Journal of Organometallic Chemistry 769 (2014) 34–37

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Halogen exchange by reaction of $CpRu(Cl)(PPh_3)_2$ with MeC(O)X (X = Br, I) and its mechanistic study

Hitoshi Kuniyasu [a, *], Atsushi Sanagawa [a], Takuya Nakajima [a], Takanori Iwasaki [a], Nobuaki Kambe [a, *], Karan Bobuatong [b, c], Masahiro Ehara [b, c, **]

[a] Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
[b] Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan
[c] Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto Daigaku-Katsura, Kyoto 615-8510, Japan

ARTICLE INFO

*Article history:*
Received 2 May 2014
Received in revised form
30 May 2014
Accepted 18 June 2014
Available online 19 July 2014

*Keywords:*
Ruthenium
Acid halide
Halogen exchange
DFT calculation
Radical mechanism

ABSTRACT

The treatment of $CpRu(Cl)(PPh_3)_2$ with MeC(O)X offers a very convenient procedure for the synthesis of $CpRu(X)(PPh_3)_2$. The proposed mechanism involves an intermediate produced by the concerted liberation of $PPh_3$ by the incoming MeC(O)X and the subsequent subtraction of the X atom by the Ru atom to form a radical pair.



## Introduction

Few ligand–exchange reactions between M–X and R–X′ (Eq. (1)), where X and X′ are halogen or pseudo-halogen atoms, M is a metal, and R is a carbon functionality, have utilized in organometallics compared to other types of ligand exchange, such as transmetalation [1,2].

$$\text{M-X} + \text{R-X'} \longrightarrow \text{M-X'} + \text{R-X} \quad (1) \qquad (1)$$

We have recently reported that the ligand exchange reaction between M–X bonds of *trans*-M(X)[C(O)Ar]$(PPh_3)_2$ and C–X′ bonds of ArC(O)X′ (M = Pt, Pd; X, X′ = Cl, Br, I) successfully occurred to give a clean equilibrium mixture of *trans*-M(X)[C(O)Ar]$(PPh_3)_2$/ArC(O)X′ and *trans*-M(X′)[C(O)Ar]$(PPh_3)_2$/ArC(O)X [3]. The Gibbs free energy ($\Delta G$) of the reaction was equivalent to the $\Delta\Delta G$ of oxidative addition of ArC(O)X and ArC(O)X′ to $M(PPh_3)_2L_n$ ($L_n = 2PPh_3$ or $CH_2{=}CH_2$), consistent with density functional theory (DFT) calculations. Moreover, the theoretical mechanistic study suggested that the reaction proceeded via concerted $\sigma$-bond metathesis. It was demonstrated that the reactions of nickel triad complexes such as *cis*-$[Pt(Cl)_2(PPh_3)_2]$, *trans*-$[Pd(Cl)_2(PPh_3)_2]$, and $Ni(Cl)_2$(dppe) with MeC(O)Br and MeC(O)I were quite convenient for halogen exchanges. Similarly, the conversion of Au(L)Cl (L = $PPh_3$, IPr) to the corresponding bromide and iodide was achieved, and a $\sigma$-bond metathesis was also identified by theoretical calculation [4]. This transformation benefits from its simple handling. Analytically pure products were obtained successfully just by mixing of reagents and the subsequent removal of the solvent, by-product (MeC(O)Cl), and excess MeC(O)X by evaporation. Procedures that are usually required in conventional syntheses involving typical LiX, KX, and NaX metal salts, such as filtration, extraction, drying in the presence of desiccant, and recrystallization, were omitted. Herein, the Cl-to-X conversion of a ruthenium chloride is reported along with its mechanistic study [5–7].

