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Rare-Earth Silylamide-Catalyzed Selective Dimerization of Terminal Alkynes and Subsequent Hydrophosphination in One Pot

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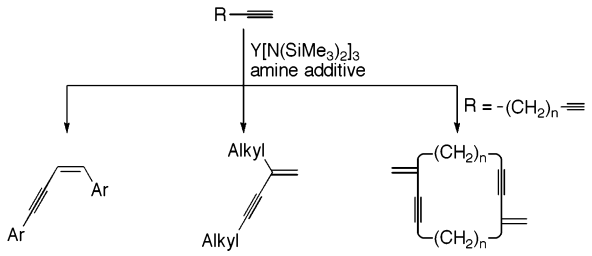

Rare-earth silylamides, $Ln[N(SiMe_3)_2]_3$ (Ln = Y, La, Sm), catalyzed regio- and stereoselective dimerization of terminal alkynes in the presence of amine additives to give conjugated enynes in high yields. The additives played a crucial role to depress the oligomerization and to control the regio- and stereochemistry of the dimerization. Thus, the selectivity for (*Z*)-head-to-head enynes was increased in the order of tertiary < secondary < primary amine additives. On the other hand, the reversed order was observed for the formation of head-to-tail dimers. When α,ω-diynes were subjected to the dimerization, very novel cyclic bisenyne compounds were given through double-dimerization in satisfactory yields. In addition, an application of the system allowed subsequent hydrophosphination of the enynes generated in situ with diphenylphosphine, giving rise to 1-phosphinyl-1,3-dienes as the sole products in excellent yields after oxidative workup.

Introduction

Enyne compounds have been known as important building blocks in organic synthesis[1] and as key units found in a variety of biologically active compounds.[2] Of their synthetic methods, the dimerization of terminal alkynes could be a very practical and straightforward approach in an atom-economical manner. For this reason, the reaction has been frequently investigated with use of many metal catalysts, which include group 4 and 8−10 metals,[3] lanthanides,[4] actinides,[5] and others.[6] However, exclusive formation of one enyne out of three possible isomers: (*Z*), (*E*)-head-to-head and head-to-tail dimers, could be achieved with only a few catalysts.[3c,f,h,4b] Moreover, effective catalysts for the dimerization of both aromatic and aliphatic alkynes have been rarely reported.[6] With respect to lanthanide catalysts, only metallocene and half-metallocene complexes have been used for the alkyne dimerization.[4] Preparation of these complexes needs multisteps despite their good catalyst activities.[7] In contrast, readily available rare-earth silylamides, $Ln[N(SiMe_3)_2]_3$, would be potentially attractive catalysts,

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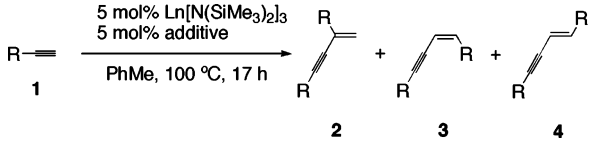
because they are found to be effective for hydroamination,[8] hydrosilylation,[9] and hydrophosphination[10] of unsaturated bonds as well as the lanthanocenes. In fact, we recently reported that regio- and stereoselective dimerization of various functional terminal alkynes was induced by the amide complexes.[11] In this paper, we describe more detailed features of the reaction, particularly, the scope and limitation, and double-dimerization of α,ω-diynes leading to cyclic bisenynes. As an application of the present method, one-pot synthesis of 1-phosphinyl-1,3-butadiene derivatives through the dimerization and subsequent hydrophosphination using the single catalyst is also documented herein.

Results and Discussion

When phenylacetylene (**1a**) was treated with $Y[N(SiMe_3)_2]_3$ (5 mol %) in toluene at 100 °C for 17 h, 97% of **1a** was consumed, but head-to-tail dimer, 2,4-diphenylbut-1-en-3-yne (**2a**), and head-to-head dimer, (*Z*)- and (*E*)-1,4-diphenylbut-1-en-3-yne (**3a**) and (**4a**) were obtained only in 5%, 11%, and 2% yields, respectively. The low mass balance was attributed to the formation of oligomers, which were not fully characterized. The selectivities of **2a**−**4a** hardly changed even by decrease of the conversion **1a** at lower temperature (60 °C). The reaction became sluggish in THF, wherein **2a** was given in 17% yield as a single product with 50% conversion after 46 h at refluxing temperature. Then, we investigated the effect of various additives in order to improve the product yield and selectivity. An addition of Ph_3P, Ph_2PH, and Ph_2O showed no significant effect and PhOH ceased the reaction. Fortunately, amine additives exhibited a different effect to produce the dimer **3a** with much improved selectivity. These results are summarized in Table 1. Tertiary aliphatic amines such as Et_3N showed no effect for inhibition of the oligomerization (entry 2), but Ph_3N slightly increased the yield of **3a** to 37% (entry 3). With secondary amine, Ph_2NH, the enyne **3a** was obtained in similar yield, but head-to-tail enyne **2a** was also provided in 22% yield (entry 4). Surprisingly, good regio- and stereospecific dimerization was caused by $C_5H_{11}NH_2$ in high yield (entry 5). Moreover, better yield was attained by the addition of $PhNH_2$ (entry 6). These results indicate that the selectivity of **3a** is increased in the order of tertiary < secondary < primary-amine, and higher reactivity is observed by aromatic amines rather than aliphatic ones. We next tested the effect of substituted aromatic primary amines. Bulky amines such as 2,6-^{i}Pr$_2$C$_6$H$_3$NH$_2$ predominantly caused the alkyne to oligomerize (entry 7), whereas both electron-donating and -withdrawing groups substituted at the *para* position

