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钌亚丙二烯基配合物与肼的反应性质: 丙烯腈配合物的生成

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摘要 以双齿 P,N-配体 8-(二苯基膦基)喹啉(DPPQ)为支撑配体的钌亚丙二烯基配合物[RuCl(=C=C=CR_2)(DPPQ)$_2$][BPh_4] (**3a**: R=苯基; **3b**: CR_2=FN=亚芴基)可由双核钌配合物[Ru(μ-Cl)(DPPQ)$_2$]$_2$[BPh_4]$_2$ (**1**)分别与过量的 1,1-二苯基炔丙醇(**2a**)或 9-乙炔-9-芴醇(**2b**)反应得到. 配合物 **3** 易与肼在室温下反应生成丙烯腈的钌配合物[RuCl(N≡C—CH=CR_2)(DPPQ)$_2$][BPh_4] (**4a**: R=苯基; **4b**: CR_2=FN=亚芴基), 该反应涉及肼对亚丙二烯基配体 α-碳原子的分子间亲核进攻, 是首例肼对金属亚丙二烯基加成生成丙烯腈的反应. 配合物 **4** 与过量的丙炔醇 **2** 反应可释放出 3,3-二苯基丙烯腈(**5a**)或3-芴基丙烯腈(**5b**), 并再生亚丙二烯基配合物**3**. 此外, 初步考察了配合物**1**对端基炔丙醇与肼反应生成丙烯腈的催化活性, 结果表明该催化反应的确可以进行, 但是得到的丙烯腈产物的产率不高. 尽管结果不是很理想, 但是这些研究表明可望发展端基炔丙醇与肼经由过渡金属亚丙二烯基中间体转化为丙烯腈的新催化反应.
关键词 钌; 亚丙二烯基; 炔烃; 肼; 腈

Reactivity of Ruthenium Allenylidene Complexes with Hydrazines: Formation of Acrylonitrile Complexes

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Abstract The cationic ruthenium allenylidene complexes [RuCl(=C=C=CR_2)(DPPQ)$_2$][BPh_4] (**3a**: R=Ph; **3b**: CR_2=FN=9*H*-fluoren-9-ylidene) supported by the heterobidentate P,N-donor ligand 8-(diphenylphosphanyl)quinoline (DPPQ) have been synthesized from the reactions of the dimeric complex [Ru(μ-Cl)(DPPQ)$_2$]$_2$[BPh_4]$_2$ (**1**) with excess 1,1-diphenylprop-2-yn-1-ol (**2a**) or 9-ethynyl-9*H*-fluoren-9-ol (**2b**), respectively. Addition of hydrazines to the ruthenium-allenylidenes **3** led to the facile formation of ruthenium-bound acrylonitrile complexes [RuCl(N≡C—CH=CR_2)(DPPQ)$_2$][BPh_4] (**4a**: R=Ph; **4b**: CR_2=FN) at room temperature. This reaction involves the intermolecular nucleophilic attack of hydrazines at the C_α atom of the allenylidene ligand, which represents the first examples of addition of hydrazines to metal-allenylidenes affording acrylonitrile derivatives. Reaction of acrylonitrile complex **4** with an excess of propargyl alcohols **2a** or **2b** (4 equiv.) could release the organic acrylonitriles 3,3-diphenylacrylonitrile (**5a**) or 2-(9*H*-fluoren-9-ylidene)-acetonitrile (**5b**) along with regeneration of allenylidene complex **3**. In addition, the catalytic activity of **1** for the transformation of terminal propargyl alcohols and hydrazines into acrylonitriles has been investigated preliminarily. The results showed that the catalytic reaction did proceed to give the desired acrylonitrile products, albeit the yield not good. Nevertheless, our results of the catalytic reactions demonstrated that it is very promised to develop new catalytic reactions for the transformation of terminal propargylic alcohols and hydrazines into acrylonitriles via allenylidene intermediates.
Keywords ruthenium; allenylidene; alkyne; hydrazine; nitrile

1 Introduction

Transition metal allenylidene complexes ($L_nM=C_\alpha=C_\beta=C_\gamma RR'$) have attracted a great deal of attention and achieved rapid development in past decades, due to their potential performance in many stoichiometric and catalytic transformations of organic molecules.[1] Especially, the ruthenium allenylidene complexes have been widely studied.[1d~1i,2]

Experimental and theoretical studies have demonstrated that the α- and γ-carbon atoms of the allenylidene ligand

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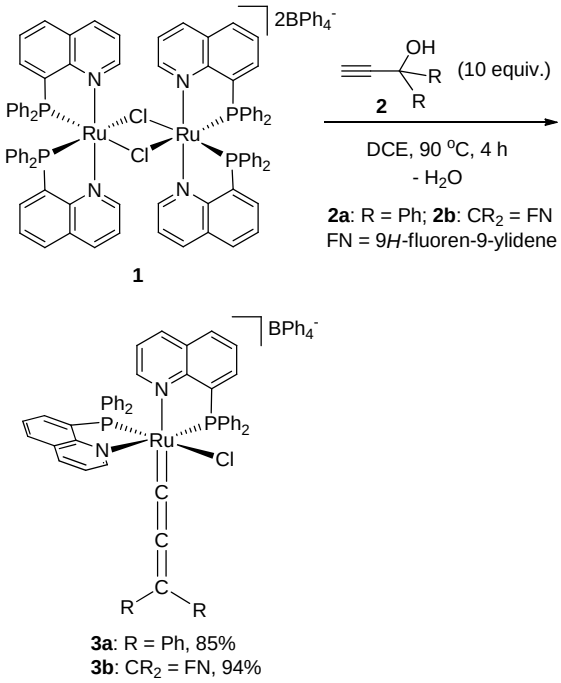
are electrophilic centers, while the β-carbon atom exhibits nucleophilic character.[3,4] Thus, electrophiles usually attack the C_β of the allenylidene chain to afford vinylcarbyne complexes,[5] while nucleophiles usually attack the C_α or C_γ atom leading to the formation of vinylcarbene, vinylidene or alkynyl complexes.[1c,1h,1i,2a,2e,2h,6] The regioselectivity of the nucleophilic addition reactions to the allenylidene chain mainly depends on both electronic and steric factors of the metallic fragment, the nucleophile and the substituents on the allenylidene chain.[2e] Numerous studies indicate that (i) anionic nucleophiles tend to react through the C_γ atom, affording neutral alkynyl complexes;[5d,7] (ii) neutral nucleophiles containing acidic hydrogens such as alcohols, water, amines, and thiols prefer the initial addition of the nucleophile to the C_α and protonation of the C_β atom of allenylidene chain to give vinylcarbene derivatives;[2a,8] (iii) nucleophiles containing phosphine usually react reversibly at the C_α or C_γ atom of allenylidene chain to afford the α-phosphonioallenyl or γ-phosphonioalkynyl adducts, respectively, and, in some cases, a mixture of both adducts.[9,10] The attack of phosphine nucleophiles at the C_α or C_γ atom is defined by a delicate balance of various factors, such as the nature of the metal atom, electronic and steric properties of ancillary ligands and substituents at the C_γ atom of the allenylidene ligand.[11]

Hydrazines have been extensively employed as nucleophiles for the atom-economic synthesis of new organonitrogen compounds.[12] In this context, a few number of stoichiometric reactions of hydrazines with transition-metal vinylidenes have been reported to yield either metal-bound nitrile complexes[13] or diaza-metallacyclobutene complexes resulting from nucleophilic attack of hydrazines at the electrophilic α-carbon of metal-vinylidenes.[14] More importantly, Fukumoto *et al.*[15c,15d] developed a series of ruthenium- or rhodium-catalyzed anti-Markovnikov addition of terminal alkynes with hydrazines, which, depending on the catalysts used as well as the nature of the alkyne and the hydrazine substrates, could lead to the production of nitriles[15a,15b] or aldimine-type hydrazones. The catalytic reactions involve the intermolecular addition of the hydrazine nitrogen to the metal-vinylidene intermediates generated from terminal alkynes. In contrast, much less attention has been paid to the reactivity of hydrazines with closely related metal-allenylidenes. To the best of our knowledge, the only one example was contributed by Fischer and coworkers[16] in 2006 using 1,2-dimethylhydrazine or 1,1-dimethylhydrozine as dinucleophiles to react with chromium-allenylidene complexes $[(CO)_5Cr=C=C=C(NMe_2)Ph]$ and $[(CO)_5Cr=C=C=C(O\text{-}endo\text{-}Bornyl)OEt]$, which afforded the corresponding heterocyclic 1,2-dimethylpyrazolylidene chromium complex or the zwitterionic 1,1-dimethylpyrazolium-5-ylidene chromium complex via 1,2,3-diheterocyclization. The reaction proceeded by a stepwise process and was initiated by addition of hydrazine to the C_γ of the allenylidene ligand followed by displacement of one NMe_2 or the OEt substituent at the C_γ and subsequent intramolecular cyclization.

