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Coupling of terminal alkynes by $RuHXL_2$ (X = Cl or $N(SiMe_3)_2$, L = P^iPr_3)

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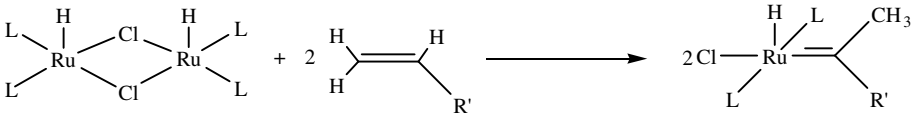
Abstract

The compounds RuL_2HX, where L = P^iPr_3 and X = Cl or $N(SiMe_3)_2$, are catalyst precursors for dimerization of terminal alkynes to enynes and also to cumulenes at 23 °C; selectivity among these products is X-dependent, but not high. Conversion of Ru species onto the catalytic cycle was undetectably small, so alternative approaches to understanding the catalytic mechanism were employed: stoichiometric reactions, independent synthesis of candidate intermediates, and trapping with CO. These show the intermediacy of vinylidenes and vinyl compounds, and reveal conversion of cumulenes to the thermodynamically more stable enynes.

Keywords: Terminal alkynes; Dimerization; Enynes; Cumulenes

1. Introduction

Back donation from a metal center containing no pi acid ligands has been shown to have the ability to isomerize hydrocarbons to the isomeric carbene complexes, especially from olefins (Eq. (1)).



1

R' = H, OR, or NR^1R^2 (1)

In this report, these 14e unsaturated ruthenium complexes are investigated for the reactivity with terminal alkynes, via possible intermediate vinylidene or vinyl complexes. The reaction of terminal alkynes with unsaturated divalent ruthenium or osmium complexes is known to form vinylidene complexes (Scheme 1) [7–11]. The present report

For example, the 14-electron ruthenium(II) complexes $RuXHL_2$ [1] (X = Cl, F, NH^tBu, O^tBu, or $N(SiMe_3)_2$, and L = P^iPr_3) were investigated for their reactivity with various vinyl compounds [2–6].

focuses especially on the reactivity of 14-electron ruthenium(II) complexes $RuXHL_2$ (X = Cl (**1**), or $N(SiMe_3)_2$ (**2**), and L = P^iPr_3) with various alkynes, but under catalytic conditions, where the alkyne/Ru ratio is much greater than unity. The dimerization of terminal alkynes [12–17] has been widely studied because of its attractive, atom-economic forming of a C–C bond which serve as a useful building block for organic synthesis [18–20]. In addition,

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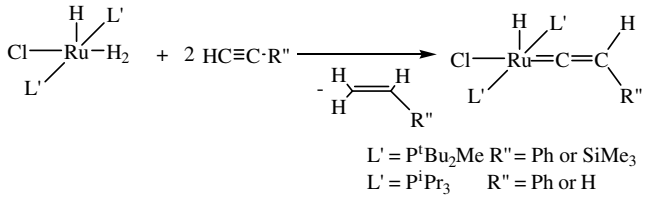


Scheme 1.

the enyne could be a monomer unit to produce conjugated polymers or oligomers. However, due to the possibility of several isomers (Scheme 2), the selectivity of RCCH dimerization is the biggest challenge to be addressed [21]. Here we present the catalytic reactivity of $RuXHL_2$ with terminal alkynes together with a mechanistic study. Ruthenium has good precedent for dimerization of terminal alkynes [20,22–29].

2. Results and discussion

2.1. Reaction of 14 electron ruthenium complexes (*1* and *2*) and terminal alkynes, RCCH

Compound **2** is a catalyst precursor for the dimerization [12,14,30] of terminal alkynes (RC≡CH, R = Ph (**a**), ^{t}Bu (**b**), and Me_3Si (**c**)) with high stereoselectivities at room temperature. **2** can be prepared *in situ* by addition of LiN(SiMe$_3$)$_2$ to **1**; this conversion is complete within 30 min. A hydride triplet is observed at −20.8 ppm and a $^{31}P\{^1H\}$ NMR singlet is seen at 98.8 ppm. Two doublet of virtual triplet Me groups in ^{i}Pr and two $SiMe_3$ signals indicate it has C_s symmetry.

2.2. R = Ph

When equimolar **2** and PhC≡CH was mixed in benzene, there is no significant change observed in ^1H NMR and $^{31}P\{^1H\}$ NMR spectra of **2** over one day, although there was no signal for the terminal hydrogen of PhC≡CH. Instead, when 5 equiv. of PhC≡CH was applied in that reaction mixture, an AB pattern grew at 5.77 and 6.39 ppm in the ^1H NMR spectrum which corresponds *cis*-PhC(H)=C(H)CCPh (**3a**). At 20:1 mol ratio, in 3.7 h, all acetylene is converted to *cis*-[13], *trans*-[13], and 1,3-disubstituted enynes [12] and cumulene (**6**, **7**) in the mole ratio 79:14:7:trace. In addition, a small amount of styrene (≈3% by the ratio of integration of vinyl protons on the ^1H NMR) was seen in the spectra. Past reported dimerization of terminal alkynes has yielded mainly three kinds of enyne (Scheme 2) [12–15]. In addition, in a few cases, the formation of cumulenes (**6** and **7**) has been reported also [13–16,31,32].

