Alkyne Reactions with Arylpalladium Compounds

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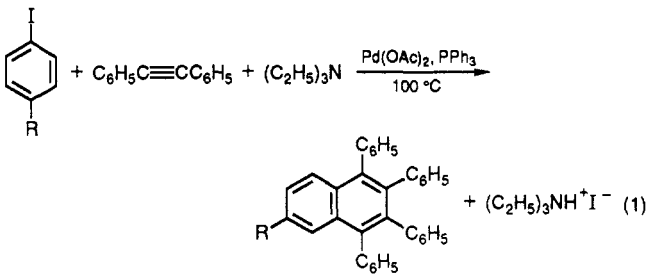
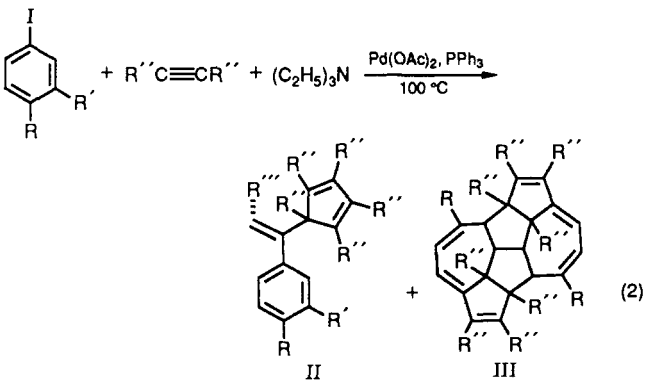
Cyclopalladated *N,N*-dimethylbenzylamine trifluoromethanesulfonate reacts with diphenylacetylene to form a benzofulvene derivative, VIII. New complexes of two alkyne units with one cyclopalladated chloro dimer were prepared including a bis(dimethyl acetylenedicarboxylate)-cyclopalladated dimethylbenzylamine product and a 3-hexyne-cyclopalladated [(dimethylamino)methyl]ferrocene complex. Several 3:1 alkyne to aryl halide compounds have been formed catalytically from aryl iodides or bromides and alkynes. They are pentaalkylcyclopentadiene derivatives II. Methyl *o*-iodobenzoate with some alkynes yields isocoumarin derivatives. In some cases hexacyclic or tetracyclic 4:2 alkyne to aryl halide products are formed, also. Mechanisms are suggested to explain these and related reactions.

We have reported that aryl iodides react differently with diphenylacetylene than they do with 3-hexyne. The diphenylacetylene reaction yields 1,2,3,4-tetraphenylnaphthalene derivatives (eq 1) while 3-hexyne forms a



(1)

hexacyclic 4:2 alkyne to aryl iodide product and/or a 3:1 pentaethylcyclopentadienyl derivative[1] (eq 2, R″ = C_2H_5).



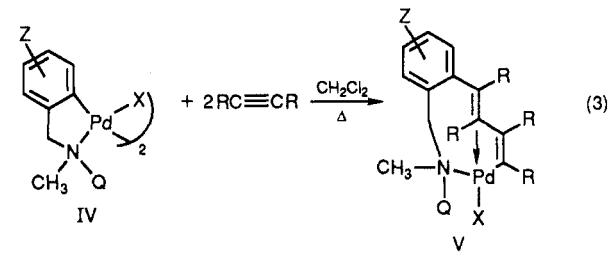
(2)

II III

R = H, CH_3O, CH_3O_2C, NO_2; R′ = H, CH_3O_2C, CH_3O; R″ = C_2H_5; R‴ = CH_3

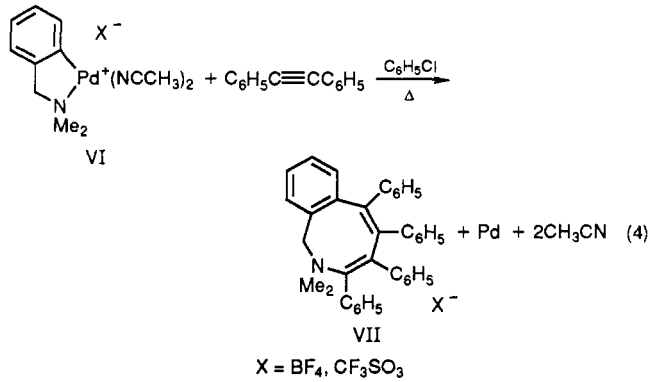
We have proposed mechanisms for these reactions, but there are still questions to be answered about them. The questions we have addressed in this study are the following: (1) are the 2:1 alkyne to cyclopalladated *N,N*-dimethylbenzylamine chloro dimer type complexes reported by Pfeffer[2] intermediates in all or any of our reactions and (2) why do diphenylacetylene and 3-hexyne react differently?

Pfeffer has reported the preparation of several 2:1 alkyne to cyclopalladated *N,N*-dimethylbenzylamine chloro dimers,[2,3] for example, V (R = C_6H_5, Q = CH_3, X = Cl, Z = H). These complexes have been prepared either directly from the cyclopalladated complex IV and two alkynes[2] (eq 3) or from a preformed 1:1 complex and a second alkyne.[3]



IV V (3)

A crystal structure for V (R = C_6H_5, Q = CH_3, X = Cl, Z = H) was determined. The structure showed that the first double bond attached to the aromatic ring was trans and the second one was cis.[2] A *cis,cis*-diene would be expected initially, but a subsequent isomerization occurs to give a more favorable structure for coordination of the double bond next to the aromatic ring with the palladium and perhaps to relieve strain between the five adjacent phenyl groups in the cis,cis complex. Pfeffer has proposed that the isomerization proceeds by an initial decoordination of the nitrogen atom followed by a "metallocyclic flip" involving intermediate formation of a metallacyclopentenyl complex.[3] No reactions of complex V were reported. However, a curious reaction of cyclopalladated *N,N*-dimethylbenzylamine bis(acetonitrile) tetrafluoroborate (prepared from IV and silver tetrafluoroborate in acetonitrile solution) with diphenylacetylene in boiling chlorobenzene was reported.[3] The product of this reaction was proposed to be a benzoazacyclooctatriene (VII) on the basis of its molecular weight and ^1H NMR spectrum and by analogy with other reactions. The peculiar ^1H NMR spectrum observed with the two *N*-methyl groups being a very broad singlet at room temperature and a sharp doublet at −80 °C was explained as being due to nonrigidity of the eight-membered ring at room temperature (eq 4).