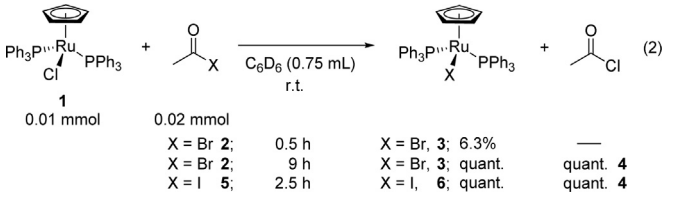
## Results and discussion

The reaction of $CpRu(Cl)(PPh_3)_2$ (**1**, 0.010 mmol) with MeC(O)Br (**2**, 0.020 mmol) in $C_6D_6$ (0.75 mL) at room temperature was monitored by $^{31}P$ and $^{1}H$ NMR spectroscopies (Eq. (2)). The gradual

* Corresponding authors. Fax: +81 6 6879 7390.
** Corresponding author. Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan. Fax: +81 6 6879 7390.
*E-mail addresses:* kuni@chem.eng.osaka-u.ac.jp (H. Kuniyasu), kambe@chem.eng.osaka-u.ac.jp (N. Kambe), ehara@ims.ac.jp (M. Ehara).

http://dx.doi.org/10.1016/j.jorganchem.2014.06.018
0022-328X/

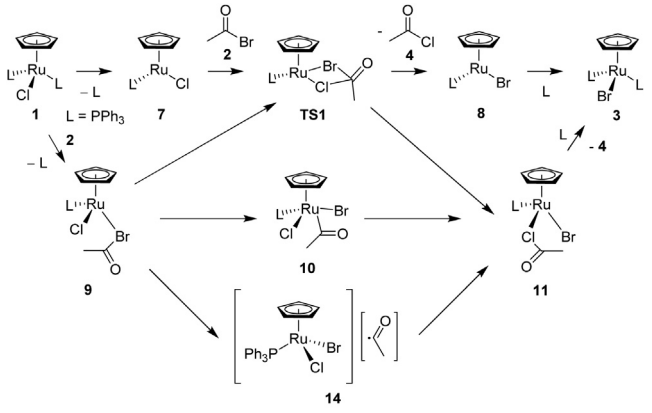
clean conversion of **1** ($\delta$ 40.1) to CpRu(Br)($PPh_3$)$_2$ (**3**) ($\delta$ 39.0) and MeC(O)Cl (**4**) was observed (6.3% of **3** after 0.5 h) [5c,8]. After 9 h, **3** was produced quantitatively. No intermediate was detected during the course of the reaction. A similar treatment of **1** with MeC(O)I (**5**) produced CpRu(I)($PPh_3$)$_2$ (**6**) ($\delta$ 38.0) after 2.5 h at room temperature. Next, preparative scale reactions were executed to demonstrate the utility of the present reaction as a synthetic method. Compounds **1** (1.0 mmol) and **2** (5.0 mmol) were added to $C_6H_6$ (50 mL) in a 100 mL flask fitted with a stirring bar in a glove box. After the reaction mixture was stirred at 25 °C for 3 h, the solvent, excess **2** (b.p. 75–77 °C), and **4** (b.p. 52 °C) were removed in vacuo. NMR spectra and elemental analysis showed that analytically pure **3** was obtained. A similar large scale reaction was conducted with **5** at 25 °C for 4 h to quantitatively afford **6** [9].




(2)

The mechanism of the reaction between **1** and **2** was theoretically investigated DFT using the M06 functional [10,11].

This computational method was shown to give reliable geometries and energies in previous studies on the ligand exchange reactions of *trans*-M(Cl)[C(O)Ph]($PPh_3$)$_2$ (M = Pt, Pd) and Au(Cl)($PPh_3$) with RC(O)Br (R = Ph, Me) [3,4]. Three possible reaction pathways, Mechanism 1–3, initially were investigated (Scheme 1). In mechanism 1, the liberation of $PPh_3$ produces the coordinately unsaturated CpRu(Cl)($PPh_3$) (**7**). Next, $\sigma$-bond metathesis between the Ru–Cl bond of **7** and the C–Br bond of **2** affords **TS1**, and the subsequent elimination of **4** yields CpRu(Br)($PPh_3$) (**8**), which can undergo recoordination by $PPh_3$ to form **3**. The associative elimination of $PPh_3$ to form **9** before **TS1** formation is considered in Mechanism 2. Mechanism 3 involves the oxidative addition of the Br–C bond to **9** that produces Ru(IV) complex **10** [8d,12]. In addition to the species shown in Scheme 1, the study identified transition states **TS2**, **TS3**, **TS4** and **TS5**. The energy diagram and optimized transition state and intermediate structures are shown in Fig. 1 [13,14]. The




