min) and iodobenzene (8.32 min).

References

1. (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (b) Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431. (c) Jacobsen, E. N.; Zhang, W.; Guler, M. *J. Am. Chem. Soc.* **1991**, *113*, 6703. (d) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063.
2. (a) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922. (b) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. (c) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.
3. (a) McMurray, T. J.; Groves, J. T., in *Cytochrome P-450; Structure, Mechanism, and Biochemistry*; Oriz de Montellano, P. R., Ed.; Plenum: New York, 1986. (b) Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, *4*, 578. (c) Watanabe, Y.; Groves, J. T., in *The Enzymes* Vol. XX, Sigman, D. Ed.; Academic Press: New York, 1992, pp 406-542. (d) Quici, S.; Banfi, S.; Pozzi, G. *Gaz. Chim. Ital.* **1993**, *123*, 597.
4. (a) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791. (b) Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 7281. (c) Suslick, K. S.; Cook, B. R. *J. Chem. Soc., Chem. Commun.* **1987**, 200. (d) Collman, J. P.; Lee, V. J.; Zhang, X.; Ibers, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1993**, *115*, 3834. (e) Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 368.
5. (a) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770. (b) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786. (c) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032.
6. (a) Fujii, H. *J. Am. Chem. Soc.* **1993**, *115*, 4641. (b) Dunford, H. B. *Adv. Inorg. Biochem.* **1982**, *4*, 41.
7. Bruice, T. C.; Ostovic, D. *Acc. Chem. Res.* **1992**, *25*, 314.
8. Groves, J. T.; Kruper, W. J., Jr.; Hausthalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375.
9. Groves, J. T.; Ahn, K.-H.; Quinn, R. *J. Am. Chem. Soc.* **1988**, *110*, 4217.
10. Collman, J. P.; Zhang, X.; Hembre, R. T.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 5356.
11. Saltzman, H.; Sharefkin, J. G. *Org. Syn.* **1963**, *43*, 60.
12. H_2TNPPP; Groves, J. T.; McMurrary, T. J. unpublished result.

Selective Dimerization and Cyclotrimerization of Phenylacetylene with Rhodium and Iridium Complexes

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Oligomerization of phenylacetylene is catalyzed by $Rh(ClO_4)(CO)(PPh_3)_2$ (**Rh-1**), $[Rh(CO)(PPh_3)_3]ClO_4$ (**Rh-2**), $[Rh(COD)L_2]ClO_4$ ($L_2=(PPh_3)_2$, **Rh-3**; $(PPh_3)(PhCN)$, **Rh-4**; $(PhCN)_2$, **Rh-5**), $[Rh(C_3H_5)(Cl)(CO)(SbPh_3)_2]ClO_4$ (**Rh-6**), $[Ir(COD)L_2]ClO_4$($L_2=(PPh_3)_2$, **Ir-1**; $(PPh_3)(PhCN)$, **Ir-2**; $(PhCN)_2$, **Ir-3**; $(AsPh_3)(PhCN)$, **Ir-4**; $Ph_2PCH_2CH_2PPh_2$, **Ir-5**; COD, **Ir-6** and 2,2'-dipyridyl, **Ir-7**), $Ir(ClO_4)(CO)(PPh_3)_2$, **Ir-8**, $[Ir(PhCN)(CO)(PPh_3)_2]ClO_4$, **Ir-9** to produce dimerization products, 1,3-diphenylbut-1-yn-3-ene, **1**, (E)-1,4-diphenylbut-1-yn-3-ene, **2** and (Z)-1,4-diphenylbut-1-yn-3-ene, **3**, and cyclotrimerization products, 1,3,5-triphenylbenzene, **4** and 1,2,4-triphenylbenzene, **5**. Product distribution of the oligomers varies depending on various factors such as the nature of catalysts, reaction temperature, counter anions and excess ligand present in the reaction mixtures. Increasing reaction temperature in general increases the yield of the cyclotrimerization products. Exclusive production of dimer **1** and trimer **4** can be obtained with **Ir-1** at 0 ℃ and with **Ir-2** in the presence of excess PhCN (or CH_3CN) at 50 ℃, respectively. Dimer **2** (up to 81%) and trimer **5** (up to 98%) are selectively produced with **Rh-1** at 50 and 100 ℃, respectively. Production of **3** is selectively increased up to 85% by using PF_6^- salt of $[Ir(COD)(PPh_3)_2]^+$ at 25 ℃. Addition of CH_3I to **Rh-1** produces $CH_3PPh_3^+I^-$ and increases the rate of oligomerization(disappearance of phenylacetylene). Among the metal compounds investigated in this study, **Ir-1** catalyzes most rapidly the oligomerization where the catalytically active species seems to contain $Ir(PPh_3)_2$ moiety. The stoichiometric reaction of phenylacetylene wth **Ir-9** at 25 ℃ quantitatively produces hydridophenyl-ethynyl iridium (III) complex, $[Ir(H)(C\equiv CPh)(PhCN)(CO)(PPh_3)_2]ClO_4$ (**Ir-11**), which seems to be an intermediate for the oligomerization.