We have been interested in the chemistry of ruthenium complexes with the heterobidentate P,N-donor ligand 8-(diphenylphosphanyl)quinoline (DPPQ) and have reported recently the catalytic activity of a series of ruthenium DPPQ complexes for the *endo* cycloisomerization of terminal alkynols. It was found that, with only 1 mol% loading of the dimeric ruthenium complex $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2[BPh_4]_2$ (**1**), the *endo* cycloisomerization of a range of terminal alkynols could be achieved to give the corresponding *endo*-cyclic enol ethers in moderate to excellent yields. A series of seven-, six-, and five-membered oxacyclocarbene ruthenium complexes such as $[RuCl(DPPQ)_2\{=CCH_2C_6H_4CH_2CH_2O\}](BPh_4)$ and $[RuCl(DPPQ)_2\{=CCH_2(CH_2)_nCH_2O\}](BPh_4)$ (n=1, 2) derived from intramolecular nucleophilic addition of the O—H group to the vinylidene intermediate can be accessed from the stoichiometric reactions of **1** with corresponding alkynol substrates and have been proved to be the key intermeidates for the catalytic cycloisomerization.[17] As an extension of our study on the reactivity of ruthenium DPPQ complexes, we herein report the synthesis of the cationic bis-DPPQ ruthenium allenylidene complexes $[RuCl(=C=C=CR_2)(DPPQ)_2][BPh_4]$ (**3a**: R=Ph; **3b**: CR_2=FN=9*H*-fluoren-9-ylidene) from the reaction of precursor **1** with 1,1-diphenylprop-2-yn-1-ol (**2a**) or 9-ethynyl-9*H*-fluoren-9-ol (**2b**), as well as the reactivity of allenylidene complexes **3** toward hydrazines (Eq. 1), which lead to formation of ruthenium-bound acrylonitrile complexes $[RuCl(N\equiv CCH=CR_2)(DPPQ)_2][BPh_4]$ (**4a**: R=Ph; **4b**: CR_2=FN). The latter reaction involves the intermolecular attack of hydrazines at the C_α atom of allenylidene ligand, which provides the first examples of addition of hydrazines to metal-allenylidenes affording acrylonitrile derivatives. Meanwhile, reaction of acrylonitrile complex **4**



(1)

with an excess of progarylic alcohols **2** could release the organic acrylonitriles 3,3-diphenylacrylonitrile (**5a**) or 2-(9*H*-fluoren-9-ylidene)acetonitrile (**5b**) along with regeneration of allenylidene complex **3**. Moreover, the reactions of 1,1-diphenylprop-2-yn-1-ol (**2a**) or 9-ethynyl-9*H*-fluoren-9-ol (**2b**) with hydrazines in the presence of catalytic amount of complex **1** have been preliminarily investigated to test the catalytic activity of **1** for the transformation of terminal propargylic alcohols and hydrazines into acrylonitriles.

2 Results and discussion

2.1 Preparation of ruthenium allenylidene complexes [RuCl(=C=C=CR_2)(DPPQ)$_2$][BPh_4] (3a: R=Ph; 3b: CR_2=FN=9*H*-fluoren-9-ylidene)

The synthesis of the allenylidene complexes followed the Selegue's method[18] by using the corresponding terminal propargyl alcohols as building blocks. Thus, the reactions of [Ru(μ-Cl)(DPPQ)$_2$]$_2$[BPh_4]$_2$ (**1**) with 10 equiv. of 1,1-diphenylprop-2-yn-1-ol (**2a**) or 9-ethynyl-9*H*-fluoren-9-ol (**2b**) in 1,2-dichloroethane (DCE) at 90 ℃ to afford the corresponding allenylidene complexes [RuCl(=C=C=CPh_2)(DPPQ)$_2$][BPh_4] (**3a**) and [RuCl(=C=C=(FN))-(DPPQ)$_2$][BPh_4] (**3b**, FN=9*H*-fluoren-9-ylidene) within 4 h (Scheme 1), which were isolated as purple solids in 85% and 94% yields, respectively. When 5 equiv. of **2a** was used, the reaction proceeded very slowly and only 60% conversion of **1** was observed even after 24 h, while only trace amount of **3a** could be detected when a solution of **1** and **2a** in a molar ratio of 1∶2.5 (*i.e.*, a 1∶1.25 ratio for the monomeric species [RuCl(DPPQ)$_2$]$^+$ and **2a**) was heated at 90 ℃ for 24 h. We have also investigated the reaction at a lower temperature of 60 ℃, the reaction could not be completed when a solution of **1** with 10 equiv. of **2a** was heated for 24 h (70% conversion of **1**), and no appreciable reaction can be observed even after 24 h when 5 equiv. of **2a** was used.

Complexes **3a** and **3b** are air-stable solids and both have been fully characterized by spectroscopic methods and elemental analysis. The IR spectrum of **3a** and **3b** shows the characteristic absorption ν(C=C=C) at 1934 and 1933 cm^{-1}, respectively. At room temperature, the ^{31}P{^{1}H} NMR spectra of **3a** and **3b** in CD_2Cl_2 exhibit two doublets at δ 56.4, 48.3 ($^2J_{PP}$=27.2 Hz) and 55.2, 46.7 ($^2J_{PP}$=27.2 Hz), respectively, for the two inequivalent phosphino groups in each complex. The ^{1}H NMR spectra of both complexes shows the expected signals in the range δ 10.25～6.15 without characteristic resonance. The ^{13}C{^{1}H} NMR spectra strongly support the formation of the allenylidene complexes, which display the characteristic carbene Ru=C$_\alpha$ low-field resonance as triplet signals at δ 311.2 ($^2J_{CP}$=17.5 Hz) for **3a** and δ 312.8 ($^2J_{CP}$=17.8 Hz) for **3b**, and singlet resonances for the C$_\beta$ and C$_\gamma$ carbons at δ 209.6 and 159.1 for **3a**, and at δ 216.7 and 153.4 for **3b** (Table 1). These results are in line with those reported for other known ruthenium-allenylidene complexes.[2]

Table 1 Selected ^{31}P NMR, ^{13}C {^{1}H} NMR and IR data for the ruthenium allenylidene complexes **3a** and **3b**

Complex	^{31}P NMR δ	^{13}C {^{1}H} NMR δ			IR $\nu_{(C=C=C)}$/ cm^{-1}
		C$_\alpha$	C$_\beta$	C$_\gamma$	
3a	56.4, 48.3	311.2	209.6	159.1	1934
3b	55.2, 46.7	312.8	216.7	153.4	1933

The structures of **3a** and **3b** were further confirmed by single-crystal X-ray diffraction. Figures 1 and 2 show the X-ray structures for the cations of **3a** and **3b**, respectively, from which it can be seen that the Ru center in each complex adopts similar distorted octahedral geometry consisting of two DPPQ ligands chelating to Ru nearly perpendicularly, one chlorine ligand, and one allenylidene ligand. The N atom of one of the DPPQ ligands is *trans* to the allenylidene ligand [N(1)—Ru(1)—C(1), 177.7(2)° for **3a** and 177.10(17)° for **3b**], whereas the P atom is *trans* to the N atom of the other DPPQ ligand [P(1)—Ru(1)—N(2), 177.96(12)° for **3a** and 178.58(10)° for **3b**]. The P atom of the other DPPQ ligand is *trans* to the Cl ligand [P(2)—Ru(1)—Cl(1), 168.98(5)° for **3a** and 166.15(4)° for **3b**]. The structural features closely resemble those for the series of bis-DPPQ ruthenium oxacyclocarbene complexes [RuCl(DPPQ)$_2${=$CCH_2C_6H_4CH_2CH_2O$}](BPh_4) and [RuCl(DPPQ)$_2${=$CCH_2(CH_2)_nCH_2O$}](BPh_4) (n=1～3) we reported previously,[17] with the oxacyclocarbene ligand replaced by the allenylidene ligand. The characteristic allenylidene ligand is bound to the metal in a nearly linear fashion. Taking **3a** for an example, the bond angles associ-

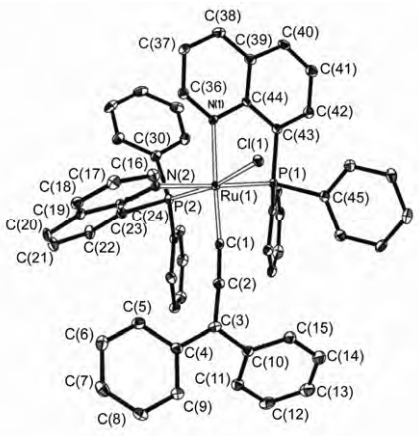


Figure 1 Molecular structure for the cation of **3a** with thermal ellipsoids drawn at 30% probability (CCDC 1567164)

Counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths (nm) and angles (°): Ru(1)—C(1) 0.1892(6), C(1)—C(2) 0.1244(8), C(2)—C(3) 0.1359(8), Ru(1)—N(1) 0.2151(4), Ru(1)—N(2) 0.2198(4), Ru(1)—P(1) 0.22655(14), Ru(1)—P(2) 0.22967(14), Ru(1)—Cl(1) 0.24291(13); C(1)—Ru(1)—N(1) 177.7(2), C(1)—Ru(1)—N(2) 87.3(2), N(1)—Ru(1)—N(2) 94.70(17), C(1)—Ru(1)—P(1) 94.68(17), N(1)—Ru(1)—P(1) 83.27(13), N(2)—Ru(1)—P(1) 177.96(12), C(1)—Ru(1)—P(2) 89.37(17), N(1)—Ru(1)—P(2) 92.00(13), N(2)—Ru(1)—P(2) 80.76(13), P(1)—Ru(1)—P(2) 99.46(5), C(1)—Ru(1)—Cl(1) 97.11(17), N(1)—Ru(1)—Cl(1) 81.84(13), N(2)—Ru(1)—Cl(1) 90.60(13), P(1)—Ru(1)—Cl(1) 88.94(5), P(2)—Ru(1)—Cl(1) 168.98(5), C(2)—C(1)—Ru(1) 174.9(5), C(3)—C(2)—C(1) 172.8(6)

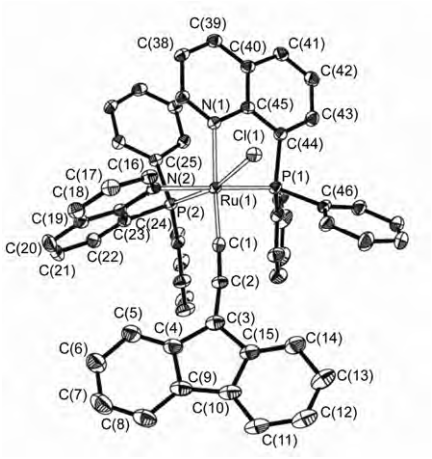


Figure 2 Molecular structure for the cation of **3b** with thermal ellipsoids drawn at 30% probability (CCDC 1567165)

Counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths (nm) and angles (°): Ru(1)—C(1) 0.1883(5), C(1)—C(2) 0.1226(7), C(2)—C(3) 0.1361(8), Ru(1)—N(1) 0.2162(4), Ru(1)—N(2) 0.2214(4), Ru(1)—P(1) 0.22705(12), Ru(1)—P(2) 0.22960(12), Ru(1)—Cl(1) 0.24551(11); C(1)—Ru(1)—N(1) 177.10(17), C(1)—Ru(1)—N(2) 84.57(17), N(1)—Ru(1)—N(2) 97.81(14), C(1)—Ru(1)—P(1) 94.82(14), N(1)—Ru(1)—P(1) 82.76(11), N(2)—Ru(1)—P(1) 178.58(10), C(1)—Ru(1)—P(2) 91.02(15), N(1)—Ru(1)—P(2) 91.02(11), N(2)—Ru(1)—P(2) 80.40(11), P(1)—Ru(1)—P(2) 100.90(4), C(1)—Ru(1)—Cl(1) 98.53(14), N(1)—Ru(1)—Cl(1) 79.83(11), N(2)—Ru(1)—Cl(1) 90.49(10), P(1)—Ru(1)—Cl(1) 88.33(4), P(2)—Ru(1)—Cl(1) 166.15(4), C(2)—C(1)—Ru(1) 174.9(4), C(3)—C(2)—C(1) 169.1(6)

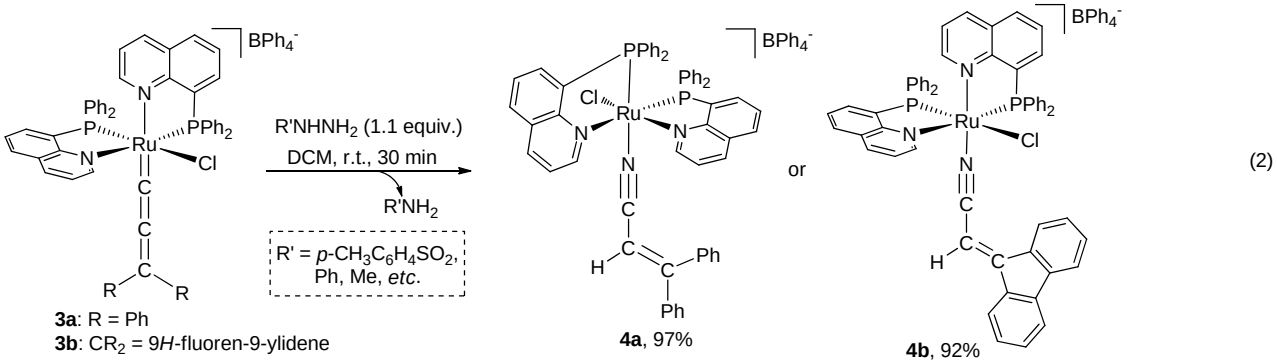
ated with the ruthenium diphenylallenylidene moiety are 174.9(5)° and 172.8(6)° for Ru(1)—C(1)—C(2) and C(1)—C(2)—C(3), respectively. The bond lengths of ruthenium allenylidene unit in **3a** [Ru(1)—C(1), 0.1892(6) nm; C(1)—C(2), 0.1244(8) nm; C(2)—C(3) 0.1359(8) nm] are comparable with those reported for other ruthenium-allenylidene complexes.[2] It is notable that C(1)—C(2) is shorter than the normal C=C double bond (about 0.130 nm), while C(2)—C(3) shows longer distance, indicating a substantial contribution of the canonical form [M]—C≡C—C^+Ph_2 to the structure of **3a**.

2.2 Reactions of 3 with hydrazines: formation of acrylonitrile complexes [RuCl(N≡CCH = CR_2)-$(DPPQ)_2$][BPh_4] (4a: R=Ph; 4b: CR_2=FN)

To test the reactivity of the allenylidene complexes **3** with hydrazine nucleophiles, we initially tried the reaction of allenylidene complex **3a** with 1.1 equiv. of 4-methylbenzenesulfonohydrazide ($TsNHNH_2$) in dichloromethane (DCM) at room temperature, with the intention to isolate the anticipated *α*-hydrazinovinylcarbene complex [RuCl(=C(NHNHSO$_2$-*p*-$C_6H_4CH_3$)CH=CPh_2)-$(DPPQ)_2$][BPh_4] or the hydrazino-alkynyl ruthenium complex [RuCl(C≡CC(NH_2NHSO$_2$-*p*-$C_6H_4CH_3$)Ph_2)$(DPPQ)_2$]-[BPh_4] resulted from the nucleophilic addition of a hydrazine to the C_α or C_γ of the allenylidene chain. However, rather than the above expected complexes, the acrylonitrile ruthenium complex [RuCl(N≡CCH = CPh_2)$(DPPQ)_2$]-[BPh_4] (**4a**) was formed exclusively along with the eliminated 4-methylbenzenesulfonamide ($TsNH_2$) within 30 min (Eq. 2), which were isolated in 97% and 85% yield, respectively. Other hydrazines including the mono-substituted hydrazines such as methylhydrazine and phenylhydrazine or the 1,1-disusbtituted ones like piperidin-1-amine, and 1,1-dimethylhydrazine, *etc.* were also tested for the reactions with complex **3a**. Again, rapid and quantitative formation of acrylonitrile complex **4a** and the corresponding amines were observed at room temperature. Moreover, reactions of hydrazones such as (diphenylmethylene)hydrazine, propan-2-ylidene-hydrazine, (9*H*-fluoren-9-ylidene)hydrazine, *etc.* with allenylidene **3a** also led to the exclusive formation of the acrylonitrile complex **4a** and the respective imines.

Similarly, the reactions of allenylidene complex **3b** with various hydrazines and hydrazones were also investigated under the same reaction condition. Indeed, analogous acrylonitrile ruthenium complex [RuCl(N≡C—CH=(FN)$(DPPQ)_2$][BPh_4] (**4b**) together with the corresponding amine or imine was isolated in high yields (Eq. 2).

Complexes **4a** and **4b** are yellow air-stable solids, which have been characterized by the spectroscopic methods as well as elemental analysis. The typical spectroscopic features are showed in Table 2. The ^{1}H NMR spectra of **4a** and **4b** show characteristic vinyl proton N≡CCH= signals at *δ* 5.70 (**4a**) and 5.86 (**4b**) as singlet in CD_2Cl_2 at the room temperature, respectively. The $^{13}C\{^1H\}$ NMR spectra of these complexes displays the characteristic CH= signal of acrylonitrile ligand at *δ* 93.2 (**4a**) and 86.1 (**4b**) and N≡C signal at *δ* 137.9 (**4a**) and 134.1 (**4b**). Due to the presence of two inequivalent phosphorous centers, the



(2)

$^{31}P\{^{1}H\}$ NMR spectra of **4a** and **4b** inCD_2Cl_2 exhibit two doublets at δ 60.4, 54.8 ($^{2}J_{PP}$=29.7 Hz) (**4a**) and 60.0, 54.5 ($^{2}J_{PP}$=29.0 Hz) (**4b**), respectively. The IR spectra of acrylonitrile complexes **4a** and **4b** show the ν(N≡C) weak absorption at 2221 and 2206 cm^{-1}, respectively.

Table 2 Selected ^{31}P NMR, $^{13}C\{^{1}H\}$ NMR and IR data for the ruthenium acrylonitrile complexes

Complex	^{31}P NMR	^{1}H NMR δ	$^{13}C\{^{1}H\}$ NMR δ		IR $\nu_{(N\equiv C)}$/
	δ	CH=	CH=	N≡C	cm^{-1}
4a	60.4, 54.8	5.70	93.2	137.9	2221
4b	60.0, 54.5	5.86	86.1	134.1	2206

X-ray difraction studies were carried out for complexes **4a** and **4b**, and the structures for the cationic moieties of **4a** and **4b** are shown in Figures 3 and 4, respectively, with selected bond lengths and angles. The overall structures of **4a** and **4b** are similar to those of the allenylidene complexes **3a** and **3b**, with the allenylidene ligands replaced by the acrylonitrile ligands. In each complex, two DPPQ ligands chelate to the Ru center nearly perpendicularly with the N atom of one of the DPPQ ligands *trans* to the P atom of the other DPPQ [P(1)—Ru(1)—N(3), 177.40(6)° for **4a** and 175.3(2)° for **4b**]. Different from the cases in the allenylidene complexes **3a** and **3b**, in which both allenylidene ligands are *trans*-disposed to the N atom of the DPPQ ligands, it is noted that the 3,3-diphenylacrylonitrile ligand in **4a** is *trans* to a P atom of one of the DPPQ ligands, while the 2-(9*H*-fluoren-9-ylidene)acetonitrile ligand in **4b** is *trans* to a N atom of DPPQ. The characteristic acrylonitrile ligands are bonded to the ruthenium centers in a

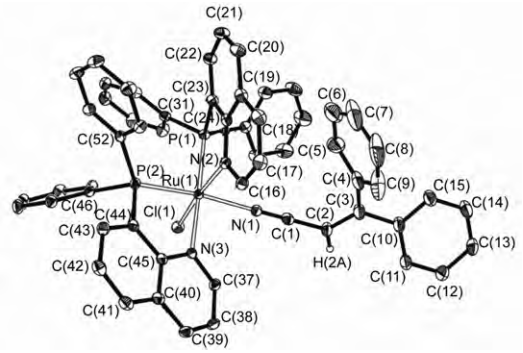


Figure 3 Molecular structure for the cation of **4a** with thermal ellipsoids drawn at 30% probability (CCDC 1567166)

Counter anion and hydrogen atoms except H(2A) are omitted for clarity. Selected bond lengths (nm) and angles (°): Ru(1)—N(1) 0.2081(2), N(1)—C(1) 0.1127(4), C(1)—C(2) 0.1436(4), C(2)—C(3) 0.1350(4), Ru(1)—N(2) 0.2075(2), Ru(1)—N(3) 0.2172(2), Ru(1)—P(1) 0.22511(6), Ru(1)—P(2) 0.22989(6), Ru(1)—Cl(1) 0.24168(6); N(2)—Ru(1)—N(1) 85.72(8), N(2)—Ru(1)—N(3) 96.07(8), N(1)—Ru(1)—N(3) 88.34(8), N(2)—Ru(1)—P(1) 82.27(6), N(1)—Ru(1)—P(1) 93.52(6), N(3)—Ru(1)—P(1) 177.40(6), N(2)—Ru(1)—P(2) 88.37(6), N(1)—Ru(1)—P(2) 167.48(6), N(3)—Ru(1)—P(2) 81.31(6), P(1)—Ru(1)—P(2) 96.62(2), N(2)—Ru(1)—Cl(1) 173.07(6), N(1)—Ru(1)—Cl(1) 87.67(6), N(3)—Ru(1)—Cl(1) 85.82(6), P(1)—Ru(1)—Cl(1) 96.07(2), P(2)—Ru(1)—Cl(1) 98.51(2), C(1)—N(1)—Ru(1) 175.4(2), N(1)—C(1)—C(2) 178.6(3), C(3)—C(2)—C(1) 121.8(3)