VI VII (4)

X = BF_4, CF_3SO_3

We now report further examples of 2:1 complexes, some of their reactions, and a correction to the structure of

(1) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941.
(2) Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bauaoud, S.-E.; LeBorgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547.
(3) Maassarani, F.; Pfeffer, M.; LeBorgne, G. *Organometallics* **1987**, *6*, 2029.

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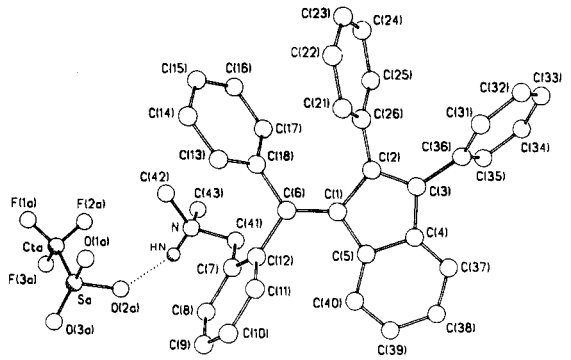
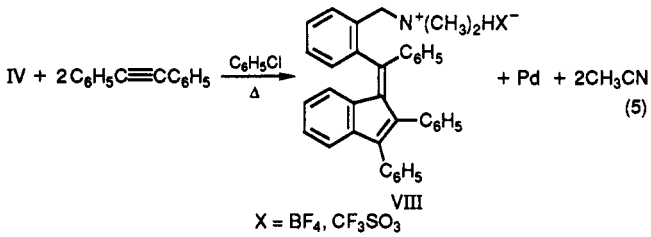


Figure 1. Structure of VIII (X = $CF_3SO_3^-$).

compound VII. These reactions will be related to the proposed mechanisms of reaction of aryl iodides with alkynes. We also report further examples of the preparation of 3:1 products (II) and the 4:2 products (III).

Results and Discussion

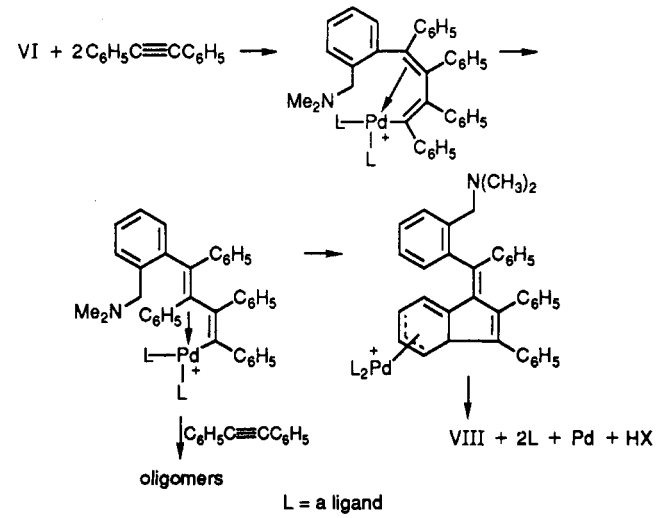
Reactions of Cyclopalladated Complexes with Alkynes. We repeated the published preparation of VII and obtained the product described, but we were unable to obtain crystals suitable for an X-ray structure determination. We then prepared the analogous trifluoromethanesulfonate and did obtain good quality crystals. The product was found to be a benzofulvene derivative, VIII (X = CF_3SO_3), rather than the proposed azacyclooctatriene, VII (X = CF_3SO_3) (eq 5). The structure is shown in Figure 1.



The ^1H NMR spectra of both salts of VIII were nearly identical. Both on treatment with aqueous sodium carbonate gave the same free base. Reaction of the free base with tetrafluoroboric acid regenerated the original salt.

The structure in Figure 1 shows hydrogen bonding between the proton of the ammonium ion and one of the sulfonate oxygens (N to O distance, 2.114 Å). Presumably, the structure of the tetrafluoroborate is similar with the hydrogen bond between F and N. The proton NMR spectra of the samples vary with conditions. The crystalline tetrafluoroborate, in our hands, shows two very broad peaks, at about 1.8 and 2.7 ppm for the two *N*-methyl groups in deuterated chloroform at room temperature. The benzylmethylene group appears as two doublets centered at 3.93 and 4.24 ppm (J = 14 Hz). If the chloroform solution is shaken with 48% aqueous tetrafluoroboric acid, the chloroform layer separated, and the spectrum retaken, the methyl groups now appear as two sharp doublets centered at 1.8 and 2.7 ppm with J = 4 Hz at room temperature. The methylene group now appears as two double doublets at the same positions as before. Treatment of the original chloroform solution with water (or D_2O), separating the chloroform solution and reruning the spectrum, then shows the two *N*-methyls as a (single) sharp singlet (at room temperature) at 2.14 ppm. The methylene group appears as two doublets centered at 3.68 and 3.87 ppm with J = 14 Hz. Heating a solution of the tetrafluoroborate in deuterated nitromethane solution, where the methyls appear as two sharp doublets at room