**Scheme 1.** Possible reaction pathways of the reaction between **1** and **2**.

energy of **TS2**, which leads to the formation of **9**, was 101.6 kJ/mol higher than the reactants. On the other hand, the formation of **7** required 147.5 kJ/mol, which was clearly energetically more demanding. Similarly, the energy of **8** (128.3 kJ/mol) was much higher than that of **TS5** (95.6 kJ/mol), which generates **3** by elimination **4**. Therefore, we concluded that Mechanism 1 is unlikely. In intermediate **9** (79.2 kJ/mol), one hydrogen of Me of the incoming acetyl bromide is found in close proximity to the Cl atom, hydrogen bond-like interaction as suggested by the Cl···H (2.53 Å). Two pathways were considered from **9**: The $\sigma$-bond metathesis that provides **11** via the transition state **TS1** (Mechanism 2), and the oxidative addition of Br–C bond, which yields Ru(IV) complex **10** via **TS3** followed by the Cl–C bond-forming reductive elimination to afford **11** via **TS4** (Mechanism 3). The energies of **TS1** and **11** amounted to 117.9 and 72.3 kJ/mol, respectively. The energies of **TS3**, **10**, and **TS4** equaled 124.7, 93.6 and 117.5 kJ/mol, respectively. The energy of **TS1** was 6.8 kJ/mol lower than that for **TS3**, suggesting that Mechanism 2 was more favorable than Mechanism 3. After the formation of **11**, in which the Br···H distance is 2.53 Å, the associative elimination of **4** via **TS5** (95.6 kJ/mol) produced **3** and **4**. A total energy change of −15.5 kJ/mol was calculated for the entire reaction ($\Delta G$ = −16.0 kJ/mol). In **TS2**, dihedral angles ∠Ru–Cl–C–O and ∠Ru–Br–C–O equaled −179.4° and 179.9°, respectively. Likewise, in **TS5**, the dihedral angles ∠Ru–Cl–C–O and ∠Ru–Br–C–O equaled −179.9° and 177.8°, respectively. This shows that Ru, Cl, C, O of the carbonyl group, and Br atoms are nearly coplanar in **TS2** and **TS5**. On the other hand, the dihedral angles ∠Ru–Cl–Br–C of **TS2**, **9**, **TS1**, **11**, and **TS5** amounted to 179.8°, 116.0°, 137.9°, 104.0°, and 179.9°, respectively. Therefore, the Ru–Cl–C–Br quadrangle bends downward from flat **TS2** to **9**, and flips back to **TS1** before bending downward again to **11** and flattening again to **TS5**. The dihedral angle ∠Ru–Cl–Br–C of **TS3**, **10**, and **TS4** equaled 102.1°, 104.8°, and 93.6° in **TS3**, **10**, and **TS4**, respectively, suggesting that this quadrangle folded similarly to the Ru–Cl–C–Br quadrangle. However, this movement in Mechanism 3 was less dynamic than in the of $\sigma$-bond metathesis mechanism. The C=O group gradually changed direction from right to left in both mechanisms during this folding process (Fig. 1).

Besides those shown in Scheme 1, another possible reaction mechanism involves the formation of the 18-electron cationic complex **12** (L′ = $PPh_3$ or solvent), which reacts with **2** to provide **13**, and the subsequent elimination of L′ to form **3** (Scheme 2) [5b,c,15]. If the reaction proceeded via **12**, the addition of free $PPh_3$ or acetonitrile would accelerate the reaction [16a]. However, the transformation was actually rather suppressed by the addition of $PPh_3$ (0.1 equiv) or hardly affected by the addition of $CD_3CN$ (20 equiv) under the same conditions described in Eq. (2), excluding the formation of **12** and this mechanism. This retardation is consistent with Mechanism 2, which involves the elimination of $PPh_3$.

