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Articles

Oxidative Addition of Phenylacetylene to $[Ir(CO)(RCN)(PPh_3)_2]ClO_4$: Preparation, Kinetics, and Mechanism

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Reactions of $PhC{\equiv}CH$ (1a) and $p\text{-}CH_3C_6H_4C{\equiv}CH$ (**1b**) with $[Ir(RCN)(CO)(PPh_3)_2]ClO_4$, **2** (R = Ph (**a**), CH_3 (**b**), CH=CHPh (**c**)), give $[Ir(H)(\text{-}C{\equiv}CR')(RCN)(CO)(PPh_3)_2]ClO_4$, **3** (R′ = Ph, R = Ph (**a**), CH_3 (**b**), CH=CHPh (**c**); R′ = $p\text{-}CH_3C_6H_4$, R = Ph (**d**)), where the hydride is *cis* both to two PPh_3 groups and *trans* to RCN. The oxidative addition of **1a** to **2a,b** is first order both in **1a** and **2a,b** and depressed by the presence of RCN added. The suggested reaction pathway involves the initial replacement of RCN of **2a,b** by **1a** to give $[Ir(PhC{\equiv}CH)(CO)(PPh_3)_2]ClO_4$, which undergoes an intramolecular oxidative cleavage of the coordinated **1a** to give $[Ir(H)(\text{-}C{\equiv}CPh)(CO)(PPh_3)_2]ClO_4$, to which RCN is added back to give the stable complexes **3a,b**. Kinetic data obtained for alkyne hydrogen deuterated phenylacetylene, $PhC{\equiv}CD$ (**1a**-*d*), support the suggested mechanism.

Introduction

Reactions of terminal alkynes with transition metal complexes produce a variety of compounds such as alkyne complexes,[1] hydrido alkynyl complexes,[2] vinylidene complexes,[1,2f,3] alkynyl complexes,[4] metallacyclopentadiene complexes,[5] and other types of complexes.[6] These metal complexes are the key intermediates of a variety of well-established reaction pathways for the metal-catalyzed reactions of alkynes.[1–6]

During our investigation of the oligomerization of terminal alkynes with iridium(I) complexes, we have isolated a stable hydrido(phenylethynyl)iridium(III) complex, $[Ir(H)(\text{-}C{\equiv}CPh)(CO)(PhCN)(PPh_3)_2]ClO_4$ (**3a**), from the reaction of phenylacetylene (**1a**) with $[Ir(CO)(PhCN)(PPh_3)_2]ClO_4$ (**2a**), which catalyzes the oligomerization of **1a** to give dimers and cyclotrimers of **1a** at 50 °C.[7] We have also observed that the rates of the oxidative addition of **1a** to **2a** are significantly decreased by the presence of excess PhCN although PhCN of **2a** remains in the product **3a**. We, therefore, decided to look into the reaction mechanism for the formation of **3** since there is no evidence that the 16-electron complex **2** reacts with RCN to give complexes containing more than one RCN in the presence of excess RCN or loses RCN in the absence of RCN in the reaction mixture. To our knowledge, there has not been a report on a kinetic study for the oxidative addition of an alkyne to a transition metal complex.

In this paper, we wish to report the characterization of $[Ir(H)(\text{-}C{\equiv}CR')(CO)(RCN)(PPh_3)_2]ClO_4$, **3** (R′ = Ph, R = Ph (**a**), CH_3 (**b**), CH=CHPh (**c**); R′ = $p\text{-}CH_3C_6H_4$, R = Ph (**d**), prepared from the oxidative addition of phenylacetylene (**1a**) and *p*-tolylacetylene (**1b**) to $[Ir(CO)(RCN)(PPh_3)_2]ClO_4$, **2** (R = Ph (**a**), CH_3 (**b**), CH=CHPh (**c**)), and detailed kinetic measurements for the formation of **3a,b** along with a suggested mechanism involving replacement of RCN by **1a** in the initial step and coordination of RCN back to iridium in the last step. Kinetic measurements have been also carried out for the oxidative addition of alkyne hydrogen deuterated phenylacetylene, $DC{\equiv}CPh$ (**1a**-*d*), to $[Ir(CO)(PhCN)(PPh_3)_2]ClO_4$ (**2a**) in order to obtain information which supports the reaction pathway suggested.

