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Rare examples of P–C reductive elimination in ruthenium complexes to generate phosphonium salts are presented. Triarylphosphines are converted to benzophospholium or phosphaphenalenium ligands via cyclometalation and 1,2-insertion of an alkyne followed by P–C reductive elimination. The intermediate in each step was successfully characterized by NMR and X-ray diffraction studies.

Reductive elimination to generate a C–E (E = heteroatom) covalent bond is a key step in many types of catalytic reactions such as cross coupling[1] and C–H functionalization.[2] Among them, P–C reductive elimination is mainly found in substituent exchange reaction of phosphines (Figure 1a),[3] synthesis of phosphonium salts $PR_4^+X^-$ (X = halogen) (Figure 1b),[4] and hydrophosphination of alkenes and alkynes.[5] In particular, P–C reductive elimination of phosphonium salts from (hydrocarbyl)(phosphine) complexes is of special interest considering the general utility of phosphine ligands in organometallic chemistry.

The mechanism for P–C reductive elimination of phosphonium salts has been well-investigated by using styrylpalladium(II) phosphine complexes.[6] Application of the reductive elimination for the synthesis of phosphacycles has attracted significant interests, because phosphine-containing π-conjugated molecules, especially five-membered phosphacycles (phospholes), have potential applications in various fields including bioimaging[7] and organic light-emitting diodes (OLEDs),[8] just to name a few. Synthesis of phosphacycles such as dibenzophosphole by using Pd(II) as a catalyst has been achieved (Figure 1c).[9] However, a large part of research on P–C reductive elimination of phosphonium salts

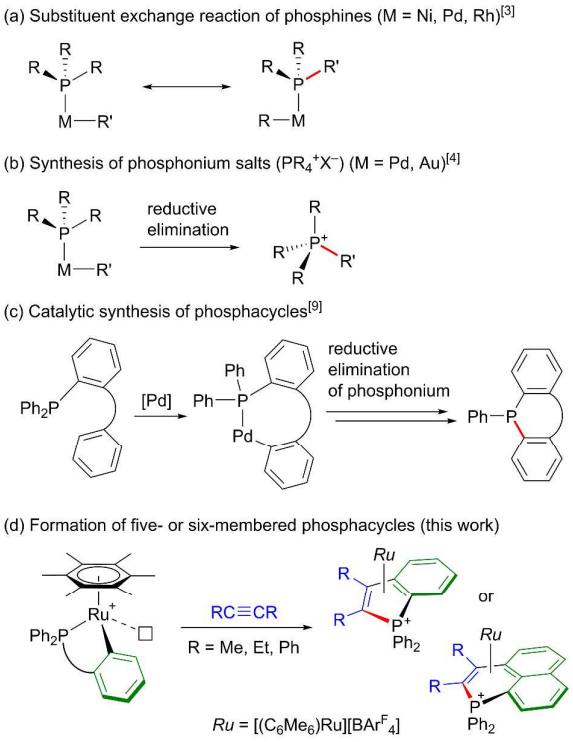

Figure 1. Examples of P–C reductive elimination and this work.

depends on palladium complexes and only a few examples have been reported with other metals.[10] Obviously more attention should be paid to the P–C reductive elimination at transition metals other than palladium, and in this context it is interesting to note that Toste and co-workers reported reductive elimination of phosphonium at an Au(III) centre in 2016.[10b] With regard to group 8 metals, to the best of our knowledge, there has been only one observation of similar P–C reductive elimination at a ruthenium centre.[10c]

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In the course of our studies on vinylidene rearrangement and insertion/remote rearrangement of internal alkynes in transition metal complexes,[11] P–C reductive elimination unexpectedly proceeded to generate five- and six-membered phosphacycles fused with aromatic systems. Herein we report the details of the reactions, mechanism for the formation of the phosphacycles, and solid-state structures of the products.

First we examined reactions of [(η^6-C_6Me_6)RuCl(Ph)(PPh_3)] **1** with 2-butyne or 3-hexyne in the presence of $NaBAr^F_4$, where BAr^F_4 is tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Scheme 1).[12, 13] In the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture using 2-butyne after 15 min, new signals were observed at δ 68.5 and 23.3 ppm in the ratio of 1:6 with complete consumption of the starting material **1**. After 1 h, the former signal disappeared, suggesting the clean formation of a single product through a metastable intermediate. The reaction with 3-hexyne proceeded similarly. Recrystallization of the reaction mixture in each case provided orange crystals in 50-53% yields, X-ray diffraction analysis of which revealed that the products are [(η^6-C_6Me_6)Ru(η^4-1,1-diphenyl-1-phosphindolium)][BAr^F_4] **2a**-**b**.