Introduction

Dimerization[1] and cyclotrimerization[1b,2] of terminal alkynes are known to be catalyzed by transition metal complexes for some time. While the head-to-tail dimerization product (type **1**) and both the E- (type **2**)[1b,c,e,f] and Z-isomer (type **3**)[1j,k] of the head-to-head dimerization products have been reported, both two isomers (type **4** and type **5**) have been

Table 1. Dimerization and Cyclotrimerization of Phenylacetylene with Rhodium and Iridium Compounds (see equation 1 for the numbers of catalysts and products) in $CDCl_3$ under N_2. PhC≡CH/catalyst = 30

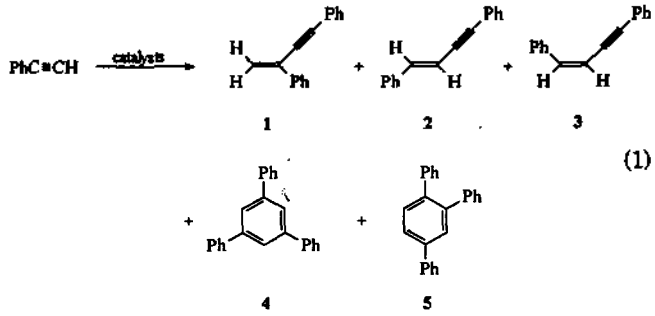
Catalyst	Temp.	Product, %[a]					Time,	Unreacted
	℃	**1**	**2**	**3**	**4**	**5**	hr	PhC≡CH, %
Rh-1	25	25	75				20	55
	50	2	81		2	15	20	5
	100				2	98	1	0
Rh-2	25	35	18		47		20	67
	50	17	67		16		20	50
Rh-3	25	36	28		33	3	12	22
	50	1	3	1	92	3	1	17
Rh-4	25	35	25		33	7	20	64
	25[b]	42	8		22	28	20	64
	50		26		34	40	20	20
	50[b]		29		31	40	20	19
Rh-5	25	2	5	3	76	14	20	66
	50				71	29	20	37
Rh-6	25	4	16		33	47	20	62
	50				45	55	7	50
Ir-1	25	60	22	16	2		1	5
	0	100					1	30
Ir-1a[c]	25		15	85			1	5
Ir-2	25	10	37	53			20	50
	50	60	11	13	16		20	5
Ir-2a[d]	50	20	12	11	19	38	70	0
Ir-2[b]	50				100		20	5
Ir-3	50				45	45	120	10
Ir-4	50	(less	than	10%)	40	50	110	10
Ir-4[b]	50	14			41	45	48	10
Ir-5	50	14			41	45	20	5
Ir-6	50				45	55	15	25
Ir-7	50	20	17	13	23	27	170	50
Ir-8	50	8	5	37	35	15	46	64
Ir-9	50	6	6	48	21	19	46	75

[a] Percentage among the products. [b] In the presence of excess CH_3CN or PhCN (RCN/M = 10, M = Rh, Ir). [c] **Ir-1a** = $[Ir(COD)(PPh_3)_2]PF_6$. [d] **Ir-2a** = $[Ir(COD)(PPh_3)(PhCN)]PF_6$.

also observed in the cyclotrimerization.[1b,2] Distribution of products (**1-5**) varies quite sensi-tively with the nature of the metals[1g,2b,e,j] and the ligands coordinated to the catalyst metals[1b,2b,g,i] as well as the substituents of alkynes[1g,2b] while a single product is selectively produced with a catalyst.[1c,g,2b] Most of these experimental observations have not been unambiguously understood in terms of properties of the catalysts, *e.g.*, the reason why **1** is the major product with the yttrium compound whereas **2** is the major one with the lanthanum and cerium analogues could not be fully explained.[1g] We have investigated the oligomerization of phenylacetylene catalyzed by rhodium and iridium complexes in hopes of i) seeing some relationship between the product distribution, properties of catalyst metal compounds and reaction conditions and ii) finding ways for production of an oligomer selectively.

Results and Discussion

Table 1 summarizes the experimental results showing that all three possible dimeric isomers, **1-3**, and two cyclotrimeric isomers, **4**, and **5** are produced in the reactions of phenylacetylene with those metal complex catalysts in equation 1. It is seen in Table 1 that the product distribution varies very much depending on the nature of catalysts and the other experimental conditions such as temperature, counter anion and presence of excess ligands (*vide infra*).



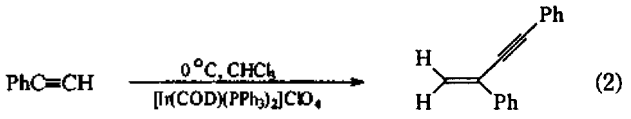
(1)