Scheme I



temperature, to 315 K results in the methyls appearing as two sharp singlets (exchange of D for H in the salt?), and heating further causes broadening; finally at 354 K, the methyl resonances collapse to a broad singlet. This behavior we believe can be explained by first proposing an increasing rate of exchange of the proton on nitrogen as the temperature is increased followed by a dissociation of the hydrogen-bonded ion pair. The dissociation allows the rigidly held methyls to rotate and become equivalent. The original salt when treated with water apparently dissociates and rotation about the C–N bond becomes possible, but rotation is still restricted about the methylene–phenyl bond since the methylene protons appear as two doublets. [A reviewer has suggested the alternative explanation that since VIII is chiral because of hindered rotation both the dimethylamino and benzylmethylene groups are diastereotopic when the N is protonated. When the proton is removed by heating or adding base, inversion of the nitrogen can occur rendering the *N*-methyls equivalent while the methylene group remains diastereotopic.] The original salt in chloroform solution shows an intermediate ^1H NMR spectrum presumably due to some water in the chloroform solution or the salt itself. Shaking the solution with strong fluoroboric acid converts the salt back to the hydrogen-bonded ion pair.

The formation of VIII is easily explained as a double insertion of diphenylacetylene into the palladium–carbon bond of the cyclopalladated complex to form the *cis,cis*-diene followed by an isomerization to the *trans,cis*-diene. The *trans,cis*-diene cannot form the naphthalene derivative, but instead it cyclizes to VIII. The steps are formulated in Scheme I.

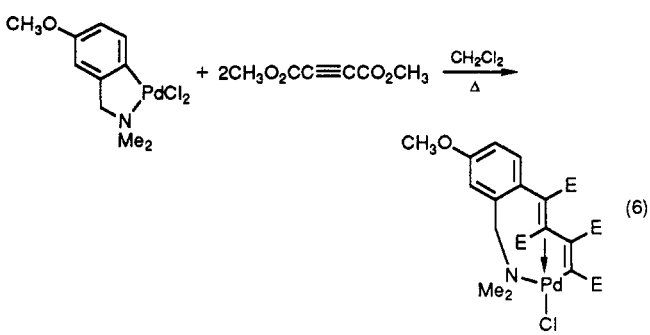
We have suggested that the isomerization and cyclization of the 2:1 alkyne to VI complex occurs without coordination of nitrogen to the palladium in order to explain the fact that treatment of V (Z = H, Q = CH_3, R = C_6H_5, X = Cl) with silver tetrafluoroborate and heating the product in chlorobenzene, with or without acetonitrile or excess diphenylacetylene, yields only about 20% of the free base of VIII and no VIII itself. According to Pfeffer the yield of product VIII from reaction 4 is nearly quantitative.[3] The only other identifiable product from our reaction is about 10% of V (Z = H, Q = CH_3, R = C_6H_5, X = Cl).

We have prepared a few additional complexes of type V to better determine the generality of their synthesis. Complexes with diphenylacetylene and cyclopalladated dimethylbenzylamine chloro dimer with a 4-nitro and 4-methoxy substituents were prepared by Pfeffer's me-