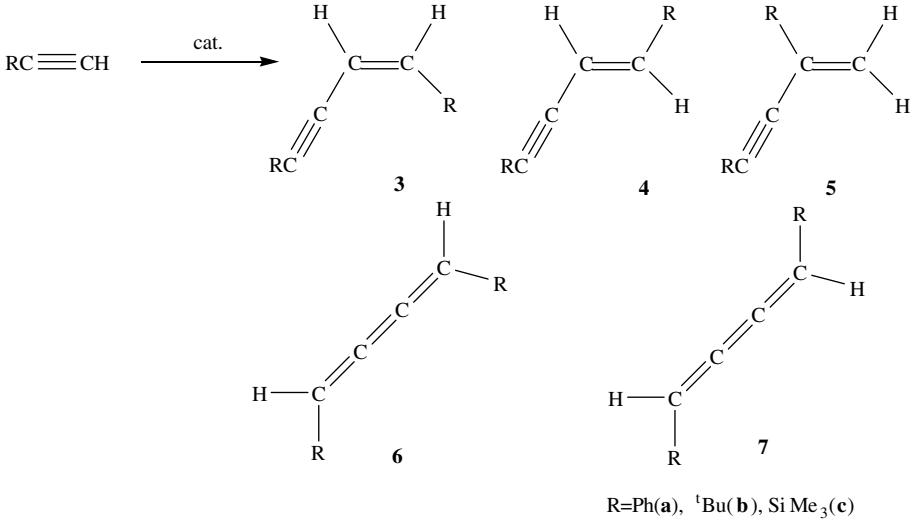
2.3. R = SiMe$_3$ and CMe$_3$

The reactivity of **2** towards *tert*-butylacetylene and trimethylsilylacetylene were also studied (Table 1) [12–16]. To periodically monitor the dimerization, ^1H NMR and $^{31}P\{^1H\}$ NMR were used. Especially in the case of ^1H NMR, the signals of dimers in the vinyl region were observed, as well as for the unreacted acetylene proton.

Table 1
Dimerization of RC≡CH by ruthenium complexes **1** and **2** in C_6D_6

R	Complex	Product ratio **3**:**4**:**5**:**6**	% Yield	Reaction time
Ph	**1**	75.9:7:17.1:trace*	100	<28 h
^{t}Bu	**1**	Trace*	0	Over 2 days
Me_3Si	**1**	21.2:trace*:73.5:5.3	84	<3 days
Ph	**2**	78.8:13.8:7.4:trace*	100	3.7 h
^{t}Bu	**2**	85.6:trace*:5.7:8.7	100	<5.5 h
Me_3Si	**2**	67.5:trace*:trace*:32.5	100	0.5 h

Reaction condition: catalyst:acetylene = 0.109 mmol:2.18 mmol, room temperature. Trace*: signals cannot be distinguished because they are too weak.



Scheme 2.

In the case of ^{t}BuC≡CH, **3b** (86%) was the major product (vinyl signals appeared at 5.56 ppm and 5.46 ppm with a 12.3 Hz coupling constant); a vinyl signal at 6.29 ppm, having $J = 1.5$ Hz, indicates formation of **5b** (6%). In addition, the signal of a vinyl proton appeared at 5.51 ppm which corresponds to cumulene (9%) [13,15,16]. Under the same conditions, $Me_3SiC{\equiv}CH$ produced mainly *cis*-enyne, **3c**, (67%) (6.22 ppm and 6.00 ppm with 14.4 Hz coupling) and a vinyl singlet at 6.37 ppm corresponding to formation of cumulene (32%) [13,14].

In the case of the cumulene, it was hard to distinguish whether it was *cis* (**6**) or *trans* (**7**) because both have the same ^{1}H NMR chemical shift [14]. However, since we observed that cumulenes were isomerized to **3b** and **3c** [14], respectively, after **2** dimerized all of ^{t}BuC≡CH or $Me_3SiC{\equiv}CH$, this suggests that cumulenes in this case might have *cis* stereochemistry, **6b** and **6c**.

2.4. Catalysis with the chloride analog, *1*

Since detection of metal-containing intermediates was not possible during catalysis by **2**, compound **1** was studied. Because it is known that the H_2 adduct of **1** consumes 2 equiv. of terminal alkyne (liberating olefin) to produce vinylidene complex (Scheme 1) [8–12], **1** itself could also form a vinylidene compound with acetylene which could be one of possible intermediates for the dimerization. In addition dimerization of alkyne with excess terminal alkynes could be studied also, to learn the impact of lone pair electron donor ability, Cl (**1**) vs. $N(SiMe_3)_2$ (**2**), on catalyst performance. Dimerization of PhC≡CH by **1** produced mainly *cis*-enyne (**3a**) with 75.9% of overall product. In addition, small amounts of *trans*-(**4a**) (7%, doublet at 6.3 ppm) and 1,3-enynes (**5a**) (17.1%, singlets at 5.74 ppm and 5.69 ppm) were also seen in ^{1}H NMR. Only one vinyl signal for **4a** is seen because of overlap of the other vinyl proton signal with the phenyl signals. Unexpectedly, the reaction of **1** and ^{t}BuC≡CH did not produce any dimer except for a weak signal of enyne **5b**. However, dimerization of $Me_3SiC{\equiv}CH$ produced 1,3-enyne (**5c**) as a major dimer (73.5% of total dimers). As minor products, **3c** with 21.2% yield and *cis*-cumulene (**6c**) with 5.3% yield were produced by **1**.

Surprisingly, over a long reaction period of dimerization by **2**, isomerization of **6b** or **6c** to the thermodynamically more stable **3b** or **3c**, respectively, occurred [14,15]. These cumulene isomerizations are slower than the rate of alkyne dimerization (Tables 1 and 2). For example, isomerization of **6c** to **3c** took 101 h, but dimerization was done in 0.5 h. This isomerization is much faster for the Me_3Si case. However, this isomerization does not take place once the ^{1}H NMR and $^{31}P\{^1H\}$ NMR signals of **2** have decayed.

Energy difference of *cis*-enyne and cumulene has been studied with Me(H)C=C=C=C(H)Me for **6b** (Fig. 1) [15] and $H_3Si(H)C{=}C{=}C(H)SiH_3$ for **6c** (Fig. 1) [14] which shows cumulenes have higher energy than *cis*-enynes (by 17.3 kcal/mol for Me(H)C=C=C=C(H)Me, and by 18.9 kcal/mol for $H_3Si(H)C{=}C{=}C{=}C(H)SiH_3$).

By comparing products from **1** and **2**, it was found that Cl vs. $N(SiMe_3)_2$ significantly influences the reaction time as well as distribution of products; this indicates that at least one of these two anionic ligands remains attached to Ru on the catalytic cycle. For example, the fastest reaction by **2** (dimerization of $Me_3SiC{\equiv}CH$) is the slowest reaction by **1** (over 78 h to completely dimerize 20 equiv. of acetylene). In addition, catalyst **2** produced mainly **3c**, but **5c** was produced only by **1** (only a trace could be seen in ^{1}H NMR spectra catalyzed by **2**). In the case of the dimerization of *tert*-butylacetylene, mainly **3b** was formed by **2**. Unexpectedly, the reaction of ^{t}BuC≡CH with **1** did not produce any dimers which might be due to steric bulk around the metal center after formation of its vinylidene. The only product, seen by ^{1}H NMR, was trace of **5b** over 2 days. However, PhC≡CH was not much influenced by change from Cl to $N(SiMe_3)_2$. These gave similar distribution of products, but the reaction rate was significantly faster for **2**.