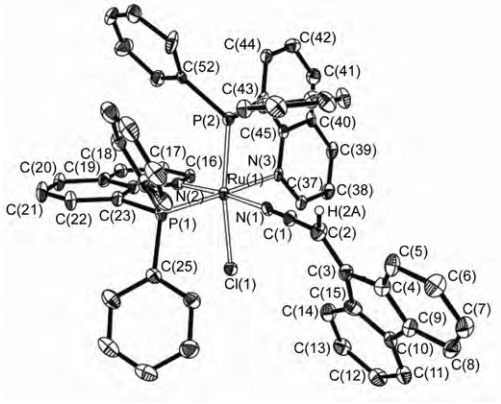


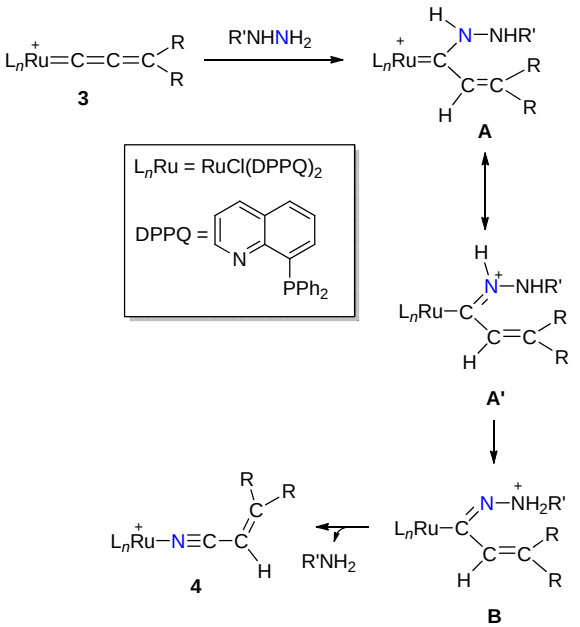
Figure 4 Molecular structure for the cation of **4b** with thermal ellipsoids drawn at 30% probability (CCDC 1834559)

Counter anion and hydrogen atoms except H(2) are omitted for clarity. Selected bond lengths (nm) and angles (°): Ru(1)—N(1) 1.992(10), N(1)—C(1) 0.1150(14), C(1)—C(2) 0.1423(16), C(2)—C(3) 0.1337(17), Ru(1)—N(2) 0.2107(9), Ru(1)—N(3) 0.2218(8), Ru(1)—P(1) 0.2261(3), Ru(1)—P(2) 0.2278(3), Ru(1)—Cl(1) 0.2447(3); N(2)—Ru(1)—N(1) 174.5(3), N(2)—Ru(1)—N(3) 92.6(3), N(1)—Ru(1)—N(3) 91.7(3), N(2)—Ru(1)—P(1) 82.8(2), N(1)—Ru(1)—P(1) 93.0(3), N(3)—Ru(1)—P(1) 175.3(2), N(2)—Ru(1)—P(2) 94.3(2), N(1)—Ru(1)—P(2) 89.8(3), N(3)—Ru(1)—P(2) 80.8(2), P(1)—Ru(1)—P(2) 99.57(10), N(2)—Ru(1)—Cl(1) 86.9(2), N(1)—Ru(1)—Cl(1) 89.7(3), N(3)—Ru(1)—Cl(1) 88.9(2), P(1)—Ru(1)—Cl(1) 90.72(10), P(2)—Ru(1)—Cl(1) 169.71 (9), C(1)—N(1)—Ru(1) 173.4(9), N(1)—C(1)—C(2) 178.3(13), C(3)—C(2)—C(1) 122.9(11).

nearly linear fashion. Taking **4a** as an example, the Ru(1)—N(1)—C(1) and N(1)—C(1)—C(2) bond angles are 175.4(2)° and 178.6(3)°, respectively, which, together with the triple-bond N≡C distance for N(1)—C(1) of 0.1127(4) nm and the single-bond C(1)—C(2) distance of 0.1436(4) nm, clearly indicate the ligand as an nitrile derivative. The Ru(1)—N(1) bond length is 0.2081(2) nm. These bonding parameters are close to those observed in ruthenium-bound nitrile complexes.[13c,19,20] The C(2)—C(3) bond length of 0.1350(4) nm and the bond angles around C(2) and C(3) are consistent with those reported for acrylonitrile ruthenium complexes.[20]

Several reactions involving transformation of metal-vinylidenes into nitrile derivatives via the use of hydrazines have been reported in literature, including the stoichiometric reactions of metal-vinylidenes with hydrazines to give metal-bound nitrile complexes,[13] as well as the catalytic transformation of terminal alkynes with hydrazines into nitriles via ruthenium- or rhodium-vinylidene intermediates.[15a,b] Formation of acrylonitrile complexes **4** from the reaction of **3** with hydrazines is closely related to the previously reported transformation of metal-vinylidenes. On the basis of the previous reports on metal-vinylidenes, a plausible mechanism for the formation of the ruthenium acrylonitrile complexes is outlined in Scheme 1. Initial nucleophilic addition of the unsubstituted nitrogen atom of the hydrazine to the C_α atom and protonation of the C_β atom of allenlidene ligand in complex **3** gave rise to the α-hydrazinovinylcarbene intermediate [RuCl(=C(NHNHR')—CH=CR_2)(DPPQ)$_2$][BPh_4] (**A**), for which

the contribution of the η^1-azoniabutadienyl resonance structure [RuCl(—C(=NHNHR')—CH=CR_2)(DPPQ)$_2$][BPh_4] (**A'**) may be also considered. Proton migration in **A** or **A'** could lead to the formation of the η^1-azabutadienyl intermediate [RuCl(—C(=NNH_2R')—CH=CR_2)(DPPQ)$_2$][BPh_4] (**B**), followed by subsequent deamination to form the final ruthenium acrylonitrile complex **4**. It is noted that Albertin and co-workers[13c] recently reported reaction of aryl vinylidene complexes [CpRu(=C=CHR)(PPh_3)L][BPh_4] (L = P(OEt)$_3$ or P(OMe)$_3$; R = Ph or *p*-tolyl) with hydrazines R'$NHNH_2$ (R'=H, Me or Ph) leading to the nitrile complexes [CpRu(N≡CCH_2R)(PPh_3)L][BPh_4] along with the eliminated amine R'NH_2. They provided an alternative mechanism based on the results of the labeling experiments with PhNH$^{15}NH_2$ and density functional theory (DFT) calculations, which involves the formation of a hydrazine-vinyl complex as an intermediate rather than the hydrazinocarbene carbene.[13c] Nevertheless, as a neutral nucleophile with acidic hydrogen, addition of hydrazines with complexes **4** to give **A** or **A'** conform to the classical behaviour expected for allenylidene complexes.[2a,2e,2h,21] Analogous addition of primary or secondary amines to the C_α—C_β bond of the allenylidenes to give vinylaminocarbene[8a,21a] or η^1-azoniabutadienyl complexes[2a,21b,21c] in ruthenium system is well known. The conversion of Cr, W,[13d] Mn,[13b] Ru[15a] and Fe[13a] hydrazino(methyl)carbene complexes into the corresponding acetonitrile complexes has also been reported. Unfortunately, our attempts to monitor the reaction of **3a** with 4-methylbenzenesulfono- hydrazide (TsNHNH_2) by NMR at low temperature range from −78 to 0 ℃ did not allow us to detect any further intermediates for this transformation.



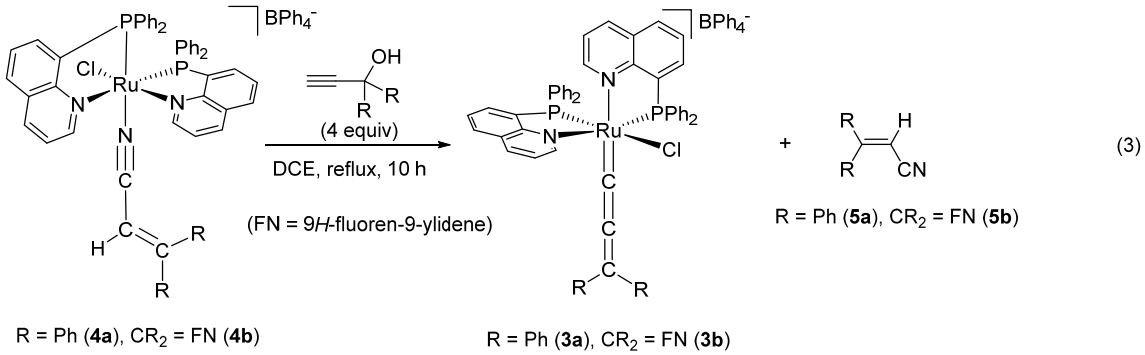
Scheme 1 Proposed mechanism for the reactions of allenylidene complex **3** with hydrazines to form acrylonitrile complex **4**

In fact, the reactivity of transition metal-allenylidenes with hydrazines remains largely unexplored, which is limited to only one published examples. Fischer and coworkers[16] reported that 1,2-dimethylhydrazine or 1,1-dimethylhydrozine served as dinucleophiles to react with chromium-allenylidene complexes [$(CO)_5$Cr=C=C=C(NMe_2)Ph] and [$(CO)_5$Cr=C=C=C(O-*endo*-Bornyl)OEt] affording the heterocyclic 1,2-dimethylpyrazolylidene chromium complex or the zwitterionic 1,1-dimethylpyrazolium-5-ylidene chromium complex via 1,2,3-diheterocyclization. In this case, the diheterocyclization took place with addition of hydrazines to the C_γ of the π-donor- substituted allenylidene ligand as the initiate step, which was then followed by displacement of one NMe_2 or the OEt substituent at the C_γ and subsequent intramolecular addition of the second NHMe or NMe_2 functionality to the C_α atom to complete the cyclization. We provide here the first examples of addition of hydrazines to metal-allenylidenes to give acrylonitrile derivatives.