Table I. Properties of 2:1 Alkyne Cyclopalladated Benzylamine Complexes

product	% yield	mp, °C	^{1}H NMR ($CDCl_3$), ppm	^{13}C NMR ($CDCl_3$), ppm	anal. found C	found H	found N	calcd C	calcd H	calcd N
V, R = C_6H_5, Q = CH_3, X = Cl, Z = *p*-NO_2	18	220 dec	8.28–6.55 (m, 23 H), 2.83 (s, 3 H, 2.89 (d, J = 7.3 Hz, 2 H), 2.43 (s, 3 H)	168.2 (s), 150.7 (s), 141.7 (s), 139.8 (s), 138.4 (s), 137.2 (s), 136.5 (s), 135.6 (s), 131.7 (s), 128.7 (s), 128.0 (s), 127.9 (s), 126.6 (s), 116.25 (s), 114.3 (s), 113.0 (s), 67.6 (t), 51.8 (q), 46.2 (q)	65.90	4.91	4.53	65.59	4.61	4.13
V, R = C_6H_5, Q = CH_3, X = Cl, Z = *p*-CH_3O	57	200 dec	7.30–6.45 (m, 23 H), 3.78 (s, 3 H, OCH_3), 2.81 (d, J = 13.3 Hz, 1 H), 2.72 (s, J = 3 Hz, 1 H), 2.62 (d, J = 13.4 Hz, 1 H), 2.35 (s, 3 H, N–CH_3)	166.8 (s), 166.6 (s), 164.0 (s), 159.3 (s), 143.4 (s), 131.2 (s), 129.9 (s), 129.6 (s), 128.3 (s), 66.2 (q), 53.8 (q), 53.4 (q), 52.5 (q), 52.1 (q), 51.6 (q), 44.6 (q), 30.8 (q)	68.41	5.58	1.82	68.90	5.13	2.12
V, R = CH_3O_2C, X = Cl, Q = CH_3, Z = H	62	220 dec	7.5–7.1 (m, 4 H), 3.88 (s, 3 H), 3.85 (s, 3 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.74 (d, J = 14 Hz, 1 H), 3.29 (d, J = 14 Hz, 1 H), 2.86 (s, 3 H), 2.37 (s, 3 H)	166.8 (s), 166.6 (s), 164.0 (s), 159.3 (s), 143.4 (s), 131.2 (s), 129.9 (s), 129.6 (s), 128.3 (s), 66.2 (q), 53.8 (q), 53.4 (q), 52.5 (q), 52.1 (q), 51.6 (q), 44.6 (q), 30.8 (q)	46.16	4.83	2.08	46.61	4.85	2.26
V, R = C_2H_5, X = Cl, Q = CH_3, Z = H	80	123 dec	7.4–7.0 (m, 4 H), 4.24 (d, J = 13 Hz, 1 H), 3.11 (d, J = 13 Hz, 1 H), 1.71–2.81 (m, 8 H), 2.65 (s, 3 H), 2.06 (s, 3 H), 1.36 (t, J = 7.4 Hz, 3 H), 1.16 (t, J = 7.4 Hz, 3 H), 0.95 (t, J = 7.4 Hz, 3 H)	141.1 (s), 134.9 (s), 131.1 (s), 130.8 (s), 128.6 (s), 127.5 (s), 114.1 (s), 98.4 (s), 67.4 (t), 51.7 (q), 47.2 (q), 33.3 (t), 26.3 (t), 24.3 (t), 21.9 (t), 15.2 (q), 14.9 (q), 148.8 (q), 12.4 (q)	84.59	10.68	4.49	84.85	10.44	4.71
V, R = CO_2CH_3, X = Cl, Q = CH_3, Z = *m*-CH_3O	61	195 dec	7.40 (d, J = 8.7 Hz, 1 H), 6.94 (dd, J = 8.7 Hz, 3.0 Hz, 1 H), 6.70 (d, J = 2.6 Hz, 1 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 3.79 (d, J = 13.8 Hz, 1 H), 3.75 (s, 3 H), 3.74 (s, 3 H), 3.16 (d, J = 13.8 Hz, 1 H), 2.87 (s, 3 H), 2.35 (s, 3 H)	167.2 (s), 166.9 (s), 164.3 (s), 160.3 (s), 159.3 (s), 149.0 (s), 143.3 (s), 135.3 (s), 630.1 (s), 129.7 (s), 122.8 (s), 117.5 (s), 114.0 (s), 110.2 (s), 66.4 (q), 55.4 (q), 53.7 (q), 53.3 (q), 52.2 (q), 52.1 (q), 51.6 (q), 46.3 (q)	44.48	4.49	2.31	44.76	4.44	2.31
V, R = C_6H_5, Q = H, X = Br, Z = 3,4-$(CH_3O)_2$	67	225 dec	7.26–6.41 (m, 23 H), 3.86 (s, 3 H), 3.64 (s, 3 H), 3.27 (d, J = 13.8 Hz, 1 H), 3.01 (d, J = 13.8 Hz, 1 H), 2.43 (d, J = 6.2 Hz, 3 H)		63.33	4.66		63.13	4.74	
IX	86	135 dec	4.19 (s, 5 H), 4.13–3.95 (m, 3 H), 2.64 (s, 3 H), 2.00–1.91 (m, 6 H), 1.87 (s, 3 H), 1.72 (t, J = 7.5 Hz, 3 H), 1.14 (t, J = 7.5 Hz, 3 H), 0.96 (t, J = 7.5 Hz, 3 H)	139.8 (s), 133.8 (s), 110.1 (s), 102.3 (s), 92.0 (s), 82.9 (s), 69.9 (d), 68.7 (d), 64.9 (d), 61.5 (t), 51.6 (q), 45.9 (q), 35.9 (q), 26.2 (q), 24.4 (q), 22.3 (q), 17.8 (q), 14.9 (q), 12.4 (q)	54.88	6.86	2.57	54.77	6.62	2.55

thod,[2] but the yields were low (6 and 18%, respectively). Pfeffer reports that dimethyl acetylenedicarboxylate will only insert once into IV (R = CH_3O_2C, X = Cl, Q = CH_3, Z = H);[3] however, we find no difficulty achieving two insertions under his conditions. The *m*-methoxy derivative was also obtained in moderate yield (eq 6). The *trans*,-



(6)

cis-diene system is assumed in these complexes. A stable complex with diphenylacetylene and a secondary amine,

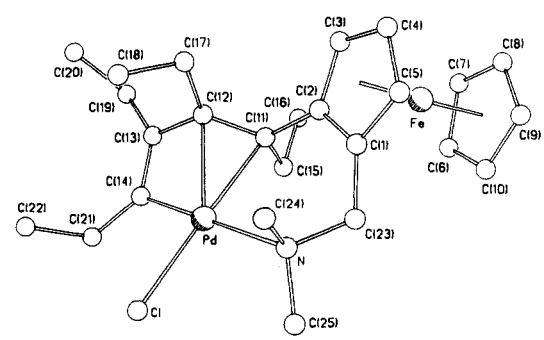


Figure 2. Structure of the product formed from cyclopalladated [(dimethylamino)methyl]ferrocene–chloro dimer and 3-hexyne.

cyclopalladated *N*-methyl-3,4-dimethoxybenzylamine bromo dimer,[4] was also obtained readily. We found that 3-hexyne formed stable 2:1 complexes, also. Complex IV

(4) Clark, P.; Dyke, S. *J. Organomet. Chem.* **1985**, *281*, 389; **1984**, *276*, 421.

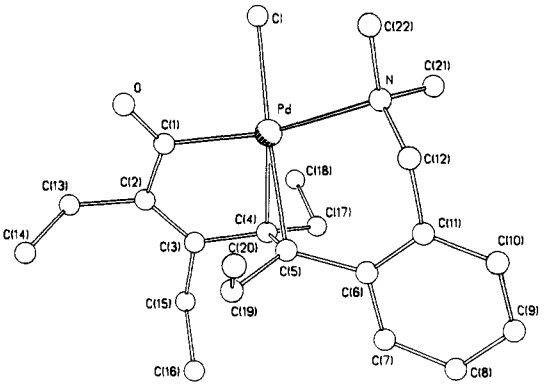
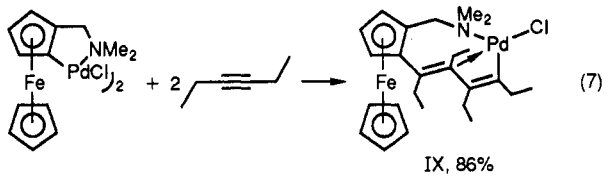


Figure 3. Structure of the carbonylation product of V (R = C_2H_5).

and cyclopalladated [(dimethylamino)methyl]ferrocene chlorodimer both gave complexes with 3-hexyne (eq 7). A