2.5. Mechanism

By various studies [12–16], mainly two pathways were proposed for dimerization of terminal acetylene catalyzed

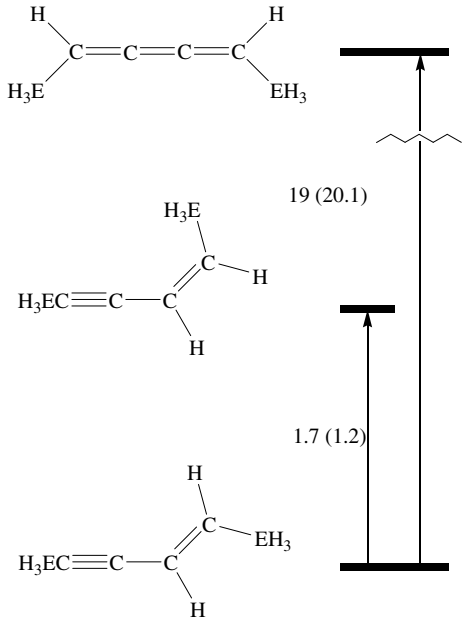
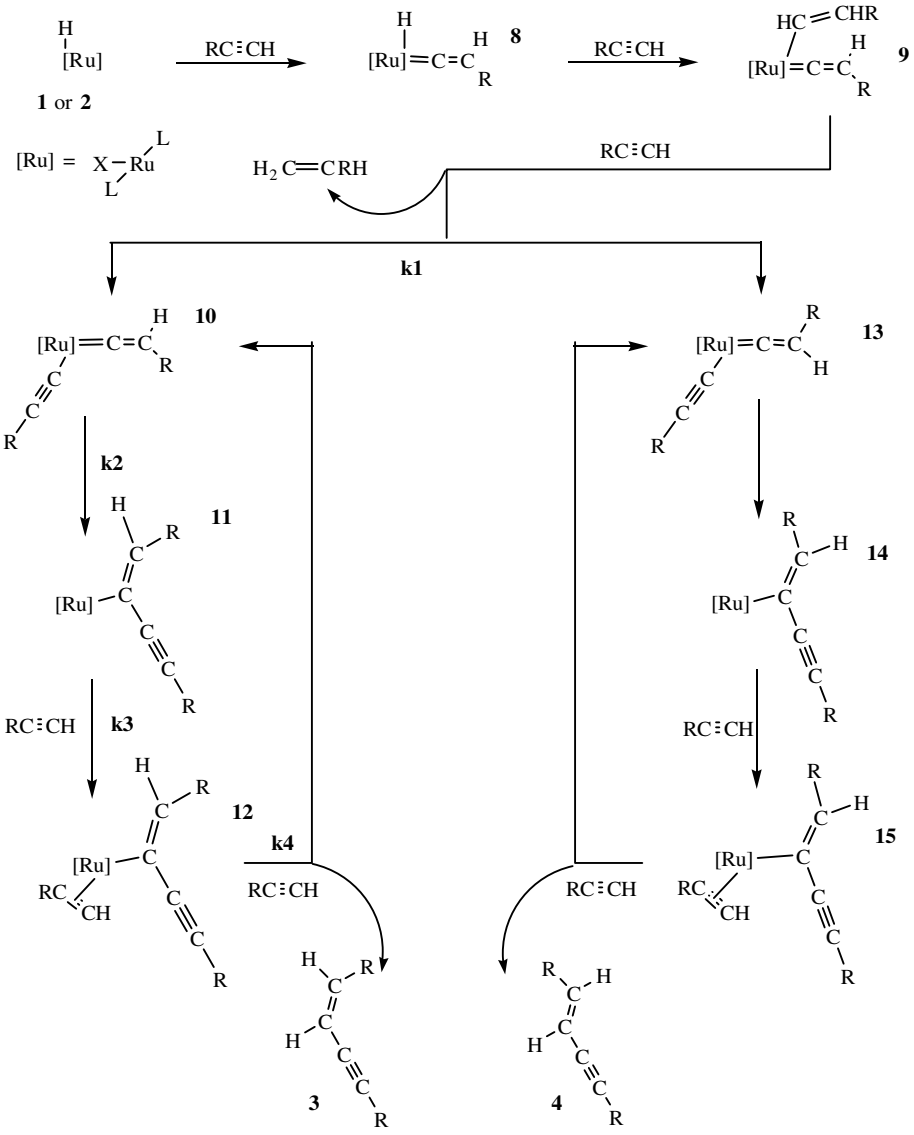


Fig. 1. Relative isomer energies (kcal/mol) for E=C(Si).

Table 2
Isomerization of cumulene to *cis*-disubstituted enyne by complex **2**

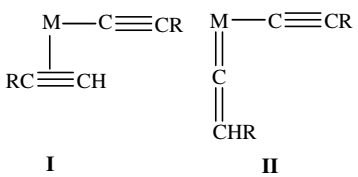
R	Ratio of product after isomerization **3**:**4**:**5**:**6**	Isomerization time (h)
^{t}Bu	87.5:trace*:6.5:6	26
Me_3Si	100:trace*:trace*:trace*	<101

Trace*: signals cannot be distinguished because they are too weak.



Scheme 3.

by metal complexes. These differ by isomeric catalyst structures **I** or **II** (below). Studying the mechanism of alkyne dimerization catalyzed by **2** was frustrated because ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectra showed no detectable amount of ruthenium–substrate complex converted onto the catalytic cycle. Therefore catalyst **1** was chosen for mechanistic study since it reacts slower than **2** (Table 1). 1:1 mol ratio(RC≡CH:**1**) reactions were performed to see whether vinylidene complexes, **8** (Scheme 3), were produced (Scheme 1). In reactions of all three terminal acetylenes, **8** was formed.