2.3 Catalytic tests on the activity of 1 for the transformation of propargyl alcohol with hydrazines into acrylonitriles.

Fukumoto and co-workers have demonstrated that the ruthenium complex TpRuCl(PPh_3)$_2$[15a] and the rhodium system TpRh(C_2H_4)$_2$/P(2-furyl)$_3$[15b] [Tp = hydrotris(pyrazolyl)borate] can serve as efficient catalyst for the transformation of terminal alkynes and hydrazines into nitrile products through ruthenium- or rhodium-vinylidene intermediate, among which the ruthenium catalyst is effective for aryl-substituted or primary and secondary alkyl-substituted alkynes, while the rhodium catalyst is applicable for the tertiary alkyl-substituted alkynes. In addition, nitriles are usually labile ligands, which can readily dissociate from metal center to regenerate reactive species for further reaction. In view of the facile formation of acrylonitrile complex **4** at room temperature from the reaction of allenylidene complex **3** with hydrazines and the fact that allenylidene complex **3** can be accessed from the reaction of complex **1** with the respective propargyl alcohols, it seems to be very promised to develop the related catalytic reaction based on this chemical behavior by employing **1** as catalyst. More encouragingly, reaction of complex **4a** with 4 equiv. of 1,1-diphenylprop-2-yn-1-ol (**2a**) in refluxing DCE for 10 h does regenerate the allenylidene complex **3a** along with releasing 3,3-diphenylacrylonitrile (**5a**) almost quantitatively, which were isolated in 96% and 90% yield, respectively. Similarly, under the same reaction condition, reaction of allenylidene **4b** with 9-ethynyl-9*H*-fluoren-9-ol (**2b**) gave the corresponding allenylidene complex **3b** and 2-(9*H*-fluoren-9-ylidene)acetonitrile (**5b**) in high yields (92% and 85%, respectively) (Eq. 3).

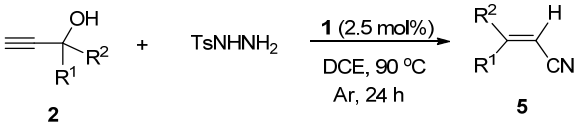
We then investigated the reactions of propargyl alcohols **2** with various *N*-substituted hydrazines such as TsNHNH_2, NH_2NH_2•H_2O, Me_2NHNH_2, $PhNHNH_2$ and $MeCONHNH_2$ in the presence of catalytic amount of complex **1** to test its catalytic activity for the formation of the respective acry-

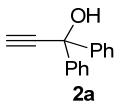
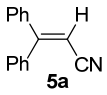
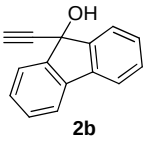
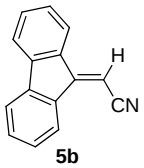
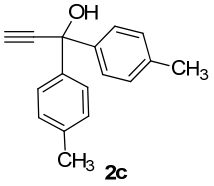
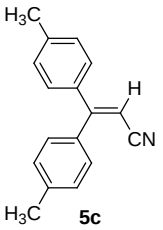
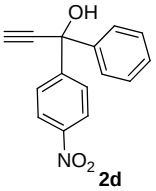
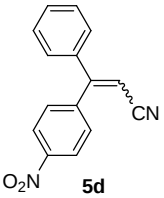
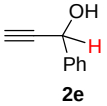
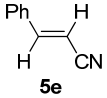


lonitriles. After our efforts for the screening of the reaction conditions, it is found that, the catalytic reaction does proceed to give the desired acrylonitrile product, yet the yield is not good. In the presence of 2.5 mol% complex **1**, the reaction of **2a** with 5.0 equiv. of $TsNHNH_2$ in DCE at 90 ℃ for 24 h gave the best result to produce 3,3-diphenylacrylonitrile (**5a**) in 30% isolated yield only (*ca.* 6 turnover for the monomeric $[RuCl(DPPQ)_2]^+$ species) (Table 3, Entry 1). Formation of the amine $TsNH_2$ was also detected. It was also the case for the reaction of 9-ethynyl-9*H*-fluoren-9-ol (**2b**) with $TsNHNH_2$ under the same conditions, which gave 2-(9*H*-fluoren-9-ylidene)- acetonitrile (**5b**) in 28% isolated yield only (Table 3, Entry 2). In both reactions, the substrate **2** was recovered in *ca.* 40% yield.[22,23] Our attempts to further improve the yields of the acrylonitrile products were unsuccessful. In this context, it should be mentioned that Zhan and co-workers[24] reported recently an efficient $FeCl_3$-catalyzed synthesis of acrylonitriles by employing propargyl alcohols and $TsNHNH_2$ as a combined cyano source through a domino propargylic substitution/aza- Meyer-Schuster rearrangement route. It is also noted that, in Fukumoto's $TpRh(C_2H_4)_2/P(2\text{-furyl})_3$ catalyst system, when 1,1-disubstituted propargyl alcohols including 1,1-diphenylprop-2-yn-1-ol (**2a**) were employed as the alkyne substrates, the corresponding *β*-cyanohydrins were obtained as the products instead of the respective acrylonitriles,[15b] which suggested that the catalytic reactions proceeded through the rhodium *γ*-hydroxyl vinylidene intermediates rather than allenylidenes.

At first glance, we envisioned that the unsatisfied result of the catalytic reaction could be probably due to the relatively stronger binding of the acrylonitrile to the ruthenium center in complex **4**, which then make it difficult to regenerate the reactive allenylidene **3** in the catalytic cycle. In fact, when the solution of the catalytic reaction was checked by ^{31}P NMR after the reaction was stopped, the acrylonitrile complexes **4a** and **4b** were the only detectable metal species. Thus, we looked into the reaction of complex **4** with the propargyl alcohol **2** in more details. As monitored by the *in situ* $^{31}P\{^1H\}$ NMR, no appreciable reaction occurred when a mixture of **4a** with **2a** in a molar ratio of 1∶1 in DCE was refluxed for 10 h. When the reaction was performed using 1∶2.5 molar ratio of **4a** and **2a**, the reaction could not be completed and became very slow after the solution was refluxed for 10 h, which seemed to reach a steady state with the acrylonitrile complex **4a** and

Table 3 Reaction of propargyl alcohol with $TsNHNH_2$ leading to acrylonitrile catalyzed by complex **1**[a]



Entry	Substrate	Product	Yield[b,c]/%
1	 **2a**	 **5a**	30
2	 **2b**	 **5b**	28
3	 **2c**	 **5c**	36
4	 **2d**	 **5d**	Trace
5	 **2e**	 **5e**	20

[a] Typical reaction conditions: oil bath, 90 ℃, propargyl alcohol (0.2 mmol), $TsNHNH_2$ (1.0 mmol), complex **1** (0.005 mmol) in DCE (2 mL) under reflux. [b] Isolated yield. [c] Substrates **2a** and **2b** were recovered in *ca.* 40% yield and benzophenone or 9*H*-fluoren-9-one was identified as the byproducts of the reactions (*ca.* 25%).[23]

the allenylidene product **3a** in about a molar ratio of 1∶1. This result clearly showed that the dissociated acrylonitrile presented in the solution could compete with alkyne substrate **2** to re-coordinate to the metal center, which may furnish an equilibrium for **4a**, alkyne **2a** and the allenylidene species **3a** in the solution, and thus inhibited further reaction. As a result, a large excess of **2** were needed to complete the reaction (Eq. 3). The relatively stronger coordination of the acrylonitrile to the ruthenium center than the propargilic alcohols **2** can be also expected based on above results. These observations are also consistent with our before-mentioned circumstances on the preparation of allenylidene complexes **3** from the reactions of the dimeric complex **1** with propargylic alcohols **2**, in which 10 equiv. of **2** were needed to complete the reaction (Eq. 1, 4 h for a 1∶5 ratio between the monomeric species $[RuCl(DPPQ)_2]^+$ and **2**). Moreover, these results also reflected the fact that the monomeric $[RuCl(DPPQ)_2]^+$ species is not so reactive in the reaction with propargyl alcohols **2** for the formation of the allenylidene complex, which then suggested that formation of allenylidene intermediates **3** (or the related γ-hydroxyl vinylidene precursors) from the reaction of $[RuCl(DPPQ)_2]^+$ species with **2** should be rate-determining step in the catalytic reaction. Consequently, all these factors taken together lead to the poor catalytic activity of **1** in the catalytic reaction, although the conversion of allenylidene complexes **3** with hydrazines into acrylonitrile can take place readily.

We have also preliminarily investigated the scope of the propargyl alcohols as well as electronic effect of the substituents. The 1,1-di-*p*-tolylprop-2-yn-1-ol (**2c**) with electron-donating methyl groups at 4-position of the phenyl substituents of the propargyl alcohol led to slightly increasing of the yield of the 3,3-di-*p*-tolylacrylonitrile product **3c** (36% isolated yield), while introducing electron-withdrawing NO_2 group at the phenyl ring (substrate **2d**) only gave trace amount of the desired acrylonitrile **3d** (Table 3, Entries 3 and 4). The reaction of $TsNHNH_2$ with other propargyl alcohol such as 1-phenylprop-2-yn-1-ol (**2e**) which can form ruthenium allenylidene intermediate also led to the formation of the corresponding cinnamonitrile (**5e**), with a low isolated yield of 20% only (Entry 5). Although the results are not good, our preliminary studies provide a new idea for the design of catalytic transformation of terminal propargylic alcohols and hydrazines into acrylonitriles via allenylidene intermediates.

