopic data for **1**·THF: $^1$H NMR (THF-$d_8$, 300 MHz) $\delta$ 1.21 (s, $C_5Me_5$); $^{13}$C{$^1$H} NMR (THF-$d_8$, 75 MHz) $\delta$ 124.5 (d, $J_{PC}$ = 24.5 Hz, Ru−C≡), 114.5 (Ru−C≡*C*), 94.4 (*C*$_5$Me$_5$), 10.1 (C$_5$*Me*$_5$); $^{31}$P{$^1$H} NMR (THF-$d_8$, 121.6 MHz) $\delta$ 53.0 (s, PPh$_3$); IR ($C_6H_6$) $\nu_{C\equiv C}$ 2067 cm$^{-1}$.

[13] For recent reviews, see: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: New York, 1988. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988. (d) Leitner, W. *Angew. Chem. Int. Ed., Engl.* **1995**, *34*, 2207.

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[15] Yi, C. S.; Liu, N.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* in press.