catalyst = $Rh(ClO)_4(CO)(PPh_3)_2$(**Rh-1**), $[Rh(CO)(PPh_3)_3]ClO_4$ (**Rh-2**), $[Rh(COD)(PPh_3)_2]ClO_4$ (**Rh-3**), $[Rh(COD)(PPh_3)(PhCN)]ClO_4$ (**Rh-4**), $[Rh(COD)(PhCN)_2]ClO_4$ (**Rh-5**), $[Rh(C_3H_5)(Cl)(CO)(SbPh_3)_2]ClO_4$(**Rh-6**), $[Ir(COD)(PPh_3)_2]ClO_4$, (**Ir-1**), $[Ir(COD)(PPh_3)(PhCN)]ClO_4$, (**Ir-2**), $[Ir(COD)(PhCN)_2)]ClO_4$ (**Ir-3**), $[Ir(COD)(AsPh_3)(PhCN)]ClO_4$ (**Ir-4**), $[Ir(COD)(Ph_2PCH_2CH_2PPh_2)]ClO_4$ (**Ir-5**), $[Ir(COD)_2]ClO_4$ (**Ir-6**), [Ir(COD)(2,2′-dipyridyl)]ClO_4 (**Ir-7**), $Ir(ClO_4)(CO)(PPh_3)_2$ (**Ir-8**), $[Ir(CO)(PhCN)(PPh_3)_2]ClO_4$ (**Ir-9**), $[Ir(CO)(PPh_3)_3]ClO_4$ (**Ir-10**)

Production of 1,3-Diphenylbut-1-yn-3-ene, 1

It is seen in Table 1 that increasing the reaction temperature in general increases the yields of cyclotrimerization products with both rhodium and iridium catalysts. The temperature effect on the product distribution is remarkable for production of **1**: it is striking to see the head-to-tail dimerization product, **1** as the only product with **Ir-1** when the reaction temperature is decreased down to 0 ℃ where the dimerization is still fairly fast (eq. 2). Head-to-tail dimerization products of alkynes have been produced in good purity with other catalysts for alkynes with different substituents for which detailed mechanisms were suggested.[1c,d,g-i] The exclusive formation of **1** with **Ir-1** at low temperature (0 ℃) could not be understood simply by the far lower activation energy process for the formation of **1** than those for others, **2-5**, since i) **1** is not produced at all while **2** and **3** are rapidly formed in the presence of **Ir-1a** ($[Ir(COD)(PPh_3)_2]PF_6$) at 25 ℃, and ii) **1** is only a minor product while larger amounts of **2** and **3** are obtained with **Ir-2** at 25 ℃ (see Table 1). The temperature effect may be understood by the dissociation of a ligand (COD or PPh_3) from **Ir-1**. The ligand dissociation could be negligible at 0 ℃ but significant at 25 ℃. In fact, we observed by following the ^1H NMR spectral changes that a considerable amount of free COD (dissociated from **Ir-1**) was present in the reaction mixture of **Ir-1** with phenylacetylene at 25 ℃ while at 0 ℃, free COD was not found in the reaction mixture of **Ir-1** and phenylacetylene. Dissociation of PPh_3 from **Ir-1** was not detected in the reaction of phenylacetylene both at 25 and 0 ℃. Then it may be said that [Ir(COD)

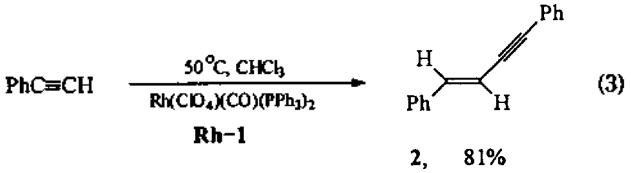
$(PPh_3)_2]ClO_4$ (**Ir-1**) is catalytically active only for the formation of **1** while the ligand (COD) dissociation from **Ir-1** leads to species which produce all the products, **1-4**.



(2)

Production of (E)-1,4-Diphenylbut-1-yn-3-ene, 2

The E-isomers (type **2**)[1b,c,e,f] of the head-to-head dimerization products have been more frequently reported than the Z-isomers (type **3**).[1j,k] We found that at 50 °C, the yield of **2** is considerably high (81%) when **Rh-1** is used as the catalyst (Eq. 3). The yield of **2** decreases both at lower (25 °C) and higher (100 °C) temperature (see Table 1). Formation of **2** seems less favorable (higher activation energy) than that of **1** for steric reasons around the metal in **Rh-1** since increasing reaction temperature in general increases the relative yield of **2** to **1** except that it is smaller at 50 °C than that at 25 °C when **Ir-2** is used as the catalyst (see Table 1). The smaller relative yield of **2** to **1** at 50 °C than at 25 °C with **Ir-2** is not fully understood yet. The absence of **2** (and **1**) in the reaction mixture of **Rh-1** and phenylacetylene at 100 °C may be simply understood in terms of increase in yield of the cyclotrimerization products (*vide infra*).

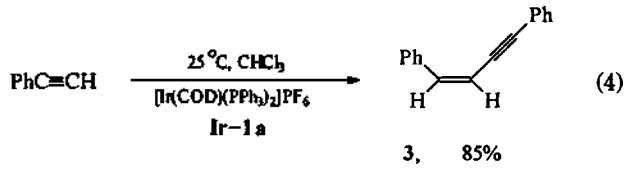


(3)

Production of (Z)-1,4-Diphenylbut-1-yn-3-ene, 3.

Metal catalyzed production of the Z-isomers of the head-to-head dimerization of alkynes has been reported only in few papers.[1j,k] It is striking to see that significant amounts of the Z-dimer, **3** are produced in the presence of those iridium complexes in Table 1 while the rhodium analogues (**Rh-1** to **Rh-6**) barely produce **3** (see Table 1).