The molecular structure of **2b** is shown in Figure 2. The ruthenium atom is coordinated by the hexamethylbenzene and the phosphindolium in η^6- and η^4-fashions, respectively. The η^4-diene moiety in the five-membered PC_4 ring is essentially planar but the phosphorous atom deviates from planarity with the dihedral angle between the C1–C2–C3–C4 and C1–P–C4 planes at 29.5°, which is similar to those observed for other η^4-phospholium complexes.[14] The C–C bond lengths of the butadiene parts are not alternating (1.440(4) to 1.460(4) Å) as was found in other Ru(0) complexes bearing η^4-butadiene and η^6-arene ligands.[15] In the $^{13}C\{^1H\}$ NMR spectra of **2a**-**b**, signals assignable to the C_α and C_β (C1, C4 and C2, C3 for **2b** in Figure 2, respectively) of the PC_4 ring were observed at around δ 40 (d, $^1J_{PC} \cong 90$ Hz) and 80 ppm (d, $^2J_{PC} \cong 20$ Hz), respectively, which fall in the typical region of those for [(η^6-arene)Ru(0)(η^4-butadiene)] type complexes.[15c, 15d] The ^1H NMR spectrum of **2a** shows a doublet (δ 1.53 ppm, $^3J_{PH}$ = 16 Hz) and a singlet (δ 2.14 ppm) signals attributable to the Me groups, while in the case of **2b**, four signals derived from the diastereotopic methylene protons are observed.

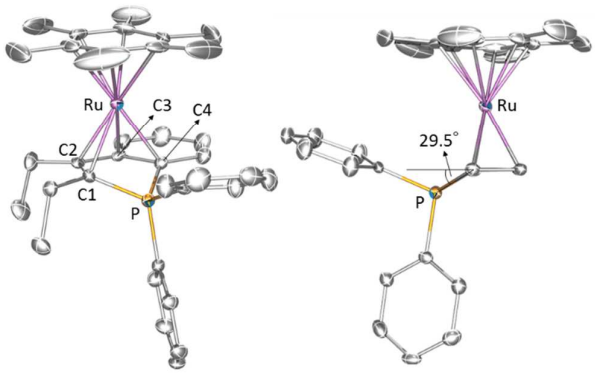
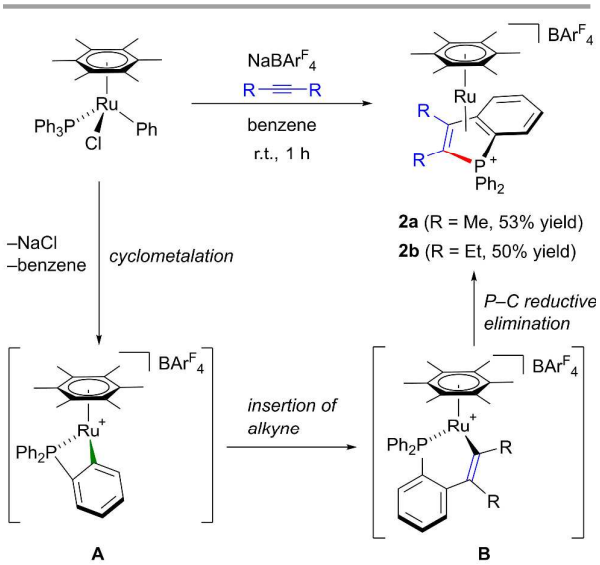
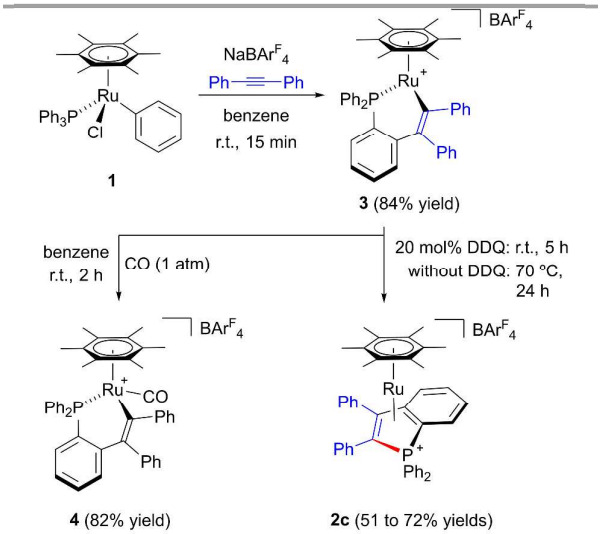


Figure 2. Molecular structure of the cationic part of **2b** with thermal ellipsoid plots at 50% probability. Left: front view, right: side view without the Et and fused Ph groups. Selected bond lengths [Å]: C(1)–C(2): 1.457(5), C(2)–C(3): 1.438(5), C(3)–C(4): 1.459(4), Ru–C(1): 2.179(3), Ru–C(2): 2.132(3), Ru–C(3): 2.168(3), Ru–C(4): 2.241(3).