In agreement with the concerted $\sigma$-bond metathesis mechanism, no significant effect was observed by the addition of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and galvinoxyl during the transformation of *trans*-Pt(Cl)[C(O)Ph]($PPh_3$)$_2$ to the corresponding bromide [3]. In stark contrast, the radical and radical inhibitor remarkably affected the present Ru-system. The reaction of **1** with **2** in the presence of 0.1 equiv of TEMPO under otherwise similar conditions only gave 19% of **3** after 9 h (Eq. (3), compare this with the result of Eq. (2)). On the other hand, the same reaction in the presence of 1.0 equiv of 9,10-dihydroanthracene (DHA) produced **3** in 75% after 0.5 h and quantitatively within 2 h [16]. These results clearly show the participation of a radical species in the reaction mechanism. Reports have shown that Cp*Ru(Cl)($PPh_3$)$_2$, an analog of **1**, subtracted a halogen from halogenated compounds during the process of the atom transfer radical addition (ATRA) to alkenes [17]. A revised mechanism, Mechanism 4, is therefore proposed in

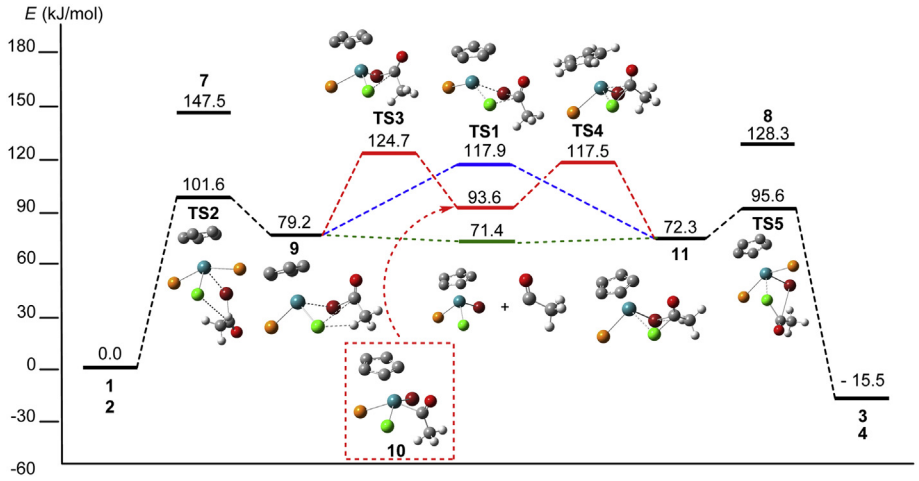
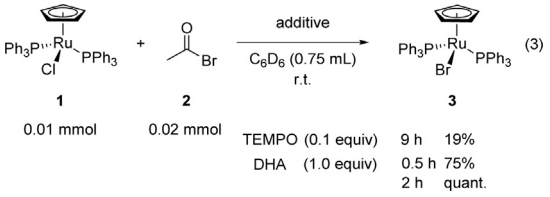



**Fig. 1.** Energy diagram for the reaction of **1** with **2**. Phenyl of $PPh_3$ and hydrogen atoms of Cp are omitted for clarity. Atoms in blue, orange, green, dark red, and red represent Ru, P, Cl, Br, and O, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Scheme 1. After the formation of **9** via **TS2**, the Br atom is subtracted by the Ru atom to give radical pair **14** consisting of a Ru(III) fragment and an acetyl radical. Subsequent Cl atom subtraction by the acetyl radical would afford **11**. This process could be affected by the radical inhibitor or promoter. The energy of **14** would be lower than **TS1**. In fact, the combined energy of CpRu(Cl)(Br)($PPh_3$) and $CH_3C(O)^{\bullet}$ is 71.4 kJ/mol, implicating the presence of radical process with lower energy (Fig. 1).




(3)

## Conclusion

This paper clearly demonstrates acetyl bromide (**2**) and iodide (**5**) as convenient Cl-to-Br and Cl-to-I conversion reagents in CpRu(Cl)($PPh_3$)$_2$ reaction. Moreover, DFT calculations suggest that the associative liberation of $PPh_3$ before the generation of associated complex intermediate. The significant influence by the radical inhibitor and promoter suggests the participation of the radical species during the process. Further efforts are underway to validate the mechanistic involvement of the radical pair species.

## Experimental

### *General comments*

The $^{31}P$ and $^{1}H$ NMR spectra in benzene-$d_6$ were measured with a ECS400 (400 MHz) spectrometer. The chemical shifts of the $^{31}P$ NMR spectra in benzene-$d_6$ were recorded relative to 85% $H_3PO_4$ (aq) as an external standard, and S=P($C_6H_4OMe$-*p*)$_3$ was used as an internal standard to calculate the yields of products (The sensitivities of ruthenium complexes to the internal standard were measured individually). Acetyl halides and benzoyl bromide were commercially obtained. Benzene-$d_6$ was purified by distillation from sodium benzophenone ketyl before use. CpRu(Cl)($PPh_3$)$_2$ (**1**) was prepared according to a literature [18]. Registry No. of **1**: 32993-05-8; **3**: 32993-06-9; **6**: 34692-10-9.