Counter anion effects on the product distribution seem rather prominent for the cation $[Ir(COD)(PPh_3)_2]^+$: only the head-to-head dimerization products, **2** and **3** are observed with PF_6^- salt, $[Ir(COD)(PPh_3)_2]PF_6$ (**Ir-1a**) while the ClO_4^- salt (**Ir-1**) of the same cation produces all three dimers **1-3** and a cyclotrimer, **4** (see Table 1). Similar effects were observed for the cation, $[Ir(COD)(PPh_3)(PhCN)]^+$: the dimer **1** is the major product (60%) with ClO_4^- salt (**Ir-2**) while the PF_6^- salt, **Ir-2a** gives more trimers (57%) than dimers (see Table 1). These counter anion effects observed for salts of ClO_4^- (**Ir-1** and **Ir-2**) and PF_6^- (**Ir-1a** and **Ir-2a**) have not been clearly understood. It should be mentioned, however, that the anion ClO_4^- is known to coordinate to iridium (**I**, **III**) as a labile ligand[3] while the other anion PF_6^- had never been found to coordinate to iridium. Of those iridium compounds that produce the Z-dimer **3**, the PF_6^- salt (**Ir-1a**) gives the highest yield (85%) at 25 °C (Eq. 4).

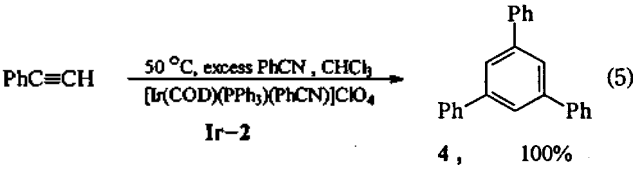


(4)

Production of 1,3,5-Triphenylbenzene, 4

It is apparent that increasing reaction temperature leads to increase in yields of cyclic trimers, **4** and **5** both with rhodium and iridium compounds (see Table 1). We found that 1,3,5-triphenylbenzene, **4** can be exclusively produced with **Ir-2** at 50 °C in the presence of excess nitrile (PhCN or CH_3CN) (Eq. 5) without a significant change in the reaction rate compared with that in the absence of excess nitrile. The presence of excess nitrile would definitely prevent the dissociation of the nitrile from $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ (**Ir-2**) but would not replace COD or PPh_3.[4] Addition of excess PPh_3 or COD to **Ir-2**, on the other hand, does not increase the selectivity to produce **4** although it increases the rate of disappearance of phenylacetylene to give oligomers. Reactions of **Ir-2** with PPh_3 and COD are known to produce **Ir-1**[5] and a mixture of **Ir-1** and $[Ir(COD)_2]ClO_4$[6] (Eq. 8), respectively. It is less likely that the anion ClO_4^- occupies a coordination site around the iridium in **Ir-2** in the presence of excess nitrile during the cyclotrimerization since ClO_4^- is known to be readily replaced by a nitrile.[5] It has been, however, observed that **Ir-2** readily loses COD in the reaction with excess PhC≡CH. These observations suggest that the actual catalytic species effective for the selective production of **4** at 50 °C contains $Ir(PPh_3)(PhCN)_n$ ($n=2$ or 3) moiety. It has been also found in separate experiments that the dimers, **1-3** are not converted into cyclic trimers, **4** and **5** at 50 °C with **Ir-2** in the presence of excess PhC≡CH with or without excess PhCN in the reaction mixtures.

It is interesting to see somewhat different results with rhodium compounds from those above with iridium compounds: i) the higher yield of **4** is obtained with $[Rh(COD)(PPh_3)_2]^+$ (**Rh-3**) (up to 92%) than with $[Rh(COD)(PPh_3)(PhCN)]^+$ (**Rh-4**) (34%) at 50 °C and ii) the addition of excess nitrile shows practically no effects on the product distribution (see Table 1). Temperature effects for the selective production of **4** with **Rh-3** is also significant as observed for the selective production of **1** with **Ir-1**: lowering the reaction temperature from 50 °C to 25 °C gives rise to a large decrease in the yield of **4** (see Table 1).



(5)

Production of 1,2,4-Triphenylbenzene, 5

At 100 °C, the disappearance of phenylacetylene in the presence of **Rh-1** is fairly fast and selectively produces **5** (98%) (Eq. 6) while at 50 °C, the dimer **2** is the major product with a small amount of **5** (see Table 1). We found that **Rh-1** slowly loses CO in solution at 100 °C while it firmly

Table 2. Relative Rates of Disappearance of Phenylacetylene in the Presence of Excess Ligands. PhC≡CH/catalyst=30. L/catalyst=10. See Equation 1 for the Numbers of Catalysts. Product Distribution in the Presence of Excess Ligands is Practically the Same with Those Values in Table 1 within the Experimental Errors

Catalyst	L	Temp., ℃	Time, hr	Unreacted PhC≡CH, %
RH-1		25	20	55
	CH_3I	25	8	5
	COD	25	20	13
	PPh_3	25	20	80
Ir-1		25	1	5
	PPh_3	25	1	7
	COD	25	1	40
Ir-2		25	20	50
	PPh_3	25	1	60
	COD	25	1	60

holds CO at 50 ℃. Therefore, the dissociation of CO from **Rh-1** seems to give rise to the catalytic species selectively effective for the production of **5** while the nature of the catalytic species is yet to be investigated.