Results and Discussion

Synthesis. The oxidative addition (eq 1) of **1** to **2** smoothly proceeds to quantitatively give **3** at room temperature. Triplets at *ca.* −17 ppm with small coupling constants (*ca.* 11 Hz) observed in the ^1H NMR spectra of **3** (Table I) unambiguously indicate that the hydride of **3** is *cis* to both PPh_3 groups and *trans* to NCR for the following reasons: (i) The coupling constants between a hydride and *trans* phosphorus are relatively large (53–194 Hz) compared with those between a hydride and *cis* phosphorus (8–20 Hz).[2,8] (ii) The chemical shift of a hydride coordinated to a transition metal largely depends on the *trans* atom, and the hydrides *trans* to nitrogen (RCN) in related metal complexes are seen at relatively high field (−16 to −20 ppm)[8a,b,d,9] compared

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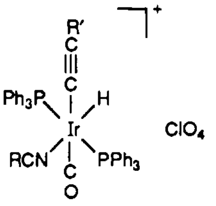
Table I. ^{1}H (at 300 MHz, Relative to TMS), ^{13}C (at 75.4 MHz, Relative to TMS), and ^{31}P (at 121.4 MHz, Relative to PO(MeO)$_3$) NMR (CDCl$_3$) and Infrared (Nujol) Spectra Data for $[Ir(H)(-C{\equiv}CPh)(CO)(RCN)(PPh_3)_2]ClO_4$ (**3**) (R = Ph (a), CH$_3$ (b), CH=CHPh (c)) and $[Ir(H)(-C{\equiv}CC_6H_4CH_3)(CO)(PhCN)(PPh_3)_2]ClO_4$ (**3d**)

	NMR		infrared, cm^{-1}		
compd	δ, ppm	assgnt, J, Hz	ν(C≡O)	ν(C≡N)	ρ(Ir–H)
3a	−17.10 (t, 1H)	Ir–H, J(PH) = 11.4	2062, s	a	820, m
	6.4–7.9 (m, 40H)^b	≡CC$_6$$H_5$, P–C$_6$$H_5$			
	83.0 (t)^c	Ir–C, J(PC) = 17.0			
	112.3 (s)^c	Ir–C≡C			
	−5.06 (s)	Ir–P			
3b	−17.44 (t, 1H)	Ir–H, J(PH) = 11.4	2060, s	2235, w	821, m
	1.90 (s, 3H)	CH_3			
	6.4–7.9 (m, 35H)^b	≡CC$_6$$H_5$, P–C$_6$$H_5$			
	83.3 (t)^c	Ir–C, J(PC) = 17.0			
	111.6 (s)^c	Ir–C≡C			
	−4.92 (s)	Ir–P			
3c	−17.12 (t, 1H)	Ir–H, J(PH) = 11.4	2054, s	2230, w	816, m
	5.99 (d, 1H)	CH=CHPh, CH=CHPh			
	6.83 (d, 1H)	J(HH) = 16.7			
	6.5–8.0 (m, 40H)^b	≡CC$_6$$H_5$, P-C$_6$$H_5$, =CHC$_6$$H_5$			
	83.1 (t)^c	Ir–C, J(PC) = 17.0			
	112.8 (s)^c	Ir–C≡C			
	−4.96 (s)	Ir–P			
3d	−17.10 (t, 1H)	Ir–H, J(PH) = 11.4	2065, s	2233, w	820, m
	2.25 (s, 3H)	CH_3			
	6.4–7.9 (m, 39H)^b				
	83.1 (t)^c	Ir–C, J(PC) = 17.0			
	112.0 (s)^c	Ir–C≡C			
	−5.02 (s)	Ir–P			

[a] Not observed. [b] Somewhat detailed assignments can also be made. [c] Proton-decoupled signals.