TABLE 1. Effect of Amine Additives for Dimerization of Terminal Alkynes 1 Catalyzed by the Rare-Earth Silylamide



entry	R	Ln	additive[a]	conv[b] (%)	product and yield[b] (%) 2	3	4
1	Ph (**1a**)	Y	none	97	5	11	2
2			Et_3N	95	2	7	3
3			Ph_3N	94	1	37	0
4			Ph_2NH	88	22	35	2
5			$C_5H_{11}NH_2$	99	0	70	0
6			$PhNH_2$	90	0	87	0
7			2,6-^{i}Pr$_2$C$_6$H$_3$NH$_2$	>99	0	9	0
8			4-MeOC$_6$H$_4$NH$_2$	97	0	95	0
9			4-MeC$_6$H$_4$NH$_2$	98	0	76	0
10			4-FC$_6$H$_4$NH$_2$	96	0	94	0
11			4-ClC$_6$H$_4$NH$_2$	92	0	91	0
12		Sm		94	0	48	0
13		La		95	0	58	0
14	hexyl (**1h**)	Y	none	98	62	5	0
15			Et_3N	>99	73	7	0
16			Ph_3N	92	69	20	0
17			Et_2NH	90	48	8	1
18			Ph_2NH	93	60	45	0
19			$C_5H_{11}NH_2$	94	0	13	0
20			$PhNH_2$	30	0	17	0
21			DBU	>99	9	8	0
22			quinuclidine	>99	58	9	0
23			$N(SiMe_3)_3$	>99	92	5	0
24		Sm		>99	29	7	0
25		La		>99	35	13	0

[a] The additive was pretreated with the catalyst for 1 h at room temperature. [b] Determined by GC.

gave exclusively the enyne **3a** in more than 90% yield, except for 4-$MeC_6H_4NH_2$ (entries 8−11). Comparing the metal size of the lanthanide catalysts, smaller Y is superior to larger Sm and La (entries 11−13).

In the reaction of oct-1-yne (**1h**) without an additive, the dimerization proceeded mainly to afford the 2-hexyldec-1-en-3-yne (**2h**) and (*Z*)-hexadec-7-en-9-yne (**3h**) in 62% and 5% yield, respectively. When the screening of various amine additives was performed in a similar manner, their effect was found to be very different from that observed in the dimerization of the aromatic alkyne **1a** (Table 1, entries 14−23). Addition of Et_3N gave a better yield of **2h** (73%) than Ph_3N (entries 15 and 16). The yield and selectivity decreased with the secondary amines, wherein Et_2NH gave the lowest product selectivity in the screening (entries 17 and 18). Although the addition of $C_5H_{11}NH_2$ and $PhNH_2$ resulted in the exclusive formation of **3h** (entries 19 and 20), they seemed to depress the catalyst activity. Thus, it can be concluded that selectivity for the synthesis of the head-to-tail dimer from the aliphatic alkyne **1h** increased in the order of primary < secondary < tertiary-amine additive, and that aliphatic amines were superior to aromatic additives, in sharp contrast to the results in the dimerization of **1a**. Other strong organic bases such as DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) and quinuclidine (1-azabicyclo[2.2.2]-octane) exhibited an undesirable effect, resulting in the predominant oligomerization with the former base and

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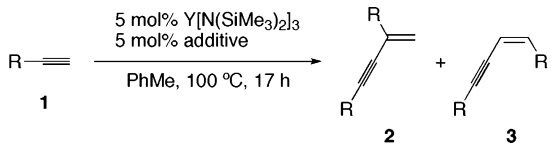
TABLE 2. Examples of Dimerization of Terminal Alkynes 1



			product and yield[a] (%)	
entry	R	additive	**2**	**3**
1	Ph (**1a**)	4-$ClC_6H_4NH_2$	0	90 (91)
2	4-$MeOC_6H_4$ (**1b**)		0	93 (95)
3	4-MeC_6H_4 (**1c**)		0	90 (97)
4	4-BrC_6H_4 (**1d**)		0	89 (90)
5	4-FC_6H_4 (**1e**)		0	80 (95)
6	2-MeC_6H_4 (**1f**)		0	(27)
7[b]			0	75 (77)
8	butyl (**1g**)	$N(SiMe_3)_2$	85 (99)	tr
9	hexyl (**1h**)		89 (92)	(5)
10		$C_5H_{11}NH_2$	0	43 (45)

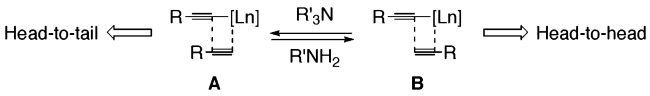
[a] Isolated yield. The value in parentheses indicates GC yield. [b] 10 mol % of the catalyst and additive were used.

lower yields with the latter (entries 21 and 22). Finally, a bulky tris(trimethylsily)amine, $N(SiMe_3)_3$, gave **2h** and **3h** in 92% and 5% yields, respectively (entry 23). The smaller metal, i.e., Y, gave better results as in the case of **1a** (entries 23−25).

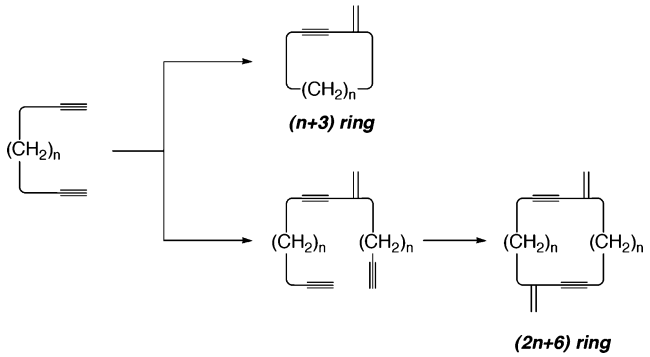
We next investigated the scope of terminal alkynes under the optimized conditions (Table 2). The reaction of aromatic alkynes **1b**−**e** with electron-donating and -withdrawing groups at the para position of the aromatic ring gave the corresponding enynes **3b**-**e** in high yields (entries 2−5). However, the presence of an ortho substituent such as 1-ethynyl-2-methylbezene (**1f**) resulted in lower yield of the product **3f** (27%) with retention of the substrate (entry 6). The problem could be overcome by increasing the catalyst loading to give **3f** in 77% yield (entry 7). The dimerization could not be applied to aromatic alkynes containing acetyl, ester, and dioxolanyl groups at the para position.[12] In the reaction of aliphatic alkynes using $N(SiMe_3)_3$, **2g** and **2h** were provided in 92% and 99% yield, respectively (entries 8 and 9). Substitution of the tertiary amine by a primary amine like amylamine enabled exclusive formation of (*Z*)-head-to-head dimer **3g,** though in low yield (entry 10).