Judging from the structure of the products, we assumed the reaction mechanism as shown in Scheme 1. After treatment of **1** with $NaBAr^F_4$, cyclometalation reaction took place to form the ruthenaphosphacyclobutene **A** along with the release of a benzene molecule.[16] An alkyne then inserted to the strained Ru–C bond in the four-membered metallacycle of **A**. In the resulting vinyl complex **B**, which is assigned as the unstable intermediate observed by $^{31}P\{^1H\}$ NMR (*vide infra*), P–C reductive elimination proceeded to generate the phosphindolium skeleton. Notably, this P–C reductive elimination completed within 1 h at room temperature. The major driving force of the facile P–C reductive elimination is considered to be the formation of 18e complex **2** from 16e species **B**.



Scheme 1. Reactions of **1** with 2-butyne or 3-hexyne.

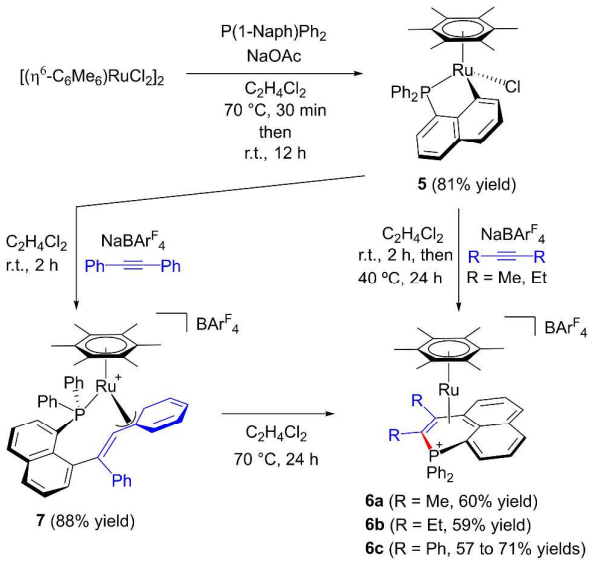


Scheme 2. Isolation of the intermediate **3** and its reactions.

To investigate the generality of the reaction, we performed the experiments using diphenylacetylene (Scheme 2).[12] In the $^{31}P\{^1H\}$ NMR of the reaction mixture after 15 min, only one signal at 73.4 ppm was observed. Notably, a complex corresponding to the intermediate **B**, [(η^6-C_6Me_6)Ru{P(Ph)$_2$[C_6H_4C(Ph)=C(Ph)-κ^2-*P*,*C*]}[BAr^F_4] **3**, was successfully isolated in 84% yield as black green crystals. Although single-crystals of **3** suitable for X-ray diffraction analysis could not be obtained so far,[17] **3** could be converted readily into its CO adduct **4** and the solid state structure of the latter was unambiguously determined by X-ray diffraction analysis (Figure S2).[12] It should be mentioned that the $^{31}P\{^1H\}$ NMR chemical shift of **3** (73.4 ppm) is similar to those found in the early stage of the reactions using dialkylalkynes (68.5 and 66.2 ppm for 2-butyne and 3-butyne, respectively). Thus these observations confirm the structure of the intermediate **B** in Scheme 1.

To confirm that compound **3** actually works as the intermediate of the P–C reductive elimination, reactivity of **3** was investigated (Scheme 2). In fact, heating a benzene solution of **3** at 70 °C afforded the corresponding phosphindolium complex **2c** in 72% yield, although long reaction time (ca. 24 h) was required to complete the conversion. It is known that electron-accepting alkenes such as DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) promote reductive elimination through π-coordination or electron-transfer oxidation.[18] As expected, the reaction of **3** with 20 mol% DDQ at room temperature for 5 h resulted in isolation of **2c** in 51% yield. These experiments strongly support the proposed mechanism.