$HC{\equiv}CR' + [Ir(CO)(RCN)(PPh_3)_2]ClO_4 \longrightarrow$

1 **2**



(1)

3

1: R' = Ph (**a**), *p*-CH$_3$C$_6$H$_4$ (**b**)

2: R = Ph (**a**), CH$_3$ (**b**), CH=CHPh (**c**)

3: R' = Ph, R = Ph (**a**), CH$_3$ (**b**), CH=CHPh (**c**); R' = *p*-CH$_3$C$_6$H$_4$, R = Ph (**d**)

with hydrides *trans* to carbon (CO, CNR, olefin) seen at −7 to −14 ppm.[2d,e,8a,b,e,10]

The ν(C≡O) stretches are observed at higher frequencies as expected, for **3** at *ca.* 2020 cm^{-1} than those of **2**.[8b] The ν(C≡N) stretches of RCN in **3** are higher than those of free RCN (2209 and 2221 cm^{-1} for PhCH= CHCN and PhCN, respectively), which suggests RCN is coordinated *via* the nitrogen.[11] While ν(Ir–H) and ν(C≡C) of **3** are not observed (probably obscured by the nearby strong absorptions due to ν(C≡O) and ν(C≡N)), ρ(Ir–H) frequencies of **3** are clearly seen at 816–821 cm^{-1} (see Table I).

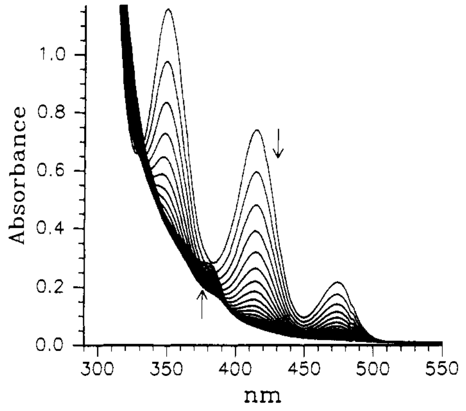


Figure 1. Spectral changes, scanned at an interval of 25 s, during the reaction of $[Ir(PhCN)(CO)(PPh_3)_2]ClO_4$ (**2a**, 2.35 × 10^{-4} M) with PhC≡CH (**1a**, 1.52 × 10^{-2} M) in CH$_2$Cl$_2$ at 25 °C in the presence of PhCN (1.48 × 10^{-4} M). The three absorption bands of **2a** at 350, 414, and 474 nm decrease as the reaction proceeds, and the absorbance at *ca.* 380 nm increases very slowly after most of **2a** disappeared. This increase in absorbance is due to the slow reaction of the product, $[Ir(H)(-C{\equiv}CPh)(PhCN)(CO)(PPh_3)_2]ClO_4$ (**3a**), with the excess **1a** to give an unknown product.

The ^{13}C NMR data for **3** (Table I) show the two carbons, IR-C and Ir–C≡C at *ca.* 83 and 113 ppm, respectively, and the one signal observed in the ^{31}P NMR of **3** (Table I) supports the structure deduced from the ^{1}H NMR data above.

Quantitative formation of **3** suggests that the iridium(I) compounds **2** catalyzed oligomerization of phenylacetylene (**1a**) (to give dimers and cyclic trimers)[7] occurs through the formation of **3**, which then reacts with another molecule of **1a** to undergo the oligomerization of **1a**.

Kinetics and Mechanism

The oxidative addition of **1a** to **2a,b** to give **3a,b** occurs slowly enough to be measured by following the absorbances of **2a,b** in the visible region (see Figure 1). Kinetic measurements for the reactions of eq 1 revealed that the reaction rate is first order both

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Table II. Selective Rate Data for the Oxidative Addition of Phenylacetylene (**1a**) to [Ir(PhCN)(CO)(PPh$_3$)$_2$]ClO$_4$ (**2a**) and [Ir(CH$_3$CN)(CO)(PPh$_3$)$_2$]ClO$_4$ (**2b**) ([Ir] = 2.35×10^{-4} M) at 25 °C in CH$_2$Cl$_2$