When the silylamide complex was substituted by lithium hexamethyldisilazane, $LiN(SiMe_3)_2$, no reactions of the terminal alkynes took place under the identical conditions. The result indicated that the present dimerization is owing to the useful characteristics of the rare-earth silylamide. By referring to the work of Teuben[4a] and Hou,[4b] it is almost certain that the dimerization proceeded through alkyne insertion to the rare-earth alkynide, followed by protonation with another molecule of the alkyne to give the enyne and the alkynide. The present reaction sharply depended on the nature of the amine additives. Although their exact role has not been clear, they would act as proton sources to inhibit the alkyne oligomerization and as ligands to prevent an aggregation of the reaction intermediates. In the latter case, it is likely that a more active species such as

SCHEME 1



SCHEME 2



monomer and dimer could be generated in situ through coordination or ligand exchange with the silylamide.[13] Of course, no reaction took place with these additives alone and their excess loading lowered the catalyst activity.[14] As regards the regioselectivity of the reaction, the alkyne would insert preferentially to the alkynide coordinated by bulky amine through the transition state **A** as depicted in Scheme 1. On the other hand, the dimerization with primary amine would proceed via **B** to avoid the steric hindrance between substituents of the alkynes. The formation of the (*Z*)-isomer of the two head-to-head dimers may be accounted for by the participation of dimeric alkynide species.[4b]

Performing the head-to-tail dimerization of α,ω-diynes potentially enables two distinctive processes, i.e., mono- and double-dimerization to afford (n + 3) and (2n + 6)-membered rings, respectively, as shown in Scheme 2. With respect to the former reaction, Trost has employed the palladium-catalyzed reaction to obtain mono cyclic head-to-tail enynes.[15] In addition, Hidai has reported the synthesis of cyclic (*Z*)-head-to-head enynes from α,ω-diynes catalyzed by ruthenium complexes.[16] To the best of our knowledge, there is no precedent of a direct synthesis of cyclic bisenynes from α,ω-diynes by the double-dimerization. However, we expected that α,ω-diynes containing a short carbon chain would dimerize intermolecularly at first due to the steric reason, which would be followed by intramolecular dimerization instead of oligomerization, because the resulting two terminal alkyne units would come close together by coordination to the electron-deficient rare-earth metal center.

When 1,7-octadiyne (**5a**) was treated with the yttrium catalyst and $N(SiMe_3)_3$ in toluene (0.7 M) at 100 °C for

(12) Molander, G. A.; Romero, J. A, C. *Chem. Rev.* **2002**, *102*, 2161−2185

(13) Evans reported that $(C_5Me_5)_2LnN(SiMe_3)_2$ did not react with phenylacetylene in toluene even at 100 °C, but the metathesis occurred in THF. Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618−2633.

(14) When **1a** was treated with $PhNH_2$ (15 mol %) and $Y[N(SiMe_3)_2]_3$ (5 mol %), no reaction commenced (see entry 4 in Table 1). The reaction of **1h** using Et_3N (15 mol %) and the Y-silylamide (5 mol %) decreased the yield of **2 g** and **3g** to 21 and 7% yields, respectively, with 49% conversion (see entry 15).

(15) Trost, M. B.; Mathubara, S.; Caringi, J. J. *J. Am. Chem. Soc.* **1989**, *111*, 8745−8746.

(16) Nishibayashi, Y.; Yamanashi, M.; Wakiji, I.; Hidai, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2909−2911.

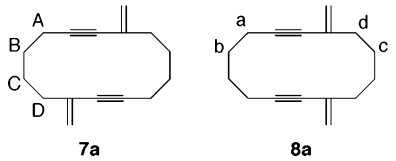
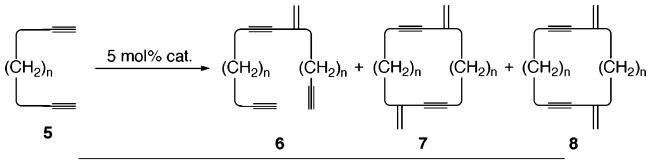
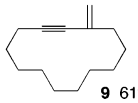


FIGURE 1. Two isomers derived from 1,7-octadiyne (**5a**).

TABLE 3. Examples for Double-Dimerization of α,ω-Diynes Leading to Bisenynes



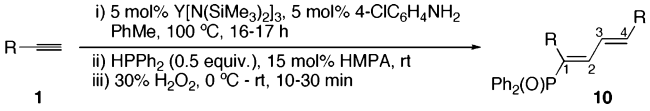
entry	n	conditions	product and yield (%)[a] 6	7 + 8 [7 : 8]
1	4 (**5a**)	19.0 h, 4.9 M	0	51 [72 : 28]
2		22.5 h, 2 .0M	53	30 [73 : 27]
3		20.0 h, 0.7 M	0	71 [76 : 24]
4		20.0 h, 0.3 M	0	90 [72 : 28]
5	5 (**5b**)	20.0 h, 0.3 M	0	78 [70 : 30]
6[b]	10 (**5c**)	20.0 h, 0.3 M	 **9** 61%	

[a] Isolated yield. The ratio was determined by NMR. [b] 10 mol % of the catalyst and additive were used.

20 h, a mixture of two dimeric products (76:24) was obtained in 71% total yield, which was inseparable even by HPLC. The mixture showed no signals assignable to carbons and protons of terminal alkynes in the ^{13}C and ^{1}H NMR spectra, but two pairs of four olefinic protons were observed in the region of 5.13−5.18 ppm, instead. Therefore, the two compounds should be double-dimerization products **7a** and **8a** (Figure 1). Considering their structural symmetry, it is reasonable to assume that four methylene protons A−D situated in linear relation for **7a**, and four methylene protons a−d separated in two parts for **8a**, would appear independently. Thus, we measured the H−H COSY spectra of the mixture to determine their structures (see Supporting Information, Figure S1). The major product exhibited four methylene signals at ca. 1.5 (B), 1.8 (C), 2.2 (D), and 2.4 (A) ppm as expected, wherein three COSY signals of A−B, B−C, and C−D were clearly found, in addition to those of D-olefinic protons. The minor product also showed three separate signals at ca. 1.6 (c), 1.7 (b), and 2.3 (a) and one obscured signal at 2.2 (d). However, only two COSY signals of a−b and c−d were observed, other than those of d-olefinic protons. On the basis of these results, the structure of the major isomer was determined as **7a** and the minor as **8a**.