$$PhC{\equiv}CH \xrightarrow[\textbf{Rh-1}]{100\,^{\circ}C,\ CHCl_3,\ Rh(ClO_4)(CO)(PPh_3)_2} \textbf{5},\ 85\% \qquad (6)$$

Rate Increase by Addition of Excess Ligands Catalytically Active Species. Table 2 summarizes rate data obtained in the presence of excess ligands whose presence considerably increases the rates of phenylacetylene disappearance without significant change in the product distribution. Addition of excess CH_3I or COD to **Rh-1** increases the rate while the rate is decreased by the presence of excess PPh_3. It is known that **Rh-1** reacts with PPh_3 to give **Rh-2**[7] which is found to be less active for the oligomerization of phenylacetylene in this study (see Table 1). Therefore, it may be said that the more PPh_3 is around **Rh-1**, the lower the rate of oligomerization becomes, which may be understood by stronger interactions between rhodium and PPh_3 than those between rhodium and phenylacetylene. Reactions of **Rh-1** with CH_3I and COD have been carried out in the absence of phenylacetylene in order to obtain information on the catalytic species which show higher rates than those with **Rh-1** in the absence of CH_3I and COD. Isolated yellow solids from the reactions of **Rh-1** with excess CH_3I both in the presence and absence of phenylacetylene show coordinated PPh_3 and uncoordinated ClO_4^- and no CO in their ^1H NMR and IR spectra. A significant amount of water soluble solid was isolated and identified as $CH_3PPh_3^+I^-$ (*ca.* one mole per **Rh-1**). The same type of slats, $RPPh_3^+Cl^-$ were also produced in the decomposition[8] and reductive elimination[9] of $Rh(Cl)_2(R)(CO)(PPh_3)_2$ in the presence of PPh_3. It may then be said that the addition of CH_3I to **Rh-1** increases the rate of oligomerization because CH_3I facilitates the removal of one PPh_3 and causes the dissociation of CO from **Rh-1** to give the coordinatively unsaturated catalytic species, $[Rh(PPh_3)]_n^{n+}(ClO_4)_n$ (Eq. 7). It should be mentioned that no dimers of phenylacetylene obtained in the presence of **Rh-1** and CH_3I containing CH_3 group.

$$\underset{\textbf{Rh-1}}{Rh(ClO_4)(CO)(PPh_3)_2} \xrightarrow[-CO,\ -CH_3PPh_3^+I^-]{25\,^{\circ}C,\ CH_3I} [Rh(PPh_3)_n]^{n+}(ClO_4)_n \qquad (7)$$

In separate experiments in the absence of PhC≡CH, it has been found that the reaction of **Rh-1** with COD gives **Rh-3** which shows the higher rate of the oligomerization than that with **Rh-1** (see Table 1). The rate increase by addition of COD to **Rh-1** may be understood by the formation **Rh-3** from the **Rh-1** with COD. Addition of excess PPh_3 to **Ir-1** shows practically no effect on the rate of oligomerization while COD addition lowers the rate and addition of both PPh_3 and COD to **Ir-2** raises the rate, respectively (see Table 2). It has been found in this study that $[Ir(COD)(PPh_3)_2]ClO_4$ (**Ir-1**) is the only isolated species from the reactions of **Ir-1** and **Ir-2** with excess PPh_3 and the reaction of **Ir-1** with excess COD in the absence of PhC≡CH. The same species, **Ir-1** is also produced in the reaction of COD with **Ir-2** (Eq. 8). The experimental results for **Ir-1** and **Ir-2** in Table 2 are then explained as follows. Addition of excess PPh_3 to **Ir-1** does not change the reaction rate since neither addition of PPh_3 to **Ir-1** nor dissociation of PPh_3 from **Ir-1** is significant during the oligomerization. The decrease in the rate by addition of COD to **Ir-1** suggests that **Ir-1** loses COD in the reaction with PhC≡CH to produce the catalytically active species containing $Ir(PPh_3)_2$ moiety. This suggestion is unambiguously supported by the observation that ^1H NMR of the reaction mixture of **Ir-1** and PhC≡CH shows free (uncoordinated) COD from the early stage of the oligomerization. The rate increases observed by the addition of either PPh_3 or COD to **Ir-2** are then understood also by the formation of $Ir(PPh_3)_2$ moiety containing species which seems to catalyze the oligomerization more rapidly than does $Ir(PPh_3)(PhCN)$ moiety containing species which is the catalytically active species for the oligomerization with **Ir-2** in the absence of excess PPh_3 and COD (*vide supra*). The slower rates with **Ir-2** in the presence of excess PPh_3 and COD than that with **Ir-1** in the absence of excess PPh_3 and COD (see Table 2) is apparently due to presence of PhCN and COD dissociated from **Ir-2**.

$$[Ir(COD)(PPh_3)(PhCN)]^+ + 1/2\,COD \longrightarrow \underset{\textbf{Ir-1}}{1/2[Ir(COD)(PPh_3)_2]^+} + \underset{\textbf{Ir-6}}{1/2[Ir(COD)_2]^+} + PhCN \qquad (8)$$

The two PPh_3 of the $Ir(PPh_3)_2$ moiety in the catalytically active species seem to be *trans* to each other since the slower rate was observed with a chelate diphosphine compound. $[Ir(COD)(Ph_2PCH_2CH_2PPh_2)]ClO_4$ (**Ir-5**) than with $[Ir(COD)(PPh_3)_2]ClO_4$ (**Ir-1**).