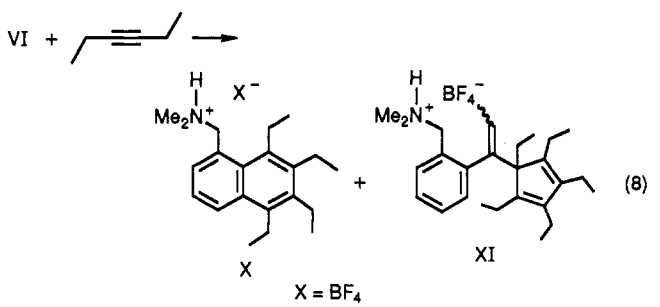


(7)

IX, 86%

crystal structure for the ferrocene complex was obtained, and this product also had the *trans,cis*-diene structure (Figure 2). The properties of the new 2:1 complexes are given in Table I. We were unable to obtain 2:1 complexes from bis(trimethylsilyl)acetylene, phenylacetylene, and 4,4'-dinitrodiphenylacetylene.

Reaction of VI (X = BF_4) with 2 equiv of 3-hexyne in chlorobenzene at 150 °C for 24 h gave 1,2,3,4-tetraethyl-5-[(dimethylammonio)methyl]naphthalene tetrafluoroborate (X) in 36% yield as the only identifiable product. We have reported this reaction at room temperature previously with the nitromethane solvate where the yield was 55%.[1] Increasing the excess of 3-hexyne to 5.3 equiv at 40 °C causes the appearance of the 3:1 alkyne to ligand product XI in 25% yield (eq 8).



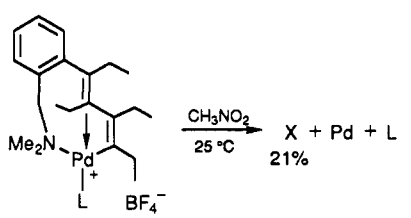
(8)

X

XI

X = BF_4

The 2:1 tetrafluoroborate XII has been prepared from the chloro complex and silver tetrafluoroborate in nitromethane solution. This complex decomposes slowly over a period of 6 days to a mixture of products from which 21% of X was isolated (eq 9).



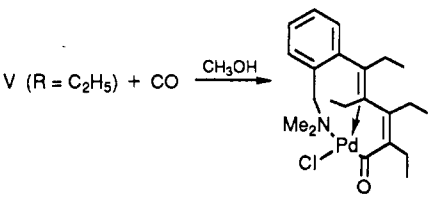
(9)

XII

L = CH_3NO_2

Inclusion of 1 equiv of 3-hexyne in the reaction mixture in eq 9 brings about the formation of about equal amounts of naphthalene X and the 3:1 complex XI (total yield of X and XI was 15%). The formation of X from XII (X = BF_4) shows that the *trans,cis*-diene structure must undergo, at least, some isomerization back to the cis,cis isomer under mild conditions. The major products from these reactions are darkly colored, intractable, viscous liquids.

An attempt to carbomethoxylate complex V (R = C_2H_5) with carbon monoxide and methanol at 50 °C and 25 psi led only to the formation of a monocarbonyl adduct. A crystal structure of the complex (Figure 3) showed that the carbonyl group had inserted between the palladium and the vinyl carbon (eq 10). At higher temperatures (100



(10)

°C) and pressure (100 psi) the complex decomposes to a mixture of at least three products. These were not identified.

Reactions of Aryl Iodides with Alkynes. The only products identified from the reaction of nonchelating aryl iodides (meta or para substituted) with diphenylacetylene are 1,2,3,4-tetraphenylnaphthalene derivatives (eq 1). We, previously, believed that the reaction occurred only with electron-donating substituents in the aryl iodide because *p*-iodonitrobenzene failed to give the naphthalene in the reaction.[1] We now have found, however, that methyl *p*-iodobenzoate undergoes the reaction in fair yield (33% yield) so there appears to be an inhibition of the reaction caused by the nitro compound (eq 1, R = CH_3O_2C).

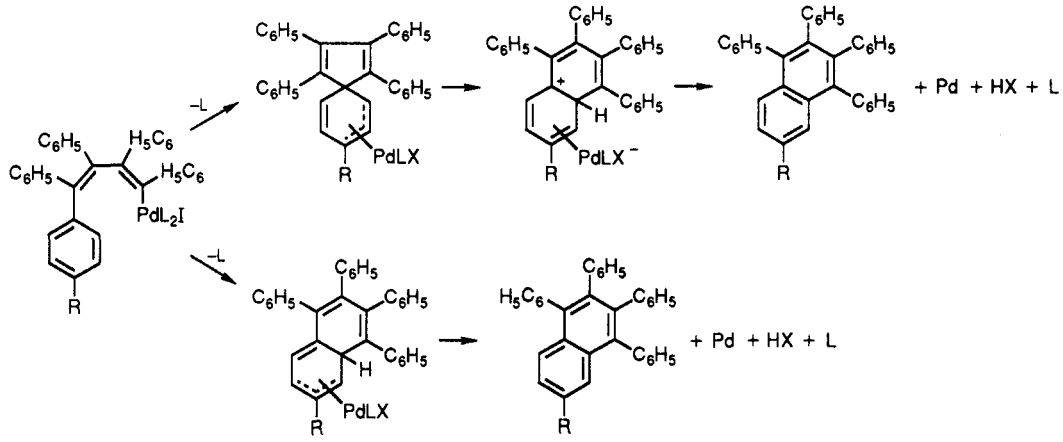
The finding that the chelated complex VI reacts with diphenylacetylene to form only benzofulvene product VIII, as described above, raises the question as to whether the aryl iodide–diphenylacetylene products might be benzofulvenes, also, rather than naphthalenes. The ^1H NMR spectrum of the iodobenzene diphenylacetylene reaction product showed the symmetry expected from 1,2,3,4-tetraphenylnaphthalene, and the melting point of our product agreed with the literature value reported for that compound prepared by another route.[1] The ^1H NMR spectra of the methoxy and methoxycarbonyl derivatives also seemed to fit best the naphthalene structures. We carried out a crystal structure determination on the product from *p*-iodotoluene, and it was found to be the naphthalene derivative, also (Figure 4, supplementary material).