The present reaction was found to be very sensitive to the reaction conditions, particularly to the concentration of the α,ω-diynes and the length of their methylene chains, because the initial products **6** were able to react further both intra- and intermolecularly to yield cyclic bisenynes and oligomers, respectively (Table 3). The reaction of **5a** in 2.0 M solution gave a mixture of the bisenynes **7a** and **8a** and mono-dimerization product **6a** in 30% and 53% yields, respectively (entry 2). Mass balance of the reaction decreased with increasing concentration to 4.9 M due to the formation of oligomers (entry 1). In contrast, **7a** and **8a** were isolated in 90% combined yield at lower concentration (0.3 M) (entry 4). Similarly, 1,8-nonadiyne (**5b**) was converted to the 16-membered cyclic bisenynes **7b** and **8b** in 78% yield in the dilute solution (entry 5). Interestingly, the ratio of **7** and **8** was always ca. 73:26 irrespective of the concentration and carbon-chain length. The reaction mode was changed in the dimerization of 1,13-tetradecadiyne (**5c**), which gave 13-membered monoenyne **9** in 61% yield exclusively (entry 6).

TABLE 4. Examples of One-Pot Synthesis of 1-Phosphinyl-1,3-butadienes 10 by the Dimerization and Subsequent Hydrophosphination



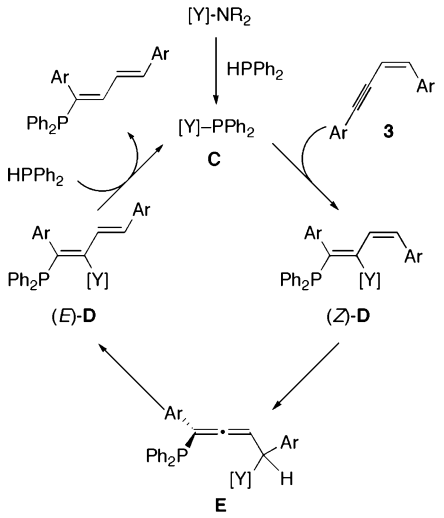
entry	R	time (min)	yield of **10**[a] (%)	
1	Ph (**1a**)	5	**10a**	94
2[b]	4-MeOC$_6$H$_4$ (**1b**)	40	**10b**	81
3	4-MeC$_6$H$_4$ (**1c**)	60	**10c**	81
4	4-BrC$_6$H$_4$ (**1d**)	120	**10d**	80
5	4-FC$_6$H$_4$ (**1e**)	10	**10e**	92 (94)[c]
6[d]	2-MeC$_6$H$_4$ (**1f**)	35	**10f**	76

[a] Isolated yield based on the phosphine. [b] Carried out at 100 °C. [c] The value in parentheses indicates an NMR yield. [d] 10 mol % of the catalyst and additive were used.

Last, we investigated one-pot synthesis of 1-phosphinyl-1,3-butadienes from two moles of terminal alkyne and one mole of phosphine in order to explore the synthetic utility of the present dimerization. This idea evolved from the fact that the rare-earth amide catalysts did not decompose after completion of the alkyne dimerization in the first step, and that they could catalyze hydrophosphination of the alkyne moiety of the thus-generated enyne in the second step.[10b] It turned out that the reaction worked successfully (Table 4). Thus, after generation of (*Z*)-1,4-diphenylbut-1-en-3-yne (**3a**) from phenylacetylene (**1a**) with the yttrium catalyst and 4-chloroaniline under the standard conditions, the mixture was subsequently treated with half-molar amounts of diphenylphosphine in the presence of the HMPA ligand (15 mol %) at room temperature and then, oxidized with hydrogen peroxide to give 1-diphenylphosphinyl-1,3-butadiene **10a** in 94% yield (entry 1). Similarly, various phosphinylbutadienes **10** were prepared in high yields via the head-to-head dimers **3**, starting from aromatic terminal alkynes. In the reaction of **1b**, the hydrophosphination in the second step took place only at elevated temperature probably because the chelate effect of the methoxy substituent would retard the reaction.

All products **10** were obtained as single isomers whose structures were determined unambiguously by X-ray crystallographic analysis of **10c** (see the Supporting Information, Figure S2). The $Ph_2(O)P$ group was attached to C(1) to form an (*E*)-double bond between C(1)−C(2), in agreement with the previous results,[10b] whereas the original (*Z*)-stereochemistry of C(3)−C(4) in **3c** was reversed to (*E*). The change of the stereochemistry of the C(3)−C(4) double bond would be explained as shown in Scheme 3. Initially, some yttrium amide species remained

SCHEME 3



after the dimerization reacted with Ph_2PH to yield phosphide complex C.[10b] *syn*-Addition of C to the alkyne moiety of **3** affords dienyl yttrium (*Z*)-D. Because the (*Z*)-stereochemistry causes severe steric repulsion, (*Z*)-D would isomerize to more stable (*E*)-D via an allenic intermediate E. Subsequent protonation with Ph_2PH affords the product **10** and phosphide C.

Summary

Regio- and stereoselective dimerization of terminal alkynes to produce conjugated enynes has been achieved using rare-earth silylamide catalysts and amine additives. The yttrium catalyst is superior to larger metals such as Sm and La. The amine additives play a crucial role to control efficiency of the reaction and regiochemistry of the products. Oligomerization of the alkynes predominates or competes with the dimerization in the absence of the additives. As a rule, primary amines tend to produce (*Z*)-head-to-head dimers preferentially and, in contrast, tertiary amines bring about the head-to-tail products. Thus, nearly complete formation of (*Z*)-head-to-head dimers from aromatic terminal alkynes with aniline derivatives and head-to-tail dimers from aliphatic alkynes with $N(SiMe_2)_3$ is realized. When this reaction is extended to α,ω-diynes, unprecedented double dimerization takes place to afford cyclic bisenyne compounds, depending on the length of the carbon chain and concentration of the reaction mixture. Moreover, dimerization of aromatic terminal alkynes, followed by hydrophosphination with diphenylphosphine enables highly efficient synthesis of 1-phosphiny-1,3-butadienes in one-pot using single rare-earth catalysts.