3 Conclusions

In summary, the new cationic ruthenium allenylidene complexes $[RuCl(=C=C=CR_2)(DPPQ)_2][BPh_4]$ (**3a**: R＝Ph; **3b**: CR_2＝FN＝9*H*-fluoren-9-ylidene) supported by the heterobidentate P,N-donor ligand 8-(diphenylphosphanyl)quinoline (DPPQ) have been synthesized from the reactions of $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2[BPh_4]_2$ (**1**) with excess 1,1-diphenylprop-2-yn-1-ol (**2a**) or 9-ethynyl-9*H*-fluoren-9-ol (**2b**), respectively. Addition of hydrazines to the ruthenium-allenylidenes **3** led to the facile formation of ruthenium-boubd acrylonitrile complexes $[RuCl(N{\equiv}C{-}CH{=}CR_2)(DPPQ)_2][BPh_4]$ (**4a**: R＝Ph; **4b**: CR_2＝FN) at room temperature. This reaction involves the intermolecular attack of hydrazines at the C_α atom of the allenylidene ligand, which represents the first examples of addition of hydrazines to metal-allenylidenes affording acrylonitrile derivatives. In addition, reaction of acrylonitrile complex **4** with an excess of progarylic alcohols **2** (4 equiv.) could release the organic acrylonitriles 3,3-diphenylacrylonitrile (**5a**) or 2-(9*H*-fluoren-9-ylidene)acetonitrile (**5b**) along with regeneration of allenylidene complex **3**. Inspired by these chemical behaviors, the catalytic activity of **1** for the transformation of terminal propargyl alcohols and hydrazines into acrylonitriles has been investigated preliminarily. The results show that the catalytic reaction proceeds to give the desired acrylonitrile product, albeit the yield is not good. On the basis of the results on the examination of the reaction of complexes **1** or **4** with different amount of proparyl alcohols **2a** and **2b**, the relatively poor catalytic activity of **1** could be probably ascribed to the relative low reactivity of the monomeric $[RuCl(DPPQ)_2]^+$ species in terms of the reaction with proparyl alcohol **2** for the formation of the allenylidene complex, as well as the relatively stronger coordination of the acrylonitrile to the ruthenium center than the propargyl alcohols **2**. Nevertheless, our preliminary results of the catalytic reactions demonstrated that it is very promised to develop new catalytic reactions for the transformation of terminal propargylic alcohols and hydrazines into acrylonitriles via allenylidene intermediates. Further studies aimed at improving the activity of catalyst by modification of the 8-phosphinoquinoline ligand and investigations on the substrate scope for the catalytic reaction, as well as the electronic effect of the substituents of the propargylic alcohol substrates are underway.

4 Experimental section

4.1 General details

NMR spectroscopic experiments were carried out on Bruker AV400 and Bruker AV500. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are relative to TMS, and $^{31}P\{^1H\}$ NMR is relative to the external standard (85% H_3PO_4). Elemental analyses data were obtained on an Elementar Analysensysteme GmbH Vario EL III instrument. Infrared spectra (4000～400 cm^{-1}) as obtained from Nujol mulls between KBr disks were recorded on a Nicolet 380 spectrometer. Melting points were obtained from a Yanaco MP-500.

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise noted. Solvents were distilled from sodium/benzophenone (THF, Et_2O and *n*-hexane) or calciumhydride (CH_2Cl_2) under argon prior to use. The starting material $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2[BPh_4]_2$,[17] 9-ethynyl-9*H*-fluoren-9-ol[25] and (9*H*-fluoren-9-ylidene)hydrazine[26]

were prepared according to literature methods. All other reagents were used as received from commercial sources without further purification, unless otherwise noted.

4.2 Experimental procedures

4.2.1 Synthesis of allenylidene complexes [RuCl(=C=C=CR_2)$(DPPQ)_2$][BPh_4] (**3a**: R=Ph; **3b**: CR_2=FN)

A mixture of [Ru(*u*-Cl)$(DPPQ)_2]_2[BPh_4]_2$ (0.4 g, 0.185 mmol) and the corresponding terminal propargyl alcohol (10.0 equiv.) in 1,2-dichloroethane was stirred at 90 ℃ for 4 h to give a purple solution. The solvent was concentrated to *ca.* 2 mL under reduced pressure and diethyl ether (20 mL) was added to the residue. The mixture was vigorously stirred about 10 min to give amount of purple precipitate. The solid was collected by filtration, washed with Et_2O (10 mL×3) and dried under vacuum, which was identified to be the allenylidene complex **3**. Crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **3**.

[RuCl(=C=C=CPh_2)$(DPPQ)_2$][BPh_4] (**3a**): Yield 85%. m.p. 168～170 ℃; ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 10.30～10.16 (m, 1H, quinolyl), 8.68 (d, *J*=10.0 Hz, 1H, quinolyl), 8.37～8.33 (m, 2H), 8.25 (d, *J*=10.0 Hz, 1H, quinolyl), 8.20～8.13 (m, 3H), 7.95 (t, *J*=10 Hz, 1H, PPh_2-*para*), 7.85 (dd, *J*=10.5, 6.5 Hz, 1H), 7.77 (t, *J*=10 Hz, 1H, PPh_2-*para*), 7.72 (d, *J*=6.5 Hz, 1H), 7.65 (t, *J*=10 Hz, 2H, Ph-*para*), 7.53～7.50 (m, 1H), 7.43～7.35 (m, 15H, BPh_4-*ortho* and other aromatic), 7.32～7.29 (m, 1H), 7.26～7.23 (m, 1H), 7.18 (t, *J*=10 Hz, 4H), 7.10～6.99 (m, 12H, BPh_4-*meta* and other aromatic), 6.94～6.84 (m, 6H, BPh_4-*pata* and other aromatic), 6.82～6.70 (m, 6H), 6.18 (dd, *J*=14.0, 10 Hz, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 311.2 [t, *J*(PC)=17.5, Ru=$\mathbf{C}_\alpha$], 209.6 (s, Ru=C=$\mathbf{C}_\beta$), 164.1 [dd, *J*(PC)=122.9, 61.7 Hz, quinolyl], 159.1 (s, Ru=C=C=C_γ), 155.7, 153.1, 151.8, 151.7, 151.2, 151.0, 144.1, 139.41, 139.39, 138.2, 137.6, 135.9 (BPh_4-*ortho*), 135.5, 135.4, 132.8, 132.7, 132.1, 131.8, 131.7～130.6 (m), 130.5 (Ph-*ortho*), 130.2～129.3 (m), 129.0 (Ph-*meta*), 128.8～127.7 (m), 126.6 (br, BPh_4-*meta*), 123.8, 122.6, 121.7 (BPh_4-*pata*); ^{31}P NMR (202 MHz, CD_2Cl_2) δ: 56.4 [d, *J*(PP)=27.0 Hz], 48.3 [d, *J*(PP)=27.0 Hz]; IR (KBr) *v*: 1934 (s, C=C=C) cm^{-1}. Anal. calcd for $C_{81}H_{62}BClN_2P_2Ru$: C 76.44, H 4.91, N 2.20; found C 76.74, H 4.87, N 2.08.

[RuCl(=C=C=FN)$(DPPQ)_2$][BPh_4] (**3b**): Yield 94%. m.p. 176～178 ℃; ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 10.12～10.10 (m, 1H, quinolyl), 8.67 (dt, *J*=7.9, 1.6 Hz, 1H), 8.41～8.37 (m, 2H), 8.29 (dt, *J*=7.9, 1.6 Hz, 1H), 8.26～8.22 (m, 3H), 8.01～7.95 (m, 1H), 7.85～7.81 (m, 2H), 7.72 (dd, *J*=5.0, 2.0 Hz, 1H), 7.59～7.55 (m, 4H), 7.49～7.40 (m, 6H), 7.39～7.29 (m, 10H, BPh_4-*ortho* and other aromatic), 7.12～6.98 (m, 10H, BPh_4-*meta* and other aromatic), 6.97～6.92 (m, 5H, BPh_4-*pata* and other aromatic), 6.91～6.87 (m, 5H), 6.85～6.82 (m, 2H), 6.78～6.74 (td, *J*=7.5, 2.5 Hz, 2H), 6.60 (d, *J*=7.5 Hz, 2H), 6.22～6.18 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 312.8 [t, *J*(PC)=17.8, Ru=$\mathbf{C}_\alpha$], 216.7 (Ru=C=$\mathbf{C}_\beta$), 164.1 [dd, *J*(PC)=98.9, 48.5 Hz, quinolyl], 155.7, 153.4 (s, Ru=C=C=$\mathbf{C}_\gamma$), 153.2, 151.7 [d, *J*(PC)=18.0 Hz], 151.0 (d, *J*(PC)=18.0 Hz), 145.7, 142.0, 139.7, 138.4, 137.8, 136.0 (BPh_4-*ortho*), 135.5 [d, *J*(PC)=10.1 Hz], 133.1, 132.9, 132.8 [d, *J*(PC)=10.1 Hz], 131.6～127.0 (m), 125.6 (br, BPh_4-*meta*), 123.8, 123.0, 122.7, 121.7 (BPh_4-*pata*), 121.5; ^{31}P NMR (202 MHz, CD_2Cl_2) δ: 55.2 [d, *J*(PP)=27.2 Hz], 46.7 [d, *J*(PP)=27.2 Hz]; IR (KBr) *v*: 1935 (s, C=C=C) cm^{-1}. Anal. calcd for $C_{81}H_{60}BClN_2P_2Ru$: C 76.57, H 4.76, N 2.20; found C 76.41, H 5.11, N 2.17.

4.2.2 Typical procedure for the synthesis of acrylonitrile complexes [RuCl(N≡C—CH=CR_2)$(DPPQ)_2$][BPh_4] (**4a**: R=Ph; **4b**: CR_2=FN)

A mixture of the allenylidene complex **3** (0.2 g, 0.16 mmol) and hydrazines (1.1 equiv.) in CH_2Cl_2 was stirred at room temperature for 30 min to give a yellow solution, then the solvent was removed under reduced pressure. Addition of diethyl ether (15 mL) to the residue with stirring produced a yellow solid. The solid was collected by filtration, washed with Et_2O (10 mL×3) and dried under vacuum, which was identified to be the acrylonitrile complex **4**. The filtrate was also collected and evaporated to *ca.* 1 mL under vacuum. The residue was purified by silica gel column chromatography to give the corresponding amine product. Crystals of **4** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **4**.