Ir	[PhC≡CH], M	[PhCN], M	[CH$_3$CN], M	k_{obs}, s^{-1} [a]
2a	9.11×10^{-3}	1.48×10^{-4}		$(5.86 \times 0.02) \times 10^{-3}$
	1.21×10^{-2}	1.48×10^{-4}		$(7.81 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}	1.48×10^{-4}		$(9.63 \pm 0.01) \times 10^{-3}$
	1.82×10^{-2}	1.48×10^{-4}		$(1.18 \pm 0.01) \times 10^{-2}$
	2.12×10^{-2}	1.48×10^{-4}		$(1.34 \pm 0.01) \times 10^{-2}$
	2.43×10^{-2}	1.48×10^{-4}		$(1.52 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}	3.71×10^{-5}		$(2.05 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}	8.16×10^{-5}		$(1.43 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}	1.26×10^{-4}		$(1.05 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}	1.48×10^{-4}		$(9.63 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}	1.86×10^{-4}		$(8.44 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}	2.04×10^{-4}		$(7.31 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}	2.78×10^{-4}		$(5.85 \pm 0.01) \times 10^{-3}$
2b	9.11×10^{-3}		1.48×10^{-4}	$(9.63 \pm 0.01) \times 10^{-3}$
	1.21×10^{-2}		1.48×10^{-4}	$(1.26 \times 0.01) \times 10^{-2}$
	1.52×10^{-2}		1.48×10^{-4}	$(1.63 \pm 0.01) \times 10^{-2}$
	1.82×10^{-2}		1.48×10^{-4}	$(1.92 \pm 0.01) \times 10^{-2}$
	2.12×10^{-2}		1.48×10^{-4}	$(2.25 \pm 0.01) \times 10^{-2}$
	2.43×10^{-2}		1.48×10^{-4}	$(2.54 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}		8.68×10^{-5}	$(2.37 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}		1.16×10^{-4}	$(1.99 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}		1.48×10^{-4}	$(1.63 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}		1.74×10^{-4}	$(1.48 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}		2.32×10^{-4}	$(1.15 \pm 0.01) \times 10^{-2}$
	1.52×10^{-2}		3.19×10^{-4}	$(8.87 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}		4.34×10^{-4}	$(6.64 \pm 0.01) \times 10^{-3}$
2a	1.52×10^{-2} [b]	5.73×10^{-5}		$(9.62 \pm 0.02) \times 10^{-3}$
	1.52×10^{-2}	1.15×10^{-4}		$(5.98 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}	1.72×10^{-4}		$(4.26 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}	2.29×10^{-4}		$(3.33 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}	3.15×10^{-4}		$(2.48 \pm 0.01) \times 10^{-3}$
	1.52×10^{-2}	4.30×10^{-4}		$(1.81 \pm 0.01) \times 10^{-3}$

[a] Pseudo-first-order rate constants obtained by following the absorbances of **2a,b** in the presence of **1a** and RCN. [b] These values are for [PhC≡CD], M.

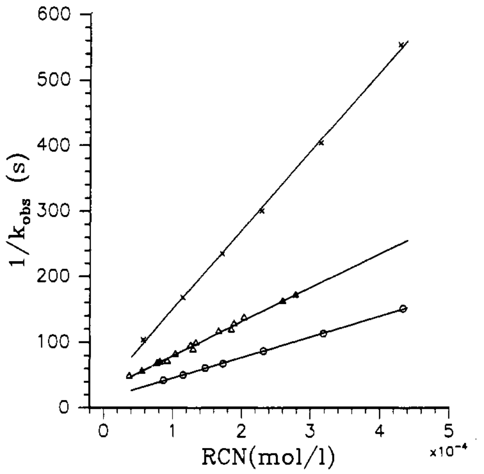

Figure 2. Plots of [RCN] (R = PhCN, CH$_3$) *vs* $1/k_{obs}$, reciprocal of the pseudo-first-order rate constant, obtained at 25 °C in CH$_2$Cl$_2$ for the reaction PhC≡CH (PhC≡CD) + [Ir(CO)(RCN)(PPh$_3$)$_2$]ClO$_4$ → [Ir(H)(–C≡CPh)(RCN)(CO)(PPh$_3$)$_2$]ClO$_4$ ([Ir(D)(–C≡CPh)(RCN)(CO)(PPh$_3$)$_2$]ClO$_4$). Key: Δ-Δ-Δ, PhC≡CH, CH$_3$CN; o-o-o, PhC≡CH, PhCN; x-x-x, PhC≡CD, PhCN.