Experimental Section

General Procedure for the Dimerization of Terminal Alkynes Catalyzed by $Y[N(SiMe_3)_2]_3$ with Amine Additives. According to entry 1 in Table 2, $Y[N(SiMe_3)_2]_3$ (39 mg, 0.07 mmol) and $4\text{-}ClC_6H_4NH_2$ (8.9 mg, 0.07 mmol) were placed in a 20-mL Schlenk tube and dissolved in toluene (1.4 mL). After the mixture was stirred for 1 h at room temperature, phenylacetylene (**1a**) (146 mg, 1.4 mmol) was added. The Schlenk tube was sealed, and stirring was continued for 17 h at 100 °C. The reaction mixture was cooled, quenched with H_2O (2 mL) and saturated NH_4Cl solution (1 mL), and diluted with ether (2 mL). GC yield was determined by using methyl benzoate as an internal standard. The aqueous layer was extracted with ether (30 mL). The combined organic layer was washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude mixture gave 129 mg (90%) of the dimer **3a** by flash column chromatography on silica gel with hexane eluent.

2-Butyloct-1-en-3-yne (2 g) [CAS Registry No. 5663-86-5]: isolated in 85% yield as a yellow liquid; IR (neat) 3094, 2957, 2930, 2224 cm^{-1}; MS *m/z* 164 (M^+, 1), 149 (4), 122 (60), 107 (91), 93 (86), 79 (100); ^1H NMR ($CDCl_3$) δ 0.91 (3H, t, *J* = 7.3 Hz), 0.92 (3H, t, *J* = 7.3 Hz), 1.25−1.55 (8H, m), 2.12 (2H, t, *J* = 7.4 Hz), 2.31 (2H, t, *J* = 6.9 Hz), 5.12 (1H, s), 5.20 (1H, s); ^{13}C NMR ($CDCl_3$) δ 10.8, 11.1, 16.2, 19.1, 19.2, 27.5, 28.1, 34.5, 78.2, 87.2, 116.5, 129.6.

2-Hexyldec-1-en-3-yne (2h) [CAS Registry No. 13343-81-2]: isolated in 89% yield as a yellow liquid; IR (neat) 3427, 2928, 2858, 2212 cm^{-1}; MS *m/z* 220 (M^+, 10), 29 (100); ^1H NMR ($CDCl_3$) δ 0.89 (3H, t, *J* = 6.8 Hz), 0.90 (3H, t, *J* = 6.9 Hz), 1.20−1.57 (16H, m), 2.11 (2H, t, *J* = 7.5 Hz), 2.30 (2H, t, *J* = 7.0 Hz), 5.12 (1H, d, *J* = 1.2 Hz), 5.20 (1H, d, *J* = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.1, 19.3, 22.57, 22.62, 28.1, 28.5, 28.6, 28.8, 31.4, 31.7, 37.6, 81.0, 90.0, 119.2, 132.4.

(*Z*)-1,4-Diphenylbut-1-en-3-yne (3a) [CAS Registry No. 13343-78-7]: isolated in 90% as a yellow liquid; IR (neat) 3061, 3020, 2189, 1489, 1447 cm^{-1}; MS *m/z* 204 (M^+, 59), 202 (100), 101 (50); ^1H NMR ($CDCl_3$) δ 5.93 (1H, d, *J* = 11.8 Hz), 6.71 (1H, d, *J* = 11.8 Hz), 7.29−7.41 (6H, m), 7.48−7.50 (2H, m), 7.93 (2H, d, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 88.2, 95.8, 107.4, 123.4, 128.27, 128.34, 128.4, 128.5, 128.7, 131.4, 136.5, 138.6.

(*Z*)-1,4-Di(4-anisyl)but-1-en-3-yne (3b) [CAS Registry No. 500906-72-9]: isolated in 93% as a yellow liquid; IR (neat) 3005, 2957, 2930, 2835, 2185 cm^{-1}; MS *m/z* 264 (M^+, 100), 249 (38); ^1H NMR ($CDCl_3$) δ 3.80 (3H, s), 3.81 (3H, s), 5.77 (1H, d, *J* = 11.8 Hz), 6.58 (1H, d, *J* = 11.8 Hz), 6.87 (2H, d, *J* = 8.9 Hz), 6.89 (2H, d, *J* = 8.9 Hz), 7.42 (2H, d, *J* = 8.9 Hz), 7.88 (2H, d, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 55.22, 55.23, 87.4, 95.4, 105.1, 113.6, 114.0, 115.7, 129.7, 130.1, 132.8, 137.3, 159.5, 159.6.

(*Z*)-1,4-Di(4-tolyl)but-1-en-3-yne (3c) [CAS Registry No. 189331-74-6]: isolated in 90% as a yellow solid; mp 61−63 °C; IR (KBr) 3026, 2920, 2856, 2361 cm^{-1}; MS *m/z* 232 (M^+, 100), 215 (58), 202 (67); ^1H NMR ($CDCl_3$) δ 2.37 (6H, s), 5.85 (1H, d, *J* = 11.8 Hz), 6.65 (1H, d, *J* = 11.8 Hz), 7.16 (2H, d, *J* = 8.2 Hz), 7.19 (2H, d, *J* = 8.2 Hz), 7.38 (2H, d, *J* = 8.0 Hz), 7.83 (2H, d, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 21.5, 87.9, 95.9, 106.5, 120.5, 128.7, 129.0, 129.2, 131.3, 133.9, 138.2, 138.4, one signal was obscured.

(*Z*)-1,4-Di(4-bromophenyl)but-1-en-3-yne (3d) [CAS Registry No. 500906-74-1]: isolated in 89% as a yellow liquid; IR (CCl_4) 2957, 2926, 2854, 2359, 2340 cm^{-1}; MS *m/z* 364 (M^+ + 4, 5), 362 (M^+ + 2, 12) (M^+, 7), 202 (100); ^1H NMR ($CDCl_3$) δ 5.92 (1H, d, *J* = 11.8 Hz), 6.66 (1H, d, *J* = 11.8 Hz), 7.32 (2H, d, *J* = 8.4 Hz), 7.49 (2H, d, *J* = 7.6 Hz), 7.51 (2H, d, *J* = 7.6 Hz), 7.76 (2H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 88.9, 95.4, 107.9, 122.1, 122.5, 122.9, 130.1, 131.5, 131.8, 132.8, 135.3, 137.8.