**1**: $^{31}P$ NMR (160 MHz, $C_6D_6$) $\delta$ 40.10.
**3**: $^{31}P$ NMR (160 MHz, $C_6D_6$) $\delta$ 38.97.
**6**: $^{31}P$ NMR (160 MHz, $C_6D_6$) $\delta$ 37.97.

### *A ligand exchange reaction between Cl of CpRu(Cl)($PPh_3$)$_2$ (**1**) and Br of MeC(O)Br (**2**) (Eq. (2))*

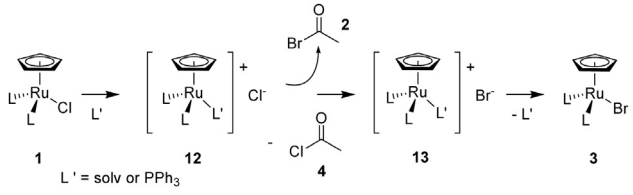
Into a dry Pyrex NMR tube were added a solution of CpRu(Cl)($PPh_3$)$_2$ (**1**, 0.010 mmol, 500 $\mu$L/20 mM in benzene-$d_6$), a solution of S=P($C_6H_4OMe$-*p*)$_3$ (0.0050 mmol, 50 $\mu$L/100 mM in benzene-$d_6$), and benzene-$d_6$ (180 $\mu$L). After the sensitivity of **1** to the internal standard was measured by $^{31}P$ NMR spectroscopy, a solution of MeC(O)Br (**2**, 0.020 mmol, 20 $\mu$L/1.0 M in benzene-$d_6$) was added and the reaction was monitored by $^{31}P$ NMR spectroscopy. The gradual conversion of **1** to **3** was confirmed. The reaction time and yield are as follows: 0.5 h, 6.3%; 1 h, 15%; 2 h, 38%; 3 h, 62%; 4 h, 80%; 5 h, 90%; 6 h, 95%; 7 h, 98%; 8 h, 99%; 9 h, 100%.

### *Preparative scale ligand exchange reactions*

Into a 100 mL flask were added CpRu(Cl)($PPh_3$)$_2$ (**1**, 726.2 mg, 1.0 mmol), MeC(O)Br (**2**, 614.8 mg, 5.0 mmol), and $C_6H_6$ (50 mL) in a glove box at room temperature. After the solution was stirred for 3 h, the solvent, excess **2** (b.p. 75–77 °C) and MeC(O)Cl (**4**, b.p. 52 °C) were removed in vacuo to give analytically pure **1** quantitatively (764.8 mg, 99%). Similarly, CpRu(I)($PPh_3$)$_2$ (**6**) was isolated by the treatment of **1** with MeC(O)I (**5**, b.p. 108 °C) (812.5 mg, 99%).

### *Computational details*

All the calculations in this study were performed using the GAUSSIAN 09 suite of programs [10]. We applied the M06 functional, which has demonstrated as a useful functional for




**Scheme 2.** Another possible mechanism via cationic complexes.

investigating chemical processes of transition metal chemistry [11]. The effective core potentials including relativistic effects (RECP) was employed to describe the inner core electrons for the Ru (Kr core). Under this approximation, the 16 valence electrons in the outer shell (4p4d5s) of the Ru atom are described through the corresponding LanL2DZ basis set. The 6-31G(d,p) basis sets were employed for cyclopentadienyl ligand, phosphorus atom of $PPh_3$, Cl, Br, and carbon and oxygen atoms of carbonyl group of acetyl bromide and acetyl chloride. The STO-6G basis sets were applied for phenyl group of $PPh_3$ and methyl group of acetyl bromide and acetyl chloride. During the optimization, all the molecular structures were fully relaxed without any symmetry constraints. All the ground state structures optimized are local minima; vibrational analyses performed at the optimized structures contained no imaginary frequencies. All the optimized transition state structures possessed only one imaginary frequency.