Various Acetylenes

Oligomerization of several acetylene derivatives were also

investigated. While diphenylacetylene does not undergo oligomerization, reactions of *p*-tolylacetylene (*p*-$CH_3C_6H_4C{\equiv}CH$) with those rhodium and iridium compounds in Eq. 1 produce oligomers in a similar product distribution as observed for the oligomerization of $PhC{\equiv}CH$: the head-to-head dimerization product, (E)-*p*-$CH_3C_6H_4CH{=}CHG{\equiv}CC_6H_4$(*p*-$CH_3$) (**2a**) is the major product (70%) with 30% of the head-to-tail dimerization product, $H_2C{=}C$(*p*-$CH_3C_6H_4$)$C{\equiv}CC_6H_4$(*p*-CH_3) (**1a**) with **Rh-1** at 50 ℃ while **1a** is the major product (62%) with **2a** (15%) and **3a** ((Z)-*p*-$CH_3C_6H_4CH{=}CHC{\equiv}CC_6H_4$(*p*-$CH_3$)) (23%) as minor ones with **Ir-1** at 25 ℃.

Alkynes with ester and ether groups behave differently: ethyl propiolate, $C_2H_5CO_2C{\equiv}CH$ is converted mainly into the cyclotrimers (70%) and the E-type head-to-head dimerizationproduct (30%), and methyl propargyl ether, $CH_3OCH_2C{\equiv}CH$ into the head-to-tail dimerization product (50%), E-type head-to-head product (40%) and cyclotrimers (10%) in the presence of **Rh-1** at 25 ℃.

It may be said that both ester and ether groups of terminal alkynes seem to facilitate the cyclotrimerization probably through the interactions with metal while the single bond between two sp^3 carbons does not seem to be cleaved by those metal compounds in Eq. 1.

Stoichiometric Reactions of [Ir(RCN)(CO)(PPh$_3$)$_2$]ClO$_4$ with Phenylacetylene. While most metal containing materials isolated from reactions of metal compounds in Eq. 1 with phenylacetylene have not been well characterized, the beige microcrystals obtained from the reactions of **Ir-9** with $PhC{\equiv}CH$ have been identified as $[IrH(-C{\equiv}CPh)(PhCN)(CO)(PPh_3)_2]ClO_4$ (**Ir-11**).[10] This oxidative addition of $PhC{\equiv}CH$ to **Ir-9** occurs at 25 ℃ within 5 minutes to give **Ir-11** quantitatively. Related hydrido(phenylethynyl)-iridium(III) compounds, $IrH(-C{\equiv}CPh)(OClO_3)(CO)(PPh_3)_2$, $[IrH(-C{\equiv}CPh)(RCN)(CO)(PPh_3)_2]ClO_4$ (R = CH_3, $C_6H_5CH{=}CH$) and $[IrH(-C{\equiv}CPh)(CO)(PPh_3)_3]ClO_4$ are also quantitatively obtained from reactions of $PhC{\equiv}CH$ with the related compounds, $Ir(OClO_3)(CO)(PPh_3)_2$ (**Ir-8**), $[Ir(RCN)(CO)(PPh_3)_2]ClO_4$ and $[Ir(CO)(PPh_3)_3]ClO_4$ (**Ir-10**), which undergo dimerization and cyclotrimerization in the presence of excess $PhC{\equiv}CH$. The isolated solid from the reaction of **Ir-8** with 1,7-octadiyne also shows signals at −15.4 ppm (J_{H-P} = 11.6 Hz) due to Ir-H in ^1H NMR spectra while it has not been fully characterized (1,7-octadiyne undergoes dimerization to give the head-to-tail dimerization product (90%) in the presence of **Ir-8** and **Rh-1** at 25 ℃).

These observations strongly suggest that the oligomerization of $PhC{\equiv}CH$ with **Ir-9** occurs *via* the cleavage of C-H bond of $PhC{\equiv}CH$ to form hydridoethynyl complex (Eq. 9), which is well-known reaction pathway[11] rather than *via* the metallacyclopentadiene intermediates, which is also well-established pathway.[2,12]

$$PhC{\equiv}CH + M \longrightarrow \overset{H}{\underset{|}{M}}-C{\equiv}CPh \xrightarrow{PhC{\equiv}CH} \overset{H}{\underset{|}{M}}-C{\equiv}CPh \xrightarrow{nPhC{\equiv}CH} \text{oligomers} \quad (9)$$
$$\underset{|}{PhC{\equiv}CH}$$

Conclusion

Each of the oligomers, **1-5**, of phenylacetylene can be selectively obtained in relatively good purity by choosing appropriate metal compounds, varying reaction temperature, adding excess ligands and employing different counter anions, and detailed mechanisms for the selective production of each oligomer are currently under investigation.