(*Z*)-1,4-Di(4-fluorophenyl)but-1-en-3-yne (3e) [CAS Registry No. 557083-83-7]: isolated in 80% as a yellow liquid; IR (CCl_4) 3024, 2925, 2855, 2186 cm^{-1}; MS *m/z* 240 (M^+, 76), 239 (60), 238 (100); ^1H NMR ($CDCl_3$) δ 5.87 (1H, d, *J* = 11.8 Hz), 6.66 (1H, d, *J* = 11.8 Hz), 7.03−7.09 (4H, m), 7.43−7.47 (2H, m), 7.87−7.91 (2H, m); ^{13}C NMR ($CDCl_3$) δ 87.6, 94.8, 106.8 (d, *J* = 2.5 Hz), 115.2 (d, *J* = 21.3 Hz), 115.7 (d, *J* = 23.0 Hz), 119.4 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 8.2 Hz), 132.7 (d, *J* = 4.1 Hz), 133.3 (d, *J* = 8.2 Hz), 137.4 (d, *J* = 8.2 Hz), 162.5 (d, *J* = 249.4 Hz), 162.6 (d, *J* = 250.2 Hz).

(*Z*)-1,4-Di(2-tolyl)but-1-en-3-yne (3f) [CAS Registry No. 259090-89-6]: isolated in 75% as a yellow liquid; IR (neat) 3005, 2957, 2930, 2835, 2185 cm^{-1}; MS *m/z* 232 (M^+, 92), 215 (100), 202 (75), 115 (79); ^1H NMR ($CDCl_3$) δ 2.33 (3H, s), 2.43 (3H, s), 5.99 (1H, d, *J* = 11.8 Hz), 6.86 (1H, d, *J* = 11.8 Hz),

7.12−7.22 (6H, m), 7.38 (1H, d, J = 7.3 Hz), 8.25−8.27 (1H, m); ^{13}C NMR ($CDCl_3$) δ 19.7, 20.7, 91.6, 93.9, 108.5, 123.2, 125.5, 128.2, 128.3, 129.4, 130.1, 132.1, 135.3, 136.4, 136.5, 140.2, two signals were obscured.

(*Z*)-Hexadec-7-en-9-yne (3h) [CAS Registry No. 13343-80-1]: isolated in 43% as a yellow liquid; IR (neat) 3020, 2925, 2856, 1466 cm^{-1}; MS *m/z* 220 (M^+, 5), 29 (100); ^{1}H NMR ($CDCl_3$) δ 0.86−0.90 (6H, m), 1.27−1.44 (14H, m), 1.48−1.57 (2H, m), 2.26 (2H, q, J = 7.2 Hz), 2.32 (2H, dt, J = 1.8, 7.0 Hz), 5.42 (1H, dt, J = 10.6, 1.8 Hz), 5.80 (1H, dt, J = 10.6, 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.04, 14.08, 19.5, 22.58, 22.61, 28.6, 28.85, 28.86, 28.89, 30.0, 31.4, 31.7, 77.4, 94.3, 109.3, 142.6.

3,10-Dimethylidenecyclotetradeca-1,8-diyne (7a) and 3,8-dimethylidenecyclotetradeca-1,9-diyne (8a): isolated as a 72:28 mixture in 90% combined yield; IR (neat) 2928, 2858, 2218 cm^{-1}; MS *m/z* (**7a**) 212 (M^+, 14), 211 (4), 197 (4), 183 (24), 169 (45), 155 (58), 141 (84), 129 (61), 115 (49), 91 (82), 77 (68), 65 (46), 51 (59), 39 (100), (**8a**) 212 (M^+, 2), 211 (8), 197 (20), 183 (29), 169 (60), 155 (83), 141 (100), 129 (60), 115 (47), 91 (77), 77 (67), 65 (51), 51 (54), 39 (99); ^{1}H NMR ($CDCl_3$) (**7a**) δ 1.46−1.53 (4H, m), 1.81−1.88 (4H, m), 2.18 (4H, t, J = 7.5 Hz), 2.38 (4H, t, J = 6.1 Hz), 5.13 (2H, m), 5.18 (2H, m), (**8a**) δ 1.61 (4H, m), 1.74 (4H, m), 2.18 (4H, m), 2.35 (4H, m). 5.13 (2H, m), 5.19 (2H, m); ^{13}C NMR ($CDCl_3$, 67.8 Hz) (**7a**) δ 19.0, 26.9, 27.3, 37.7, 81.2, 90.6, 119.3, 132.2, (**8a**) δ 19.1, 27.6, 27.8, 37.6, 81.2, 91.0, 119.7, 132.3. Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.54; H, 9.46.

3,11-Dimethylidenecyclohexadeca-1,9-diyne (7b) and 3,9-dimethylenecyclohexadeca-1,10-diyne (8b): isolated as a 70:30 mixture in 78% combined yield; a pale yellow liquid; IR (neat) 2936, 2856, 2224 cm^{-1}; MS *m/z* (**7b**) 240 (M^+, 1), 239 (3), 225 (11), 211 (29), 197 (64), 183 (52), 169 (72), 155 (94), 141 (75), 129 (83), 91 (100), (**8b**) 240 (M^+, 0.2), 239 (0.4), 211 (4), 197 (11), 183 (15), 169 (24), 141 (35), 129 (46), 91 (100); ^{1}H NMR ($CDCl_3$) signals of **7b** and **8b** were overlapped δ 1.17−1.25 (8H, m), 1.48−1.69 (4H, m), 2.13−2.18 (4H, m), 2.32−2.40 (4H, m), 5.12−5.13 (2H, m), 5.18−5.20 (2H, m); ^{13}C NMR ($CDCl_3$) (**7b**) 19.4, 28.0, 28.2, 28.4, 37.4, 80.8, 90.4, 119.7, 132.2, (**8b**) δ 18.6, 27.1, 27.4, 27.8, 28.3, 38.1, 81.2, 90.4, 119.8, 132.3. Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 89.75; H, 10.25.