[RuCl(N≡C—CH=CPh_2)$(DPPQ)_2$][BPh_4] (**4a**): Yield 97%. m.p. 196～198 ℃; ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 10.55～10.53 (m, 1H, quinolyl), 8.60 (dt, *J*=7.9, 1.6 Hz, 1H), 8.28～8.25 (m, 2H), 8.05～7.97 (m, 4H), 7.85～7.75 (m, 4H), 7.55～7.51 (m, 1H), 7.50～7.43 (m, 4H), 7.42～7.41 (m, 1H), 7.40～7.35 (m, 10H, BPh_4-*ortho* and other aromatic), 7.31 (dd, *J*=5.0, 1.5 Hz, 1H), 7.28～7.24 (m, 2H), 7.19～7.17 (m, 2H), 7.11～7.02 (m, 14H, BPh_4-*meta* and other aromatic), 7.02～6.98 (m, 3H), 6.96～6.93 (m, 1H), 6.92～6.87 (m, 4H, BPh_4-*pata*), 6.71～6.65 (m, 5H), 6.05～6.01 (m, 2H), 5.71 (s, 1H, CH=CPh_2); ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 164.5 [dd, *J*(PC)=102.4, 51.7 Hz, quinolyl], 156.1, 154.7, 154.6, 151.8 [d, *J*(PC)=17.9 Hz], 138.9, 137.9 (C≡N), 137.6, 136.6, 135.9 (BPh_4-*ortho*), 135.4, 134.8 [d, *J*(PC)=10.7 Hz], 134.4, 132.3～127.7 (m), 126.3, 125.6 (br, BPh_4-*meta*), 123.9, 121.9, 121.7 (BPh_4-*pata*), 93.2 (s, CH=CPh_2); ^{31}P NMR (202 MHz, CD_2Cl_2) δ: 60.4 [d, *J*(PP)=29.6 Hz], 54.8 (d, *J*(PP)=29.6 Hz); IR (KBr) *v*: 2210 (N≡C) cm^{-1}. Anal. calcd for $C_{81}H_{63}BClN_3P_2Ru$: C 75.55, H 4.93, N 3.26; found C 75.89, H 5.24, N 3.25.

[RuCl(N≡C—CH=FN)$(DPPQ)_2$][BPh_4] (**4b**): Yield 92%. m.p. 205～207 ℃; ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 10.82 (t, *J*=3.0 Hz, 1H, quinolyl), 8.63 (d, *J*=8.5 Hz, 1H), 8.29 (dd, *J*=16.5, 8.0 Hz, 2H), 8.09 (dd, *J*=16.5, 8.0 Hz, 2H), 7.98～7.86 (m, 6H), 7.78 (t, *J*=7.5 Hz, 2H), 7.63 (dd, *J*=7.5, 3.5 Hz, 2H), 7.53 (d, 7.5 Hz, 2H), 7.49～7.44

(m, 4H), 7.43～7.27 (m, 12H, BPh_4-*ortho* and other aromatic), 7.18～7.10 (m, 6H), 7.05 (t, J＝7.5 Hz, 8H, BPh_4-*meta*), 6.93～6.87 (m, 6H, BPh_4-*para* and other aromatic), 6.83～6.73 (m, 4H), 6.14 (dd, J＝11.0, 7.5 Hz, 2H), 5.86 (s, 1H, C**H**＝FN); ^{13}C NMR (126 MHz, CD_2Cl_2) δ: 164.1 [dd, J(PC)＝98.2, 49.1 Hz, quinolyl], 156.3, 155.9, 154.9 [t, J(PC)＝10.1 Hz], 152.1, 151.9, 141.7, 140.8, 139.3, 138.2, 137.9 [d, J(PC)＝7.6 Hz], 136.0 (BPh_4-*ortho*), 134.4 [d, J(PC)＝10.1 Hz], 134.1 (**C**≡N), 132.6～127.8 (m), 125.6 (br, BPh_4-*meta*), 125.4, 124.0, 122.1, 121.73, 121.67 (BPh_4-*pata*), 120.5, 120.3, 86.1 (s, CH＝FN); ^{31}P NMR (202 MHz, CD_2Cl_2) δ: 60.0 [d, J(PP)＝29.0 Hz], 54.5 (d, J(PP)＝29.0 Hz); IR (KBr) ν: 2200 (N≡C) cm^{-1}. Anal. calcd for $C_{81}H_{61}BClN_3P_2Ru$: C 75.67, H 4.78, N 3.27; found C 75.65, H 5.09, N 3.12.

4.2.3 Reaction of complex **4a** with 1,1-diphenylprop-2-yn-1-ol (**2a**) to form complex **3a**

A mixture of complex **4a** (0.1 g, 0.08 mmol) and **2a** (65 mg, 0.32 mmol) in 1,2-dichloroethane (6 mL) was stirred at 90 ℃ for 10 h to give a purple solution, then the solvent was removed under reduced pressure. Addition of diethyl ether (10 mL) to the residue produced a purple solid, which was collected by filtration, washed with Et_2O (10 mL×3) and dried under vacuum. The purple solid was identified as complex **3a** (95 mg, 96% yield). In order to isolate the organic compound, the filtrate was collected and evaporated to *ca*. 1 mL under vacuum. The residue was purified by silica gel column chromatography to give 3,3-diphenylacrylonitrile (**5a**)[24] as a white solid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53～7.43 (m, 6H), 7.41 (t, J＝7.7 Hz, 2H), 7.33 (d, J＝7.7 Hz, 2H), 5.77 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.1, 139.0, 137.1, 130.4, 130.0, 129.6, 128.7, 128.6, 128.5, 117.9, 94.9.

4.2.4 Reaction of complex **4b** with 9-ethynyl-9*H*-fluoren-9-ol (**2b**) to form complex **3b**

A mixture of complex **4b** (0.13 g, 0.1 mmol) and **2b** (0.11 g, 0.4 mmol) in 1,2-dichloroethane (6 mL) was stirred at 90 ℃ for 10 h to give a purple solution, then the solvent was removed under reduced pressure. Addition of diethyl ether (10 mL) to the residue produced a purple solid, which was collected by filtration, washed with Et_2O (10 mL mL×3) and dried under vacuum. The purple solid was identified as complex **3b** (94 mg, 92% yield). In order to isolate the organic compound, the filtrate was collected and evaporated to ca.1 mL under vacuum. The residue was purified by silica gel column chromatography to give 2-(9*H*-fluoren-9-ylidene)acetonitrile (**5b**)[24] as a pale yellow solid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.43 (d, J＝7.5 Hz, 1H), 7.64 (q, J＝7.5 Hz, 3H), 7.47 (dtd, J＝12.5, 7.5, 1.1 Hz, 2H), 7.38 (td, J＝7.5, 1.1 Hz, 1H), 7.33～7.28 (m, 1H), 6.11 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 153.5, 141.9, 140.7, 136.5, 134.9, 131.8, 131.7, 128.4, 127.9, 125.4, 121.5, 120.2, 120.1, 117.4, 88.5.

4.2.5 Typical procedure for the catalytic reactions

Catalyst **1** (0.005 mmol), terminal propargylic alkynols (0.2 mmol), $TsNHNH_2$ (1.0 mmol) and DCE (2 mL) were added to a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred at 90 ℃ for 24 h under argon atmosphere. The solvent was then removed under reduced pressure, and the residue was purified by column chromatography on silica gel [V(petroleum ether)∶V(ethyl acetate)＝20∶1] to afford the corresponding acrylonitrile **5**.

3,3-Di-*p*-tolylacrylonitrile (**5c**)[24]: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37 (d, J＝7.8 Hz, 2H), 7.28 (d, J＝7.8 Hz, 2H), 7.24～7.20 (m, 4H), 5.69 (s, 1H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.2, 140.8, 140.2, 136.4, 134.4, 129.6, 129.3, 129.2, 128.5, 118.3, 93.4, 21.4, 21.3.

Cinnamonitrile (**5e**)[27]: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58～7.34 (m, 6H), 5.90 (d, J＝16.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 150.6, 133.6, 131.2, 129.1, 127.4, 118.2, 96.4.

Supporting Information X-ray crystallographic details for complexes **3a**, **3b**, **4a** and **4b**. ^{31}P NMR, ^{1}H NMR, ^{13}C NMR spectra of complexes **3**～**5**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

References

[1] (a) Bruce, M. I. *Chem. Rev*. **1998**, *98*, 2797.
(b) Herndon, J. W. *Coord. Chem. Rev*. **2018**, *356*, 1 and references therein.
(c) Cadierno, V.; Gimeno, J. *Chem. Rev*. **2009**, *109*, 3512.
(d) Che, C. M.; Ho, C. M.; Huang, J. S. *Coord. Chem. Rev*. **2007**, *251*, 2145.
(e) Varela, J. A.; González-Rodríguez, C.; Saá, C. *Top. Organomet. Chem*. **2014**, *48*, 237.
(f) Lozano-Vila, A. M.; Monsaert, S.; Bajek, A.; Verpoort, F. *Chem. Rev*. **2010**, *110*, 4865.
(g) Nishibayashi, Y. *Synthesis* **2012**, *44*, 489.
(h) Rigaut, S.; Touchard, D.; Dixneuf, P. H.; *Coord. Chem. Rev*. **2004**, *248*, 1585.
(i) Bruneau, C.; Dixneuf, P. H. *Angew. Chem., Int. Ed*. **2006**, *45*, 2176.