Next, the scope of this rare example of P–C reductive elimination reaction at a ruthenium centre was expanded to another phosphine ligand, 1-naphthyl(diphenyl)phosphine (Scheme 3).[12] In this case, the cyclometallated complex that corresponds to the intermediate **A** in Scheme 1 is expected to be generated from 18e metallacycle complex **5** on reaction with $NaBAr^F_4$. Complex **5** was obtained from the reaction of [(η^6-C_6Me_6)$RuCl_2$]$_2$,[19] P(1-Naph)Ph_2[20] and NaOAc in 81% yield.[21]



Scheme 3. Reaction of complex **5** with internal alkynes.

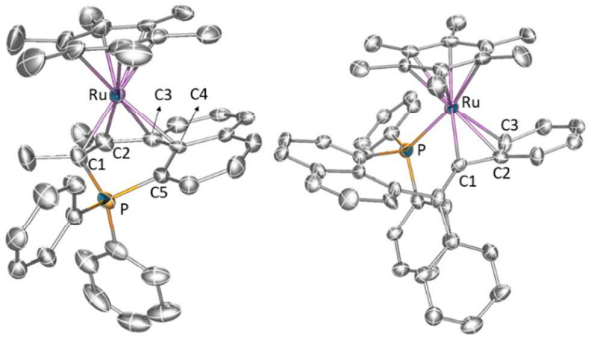


Figure 3. Molecular structures of the cationic parts of **6a** (left) and **7** (right) with thermal ellipsoid plots at 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths of **6a** [Å]: C(1)–C(2): 1.461(6), C(2)–C(3): 1.427(6), C(3)–C(4): 1.469(5), Ru–C(1): 2.160(4), Ru–C(2): 2.111(4), Ru–C(3): 2.233(4), Ru–C(4): 2.370(4).

As expected, further reactions of **5** with 2-butyne and 3-hexyne at 40 °C in the presence of $NaBAr^F_4$ afforded [(η^6-C_6Me_6)Ru(η^4-1,1-diphenyl-1-phosphaphenalenium)][BAr^F_4] **6a-b** in 60 and 59% yields, respectively, via 1,2-insertion of an alkyne and subsequent P–C reductive elimination. When diphenylacetylene was used as a substrate, η^3-benzyl complex **7** was isolated in 88% yield at room temperature, and heating a 1,2-dichloroethane solution of **7** at 70 °C for 24 h gave **6c** in 57% yield.[22] Higher temperature was required for the Ph case because η^3-coordination of the benzyl group stabilize the seven-membered ruthenacycle **7**.[23] It is interesting to note that no P–C reductive elimination takes place in the reaction of diphenylacetylene and a ruthenacycle related to **5** adopting an η^6-*p*-cymene ligand instead of η^6-hexamethylbenzene without $NaBAr^F_4$.[21a]

The structures of complexes **6a-c** and **7** were determined by X-ray diffraction analysis. Molecular structures of **6a** and **7** are shown in Figure 3. Complex **6a** has a sandwich structure with the η^6-C_6Me_6 and the η^4-phosphacycle ligands, while complex **7** has a typical piano stool structure with the η^6-C_6Me_6, the phosphorous atom and the η^3-benzyl carbon atoms. The C–C bond lengths of the butadiene moiety in **6a** are similar to those of **2b**. Interestingly, the Ru–C(η^4-phosphacycle) distances in **6a** varies considerably (10%) depending on the position in the phosphacycle: the Ru–C(3), C(4) distances (2.233(4), 2.370(4) Å, respectively) are considerably longer than the Ru–C(1), C(2) lengths (2.160(4), 2.111(4) Å, respectively). Moreover, the C2–C3–C4–C5 torsion angle is 28.7°, reflecting the naphthalene moiety is skewed from planarity. This deformation in **6a** may be explained by the orbital symmetry of the naphthalene HOMO where the C3 and C5 atoms have opposite phase signs.

In summary, we have developed P–C reductive elimination at a ruthenium centre to generate ruthenium complexes bearing five- or six-membered phosphacycles as η^4-diene ligands. The intermediates of the reaction were successfully characterized by NMR spectroscopy as well as single-crystal X-ray studies, revealing that the mechanism for the formation of the phosphacycles is cyclometallation and alkyne 1,2-insertion

followed by P–C reductive elimination. Investigation into dissociation of the phosphaphenalene derivatives from complex **6** and their photophysical properties is currently under way.[24]

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Conflicts of interest

There are no conflicts to declare.

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Phosphindolium and phosphaphenalenium complexes were obtained from PPh_2Ar (Ar = Ph, 1-Naph) *via* cyclometallation, alkyne insertion and P-C reductive elimination at a Ru centre.