I **II**

In all cases, species **8** were identified by triplets due to the vinylidene proton and to the hydride signal(Table 3). This suggests that isomerization to vinylidene from acetylene is favorable which implicates **II** (above) as on the catalytic cycle.

Therefore, the mechanism for formation of **3** and **4** in Scheme 3 is proposed. Here, stereoselectivity is determined by vinylidene conformers **10** vs. **13**, which lead to **3** or **4**, respectively. Since **1** and **2** both have bulky L, when R

Table 3
Chemical shift of vinylidene complexes

R	^{1}H NMR		$^{31}P\{^{1}H\}$ (ppm)
	Hydride (ppm)	Vinylidene proton (ppm)	
Ph	−12.53	4.35	51.0
^{t}Bu	−13.79	2.77	50.88
Me_3Si	−15.09	2.41	51.00

was bulky, **3** was the major product (Table 1) since the formation of **11** is apparently more favorable than **14** [14].

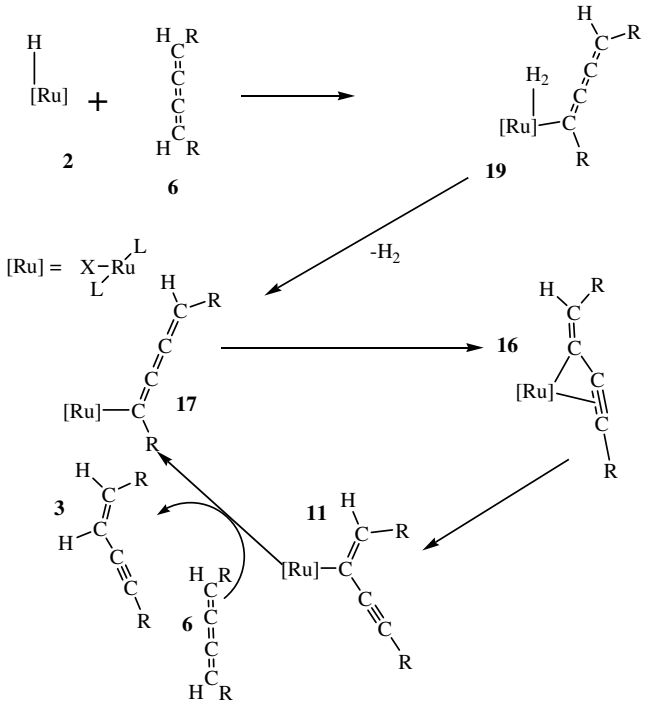
Formation of **9** was demonstrated by an osmium analog [33], where reaction of OsH_3ClL_2 with 2 equiv. Me_3SiCCH produces a vinylidene compound, which is then transformed into the vinyl vinylidene compound, $OsClL_2(C(H)=C(H)SiMe_3)(=C=C(H)SiMe_3)$. In the present work, when 1 or 2 equiv. of phenyl acetylene was added to **8a** in an attempt to observe any of the proposed intermediate **9**, **10** or **13**, not all of **8a** was consumed. Even when 3 equiv. of phenyl acetylene was added, **8a** was not consumed completely. Instead, dimerization of acetylene was observed, consistent with only small conversion of Ru onto the catalytic cycle. That is, k_1 limits the amount of active catalyst formed from precatalyst.

Transformation of η^3-PhC_4HPh ligand (**16**, Scheme 4), an isomer of **11**, has been suggested as the source of cumulene [16,30].

Compound **16** could be isomerized to cumulenyl ligand (**17**) by additional acetylene and then could be released as cumulene by another acetylene addition. In addition, **16** serves as an entry point into a catalytic cycle to isomerize **6** to **3** (Scheme 5). Oxidative addition of cumulene to **1** or **2** yields **17** with liberation of H_2 (Scheme 5).

Binding site exchange of the cumulenyl ligand in **17** causes isomerization from cumulenyl to enynyl ligand (**17** to **16**). When the second cumulene adds to **11**, enyne is released.

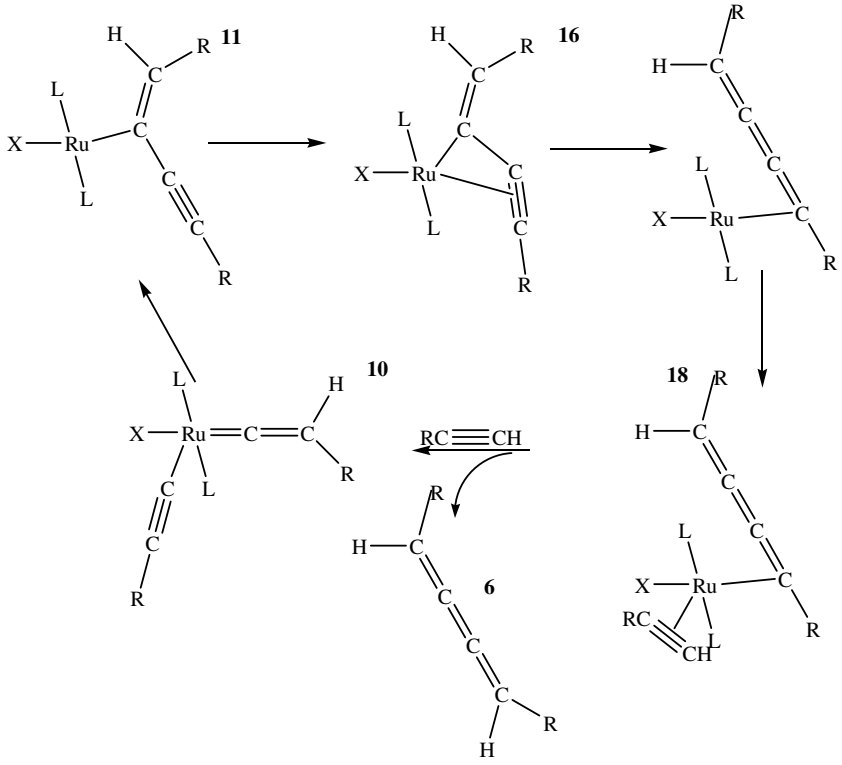
For the formation of **5** [12,34], compound **20** is required. Two pathways are possible (Scheme 6). One is migration of