Experimental

Caution. Extensive precautions should be taken in handling perchlorate salts and perchlorato complexes of transition metals since they are potentially explosive.[13]

Methods. A standard vacuum line and Schlenk glassware were used in handling metal complexes. ^1H NMR spectra were measured on a Varian 60 MHz (EM-360) for rate measurements and on a Varian Gemini 300 MHz spectrometer for identification of products. Gas chromatographs and mass spectra were recorded on a VG-trio 2000.

Materials. $Rh(OClO_3)(CO)(PPh_3)_2$,[3] $[Rh(CO)(PPh_3)_3]ClO_4$,[5] $[Rh(COD)L_2]ClO_4$ (L_2 = $(PPh_3)_2$, $(PPh_3)(PhCN)$, $(PhCN)_2$),[14] $[Rh(C_3H_5)(Cl)(CO)(SbPh_3)_2]ClO_4$[15] and $[Ir(COD)L_2]ClO_4$ (L_2 = $(PPh_3)_2$, $(PPh_3)(PhCN)$, $(PhCN)_2$, $(AsPh_3)(PhCN)$, $(Ph_2PCH_2CH_2PPh_2)$, (2,2′-dipyridyl)[5,6] were prepared by the literature methods. Phenylacetylene, *p*-tolylacetylene, ethyl propiolate and methyl propargyl ether were purchased from Aldrich and used without further purification.

Oligomerization of Phenylacetylene. A 3.0 mmole of $PhC{\equiv}CH$ was added into the $CDCl_3$ (2.5 cm^3) solution of a metal compound (0.1 mmole) in a 25 cm^3 round bottom flask under nitrogen and a part (*ca.* 0.5 cm^3) of the resulting reaction mixture was immediately transferred in a NMR tube which was then sealed. Both the flask and NMR tubes were kept on a constant temperature bath. The reaction was followed by measuring the disappearance of $PhC{\equiv}CH$ signal at δ 3.08 ppm. The reaction mixture in the flask was analyezd through column chromatographic separation on silica gel with hexane followed by ^1H NMR and mass spectrum measurements. Product analysis for dimers, **1-3** could also be obtained only by ^1H NMR measurements for the reaction mixtures since each product could be quantitatively analyzed by their characteristic signals given below. ^1H NMR: $H_2C{=}C$(Ph)$C{\equiv}CPh$ (**1**), δ 6.03 (d, J = 1 Hz), 5.18 (d); (E)-$PhHC{=}CHC{\equiv}CPh$ (**2**), δ 7.09 (d, J = 16.3 Hz), 6.43 (d); (Z)-$PhHC{=}CHC{\equiv}CPh$ (**3**), δ 6.75 (d, J = 11.9 Hz), 5.97 (d). Trimers, **4** and **5** were analyzed by GC with coinjection of authentic samples of **4** and **5** followed by mass spectrum measurements. Infrared spectral measurements for the isolated solid products from the metal catalysts were also very useful for the identification of **4** and **5**.[16,7]

Oligomerization of other Alkynes, Ethyl Propiolate, Methyl Propargyl Ether, and *p*-Tolylacetylene. These reactions were carried out in the same manner as described above for phenylacetylene. ^1H NMR: (E)-$C_2H_5O_2C$-C(H)$C{=}CHC{\equiv}CCO_2C_2H_5$ (**2b**), δ 6.9-6.1 (2H, m), 3.9-4.1 (4H, m), 1.15 (6H, m); triethyl 1,3,5-benzenetricarboxylate (**4b**), δ 1.05 (9H, t), 3.90-4.10 (6H, q), 8.60 (3H, s); triethyl 1,2,4-benzenetricarboxylate (**5b**), δ 1.05 (9H, t), 3.9-4.1 (6H, q), 7.4-8.2 (3H, m); $H_2C{=}C(CH_2OCH_3)C{\equiv}CCH_2OCH_3$ (**1c**), δ 5.46 (1H, d, J = 2.0 Hz), 5.47 (d); (E)-$CH_3OCH_2(H)C{=}C(H)C{\equiv}CCH_2OCH_3$ (**2c**), δ 5.72 (1H, dt, J = 16.1 Hz), 6.09 (1H, dt); 1,3,5-benzenetrimethanol trimethyl ether (**4c**), δ 3.37-3.40 (9H, m), 4.52 (6H, d, J = 3.0 Hz), 7.27 (3H, s); 1,2,4-benzenetrimethanol trimethyl

ether (**5c**), δ 3.37-3.40 (9H, m), 4.46 (6H, s), 7.28-7.38 (3H, m). ^{1}H NMR spectra of *p*-tolylacetylene oligomers are very similar with those of PhC≡CH except the signals due to CH_3.