3-Methylidenecyclotridec-1-yne (9): isolated in 61% as a colorless liquid; IR (neat) 2932, 2858, 2210 cm^{-1}; MS *m/z* 190 (M^+, 0.01), 147 (1), 133 (4), 119 (7), 105 (14), 93 (36), 79 (81), 67 (100); ^{1}H NMR ($CDCl_3$) δ 1.38 (10H, m), 1.52−1.62 (6H, m), 2.17 (2H, t, J = 6.9 Hz), 2.33 (2H, t, J = 5.5 Hz), 5.12 (1H, m), 5.18 (1H, m); ^{13}C NMR ($CDCl_3$) δ 19.2, 25.4, 25.6, 26.1, 26.2, 26.3, 26.9, 27.0, 36.7, 81.7, 91.1, 119.3, 132.8, one signal was obscured. Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.54; H, 11.46.

General Procedure for One-Pot Synthesis of 1-Diphenylphosphinyl-1,3-butadienes 10. According to entry 1 in Table 4, after treatment of $Y[N(SiMe_3)_2]_3$ (136 mg, 0.24 mmol) with 4-$ClC_6H_4NH_2$ (26 mg, 0.25 mmol) in toluene at room temperature for 1 h, **1a** (507 mg, 5.0 mmol) was added to the mixture and stirring was continued at 100 °C for 16 h. The reaction mixture was cooled to room temperature, and then HMPA (125μL, 0.72 mmol) and diphenylphosphine (466 mg, 2.5 mmol) were added. The mixture was stirred for 5 min at room temperature with monitoring by GC. The reaction mixture was quenched with saturated NH_4Cl solution (3 mL), diluted with ether (3 mL), and oxidized with 30% H_2O_2 solution (2 mL) for 30 min at room temperature. The aqueous layer was extracted with ether (30 mL). The combined organic layer was washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 20% EtOAc/Hexane as an eluent to give 711 mg (94%) of 1-diphenylphosphinyl-1,3-butadieynes **10a**.

(*E*,*E*)-1,4-Diphenyl-1-(diphenylphosphinyl)-1,3-butadiene (10a): isolated in 94% as a white solid; mp 137−139 °C; IR (Nujol) 1177 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.77 (1H, ddd, J = 15.7, 9.9, 1.7 Hz), 6.83 (1H, br d, J = 15.7 Hz), 7.08−7.10 (2H, m), 7.20−7.30 (9H, m), 7.39−7.4 (4H, m), 7.48−7.53 (2H, m), 7.65−7.71 (4H, m); ^{13}C NMR ($CDCl_3$) δ 124.8 (d, $^3J_{C-P}$ = 16.4 Hz), 127.1, 127.7, 128.2, 128.3 (d, $^2J_{C-P}$ = 12.3 Hz), 128.6, 128.7, 130.3 (d, $^3J_{C-P}$ = 4.1 Hz), 131.5 (d, $^1J_{C-P}$ = 104.2 Hz), 131.7 (d, $^4J_{C-P}$ = 2.5 Hz), 132.1 (d, $^3J_{C-P}$ = 9.0 Hz), 135.2 (d, $^1J_{C-P}$ = 95.6 Hz), 135.3 (d, $^2J_{C-P}$ = 9.0 Hz), 136.2, 139.9, 143.5 (d, $^2J_{C-P}$ = 10.6 Hz); ^{31}P NMR ($CDCl_3$) δ 28.64. Anal. Calcd for $C_{28}H_{23}OP$: C, 82.74; H, 5.70. Found: C, 82.55; H, 5.45.

(*E*,*E*)-1,4-(4-Anisyl)-1-(diphenylphosphinyl)-1,3-butadiene (10b): isolated in 81% as a yellow solid; mp 58−60 °C; IR (Nujol) 1177 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.781 (3H, s), 3.784 (3H, s), 6.60 (1H, ddd, J = 15.5, 9.9, 1.7 Hz), 6.67 (1H, br d, J = 15.5 Hz), 6.71 (2H, d, J = 8.7 Hz), 6.72 (2H, d, J = 8.7 Hz), 6.96 (2H, dd, J = 8.8, 1.6 Hz), 7.05 (1H, dd, J = 18.8, 9.9 Hz), 7.16 (2H, d, J = 8.8 Hz), 7.31−7.36 (4H, m), 7.40−7.44 (2H, m), 7.58−7.64 (4H, m); ^{13}CNMR ($CDCl_3$) δ 55.1, 55.2, 113.7, 114.1, 112.4 (d, $^3J_{C-P}$ = 9.8 Hz), 128.2 (d, $^2J_{C-P}$ = 12.3 Hz), 128.3, 128.5, 129.1, 131.4 (d, $^2J_{C-P}$ = 9.0 Hz), 131.6, 131.8 (d, $^1J_{C-P}$ = 103.2 Hz), 132.1 (d, $^3J_{C-P}$ = 16.4 Hz), 133.3 (d, $^1J_{C-P}$ = 99.1 Hz), 139.2, 143.7 (d, $^2J_{C-P}$ = 10.6 Hz), 159.0, 160.1; ^{31}P NMR ($CDCl_3$) δ 28.99. Anal. Calcd for $C_{30}H_{27}O_3P$: C, 77.24; H, 5.83. Found: C, 77.13; H, 5.96.

(*E*,*E*)-1,4-(4-Tolyl)-1-(diphenylphosphinyl)-1,3-butadiene (10c): isolated in 81% as a white solid; mp 177−182 °C; IR (Nujol) 1167 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (3H, s), 2.31 (3H, s), 6.76−6.77 (2H, m), 6.98 (2H, d, J = 8.3 Hz), 7.05 (2H, d, J = 8.3 Hz), 7.07 (2H, d, J = 8.3 Hz), 7.16 (1H, ddd, J = 15.8, 6.5, 3.6 Hz), 7.19 (2H, d, J = 8.3 Hz), 7.41−7.44 (4H, m), 7.48−7.50 (2H, m), 7.65−7.71 (4H, m); ^{13}C NMR ($CDCl_3$) δ 21.2, 21.3, 123.6 (d, $^3J_{C-P}$ = 17.2 Hz), 127.1, 128.3 (d, $^2J_{C-P}$ = 11.4 Hz), 129.0, 129.4, 130.3 (d, $^3J_{C-P}$ = 5.0 Hz), 131.6 (d, $^4J_{C-P}$ = 2.5 Hz), 131.9 (d, $^1J_{C-P}$ = 104.1 Hz), 132.2 (d, $^3J_{C-P}$ = 9.9 Hz), 133.6, 134.6 (d, $^1J_{C-P}$ = 98.4 Hz), 137.4, 138.9, 139.7, 143.6 (d, $^2J_{C-P}$ = 10.6 Hz), one signal was obscured; ^{31}P NMR ($CDCl_3$) δ 28.77. Anal. Calcd for $C_{30}H_{27}OP$: C, 82.93; H, 6.26. Found: C, 82.76; H, 6.34.