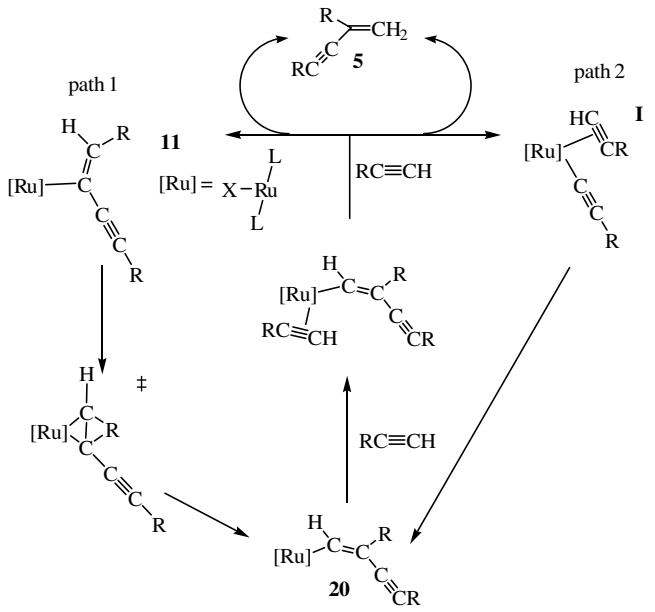
Scheme 5.

R group [33,35] with binding site exchange in Ru-vinyl group in **11** (path 1). The other possibility is from activated catalyst form **I** (path 2).

Another pathway to produce enyne, Scheme 7, involves species **I** then **IV**. Vinyl diacetylide compound (**V**) could be



Scheme 4.



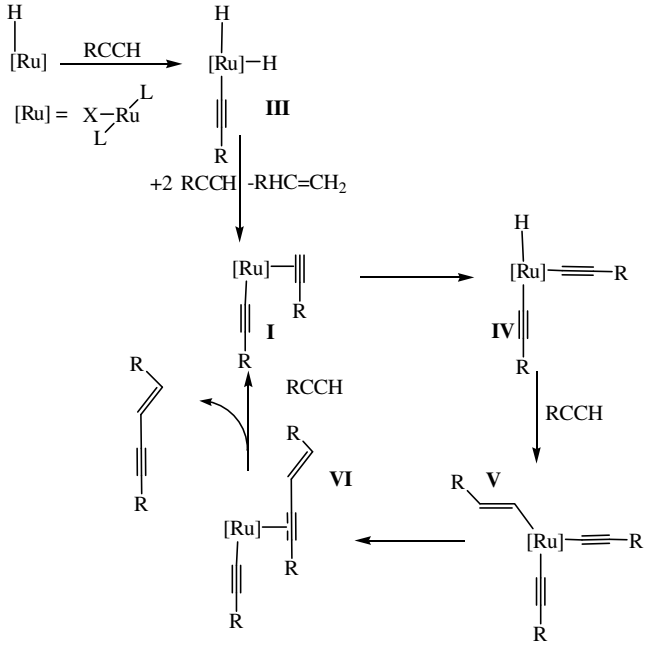
Scheme 6.

formed by another acetylene addition. Enyne could be produced by migration of one of acetylide to the vinyl ligand (**V** → **VI**), followed by addition of acetylene. In this system, *trans* vinyl product is more favorable than *cis*, which contrasts to experiment.

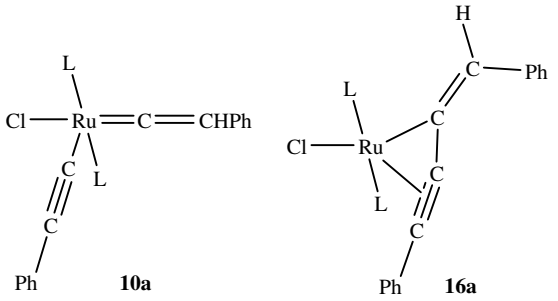
2.6. Independent study of the mechanism: attempted synthesis of proposed intermediates

For independent study of the mechanism, synthesis of $RuClL_2(=C=CHPh)(C\equiv CPh)$ (**10a**, cf. **10** and **13**) was attempted through the addition of $LiC\equiv CPh$ to $RuCl_2L_2(=C=CHPh)$ [36,37] in benzene over 2 days. Slow exchange of Cl^- with $PhC\equiv C^-$ was observed due to the insolubility of $LiC\equiv CPh$ in the solvent. Characterization by NMR indicates that **16a**, not **10a**, is the product formed. While a triplet of the vinylidene proton ($RuCl_2L_2(=C=CHPh)$) (4.7 ppm) has disappeared, appearance of a singlet at 7.5 ppm suggests formation of vinyl ligand by migration of acetylide ($PhCC^-$) to C(α). In addition, the absence of a C(α) ^{13}C NMR signal around 250–300 ppm confirms the absence of any Ru=C(α) bond. Instead, one triplet at 163.4 ppm ($J_{P-C} = 8$ Hz) is due to a vinyl C(α) and 11 signals from 137 to 124 ppm which include acetylene C (in addition to phenyl) are also observed. Observing acetylene C in that region also indicates the acetylene binds to Ru, as shown in **16a**.

For complete identification of **16a**, CO was added to this compound in C_6D_6 at room temperature (Scheme 8) as an analog to the formation of **12a** or **18a**. Two carbonyl triplets at 200.7 and 198.1 ppm indicate two CO bind to Ru. $^{13}C\{^1H\}$ NMR supports formation of **21**, not **22**, in Scheme 8. A C(α) triplet observed at 145.2 ppm ($J_{P-C} = 4$ Hz) and a C(β) triplet is seen at 141.1 ppm but its J_{P-C} is not fully resolved. Eight phenyl singlets and two cumulene (C(γ) and C(δ)) singlets were observed between 131.4 and 99.1 ppm. In further confirmation of the ligand structure, protonation of **21** was performed with HCl, which liberated cumulene (not enyne), with formation of $Ru(CO)_2Cl_2L_2$ [38,39].