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References

1. (a) Nieuwland, J. A.; Calcott, W. S.; Downing, F. B.; Cater, A. S. *J. Am. Chem. Soc.* **1931**, *53*, 4197. (b) Meriwhether, L. S.; Leto, M. F.; Kennerly, G. W. *J. Org. Chem.* **1962**, *27*, 3930. (c) Kern, R. J. *Chem. Commum.* **1968**, 706. (d) Yamazaki, H. *Chem. Commum.* **1976**, 841. (e) Singer, H.; Wilkinson, G. *J. Chem. Soc. (A)* **1968**, 849. (f) Carlton, L.; Read, G. *J. Chem. Soc. Perkin I.* **1978**, 1631. (g) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980 and the references therein. (h) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525. (i) Horton, A. D. *Chem. Commun.* **1992**, *atn.* (j) Berry, H. H.; Eisenberg, R. *Organometallics* **1987**, *6*, 1796. (k) Akhter, M.; Richards, T. A.; Weedon, B. C. L. *J. Chem. Soc.* **1959**, 933.
2. (a) Lutz, E. F. *J. Am. Chem. Soc.* **1961**, *83*, 2551. (b) Hübel, W.; Hoogzand, C. *Chem. Ber.* **1961**, *93*, 1403. (c) Donda, A. F.; Moretti, G. J. *J. Org. Chem.* **1966**, *33*, 985. (d) Dieti, H.; Reinheimer, H.; Moffatm, J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2276. (e) Masuda, T.; Mouri, T.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1152. (f) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51. (g) Kumar, V. G.; Shoba, T. S.; Rao, K. V. G. *Tetrahedron Lett.* **1985**, *25*, 6245. (h) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry* 2nd edn. University Science Books **1987**, Chap. 9 and 18. (i) Strickler, J. R.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 2814. (j) Bianchini, C.; Caulton, K. G.; Chardon, C.; Einstein, O.; Folting, K.; Jhonson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, W. E. *J. Chem. Soc.* **1991**, *113*, 5127. (k) Lambregts, M. J.; Munson, E. J.; Kheir, A. A.; Haw, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 6875.
3. Peone, J. Jr.; Vaska, L. *Angew. Chem. Int. Ed.* **1971**, *10*, 511.
4. The reaction of $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ with excess PhCN does not show any evidence for the replacement of COD or PPh_3 by PhCN.
5. Chin, C. S.; Lee, B. *J. Chem. Soc. Dalton Trans.* **1991**, 1323.
6. Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc. (A)* **1971**, 2334.
7. Vaska, A.; Peone, J. Jr. *Suom. Kemistil.* **1971**, *B44*, 37.
8. Weinberg, E. L.; Baird, M. C. *J. Organomat. Chem. Soc.* **1979**, *179*, C61.
9. Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478.
10. Chin, C. S.; Yoon, J.; Song, J. *Inorg. Chem.* **1993**, *32*, 5901.
11. (a) Marder, M. A.; Zargarian, D.; Calabrese, J. C.; Herskovitz, T. H.; Milstein, D. *Chem. Commum.* **1987**, 1485. (b) Bianchini, C.; Laschi, F.; Ottaviani, F.; Pereuzzini, M.; Zanello, P. *Organometallics* **1988**, *7*, 1660. (c) Chow, P.; Zagarian, D.; Taylor, N. J.; Marder, T. B. *Chem. Commun.* **1989**, 1545. (d) Bianchini, C.; Mas, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1990**, *29*, 4565. (f) Boese, W. T.; Goldman, A. S. *Organometallics* **1991**, *10*, 782. (g) Schafer, M.; Wolf, J.; Werner, H. *Chem. Commum.* **1991**, 1341. (h) Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Oro, L. A.; Schlüunken. C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034. (i) Billeb, G.; Brauer, H.; Neumann, W. P.; Weisbeck, M. *Organometallics* **1992**, *11*, 2069. (j) Rappert, T.; Nurmberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156.
12. (a) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc. Perkin Trans. I* **1988**, 1357. (b) Strickler, J. R.; Wexsler, P. A.; Wiegley, E. *Organometallics* **1988**, *7*, 2067. (c) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 636. (d) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 645. (e) Bianchini, C.; Cauton, K. G.; Chardon, C.; Einstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Stribe, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127. (f) Omori, H.; Suzuki, H.; Kakigono, T.; Moro-oka, Y. *Organometallics* **1992**, *11*, 989. (g) Pope, R. M.; Vanorden, S. L.; Cooper, B. T.; Bucker, S. W. *Organometallics* **1992**, *11*, 2001. (h) Yeh, W.-Y.; Liu, L.-K. *J. Am. Chem. Soc.* **1992**, *114*, 2267. (i) Hill, J. E.; Ballaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911.
13. See (a) *J. Chem. Educ.* **1978**, *55*, A355. (b) *Chem. Eng. News* **1983** (Dec. 5), *61*, 4 and **1963** (July 8)), *41*, 47 and ref. 3.
14. Uson, R.; Oro, L. A.; Artigas, J.; Sariego, R. *J. Organomet. Chem.* **1979**, *179*, 65.
15. Chin, C. S.; Shin, S. Y.; Lee, C. *J. Chem. Soc. Dalton Trans* **1992**, 1323.
16. There are prominent differences between the infrared absorptions in 1400-1600 and 850-1100 cm^{-1} due to 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene. (See Doss, R. C.; Solomon, P. W. *J. Org. Chem.* **1964**, *29*, 1567).