in **1a** and **2** in the presence of excess **1a** and a certain amount of RCN added and is significantly depressed by the presence of RCN in the reaction mixture. The plot of the reciprocal of k_{obs} (Pseudo-first-order rate constant obtained in the presence of **1a** and RCN, Table II) versus [RCN] gives a good straight line (Figure 2). The fact that the rate decreases with increasing RCN concentration suggests that the step of RCN dissociation is certainly involved in eq 1. No evidence has been obtained for the addition of another RCN to **2** in the absence or presence of **1a**.

Scheme I

$$\underset{2}{[Ir(RCN)(CO)(PPh_3)_2]^+} + \underset{1a}{HC{\equiv}CPh} \underset{k_{-1},\ +RCN}{\overset{k_1,\ -RCN}{\rightleftarrows}} \underset{4}{[Ir(HC{\equiv}CPh)(CO)(PPh_3)_2]^+}$$

$$\xrightarrow{k_2} \underset{5}{[Ir(H)(-C{\equiv}CPh)(CO)(PPh_3)_2]^+} \xrightarrow[RCN]{k_3} \underset{3}{[Ir(H)(-C{\equiv}CPh)(RCN)(CO)(PPh_3)_2]^+}$$

R = Ph, CH$_3$

Table III. Rate Constant, k_1, and Ratio of Rate Constants, k_{-1}/k_2, at 25 °C in CH$_2$Cl$_2$[a]

reactants[b]	k_1, s^{-1} M^{-1}	k_{-1}/k_2, M^{-1}
PhC≡CH + [Ir(PhCN)L$_3$]$^+$ **1a** **2a**	2.41 ± 0.16	$(1.89 \pm 0.13) \times 10^4$
PhC≡CD + [Ir(PhCN)L$_3$]$^+$ **1a-d** **2a**	2.21 ± 0.34[c]	$(4.06 \pm 0.62) \times 10^4$ [d]
PhC≡CH + [Ir(CH$_3$CN)L$_3$]$^+$ **1a** **2b**	4.54 ± 0.22	$(2.15 \pm 0.11) \times 10^4$

[a] See Scheme I for k_1 and k_{-1}/k_2. [b] L$_3$ = (CO)(PPh$_3$)$_2$. [c] k_{1D}. [d] k_{-1D}/k_{2D}.

On the other hand, RCN of **2a,b** is so labile that it is readily replaced by CO, by PPh$_3$, and even by aldehydes[12] and, therefore, expected to be readily replaced by **1a** to give [Ir(HC≡CPh)(CO)(PPh$_3$)$_2$]ClO$_4$ (**4**). Attempts to isolate **4** have been unsuccessful so far probably because the 16-electron Ir(I) complex **4** rapidly undergoes intramolecular oxidative addition to give another 16-electron complex, [Ir(H)(–C≡CPh)(CO)(PPh$_3$)$_2$]ClO$_4$ (**5**), which then takes RCN back into its coordination sphere to produce **3**. The Scheme I is, therefore, suggested for the reactions of eq 1. A steady-state approximation for **4** gives $-d[\mathbf{2}]/dt = k_1k_2[\mathbf{1a}][\mathbf{2}]/(k_{-1}\ [RCN] + k_2)$.

