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Iridium-Catalyzed Dimerization of Terminal Alkynes to (*E*)-Enynes, (*Z*)-Enynes, or 1,2,3-Butatrienes

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Summary: The iridium complex generated in situ from $[Ir(cod)Cl]_2$ and a phosphine ligand catalyzed the dimerization of terminal alkynes to give (E)-enyne, (Z)-enyne, or 1,2,3-butatriene derivatives in the presence of triethylamine. The triarylphosphine complex selectively yielded linear (E)-enynes for silylethynes, while the tripropylphosphine complex provided linear (Z)-enynes for silylalkynes or 1,2,3-butatrienes for tert-alkylethynes.

A great deal of attention has been focused on the transition-metal-catalyzed dimerization of terminal alkynes as an efficient method for the synthesis of unsaturated four-carbon compounds, which are versatile intermediates for further organic transformation.[1] The palladium complexes dimerize terminal alkynes to branched enynes,[2] while rhodium,[3] iridium,[4] and ruthenium[5] catalysts provide linear (*E*)- or (*Z*)-enynes or a mixture of the two in most cases. On the other hand, the formation of 1,2,3-butatrienes has been reported in the ruthenium-catalyzed reaction of terminal alkynes.[5g,6] Although the regio- and stereoselectivities, including their mechanistic aspects, have been extensively studied for individual transition metals and alkynes, the factors influencing different dimeric product formations have not been clearly understood. We wish to report herein the regio- and stereoselectivity and the scope and limitations in the iridium-catalyzed dimerization of terminal alkynes (Scheme 1). The reaction was greatly accelerated in the presence of a base such as triethylamine, and the products and their stereoselectivity were highly dependent on the alkynes and the phosphine ligand on the iridium catalyst. One of the three possible

(1) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12.

(2) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698.

(3) (a) Singer, H.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 849. (b) Yoshikawa, S.; Kiji, J.; Furukawa, J. *Makromol. Chem.* **1977**, *178*, 1077. (c) Ohshita, J.; Furumori, K.; Matsuguchi, A.; Ishikawa, M. *J. Org. Chem.* **1990**, *55*, 3277. (d) Kovalev, I. P.; Yevdakov, K. V.; Strelenko, Y. A.; Vinogradov, M. G.; Nikishin, G. I. *J. Organomet. Chem.* **1990**, *386*, 139. (e) Boese, W. T.; Goldman, A. S. *Organometallics* **1991**, *10*, 782.

(4) Jun, C.-H.; Lu, Z.; Crabtree, R. H. *Tetrahedron Lett.* **1992**, *33*, 7119.

(5) (a) Dahlenburg, L.; Frosin, K.-M.; Kerstan, S.; Werner, D. *J. Organomet. Chem.* **1991**, *407*, 115. (b) Echavarren, A. M.; Lopez, J.; Santos, A.; Montoya, J. *J. Organomet. Chem.* **1991**, *414*, 393. (c) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (d) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616. (e) Rappert, T.; Yamamoto, A. *Organometallics* **1994**, *13*, 4984. (f) Matsuzaka, H.; Takagi, Y.; Ishii, Y.; Nishio, M.; Hidai, M. *Organometallics* **1995**, *14*, 2153. (g) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968. (h) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275. (i) Yi, C. S.; Liu, N.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 3910. (j) Qü, J.-P.; Masui, D.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1998**, 1003.

(6) (a) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604. (b) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Johar, P. S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 987.

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Scheme 1. Dimerization of Terminal Alkynes

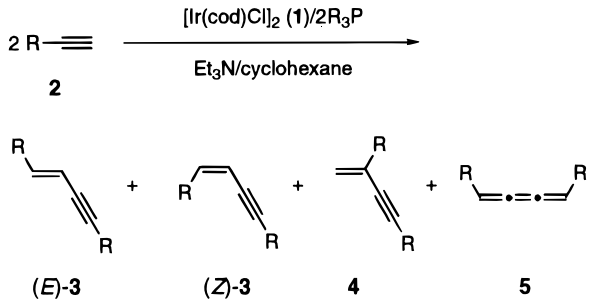


Table 1. Effect of Ligand and Base on Dimerization of 2 (R = Me_2PhSi)[a]

entry	ligand	base (amt, equiv)	time/h	yield/%[b]	isomeric ratio[c] (*E*)-**3**	(*Z*)-**3**	**5**
1	PPh_3	none	36	26	75	25	0
2	PPh_3	Et_3N (0.03)	4	92	96	4	0
3	PPh_3	Et_3N (1.0)	4	93	96	4	0
4	PPh_3	Et_3N (5.0)	4	93	96	4	0
5	PPh_3	pyridine (5.0)	4	23	96	4	0
6	$PMePh_2$	Et_3N (5.0)	4	71	95	5	0
7	PMe_2Ph	Et_3N (5.0)	4	23	87	12	1
8	PMe_3	Et_3N (5.0)	26	18	51	49	0
9	PEt_3	Et_3N (5.0)	26	45	20	78	2
10	PPr_3	Et_3N (5.0)	26	75	2	96	2
11	PBu_3	Et_3N (5.0)	26	51	16	84	0
12	P(*i*-Pr)$_3$	Et_3N (5.0)	26	trace			
13	PCy_3	Et_3N (5.0)	26	trace			

[a] A mixture of $[Ir(cod)Cl]_2$ (**1**; 0.015 mmol), a phosphine ligand (0.06 mmol), and (dimethylphenylsilyl)ethyne (1 mmol) in cyclohexane (5 mL) was stirred at 50 °C in the presence or absence of a base. [b] Isolated yields by chromatography over silica gel. [c] Determined by ^{1}H NMR.

isomers ((*E*)-**3**, (*Z*)-**3**, or **5**) was selectively synthesized by choosing an appropriate phosphine ligand and an alkyne, though formation of **4** was not observed under any reaction conditions.