It appears that the chelated palladium complex VI (X = BF_4) gives the benzofulvene VIII as a product rather than a naphthalene because the initial cis,cis two-alkyne insertion product isomerizes to the trans,cis isomer rapidly compared with closure to a naphthalene. Naphthalenes must arise totally from ring closure of a *cis,cis*-diene. Whether the closure involves a spiro-π-allylic intermediate, which later rearranged as suggested by the isolation of such a complex by Pfeffer,[5] or whether ortho ring closure occurs directly is not known (Scheme II).

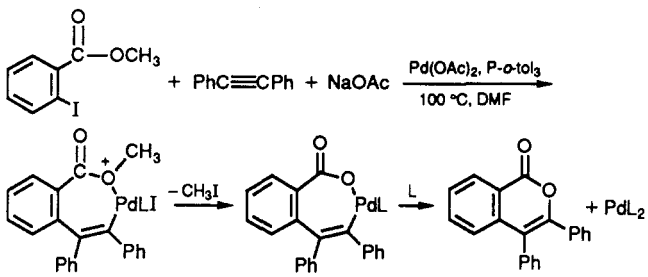
Methyl *o*-iodobenzoate reacts differently with diarylacetylenes. With diphenylacetylene employing sodium acetate and triethylamine as base, methyl *o*-iodobenzoate gives 56% of 3,4-diphenylisocoumarin. A seven-membered-ring palladacycle is presumably involved in the reaction (Scheme III). Under similar conditions, methyl

(5) Maassarani, F.; Pfeffer, M.; LeBorgne, G. *J. Chem. Soc., Chem. Commun.* **1986**, 489.

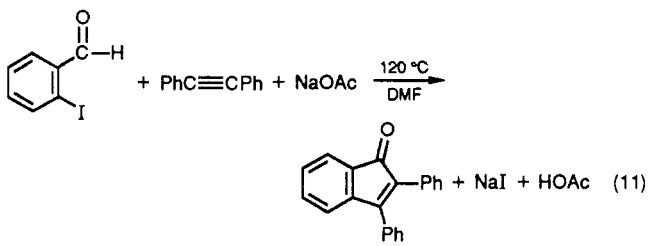
Scheme II



Scheme III



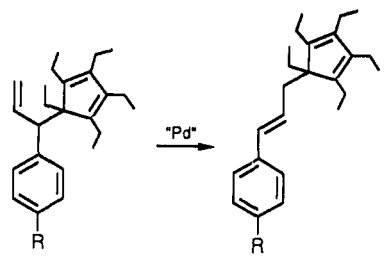
o-iodobenzoate reacts with di-*p*-anisylacetylene to give 38% of the 3,4-di-*p*-anisylisocoumarin and 1-phenyl-1-hexyne yields 29% of 3-*n*-butyl-4-phenylisocoumarin. *p*-Anisylphenylacetylene gives a ca. 1:1 mixture of the two possible regioisomers. Methyl 2-iodo-4-nitrobenzoate and diphenylacetylene give only 9% of the 6-nitroisocoumarin. Very small amounts of 2,3-diarylindenones were also found in some of these reactions, but much better yields are obtained from reactions of *o*-iodobenzaldehydes with diarylalkynes. The reaction of diphenylacetylene with *o*-iodobenzaldehyde using sodium acetate as the base for example gives 58% of 2,3-diphenylindenone (eq 11). Iodobenzene and para-substituted aryl iodides with 3-hexyne yield mixtures of 3:1 and/or 4:2 alkyne to aryl iodide complexes (eq 2). Previously, we have reported only the isolation of II (R = H) and III (R = CH_3O). We now report the formation of II from four additional aryl iodides and of III from iodobenzene, *p*-iodonitrobenzene, and methyl *p*-iodobenzoate as well as from *p*-iodoanisole in better yield than previously reported (Tables II and III). A crystal structure for III (R = H) is also reported (Figure 5, supplementary material). The electronic effects of the para ring substituents do not appear to have any significant influence on the reactions with the exception of the *p*-nitro group which has an inhibitory effect as it did in the diphenylacetylene reaction above.



(11)

Aryl bromides also react with 3-hexyne under the same conditions as aryl iodides. The products are the 3:1 alkyne to aryl halide adducts with only traces of the 4:2 products detected. Yields of the 3:1 products are as good or better from the bromides as they are from the iodides (Table II).

A second, isomeric, 3:1 alkyne to aryl halide product has been observed in these reactions, also. This minor product has been separated by preparative GLC from the mixture obtained from the reaction of 3-hexyne with methyl *p*-iodobenzoate. The ^1H and ^{13}C NMR spectra of the product indicate that it has structure XIII. Judging by the ^1H NMR spectra of the product mixtures from the other 3-hexyne–para-substituted aryl halide reactions, this type of isomeric product is formed in all cases to the extent of 5–20%. This product is likely formed by a palladium-catalyzed Cope type rearrangement of an initially formed terminal elimination 3:1 product (eq 12 and Scheme VI).