Then, k_{obs} would be equal to $k_1k_2[\mathbf{1a}]/(k_{-1}\ [RCN] + k_2)$. The k_1 values (Table III) are then obtained from the intercepts of the plot of $1/k_{obs}$ versus [RCN]. The k_{-1}/k_2 values (Table III) could also be determined from the slopes of the plots. The large k_{-1}/k_2 (in the order of 10^4) values may be understood in terms of a relatively facile ligand substitution (k_{-1}) and an intramolecular rearrangement (k_2) which requires the H–C bond cleavage of the coordinated phenylacetylene in **4**. The large values of k_{-1}/k_2 (*ca.* 10^4) makes k_{-1} [RCN] not negligible compared with k_2 through the reaction even in case where excess RCN is not added. Therefore, rate data have been obtained in the presence of a certain amount of added RCN ($(0.35–2.80) \times 10^{-4}$ M) to maintain k_{-1} [RCN] constant through the reaction. Kinetic measurements with alkyne hydrogen deuterated phenylacetylene, PhC≡CD (**1a-*d***), may provide valuable information on the suggested mechanism (Scheme I) since primary (for the k_2 step) and secondary (for the k_1 and k_{-1} steps) kinetic isotope effects are expected to be observed. Deuterated phenylacetylene (**1a-*d***) undergoes oxidative addition to **2a** more slowly than **1a** does to **2a**. For example, the half-lives of **2a** (2.35×10^{-4} M) are *ca.* 80 s ($k_{obs} = 8.62 \times 10^{-3}$ s^{-1}) and *ca.* 160 s ($k_{obs} = 4.26 \times 10^{-3}$ s^{-1}) in the reactions with **1a** and **1a-*d*** (1.52×10^{-2} M), respectively, at 25 °C in the presence of PhCN (1.67×10^{-4} M). The values of k_{1D} and k_{-1D}/k_{2D} (see eq 2 and Table III) have been obtained in the same manner described above. No significant kinetic isotope effect was found for the step of RCN substitution of *cf.* k_1 and k_{1D} in Table III) with **1a** and **1a-*d***. Accordingly, no significant isotope effect is expected for the reverse step (k_{-1} and k_{-1D}), the replacement of **1a** and **1a-*d*** with RCN. On the other hand, a relatively large kinetic isotope effect was observed for k_{-1}/k_2 value, *i.e.*, $(k_{-1D}/k_{2D})/(k_{-1}/k_2) = 2.1$. Since $k_{-1}/k_{-1,D}$ is expected to be close to

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[12] Yang, K. J.; Chin, C. S. *Inorg. Chem.* **1987**, *26*, 2732.

1, this value of 2.1 seems to be mainly due to k_2/k_{2D}, which is understood in terms of a primary isotope effect for the C–H (or C–D) bond cleavage step, k_2 (or k_{2D}), and small isotope effects on both substitution steps, k_1 and k_{-1}, of the suggested Scheme I.

$$\underset{\mathbf{1a}\text{-}d}{\mathbf{2a} + \mathrm{PhC{\equiv}CD}} \xleftarrow[\mathrm{PhCN}]{k_{-1,\mathrm{D}}} \underset{\mathbf{4a}\text{-}d}{[\mathrm{Ir(PhC{\equiv}CD)L}]^+} \xrightarrow{k_{2,\mathrm{D}}} \underset{\mathbf{5a}\text{-}d}{[\mathrm{Ir(D)(–C{\equiv}CPh)L}]^+} \quad (2)$$

$$L = (CO)(PPh_3)_2$$

k_1 for the CH_3CN complex (**2b**) has been found to be considerably larger than that for the PhCN Complex (**2a**), while the k_{-1}/k_2 values for **2a**,**b** are not much different from each other (see Table III). This lability of CH_3CN from **2a** is somewhat surprising since the dissociation of CH_3CN from the Rh analog, $[Rh(CH_3CN)(CO)(PPh_3)_2]ClO_4$, to give $Rh(ClO_4)(CO)(PPh_3)_2$ is known to be larger than that of PhCN from $[Rh(PhCN)(CO)(PPh_3)_2]ClO_4$ (dissociation of RCN from **2** is so small that it can not be measured by the spectroscopic method).[13]

Activation parameters ($\Delta H^* = 16.6 \pm 0.6$ kcal/mol and $\Delta S^* = -1.0 \pm 2.2$ cal/(deg·mol)) obtained from k_1 values for the reaction of **1a** with **2a** in the temperature region of 10–25 °C may suggest an iridium species containing both PhC≡CH and PhCN bound to Ir in the transition state.