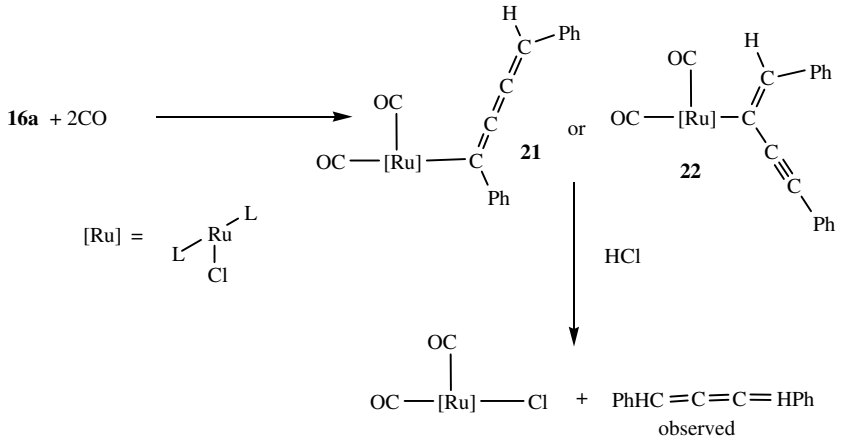
Scheme 7.



To test the catalytic viability of **16a**, 20 equiv. of $PhC\equiv CH$ was added. In 30 min, all of **16a** disappeared and three kinds of dimers appeared. Compounds **3a**, **4a**, and **5a** were produced in the ratio of 76.5:5:18.5 which ratio is very similar to that from catalytic dimerization of phenylacetylene by **1** (Table 1). However in this dimerization, cumulene was not seen. This suggests that binding $PhC\equiv CH$ to **16a** generates **12** or **15** to form *cis*- or *trans*-enyne, respectively, instead of **18**; **16a** is a precatalyst for dimerization.

3. Discussion

This work has shown that CO-free, π-electron rich Ru^{II} complexes have the ability to form C/C bonds at 23 °C. We



Scheme 8.

have not attempted to optimize conditions for best selectivity, but these would clearly be dependent on R group identity in RCCH. The lability of H on an sp carbon clearly contributes to the reactivity reported here, making vinylidene complex formation facile. Once the Ru=C bond is formed, insertion of this into a Ru–acetylide bond becomes possible. These reactions remain mechanistically obscure because a spectroscopically undetectable amount of catalyst precursor is converted onto the catalytic cycle.

A recent report [40] has provided deep insight into one mechanism of enyne formation catalyzed by one specific homogenous catalyst, $[C_6H_3(CH_2P^tBu_2)_2]Ir$, which is selective for *trans*-1,4-phenyl-but-3-ene-1-yne, **4a**. The deduced mechanism at this very sterically constrained catalyst is H–C(sp) oxidative addition, then Ir–H addition across the second alkyne C≡C bond, then reductive coupling to form enyne. The high regioselectivity is concluded to result at the reductive coupling step, and the kinetically favored σ-vinyl complex (Ph on C_α) fails at C–C coupling, so the more slowly formed alternative (Ph or C_β) is on the path to the observed enyne regioisomer. Isotope effect measurements rule out a vinylidene intermediate. No cumulene was formed.

The diversity of products formed in the present work differentiates this from the (pincer) Ir catalyst performance described above, and indicates the likelihood of participation here by more reaction channels than for (pincer)Ir. The catalysts differ in that the Ru system begins with a hydride and involves Ru^{II}, so both (vs. an Ir^{I} nonhydride) favor Ru avoiding Ru^{IV} and thus favoring a vinylidene-forming initial step. The four ^{t}Bu groups make the (pincer)Ir system more dominated by steric effects than the nonchelated P^iPr_3 groups on Ru; increased selectivity is thus favored for the former. In fact, our determination that a hydride–vinylidene is formed in a stoichiometric reaction shows this preference for a Ru^{II}–H reagent. In short, different complexes exhibit different catalytic performance by different influence of structure/composition/d-electron count (here d^6 vs. d^8).

4. Experimental

4.1. General

All reactions and manipulations were performed using standard Schlenk line and glovebox techniques under the prepurified argon. All solvents were dried and distilled from appropriate agents and stored in airtight solvent bulbs with Teflon closures under argon. $RuCl_2(P^iPr_3)_2(=C=CHPh)$ was prepared by the reported procedure (using $[RuCl_2(COD)]_x$ instead of $[RuCl_2(p\text{-cymene})]_2$) [38]. All NMR solvents were also dried with appropriate agents and vacuum transferred and stored in the glovebox under argon. All NMR spectra were taken by Varian Gemini 2000 (300 MHz ^{1}H, 121 MHz ^{31}P) spectrometers and Varian Inova (400 MHz ^{1}H, 161 MHz ^{31}P) spectrometer and referenced by residual protio solvent peaks for ^{1}H or external standard (phosphoric acid) for ^{31}P.

4.2. Preparation of $[RuHCl(P^iPr_3)_2]_2$, **1** [1]

1.2 mL of ^{t}butylethylene (6.28 mmol) was slowly added into 2.9 g of $[RuH(H_2)Cl(P^iPr_3)_2]$ (6.28 mmol) with 40 mL of toluene via syringe. Color of the solution darkened. This solution was stirred for 40 min at room temperature, and volatiles were removed into a liquid N_2 trap. The red brown precipitate was dried in vacuo. ^{1}H NMR (300 MHz, C_6D_6): δ −24.2 (t, $^2J_{P-H} = 32.8$ Hz, Ru–*H*), 1.34 (dvt, $J_{P-H} = {}^3J_{H-H} = 6.2$ Hz, 18H, $P(CHMe_2)_3$), 1.36 (dvt, $J_{P-H} = {}^3J_{H-H} = 6.2$ Hz, 18H, $P(CHMe_2)_3$), 2.19 (m, 6H, $P(CHMe_2)_3$). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 84.1 (s).

4.3. Preparation of $RuH(N(SiMe_3)_2)(P^iPr_3)_2$, **2** [1]

Fifteen grams of $[RuHCl(P^iPr_3)_2]_2$ (16.4 μmol) was dissolved with 1 mL C_6D_6 in a Teflon sealed NMR tube. Then, 0.55 mg of $LiN(SiMe_3)_2$ (32.8 μmol) was added, giving an immediate reaction. ^{1}H NMR (300 MHz, C_6D_6): δ

−20.8 (t, $^2J_{P-H} = 31$ Hz, 1H, Ru–*H*), 0.10 (s, 9H, NSi*Me*$_3$), 0.52 (s, 9H, NSi*Me*$_3$), 1.15 (dvt, $J_{P-H} = {}^3J_{H-H} = 7$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.21 (dvt, $J_{P-H} = {}^3J_{H-H} = 7$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.85 (m, 6H, P(C*H*Me$_2$)$_3$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 94.8 (s).