[2] Selected examples: (a) Hyder, I.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **2011**, *30*, 726.
(b) Smith, E. J.; Johnson, D. G.; Thatcher, R. J.; Whitwood, A. C.; Lynam, J. M. *Organometallics* **2013**, *32*, 7407.
(c) Bruce, M. I.; Burgun, A.; Fox, M. A.; Jevric, M.; Low, P. J.; Nicholson, B. K.; Parker, C. R.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Organometallics* **2013**, *32*, 3286.
(d) Alós, J.; Bolaño, T.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Valencia, M. *Inorg. Chem*. **2014**, *53*, 1195.
(e) Garcia de la Arada, I.; Díez, J.; Gamasa, M. P.; Lastra, E. *Organometallics* **2015**, *34*, 1345.
(f) Schauer, P. A.; Skelton, B. W.; Koutsantonis, G. A. *Organometallics* **2015**, *34*, 4975.
(g) Spoerler, S.; Strinitz, F.; Rodehutskors, P.; Mueller, L.; Waterloo, A. R.; Duerr, M.; Huebner, E.; Ivanovic-Burmazovic, I.; Tykwinski, R. R.; Burzlaff, N. *New J. Chem*. **2016**, *40*, 2167.
(h) Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **2016**, *35*, 388.
(i) Huang, J. B.; Zhou, X. X.; Zhao, Q. Y.; Li, S. H.; Xia, H. P. *Chin. J. Chem*. **2017**, *35*, 420.

[3] Coletti, C.; Marrone, A.; Re, N. *Acc. Chem. Res*. **2012**, *45*, 139.

[4] (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organ-*

ometallics **1996**, *15*, 2137.
(b) Auger, N.; Touchard, D.; Rigaut, S.; Halet, J.-F.; Saillard, J.-Y. *Organometallics* **2003**, *22*, 1638.
(c) Wong, C.-Y.; Lai, L.-M.; Lam, C.-Y.; Zhu, N. *Organometallics* **2008**, 27, 5806.

[5] Selected examples: (a) Pino-Chamorro, J. A.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2009**, *28*, 1546.
(b) Bustelo, E.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **2007**, *26*, 4300.
(c) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 3980.
(d) Bustelo, E.; Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 1903.

[6] Selected examples: (a) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606.
(b) Bernad, D. J.; Esteruelas, M.; López, A. M.; Oliván, M.; Oñate, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 4327.
(c) Kanao, K.; Tanabe, Y.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2010**, *29*, 2381.
(d) Queensen, M. J.; Rath, N. P.; Bauer, E. B. *Organometallics* **2014**, *33*, 5052.
(e) Strinitz, F.; Tucher, J.; Januszewski, J. A.; Waterloo, A. R.; Stegner, P.; Förtsch, S.; Hübner, E.; Tykwinski, R. R.; Burzlaff, N. *Organometallics* **2014**, *33*, 5129.
(f) Garcia de la Arada, I.; Díez, J.; Gamasa, M. P.; Lastra, E. *J. Organomet. Chem.* **2015**, *797*, 101.

[7] (a) Chen, K.-H.; Feng, Y. J.; Ma, H.-W.; Lin, Y.-C.; Liu, Y.-H.; Kuo, T.-S. *Organometallics* **2010**, *29*, 6829.
(b) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Falvello, L. R.; Llusar, R. M. *Organometallics* **2002**, *21*, 3716.
(c) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Organometallics* **1998**, *17*, 5216.

[8] (a) Serrano-Ruiz, M.; Lidrissi, C.; Mañas, S.; Peruzzini, M.; Romerosa, A. *J. Organomet. Chem.* **2014**, *751*, 654.
(b) Talavera, M.; Bolaño, S.; Bravo, J.; Castro, J.; García-Fontán, S.; Hermida-Ramón, J. M. *Organometallics* **2013**, *32*, 4402.

[9] (a) Venâncio, A. I. F. M.; Guedes da Silva, F. C.; Martins, L. M. D. R. S.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Organometallics* **2005**, *24*, 4654.
(b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; Garcıá-Granda, S. *Organometallics* **1997**, *16*, 4453.

[10] (a) Fischer, H.; Reindl, D.; Troll, C.; Leroux, F. *J. Organomet. Chem.* **1995**, *490*, 221.
(b) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modriego, J.; Oñate, E. *Organometallics* **1998**, *17*, 5434.
(c) Bolaño, S.; Rodríguez-Rocha, M. M.; Bravo, J.; Castro, J.; Oñate, E.; Peruzzini, M. *Organometallics* **2009**, *28*, 6020.
(d) Jiménez-Tenorio, J.; Palacios, M. D.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **2004**, *689*, 2776.
(e) Peruzzini, M.; Barbaro, P.; Bertolasi, V.; Bianchini, C.; Mantovani, N.; Marvelli, L.; Rossi, R. *Dalton Trans.* **2003**, 4121.
(f) Coletti, C.; Gonsalvi, L.; Guerriero, A.; Marvelli, L.; Peruzzini, M.; Reginato, G.; Re, N. *Organometallics* **2010**, *29*, 5982.

[11] Utegenov, K. I.; Krivykh, V. V. Glukhov, I. V. Petrovskii, P. V.; Ustynyuk, N. A. *J. Organomet. Chem.* **2011**, *696*, 3408.

[12] (a) Beletskaya, I. P.; Cheprakov, A. V. *Organometallics* **2012**, *31*, 7753.
(b) Hoover, J. M.; DiPasquale, A.; Mayer, J. M.; Michael, F. E. *J. Am. Chem. Soc.* **2010**, *132*, 5043.
(c) Schweizer, P. D.; Wadepohl, H.; Gade, L. H. *Organometallics* **2013**, *32*, 3697.

[13] (a) Barrett, A. G. M.; Carpenter, N. E.; Sabat, M. *J. Organomet. Chem.* **1988**, *352*, C8.
(b) Alt, H. G.; Engelhardt, H. E.; Steinlein, E.; Rogers, D. *J. Organomet. Chem.* **1987**, *344*, 321.
(c) Albertin, G.; Antoniutti, S.; Bortoluzzi, M.; Botter, A.; Castro, J. *Dalton Trans.* **2015**, *44*, 3439.

[14] Dabb, S. L.; Messerle, B. A.; Wagler, J. *Organometallics* **2008**, *27*, 4657.

[15] (a) Fukumoto, Y.; Dohi, T.; Masaoka, H.; Chatani, N.; Murai, S. *Organometallics* **2002**, *21*, 3845.
(b) Fukumoto, Y.; Tamura, Y.; Iyori, Y.; Chatani, N. *J. Org. Chem.* **2016**, *81*, 3161.
(c) Fukumoto, Y.; Ohmae, A.; Hirano, M.; Chatani, N. *Asian J. Org. Chem.* **2013**, *2*, 1036.
(d) Fukumoto, Y.; Asai, H.; Shimizu, M.; Chatani, N. *J. Am. Chem. Soc.* **2007**, *129*, 13792.

[16] Szesni, N.; Hohberger, C.; Mohamed, G. G.; Burzlaff, N.; Weibert, B.; Fischer, H. *J. Organomet. Chem.* **2006**, *691*, 5753.

[17] Cai, T.; Yang, Y.; Li, W.-W.; Qin, W.-B.; Wen, T.-B. *Chem.-Eur. J.* **2018**, *24*, 1606.

[18] Selegue, J. P. *Organometallics* **1982**, *1*, 217.

[19] (a) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1996**, *14*, 2447.
(b) Das, U. K.; Bhattacharjee, M. *Chem.-Eur. J.* **2012**, *18*, 5180.
(c) Sgro, M. J.; Stephan, D. W. *Dalton Trans.* **2013**, *42*, 10460.

[20] (a) Anil Kumar, P. G.; Pregosin, P. S.; Vallet, M.; Bernardinelli, G.; Jazzar, R. F.; Viton, F.; Kündig, E. P. *Organometallics* **2004**, *23*, 5410.
(b) Chiririwa, H.; Meijboom, R. *Acta Crystallogr.* **2011**, *E67*, m1335.

[21] (a) Kopf, H.; Holzberger, B.; Pietraszuk, C.; Hübner, E.; Burzlaff, N. *Organometallics* **2008**, 27, 5894.
(b) Jiménez-Tenorio, M.; Palacios, M. D.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **2004**, *689*, 2776.
(c) Bernad, D. J.; Esteruelas, M.; López, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995.

[22] In the catalytic reactions, benzophenone or 9*H*-fluoren-9-one was also isolated as the byproducts (*ca.* 25%). We initially envisioned that the H_2O presented in the reaction solution, which released along with the Selegue's reaction during the formation of the allenylidene complex, might lead to the hydrolysis of the acrylonitrile product **5** to give the respective ketones. We have performed the control experiments by heating a solution of 3,3-diphenylacrylonitrile (**5a**) in DCE with purposely added water at even 110 ℃ for several hours with or without 2.5 mol% of complex **1**. However, the hydrolysis issue is unlikely. As reflected by the TLC of the reaction solution, only trace amount of benzophenone can be detected. On the other hand, it has been reported that *γ*-substituted *tert*-propargyl alcohols have been involved in Sonogashira-type reactions as masked terminal alkynes via *β*-carbon elimination with liberation of ketone (see Ref. [23]). We tentatively envisioned that the ketone byproducts obtained in the catalytic reaction might come from *β*-carbon elimination of terminal *tert*-propargyl alcohols.

[23] (a) Nishimura, T.; Ariki, H.; Maeda, Y.; Uemura, S. *Org. Lett.* **2003**, *5*, 2997.
(b) Funayama, A.; Satoh, T.; Miura, M. *J. Am. Chem. Soc.* **2005**, *127*, 15354.
(c) Li, T.; Wang, Z.; Zhang, M. L.; Zhang H.-J.; Wen, T.-B. *Chem. Commun.* **2015**, *51*, 6777.
(d) Li, T.; Wang, Z.; Qin, W.-B.; Wen, T.-B. *ChemCatChem* **2016**, *8*, 2146.

[24] Hao, L.; Wu, F.; Ding, Z.-C.; Xu, S.-X.; Ma, Y.-L.; Chen, L.; Zhan, Z.-P. *Chem.-Eur. J.* **2012**, *18*, 6453.

[25] Chiarucci, M.; Mocci, R.; Syntrivanis, L. D.; Cera, G.; Mazzanti, A.; Bandini, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 10850.

[26] Hu, M. Y.; Ni, C. F.; Li, L. C.; Han, Y. X.; Hu, J. B. *J. Am. Chem. Soc.* **2015**, *137*, 14496.

[27] Shipilovskikh, S. A.; Vaganov, V. Y.; Denisova, E. I.; Rubtsov, A. E.; Malkov, A. V. *Org. Lett.* **2018**, *20*, 728.

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