(*E*,*E*)-1,4-(4-Bromodiphenyl)-1-(diphenylphosphinlyl)-1,3-butadiene (10d): isolated in 80% as a yellow solid; mp 72−74 °C; IR (Nujol) 1177 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.67 (1H, ddd, J = 15.9, 9.6, 1.7 Hz), 6.75 (1H, br d, J = 15.9 Hz), 6.98−7.00 (2H, m), 7.14 (1H, dd, J = 18.6, 9.6 Hz), 7.15−7.18 (2H, m), 7.38−7.47 (8H, m), 7.51−7.55 (2H, m), 7.65−7.70 (4H, m); ^{13}C NMR ($CDCl_3$) δ 122.2, 122.9, 124.3 (d, $^3J_{C-P}$ = 16.3 Hz), 128.4 (d, $^2J_{C-P}$ = 12.3 Hz), 128.5, 128.6, 129.8, 131.5 (d, $^4J_{C-P}$ = 2.1 Hz), 131.9, 132.0, 132.1 (d, $^3J_{C-P}$ = 9.0 Hz), 134.1 (d, $^2J_{C-P}$ = 9.0 Hz), 134.96 (d, $^5J_{C-P}$ = 1.6 Hz), 134.92 (d, $^1J_{C-P}$ = 97.6 Hz), 139.1, 143.4 (d, $^2J_{C-P}$ = 9.8 Hz); ^{31}P NMR ($CDCl_3$) δ 28.55. Anal. Calcd for $C_{28}H_{21}Br_2OP$: C, 59.60; H, 3.75. Found: C, 59.72; H, 3.68.

(*E*,*E*)-1,4-(4-Fluorodiphenyl)-1-(diphenylphosphinyl)-1,3-butadiene (10e): isolated in 92% as a white solid; mp 56−58 °C; IR (Nujol) 1176 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.65 (1H, ddd, J = 15.7, 10.6, 1.7 Hz), 6.78 (1H, d, J = 15.7 Hz), 6.93−6.99 (4H, m), 7.05−7.09 (2H, m), 7.19 (1H, dd, J = 18.5, 10.6 Hz), 7.25−7.28 (2H, m), 7.42−7.46 (4H, m), 7.51−7.53 (2H, m), 7.65−7.70 (4H, m); ^{13}C NMR ($CDCl_3$) δ 115.4 (d, $^2J_{C-F}$ = 22.1 Hz), 115.8 (d, $^2J_{C-F}$ = 21.3 Hz), 123.7 (d, J = 17.2 Hz), 128.4 (d, $^2J_{C-P}$ = 11.5 Hz), 128.8 (d, $^3J_{C-P}$ = 8.2 Hz), 130.7 (d, $^1J_{C-P}$ = 104.1 Hz), 131.1 (dd, $^2J_{C-P}$ = 8.6 Hz, $^4J_{C-F}$ = 3.7 Hz), 131.9 (d, $^4J_{C-P}$ = 2.5 Hz), 132.3 (d, $^3J_{C-P}$ = 10.6 Hz), 133.8 (d, $^1J_{C-P}$ = 98.4 Hz), 139.0, 143.7 (d, $^2J_{C-P}$ = 10.6), 162.3 (d, $^1J_{C-F}$ = 247.5 Hz), 163.0 (d, $^1J_{C-F}$ = 250.0 Hz), two signals were obscured; ^{31}P NMR ($CDCl_3$) δ 27.88. Anal. Calcd for $C_{28}H_{21}F_2OP$: C, 76.01; H, 4.78. Found: C, 76.21; H, 4.58.

(*E*,*E*)-1,4-(2-Tolyl)-1-(diphenylphosphinyl)-1,3-butadiene (10f): isolated in 76% as a white solid; mp 144−146 °C; IR (Nujol) 1177 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.72 (3H, s), 2.35 (3H, s), 6.39 (1H, ddd, J = 15.4, 11.0, 2.1 Hz), 6.76 (1H, d, J = 7.6 Hz), 6.98−7.25 (8H, m), 7.29−7.36 (2H, m), 7.42−7.54

(6H, m), 7.64 (1H, dd, J = 18.0, 11.0 Hz), 7.69−7.77 (2H, m); ^{13}C NMR ($CDCl_3$) δ 19.6, 19.7, 125.2 (d, $^3J_{C-P}$ = 17.1), 125.5, 125.6, 126.0, 127.9 (d, $^5J_{C-P}$ = 3.6 Hz), 128.4 (d, $^2J_{C-P}$ = 12.1 Hz), 128.6, 129.5 (d, $^3J_{C-P}$ = 3.7 Hz), 130.2, 130.5, 131.7 (d, $^4J_{C-P}$ = 2.4 Hz), 132.3 (d, $^3J_{C-P}$ = 9.8 Hz), 134.2 (d, $^1J_{C-P}$ = 96.3 Hz), 134.3 (d, $^2J_{C-P}$ = 8.5 Hz), 135.1, 137.5, 138.0, 138.1, 143.8 (d, $^2J_{C-P}$ = 8.5 Hz), one signal was obscured; ^{31}P NMR ($CDCl_3$) δ 26.33. Anal. Calcd for $C_{30}H_{27}OP$: C, 82.93; H, 6.26. Found: C, 82.78; H, 6.38.

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Supporting Information Available: General experimental details, H−H COSY spectra (**7a** and **8a**), and X-ray crystallographic data of **10c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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