## Acknowledgments

This study was partly supported by a grant from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Masahiro Ehara acknowledges a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS, No. 22000009) and JENESYS Programs. Computations were partly performed at the Research Center for Computational Science, Okazaki, Japan. This work was partly supported by the JSPS Japanese-German Graduate Externship.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.06.018.

## References

[1] (a) L. Han, N. Choi, M. Tanaka, J. Am. Chem. Soc. 119 (1997) 1795–1796;
(b) K. Osakada, M. Maeda, Y. Nakamura, T. Yamamoto, A. Yamamoto, J. Chem. Soc. Chem. Commun. (1986) 442–443;
(c) L.M. Martínez-Prieto, C. Melero, D. del Río, P. Palma, J. Cámpora, E. Álvarez, Organometallics 31 (2012) 1425–1438;
(d) T. Yamamoto, T. Kohara, K. Osakada, A. Yamamoto, Bull. Chem. Soc. Jpn. 56 (1983) 2147–2153;
(e) T. Yamamoto, T. Kohara, A. Yamamoto, Bull. Chem. Soc. Jpn. 54 (1981) 2010–2016.

[2] F. Diederich, P.J. Stang (Eds.), Metal-catalyzed Cross-coupling Reactions, Wiley-VCH, New York, 1998.

[3] H. Kuniyasu, A. Sanagawa, D. Nakane, T. Iwasaki, N. Kambe, K. Bobuatong, Y. Lu, M. Ehara, Organometallics 32 (2013) 2026–2032.

[4] A. Sanagawa, H. Kuniyasu, D. Nakane, T. Iwasaki, N. Kambe, K. Bobuatong, M. Ehara, Chem. Lett. 42 (2013) 831–832.

[5] For Ru–Cl to Ru–Br conversion with MBr, see: (a) I. de los Ríos, M.J. Tenorio, J. Padilla, M.C. Puerta, P. Valerga, J. Chem. Soc. Dalton Trans. (1996) 377–381;
(b) H. Brunner, M. Muschiol, T. Tsuno, T. Takahashi, M. Zabel, Organometallics 29 (2010) 428–435;
(c) R.J. Haines, A.L. du Preez, J. Organomet. Chem. 84 (1975) 357–367.

[6] For Ru–Cl to Ru–I conversion with MI, see: (a) M.O. Albers, D.J. Robinson, A. Shaver, E. Singleton, Organometallics 5 (1986) 2199–2205;
(b) U. Koelle, J. Kossakowski, J. Organomet. Chem. 362 (1989) 383–398;
(c) H.W. Bosch, H. Hund, D. Nletlispach, A. Salzer, Organometallics 11 (1992) 2087–2098.

[7] For the reactions using HX, see: (a) A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J.A. Garrido-Cárdenas, F. García-Maroto, Inorg. Chem. 45 (2006) 1289–1298;
(b) C. Kaulen, C. Pala, C. Hu, C. Ganter, Organometallics 20 (2001) 1614–1619;
(c) E. Cesarotti, M. Angoletta, N.P.C. Walker, M.B. Hursthouse, R. Vefghi, P.A. Schofield, C. White, J. Organomet. Chem. 286 (1985) 343–360;
(d) P.J. Fagan, W.S. Mahoney, J.C. Calabrese, I.D. Williams, Organometallics 9 (1990) 1843–1852;
(e) F.M. Conroy-Lewis, A.D. Redhouse, S.J. Simpson, J. Organomet. Chem. 366 (1989) 357–367.

[8] For the conversion of **1** into **3** and **6**: (a) Y. Yang, K.A. Abboud, L. McElee-White, Dalton Trans. (2003) 4288–4296;
(b) T. Wilczewski, M. Bocheńska, J.F. Biernat, J. Organomet. Chem. 215 (1981) 87–96;
(c) A. Tenaglia, L. Giordano, Synlett (2003) 2333–2336;
(d) H. Nagashima, K. Mukai, Y. Shiota, K. Yamaguchi, K. Ara, T. Fukahori, H. Suzuki, M. Akita, Y. Moro-oka, K. Itoh, Organometallics 9 (1990) 799–807;
(e) R.J. Haines, A.L. du Preez, J. Organomet. Chem. 84 (1975) 357–367.