4.4. Dimerization of terminal alkynes catalyzed by **1**

49.2 μmol of **1** was dissolved in 1.5 mL of C_6D_6 and equally divided among three NMR tubes equipped with a Teflon seal. 328 μmol of phenylacetylene, *tert*-butylacetylene, or trimethylsilylacetylene were added each tube at room temperature. By ^1H NMR, the progress of dimerization was monitored over time.

4.5. Dimerization of terminal alkynes catalyzed by **2**

Compound **2** in 1.5 mL of C_6D_6 was prepared by addition of LiN(SiMe$_3$)$_2$ (49.2 μmol) to **1** (49.2 μmol) in C_6D_6 before it was used. Then, each 0.5 mL of solution (16.4 μmol) of **2** was placed in three NMR tubes equipped with a Teflon seal. 328 μmol of phenylacetylene, *tert*-butylacetylene, or trimethylsilylacetylene were added each tube at room temperature. By ^1H NMR, the progress of dimerization was monitored.

4.6. Preparation of RuHCl(P^{i}Pr$_3$)$_2$(CCHPh), **8a**

Fifteen grams of [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ (16.4 μmol) was placed in an NMR tube equipped with a Teflon seal and dissolved in 0.5 mL of C_6D_6. 3.66 μL of phenylacetylene (32.8 μmol) was added via syringe. The color changed to dark green. This reaction was finished in 30 min. ^1H NMR (C_6D_6, 300 MHz): δ −12.48 (t, $^2J_{P-H} =$ 17.4 Hz, Ru*H*), δ 1.21 (m, P(CH(*Me*$_2$))$_3$), δ 2.49 (m, P(C*H*(Me$_2$))$_3$), δ 4.36 (t, $^4J_{P-H} = 3.9$ Hz, CC*H*(Ph)), δ 6.8–7.3 (m, CCH(*Ph*)). $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz): δ 51.0 (s).

4.7. Preparation of RuHCl(P^{i}Pr$_3$)$_2$(CCH^{t}Bu), **8b**

Fifteen grams of [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ (16.4 μmol) was placed in an NMR tube equipped with a Teflon seal and dissolved in 0.5 mL of C_6D_6. 4 μL of *tert*-butylacetylene (32.8 μmol) was added via syringe. The color changed to dark green. This reaction was finished in 30 min. ^1H NMR (C_6D_6, 300 MHz): δ −13.79 (t, $^2J_{P-H} = 18.3$ Hz, Ru*H*), δ 1.09 (s, CCH(*^{t}Bu*)), δ 1.26 (d, $^3J_{H-H} = 6.3$ Hz, P(CH(*Me*$_2$))$_3$), δ 1.30 (d, $^3J_{H-H} = 7.2$ Hz, P(CH(*Me*$_2$))$_3$), δ 2.67 (m, P(C*H*(Me$_2$))$_3$), δ 2.77 (t, $^4J_{P-H} = 3.6$ Hz, CC*H*(*^{t}*Bu)). $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz): δ 50.88 (s).

4.8. Preparation of RuHCl(P^{i}Pr$_3$)$_2$(CCHSiMe$_3$), **8c**

Fifteen grams of [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ (16.4 μmol) was placed in an NMR tube equipped with a Teflon seal and dissolved in 0.5 mL of C_6D_6. 4.7 μl of trimethylsilylacetylene (32.8 μmol) was added via syringe. Color changed to light red brown. This reaction was finished in 30 min. ^1H NMR (C_6D_6, 300 Hz): δ −15.09 (t, $^2J_{P-H} = 18.2$ Hz, Ru*H*), δ 0.15 (s, CCHSi(*Me*$_3$)), δ 1.28 (m, P(CH(*Me*$_2$))$_3$), δ 2.63 ppm (m, P(C*H*(Me$_2$))$_3$), δ 2.41 (t, $^4J_{P-H} = 3.3$ Hz, CC*H*Si(Me$_3$)). $^{31}P\{^1H\}$ NMR (C_6D_6, 121 Hz): δ 51.00 (s).

4.9. cis-PhCH=CHCCPh (**3a**) [13]

^1H NMR (C_6D_6, 300 MHz): δ 6.39 (d, $^3J_{H-H} = 12$ Hz, =C*H*), δ 5.77 (d, $^3J_{H-H} = 12$ Hz, =C*H*). δ 8.10–6.80 (m, Ph).

4.10. trans-PhCH=CHCCPh (**4a**) [13]

^1H NMR (C_6D_6, 300 MHz): δ 6.29 (d, $^3J_{H-H} = 19.9$ Hz, =C*H*), δ 8.10–6.80 (m, Ph).

4.11. CH$_2$C(Ph)(CCPh) (**5a**) [12]

^1H NMR (C_6D_6, 300 MHz): δ 5.69 (s, =C*H*H), δ 5.74 (s, =CH*H*). δ 8.10–6.80 (m, Ph).

4.12. cis-^{t}BuHCCHCC^{t}Bu (**3b**)

^1H NMR (C_6D_6, 300 MHz): δ 1.18 (s, *^{t}Bu*), δ 1.24 (s, *^{t}Bu*), 5.46 ppm (d, $^3J_{H-H} = 12.3$ Hz, =C*H*), δ 5.56 (d, $^3J_{H-H} = 12.3$ Hz, =C*H*).

4.13. CH$_2$C(*^{t}Bu*)(CC*^{t}Bu*) (**5b**)

^1H NMR (C_6D_6, 300 MHz): δ 1.17 (s, *^{t}Bu*), δ 1.19 (s, *^{t}Bu*), δ 5.11 (d, $^2J_{H-H} = 1.5$ Hz, =C*H*H), δ 5.33 (d, $^2J_{H-H} = 1.5$ Hz, =CH*H*).