The effects of a phosphine ligand and a base on the dimerization of $Me_2PhSiC{\equiv}CH$ are summarized in Table 1. The reaction suffered from low yields and low stereoselectivity (entry 1), but the presence of a catalytic amount or large excess of Et_3N greatly improved the yields and the *E* selectivity (*E*:*Z* = 96:4); the reaction was complete within 4 h at 50 °C (entries 2−4). Diisopropylethylamine and diethylamine gave similarlygood results, but less basic pyridine and cyclohexylamine were not effective (entry 5). The reaction was fast in cyclohexane and toluene but very slow in THF and acetonitrile.

The catalyst exhibited a pronounced effect of the ligand, preferring a less basic triarylphosphine for yielding (*E*)-**3** (entries 4, 6, and 7). Although the reaction significantly slowed with donating trialkylphosphines, these ligands predominantly produced (*Z*)-**3**, in improved yields and *Z* selectivity with an increase in the carbon numbers of the phosphine ligand (entries 8−10). Finally, the best *Z* selectivity exceeding 96% was achieved by the tripropylphosphine complex (entry 10), whereas bulky trialkylphosphines such as triisopropylphosphine, which have been recommended for the ruthenium-catalyzed dimerization,[5g,6] resulted in low yields or low selectivity (entries 11−13).

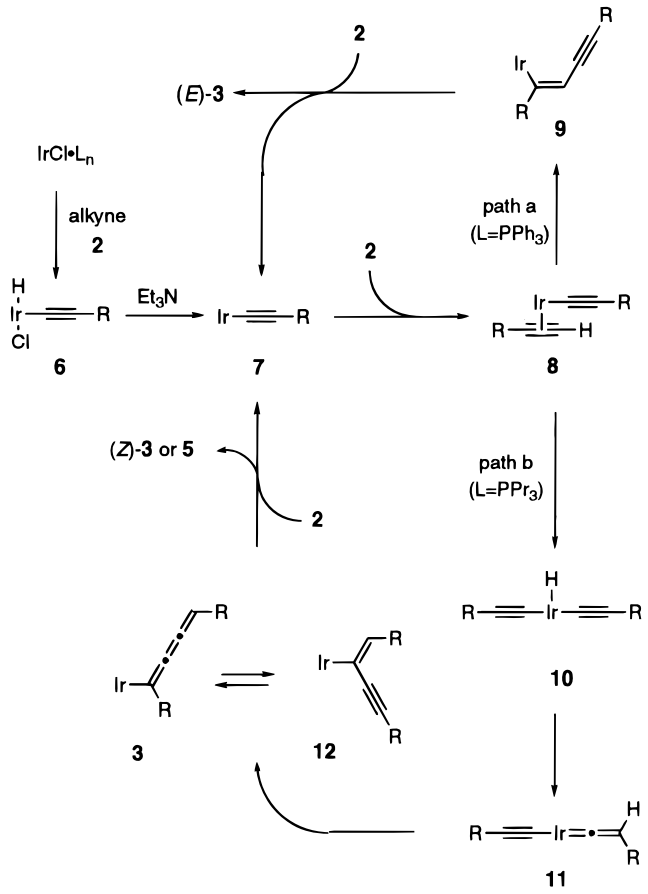
The dimerization of the representative alkynes catalyzed by the $[Ir(cod)Cl]_2/4PPh_3$ or $[Ir(cod)Cl]_2/4PPr_3$ complex are summarized in Table 2.[7] Silylacetylenes such as $Ph_2MeSiCCH$ and Me_3SiCCH selectively yielded (*E*)-**3** with the PPh_3 complex and (*Z*)-**3** with the PPr_3 complex (entries 1−4). Both ligands revealed similar