Finally, it may be worthwhile to mention why RCN of **2** has to be replaced by **1a** to give **4** and then binds back to **5** to give **3** instead of remaining intact in the coordination sphere through the reaction. The most probable intermediate for the first step (k_1) would be the 18-electron complex $[Ir(PhC{\equiv}CH)(RCN)(CO)(PPh_3)_2]ClO_4$ (**6**), whose RCN is probably even more labile than is the RCN of **2**, and therefore, the dissociation of RCN from **6** to give **4** would readily occur prior to the C–H bond cleavage of **1a** in **6** and the intramolecular rearrangement to give **3**.

Experimental Section

Extensive precautions should be taken since perchlorate slats of transition metal complexes are potentially explosive.[14]

A standard vacuum system and Schlenk type glassware were used in handling metal complexes. ^1H NMR and infrared spectra were obtained on a Varian Gemini 300-MHz spectrometer and Shimadzu Ir-440 spectrophotometer. A Hewlett Packard D8452A diode array spectrophotometer was used for the electronic absorption spectral and kinetic measurements. Elemental analysis was carried out by a Carlo Erba EA1108 at the Organic Reaction Center, Sogang University.

The starting material, $[Ir(RCN)(CO)(PPh_3)_2]ClO_4$, was prepared by the known method,[8b] and PhC≡CD was prepared by the reaction of *n*-BuLi with PhC≡CH followed by treatment with D_2O.

Synthesis of $[Ir(H)(–C{\equiv}CPh)(RCN)(CO)(PPh_3)_2]ClO_4$ (3) (R = Ph (a), CH_3 (b), CH═CHPh (c)) and $[Ir(H)(–C{\equiv}C(p\text{-}C_6H_4CH_3))(PhCN)(CO)(PPh_3)_2]ClO_4$ (3d). All compounds, **3a**-d, were prepared in the same manner as described below for **3a** and gave satisfactory elemental analyses.

To 10 mL of CH_2Cl_2 containing 0.32 mmol (18 μL) of PhC≡CH was added 0.30 mmol of **2a** (0.28 g), and the reaction mixture was stirred at 25 °C. The yellow solution became beige within 5 min. The beige solid of **3a** was filtered off after addition of hexane (10 mL), washed with hexane (10 mL), and dried under vacuum. The yield was 0.28 g and 90% based on **3a**. Anal. Calcd for $IrC_{52}H_{41}NP_2ClO_5$: C, 59.51; H, 3.94; N, 1.33. Found: C, 59.33; H, 3.83; N, 1.32.

Rate Measurements for the Reactions of PhC≡CH (1a) with $[Ir(RCN)(CO)(PPh_3)_2]ClO_4$ (2a, R = PhCN; 2b, R = CH_3CN). These reactions were followed in the same manner as described below by measuring the decrease of the absorbances at 414 nm for the reaction of **2a** (see Figure 1) and at 404 nm for **2b**. A 5.0-μL volume of phenylacetylene, **1a** (4.55×10^{-5} mol), in a microsyringe was added into a cell containing 3 mL of a CH_2Cl_2 solution of **2a** (2.34×10^{-4} M) and PhCN (1.48×10^{-4} M) kept at 25 °C; the reaction mixture was shaken for 1 s, and all of the spectral changes (see Figure 1) were measured every 25 s at 25 °C. They were measured every 2–30 s depending upon the reaction rates for different RCN compounds under different reaction conditions. The HP 89532 kinetics software stored in the instrument was used to obtain the rate data in Table II.

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(13) Lee, M. K.; Kim, I. B.; Park, H.-K.; Park, S. H.; Chin, C. S. *Polyhedron* **1985**, *9*, 1483.

(14) See: (a) *Chem. Eng. News* **1983**, *61* (Dec. 5), 4; **1963**, *41* (July 8), 47. (b) *J. Chem. Educ.* **1978**, *55*, A355.