Catalytic Head-to-Head Alkyne Dimerization to give Z-Enynes.

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Abstract The catalyst [Ir(biph)(PMe3)3Cl] (biph = biphenyl-2,2'-diyl) gives head-to-head dimerization of 1-alkynes to the corresponding Z-enynes.

Enynes can be most conveniently prepared by metal-catalyzed dimerization of 1-alkynes (eq. 1).¹ Most catalysts give head-to-tail dimers **2**, not the head-tohead compounds **1**. Ishikawa et al.¹ recently reported trialkylsilyl alkyne dimerization to the thermodynamic head-to-head product **1b** with Pd(PPh₃)₄ at 100°, RhCl(PPh₃)₃ at 25°, or NiCl₂L₂ at 200°. RuH₂(CO)(PPh₃)₂ at 100°, also gives **1b** (R = tBu) but only as a minor product (4%).²



We now find that $[Ir(biph)(PMe_3)_3Cl]$ (2, biph = biphenyl-2,2'-diyl) with 2 mol. AgBF₄ is effective for 1-alkyne dimerization and can give largely 1a or 1b, according to conditions. The complex is simply prepared from commercially available reagents.³ Table 1 shows the isolated yield of enyne and the isomeric ratio⁴ obtained. The thermodynamically less stable enyne, 1a, is preferred over the more stable 1b, except when PMe₃ is present. This probably blocks the isomerization of the intermediate vinyl complex (eq. 2). In a related Ir system, we *Present address: Agency for Defense Development, POB 35, Taejon 300 600, Korea (S.).

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showed that 1-alkynes hydrosilate via anti-addition of the Si-H to the C=C triple bond by a similar mechanism.⁵ PMe₃ is normally not readily lost from Ir(III) but the high trans effect of biph must labilize it in this case.

Table 1 Th	e results of the	catalytic runs.					
	_	Ratio					
Substrate	Additives ^a	Conditions ^b	1a	1b	Yield	(%)	- Y
PhC=CH	2AgBF ₄	rt, 24h.	74	26	85		
PhC≡CH	2AgBF ₄ ,10L	100°, 24h.	0	100	65		
tBuC=CH	$2AgBF_4$	rt, 24h.	95	5	96		
nBuC=CH	2AgBF4	rt, 24h.	54	56	91		. Ľ 9.
nBuC=CH	10AgBF4	100°, 24h.	100	0	45		

^a L = PMe₃. ^b see ref. 4. rt = room temp.

The role of the AgBF₄ is probably removal of a PMe₃ and a Cl⁻ to form the active catalyst, **3**. The preference for head to head dimerization is probably the result of the exceptionally low steric bulk of the catalyst in the plane of the insertion reaction, as suggested in diagram **3**.

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References and Notes.

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3. [Ir(cod)Cl]2 (663 mg.) is heated (90°, 2 h.) with biphenylene (300 mg) in CH₂Cl₂ (3mL) in a screw-topped vial. The resulting orange precipitate (330 mg., 89%) is isolated and treated with PMe₃ (210 μ L) at room temp. in CH₂Cl₂ (5 mL, 90 min.) to give the buff-colored catalyst, which is recrystd. from CH₂Cl₂ (78%).

4. Conditions: Ir, 33mM, Ag, 66mM, alkyne, 3.3M in thf (1 mL) in a screw-topped vial.. The products were purified by chromatography on alumina (eluent: hexane) and identified by GC-MS The E and Z isomers were identified by their characteristic 3 J(H,H') for the vinyl protons in the NMR. R = Ph: Z, 6.01 and 6.77 δ (J = 11.9 Hz); E, 6.47 and 7.03 δ (J = 16.3 Hz). R = nBu: Z, 5.42 and 5.80 δ (J = 10.6 Hz); E, 5.45 and 6.24 δ (J = 15.8 Hz). R = tBu: Z, 5.35 and 5.68 δ (J = 11.9 Hz).

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