Table 2. Dimerization of 2[a]

entry	R in **2**	ligand	time/h	yield/%[b]	isomeric ratio[c] (*E*)-**3**	(*Z*)-**3**	**5**
1	Ph_2MeSi	PPh_3	4	95	98	2	0
2	Ph_2MeSi	PPr_3	20	62	11	89	0
3	Me_3Si	PPh_3	6	83	94	6	0
4	Me_3Si	PPr_3	24	70	8	91	1
5[d]	$^i Pr_3Si$	PPh_3	12	50	86	14	0
6[d]	$^i Pr_3Si$	PPr_3	60	70	14	86	0
7[d]	2-MeC_6H_4	PPh_3	9	55	81	19	0
8[d]	2-MeC_6H_4	PPr_3	24	78	13	87	0
9[d]	4-MeC_6H_4	PPh_3	6	19	66	34	0
10[d]	4-MeC_6H_4	PPr_3	24	67	24	76	0
11[d]	$^t C_4H_9$	PPh_3	18	36	94	4	2
12	$^t C_4H_9$	PPr_3	18	74	0	7	93[e]
13[d]	Me_2PhC	PPh_3	36	53	85	10	5
14	Me_2PhC	PPr_3	24	83	0	16	84[f]
15[d]	Me_2(TBSO)C	PPh_3	36	23	81	16	3
16	Me_2(TBSO)C	PPr_3	36	71	0	22	78[f]
17[d]	C_6H_{13}	PPh_3	36	<10			

[a] A mixture of $[Ir(cod)Cl]_2$ (**1**; 0.015 mmol), a phosphine ligand (0.06 mmol), **2** (1 mmol), Et_3N (5 mmol), and cyclohexane (3 mL) was stirred at 50 °C, unless otherwise noted. [b] Isolated yields by chromatography over silica gel. [c] Determined by ^{1}H NMR. [d] Reactions were conducted at 80 °C in a sealed tube. [e] Reaction gave (*Z*)-**5**. [f] The stereochemistry was not determined.

Scheme 2. Catalytic Cycle



(7) Typical procedure: A mixture of $[Ir(cod)Cl]_2$ (0.015 mmol), a phosphine ligand (0.06 mmol), an alkyne (1 mmol), and Et_3N (5 mmol) in cyclohexane (3 mL) was stirred at 50 °C under Ar. Evaporation of volatile materials followed by chromatography over silica gel afforded the product.

stereoselectivity for $^{i}Pr_3SiCCH$, 2-MeC_6H_4CCH, and 4-MeC_6H_4CCH, though these reactions resulted in low yields and low selectivity due to the slow reaction, even at 80 °C (entries 5−10).

In contrast to the ligand-controlled reaction shown in entries 1−10, *tert*-alkylacetylenes exclusively produced 1,2,3-butatrienes **5** with the PPr_3 complex,[8] whereas the PPh_3 complex did not change the selectivity, giving (*E*)-**3**. (entries 11−16). The formation of **5** can be exclusive in bulky and presumably electron-rich alkynes, since they were in negligibly small amounts in silylacetylenes and arylacetylenes. On the other hand, all attempts at the dimerization of alkylacetylenes having propargylic hydrogens were unsuccessful (entry 17), whereas the *Z*-selective dimerization of 1-hexyne with a cationic iridium complex has been reported by Crabtree.[4]

A plausible mechanism involving two catalytic cycles (paths a and b) is shown in Scheme 2. Although the related dimerization reactions have been carried out under neutral conditions,[2−6] the phosphine ligand and the presence of a base were significant for achieving both product selectivity and fast reaction rate. The oxidative addition of the alkyne C−H bond to a low-valent transition metal yields an RCC−M−H (M = Rh, Ir, Ru, Pd) complex, which leads to vinyl−metal species through insertion of a coordinated alkyne into the M−H bond or the M−C bond, depending on the phosphine ligand on the metal catalyst. However, the addition of terminal alkyne **2** to the IrCl complex in the presence of Et_3N may afford the alkynyl−iridium(I) complex **7**, as an active species for dimerization.[9] The phosphine ligand then controls the product selectivity either by leading to the insertion process (**8** → **9**, path a) or by leading to the oxidative addition of a coordinated alkyne (**8** → **10**, path b). The "path a" giving (*E*)-**3** is predominant when using the PPh_3 complex,[9c] whereas the high electron-donating property of trialkylphosphines such as Pr_3P favors the oxidative addition of the terminal C−H bond (path b)[6,10] rather than the insertion process. The formation of (*Z*)-**3** through the alkynyl vinylidene complex **11** and the specific formation of (*Z*)-**5** in *tert*-butylacetylene from the same intermediate has been amply demonstrated by Werner[10] and Wakatsuki[6a] in the rhodium and ruthenium complexes.

Supporting Information Available: Text giving details of the synthesis of all compounds reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) *tert*-Butylacetylene gave (*Z*)-1,4-di-*tert*-butylbutatriene (Table 2, entry 12). ^1H NMR (400 MHz, $CDCl_3$): δ 5.52 (s, 2H), 1.13 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 118.5, 35.1, 29.8. The stereochemistry was assigned by comparison of ^1H NMR spectra of the corresponding *E* and *Z* isomers obtained by the catalytic dimerization of *tert*-butylacetylene with $RuH_2(CO)(PPh_3)_3$.[6a] See also: Tigchelaar, M.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1981**, *22*, 2237.

(9) Alkynyl−iridium(I) or −rhodium(I) complexes catalyze the polymerization of phenylacetylene through the *cis*-insertion process in the absence or the presence of an amine base: (a) Brown, C. K.; Georgiou, D.; Wilkinson, G. *J. Chem. Soc. A* **1971**, 3120. (b) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *22*, 1105. (c) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131.

(10) Schäfer, M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1315.