[9] For $CpRu(X)(PPh_3)_2$-catalyzed reactions, see: (a) A. Tenaglia, S. Marc, J. Org. Chem. 73 (2008) 1397–1402;
(b) P.A. Robles-Dutenhefner, E.M. Moura, G.J. Gama, H.G.L. Siebald, E.V. Gusevskaya, J. Mol. Catal. A Chem. 164 (2000) 39–47;
(c) A. Del Zotto, W. Baratta, M. Sandri, G. Verardo, P. Rigo, Eur. J. Inorg. Chem. (2004) 524–529.

[10] (a) M.J. Frisch, et al., GAUSSIAN09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2010;
(b) J. Tao, J.P. Perdew, V.N. Staroerov, G.E. Scuseria, Phys. Rev. Lett. 91 (2003) 146401.

[11] (a) Y. Zhao, D.G. Truhlar, Theor. Chem. Acc. 120 (2008) 215–241;
(b) Y. Zhao, D.G. Truhlar, Chem. Phys. Lett. 502 (2011) 1–13;
(c) Y. Zhao, D.G. Truhlar, J. Chem. Theory Comput. 7 (2011) 669–676;
(d) M. Mantina, R. Valero, D.G. Truhlar, J. Chem. Phys. 131 (2011) 064706-1–064706-5;
(e) R. Kang, J. Jiannian Yao, H. Hui Chen, J. Chem. Theory Comput. 9 (2013) 1872–1879.

[12] For Ru(IV) complexes formed by the oxidative addition to Ru(II), see: (a) H. Nagashima, K. Mukai, K. Itoh, Organometallics 3 (1984) 1314–1315;
(b) H. Nagashima, K. Mukai, Y. Shiota, K. Ara, K. Itoh, H. Suzuki, N. Oshima, Y. Moro-oka, Organometallics 4 (1985) 1314–1315;
(c) D.S. Perekalin, E.E. Karslyan, E.A. Trifonova, A.I. Konovalov, N.L. Loskutova, Y.V. Nelyubina, A.R. Kudinov, Eur. J. Inorg. Chem. (2013) 481–493.

[13] The structures, energy diagrams, selected angles and distances between two elements, Cartesian coordinates of the compounds, and IRC energy diagrams described in this manuscript are shown in the Supplementary data.

[14] The reaction of **1** with PhC(O)Br also occurs to give **3** quantitatively and the reaction mechanism has been examined theoretically. See Supplementary data.

[15] For cationic Ru-complexes, see: (a) P.M. Treichel, P.J. Vincenti, Inorg. Chem. 24 (1985) 228–230;
(b) R.F.N. Ashok, M. Gupta, K.S. Arulsamy, U.C. Agarwala, Inorg. Chim. Acta 98 (1985) 161–167;
(c) R.F.N. Ashok, M. Gupta, K.S. Arulsamy, U.C. Agarwala, Can. J. Chem. 63 (1985) 963–970;
(d) J. Amarasekera, T.B. Rauchfuss, Inorg. Chem. 28 (1989) 3875–3883;
(e) H.E. Bryndza, P.J. Domaille, R.A. Paciello, J.E. Bercaw, Organometallics 8 (1989) 379–385.

[16] (a) B.A. Howell, M.F. Debney, C.V. Rajaram, Thermochim. Acta 212 (1992) 115–122;
(b) R. Akaba, M. Iwasaki, T. Matsumura, M. Kamata, H. Itoh, J. Phys. Org. Chem. 9 (1996) 187–190.

[17] (a) M. Fernandez-Zumel, K. Thommes, G. Kiefer, A. Sienkiewicz, K. Pierzchala, K. Severin, Chem. Eur. J. 15 (2009) 11601–11607;
(b) W.J. Bland, R. Davis, J.L.A. Durrant, J. Organomet. Chem. 280 (1985) 357–406;
(c) K. Thommes, B. Içli, R. Scopelliti, K. Severin, Chem. Eur. J. 13 (2007) 6899–6907;
(d) L. Quebatte, K. Thommes, K. Severin, J. Am. Chem. Soc. 128 (2006) 7440–7441.

[18] T. Wilczewski, J. Organomet. Chem. 317 (1986) 307–325.