4.14. cis-(*^{t}Bu*)HCCCCH(*^{t}Bu*) (**6b**)

^1H NMR (C_6D_6, 300 MHz): δ 1.07 (s, *^{t}Bu*), δ 5.51 (s, =C*H*).

4.15. cis-Me$_3$SiHCCHCCSiMe$_3$ (**3c**)

^1H NMR (C_6D_6, 300 MHz): δ 0.15 (s, *Me*$_3$Si), δ 0.22 (s, *Me*$_3$Si), δ 6.00 (d, $^3J_{H-H} = 15.3$ Hz, =C*H*), δ 6.22 (d, $^3J_{H-H} = 15.3$ Hz, =C*H*).

4.16. CH$_2$C(SiMe$_3$)(CCSiMe$_3$) (**5c**)

^1H NMR (C_6D_6, 300 MHz): δ 0.12 (s, *Me*$_3$Si), δ 0.17 (s, *Me*$_3$Si), δ 5.54 (d, $^2J_{H-H} = 2.0$ Hz, =C*H*H), δ 6.10 (d, $^2J_{H-H} = 1.7$ Hz, =CH*H*).

4.17. cis-(Me$_3$Si)HCCCCH(SiMe$_3$) (**6c**)

^1H NMR (C_6D_6, 300 MHz): δ 1.22 (s, *Me*$_3$Si), δ 6.36 (s, =C*H*).

4.18. Preparation of $RuCl(P^iPr_3)_2(\eta^3CCHPh(CCPh))$ (**16a**)

Thirty-six milligrams of LiCCPh (340 μmol) was added into the solution of 0.2 g of $RuCl_2(P^iPr_3)_2(CCHPh)$ (340 μmol) in 30 mL of benzene. After 2 days stirring, volatiles were removed by high vacuum with a liquid N_2 trap. The crude compound was dissolved in pentane and filtered to remove LiCl. Pentane was removed in vacuo. This compound was washed with 10 ml of MeOH, three times and dried. 0.13 g of the dark reddish brown product (56%) was collected. ^{1}H NMR (400 MHz, C_6D_6): 1.12 (dvt, $J_{P-H} = J_{H-H} = 6$ Hz, 18H, $P(CHMe_2)_3$), 1.18 (dvt, $J_{P-H} = {}^3J_{H-H} = 6$ Hz, 18H, $P(CHMe_2)_3$), 2.14 (m, 6H, $P(CHMe_2)_3$). 7.01 (t, $J_{H-H} = 7.6$ Hz, H, *Ph*), 7.1 (t, $J_{H-H} = 7.6$ Hz, H, *Ph*), 7.21 (t, $J_{H-H} = 7.6$ Hz, 2H, *Ph*), 7.3 (t, $J_{H-H} = 7.6$ Hz, 2H, *Ph*), 7.54 (s, H, CHPh), 8.00 (d, $J_{H-H} = 7.6$ Hz, 2H, *Ph*), 8.27 (d, $J_{H-H} = 7.6$ Hz, 2H, *Ph*). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ 27.6 (s). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): 163.4 (t, $J_{P-C} = 8$ Hz), 137.3, 133.1, 131.4, 129.3, 128.4, 128.1, 127.9, 127.3, 125.6, 125.3, 124.2.

4.19. Reaction of **16a** with CO

Twenty milligrams of **16a** (30 μmol) was placed with 0.5 mL of C_6D_6 in the NMR tube equipped with Teflon seal stopcock. This solution was freeze-pump-thaw-degassed three times in liquid N_2 and the headspace evacuated. 1 atm. of CO was added. The color changed immediately to pale yellow. ^{1}H NMR (400 MHz, C_6D_6): 1.14 (dvt, $J_{P-H} = J_{H-H} = 6$ Hz, 18H, $P(CHMe_2)_3$), 1.34 (dvt, $J_{P-H} = {}^3J_{H-H} = 6$ Hz, 18H, $P(CHMe_2)_3$), 2.66 (m, 6H, $P(CHMe_2)_3$). 6.96–7.13 (m, 4H, *Ph*), 7.33 (t, $J_{H-H} = 7.6$ Hz, 2H, *Ph*), 7.7 (d, $J_{H-H} = 7.6$ Hz, 2H, *Ph*), 8.17 (s, H, CHPh), 8.32 (d, $J_{H-H} = 7.6$ Hz, 2H, *Ph*). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ 35.11 (s). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): 200.7 (t, $J_{P-C} = 10$ Hz), 198.2 (t, $J_{P-C} = 10$ Hz), 145.1 (t, $J_{P-C} = 4$ Hz), 141.1 (t, J_{P-C} not resolved), 131.4, 128.7, 128.5, 128.4, 128.1, 127.9, 127.1, 126.3, 103.4, 99.1.

4.20. Reaction of $RuCl(P^iPr_3)_2(\eta^1CCHPh(CCPh))(CO)_2$ with HCl

Twenty milligrams of **16a** (30 μmol) was placed with 0.5 mL of C_6D_6 in the NMR tube equipped with Teflon seal stopcock. This solution was freeze-pump-thaw-degassed three times in liquid N_2 and the headspace evacuated. 1 atm. of CO was added. Color change was immediate. After 1 day, 30 μL of HCl (1 M in Et_2O, 30 μmol) was added by a syringe. $Ru(CO)_2Cl_2(P^iPr_3)_2$ and PhHCCCCHPh were produced in 1 h. $Ru(CO)_2Cl_2(P^iPr_3)_2$: ^{1}H NMR (400 MHz, C_6D_6): 1.25 (vq, $J = 6$ Hz, 36H, $P(CHMe_2)_3$), 2.78 (m, 6H, $P(CHMe_2)_3$). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ 38.67 (s). PhHCCCCHPh: ^{1}H NMR (400 MHz, C_6D_6): 6.4 (s, 2H, CHPh), 6.92–7.46 (m, 10H, CH*Ph*).

4.21. Dimerization of terminal alkynes catalyzed by **16a**

Twenty-eight micromoles of **16a** was dissolved in 0.5 mL of C_6D_6 in an NMR tube equipped with a Teflon seal. 560 μmol of phenylacetylene was added. By ^{1}H NMR, the progress of dimerization was monitored. The ratio of dimers (**3a**, **4a**, and **5a**) was 76.5:5:18.5.

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