(12)

XIII

R = CH_3O_2C, CH_3O

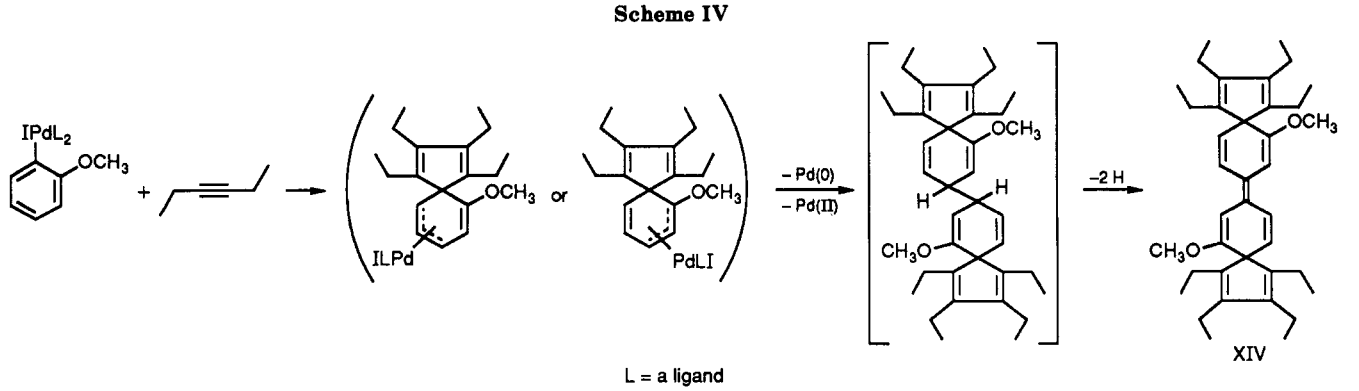
Methyl *m*-iodobenzoate and 4-iodoveratrole with 3-hexyne yield only the usual 3:1 alkyne to aryl iodide products in 20–30% yields (Table II). Both *o*-iodoanisole and methyl *o*-iodobenzoate with 3-hexyne give in low yields (with 10% $Pd(OAc)_2$) a new type of 4:2 alkyne to aryl iodide complex. These products, on the basis of their ^1H and ^{13}C NMR spectra and molecular weight appear to be dehydrogenated 2:1 alkyne to aryl iodide dimers. We have been unable to prepare crystals for obtaining an X-ray structure from either compound. In the case of the methoxy compound the precise mass indicates the formula is $C_{38}H_{52}O_2$ and NMR data provide strong evidence for its proposed structure, XIV. While we do not know if the compound is the cis or trans isomer (trans is assumed), the symmetry of the molecule is confirmed by the observation in ^1H NMR of only two kinds of ethyl groups (two of each kind of ethyl group per one vinyl-H), one kind of methoxyl, two vinyl-H doublets, and one vinyl-H singlet. The ^{13}C NMR shows only 10 peaks, also as predicted by structure XIV. The ortho methoxyl substituent apparently inhibits the rearrangement of the spiro-π-allylic intermediate to the bicyclo[5.3.0]decane derivative, and instead, the spiro complex dimerizes and the dimer is dehydrogenated by the palladium present or air oxidized to the conjugated polyene XIV (Scheme IV). The product was isolated in 26% yield.

Table II. Properties of 3:1 Alkyne to Aryl Halide Products

product	% yield from ArBr	% yield from ArI	^{1}H NMR ($CDCl_3$), ppm	^{13}C NMR ($CDCl_3$), ppm	mol wt (HRMS) found	mol wt (HRMS) calcd
II, R = R′ = H, R″ = C_2H_5, R‴ = CH_3	44	47[1]	see ref 1	see ref 1	see ref 1	
II, R = CH_3O, R′ = H, R″ = C_2H_5, R‴ = CH_3	47	24	6.72 (d, J = 8.7 Hz, 2 H), 6.60 (d, J = 8.7 Hz, 2 H), 5.73 (q, J = 6.7, 1 H), 3.72 (s, 3 H), 2.17–2.01 (m, 8 H), 1.82 (q, J = 7.1 Hz, 2 H), 1.47 (d, J = 6.6 Hz, 3 H), 1.03 (t, J = 7.6 Hz, 6 H), 0.75 (t, J = 7.5 Hz, 6 H), 0.53 (t, J = 7.1 Hz, 3 H)	143.9, 142.2, 129.5, 129.45, 128.3, 126.3, 121.5, 111.8, 67.6, 55.2, 22.65, 19.45, 18.7, 15.2, 14.2, 13.6, 8.0	352.278	352.279
II, R = CH_3OCO, R′ = H, R″ = C_2H_5, R‴ = CH_3	53	44	7.73 (d, J = 8.5 Hz, 2 H), 6.87 (d, J = 8.5 Hz, 2 H), 5.80 (q, J = 6.7 Hz, 1 H), 3.86 (s, 3 H), 2.18–1.99 (m, 8 H) 1.85 (q, J = 7.2 Hz, 2 H), 1.42 (d, J = 6.7 Hz, 3 H), 1.04 (t, J = 7.6 Hz, 6 H), 0.70 (t, J = 7.6 Hz, 6 H), 0.52 (t, J = 7.2 Hz, 3 H)	167.4, 145.0, 144.5, 143.7, 141.9, 129.5, 128.6, 127.9, 122.2, 67.5, 51.8, 22.5, 19.5, 18.7, 15.1, 14.1, 13.6, 7.9	380.271	380.272
II, R = H, R′ = CH_3OCO, R″ = C_2H_5, R‴ = CH_3	...	26	7.77 (dt, J = 7.7 Hz, 1.6 Hz, 1 H), 7.51 (t, J = 1.6 Hz, 1 H), 7.13 (t, J = 7.6, 1 H), 7.01 (dt, J = 7.6, 1.6 Hz, 1 H), 5.81 (q, J = 7.7, 1 H), 3.86 (s, 3 H), 2.30–1.98 (m, 8 H), 1.85 (q, J = 7.6 Hz, 6 H), 0.67 (t, J = 7.5 Hz, 6 H), 0.53 (t, J = 7.2 Hz, 3 H)	167.4, 144.5, 143.0, 142.5, 141.7, 133.4, 129.8, 129.6, 128.3, 127.1, 126.4, 122.1, 67.5, 51.7, 37.8, 22.2, 19.4, 18.7, 18.6, 18.2, 15.2, 14.0, 13.5, 7.97, 7.75	380.270	380.272
II, R = R′ = CH_3O, R″ = C_2H_5, R‴ = CH_3	...	21	6.62–6.63 (m, 3 H), 5.76 (q, J = 6.7 Hz, 1 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 2.19–2.00 (m, 8 H), 1.82 (q, J = 7.2, 2 H), 1.48 (d, J = 6.6, 3 H, 1.04 (t, J = 7.6, 6 H) 0.75 (t, J = 7.5, 3 H), 0.51 (t, J = 7.2, 3 H)		382.29	382.28
XIII, R = CH_3O_2C	12	17	7.89 (d, J = 8.4 Hz, 2 H), 7.19 (d, J = 8.3 Hz, 2 H), 6.26 (d, J = 15.8 Hz, 1 H), 5.60 (dt, J = 6.6, 16 Hz, 1 H), 3.88 (s, 3 H), 2.42 (dd, J = 6.6, 1.4 Hz, 2 H), 2.26 (q, J = 7.6 Hz, 4 H), 2.14 (q, J = 7.7 Hz, 4 H), 1.58, (q, J = 7.3 Hz, 2 H), 1.06 (t, J = 7.6 Hz, 6 H), 0.99 (t, J = 7.6 Hz, 6 H), 0.43 (t, J = 7.3 Hz, 3 H)	167.1, 143.1, 142.9, 142.6, 131.4, 129.7, 129.0, 127.9, 125.5, 61.4, 51.9, 38.0, 27.3, 18.7, 18.3, 15.2, 14.0, 7.8	380.270	380.272
II, R = CH_3O, R′ = H, R″ = CH_3, R‴ = H	...	94	6.87 (d, J = 8.8 Hz, 2 H), 6.60 (d, J = 8.8 Hz, 2 H), 5.22 (d, J = 1.0, 1 H), 5.15 (d, J = 1.0 Hz, 1 H), 3.68 (s, 3 H), 1.65 (s, 12 H), 1.13 (s, 3 H)	158.5, 151.5, 140.6, 135.3, 134.9, 127.6, 114.3, 112.4, 61.7, 54.7, 20.4, 10.9, 10.1	268.182	268.182
II, R = CH_3OCO, R′ = H, R″ = CH_3, R‴ = H	...	98[a]	7.76 (d, J = 8.6 Hz, 2 H), 6.98 (d, J = 8.6 Hz, 2 H), 5.35 (d, J = 1.0 Hz, 1 H), 5.22 (d, J = 1.0 Hz, 1 H), 3.87 (s, 3 H), 1.64 (s, 12 H), 1.16 (s, 3 H)	167.1, 151.5, 147.2, 140.0, 136.0, 133.0, 128.4, 126.6, 116.0, 61.5, 51.7, 19.9, 10.9, 10.0	296.178	296.178
XIII, R = CH_3O	17	...	7.10 (d, J = 8.7 Hz, 2 H), 6.75 (d, J = 8.7 Hz, 2 H), 6.2 (d, J = 15.9 Hz, 1 H), 5.35 (dt, J = 15.9, 6.7 Hz, 1 H), 3.76 (s, 3 H), 2.40 (dd, J = 6.7, 1.1 Hz, 2 H), 2.20 (q, J = 7.5 Hz, 4 H), 2.10 (q, J = 7.7 Hz, 4 H), 1.05 (t, J = 7.6 Hz, 6 H), 1.00 (t, J = 7.6 Hz, 6 H), 0.40 (t, J = 7.3 Hz, 3 H)		349[b]	349

[a] Mp 21.5–24.0 °C [b] Low-resolution MS.

Scheme IV



L = a ligand

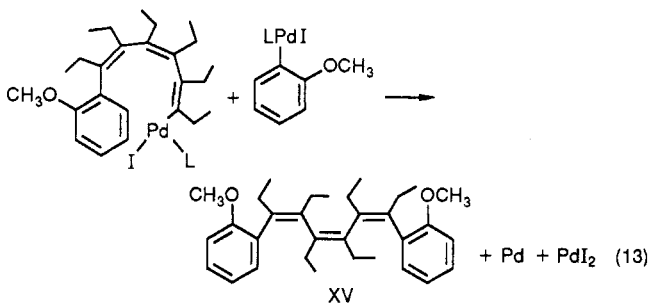
Other minor products formed from *o*-iodoanisole and 3-hexyne in addition to the 2:1 dimer XIV were 1,2,3,4-tetraethyl-5-methoxynaphthalene (5%) and a linear 3:2 alkyne to aryl group product (4%), XV. Again, the

Table III. Properties of 4:2 Alkyne to Aryl Iodide Products

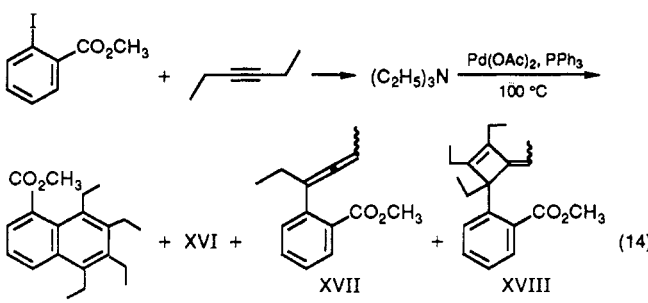
compound	% yield	Mp, °C	^{1}H NMR ($CDCl_3$), ppm	^{13}C NMR ($CDCl_3$), ppm	mol wt (HRMS) found	mol wt (HRMS) calcd
III, R = R′ = H, R″ = C_2H_5	1	164–174 dec	5.72–5.66 (dd, J = 5.7, 5.7 Hz, 2 H), 5.61–5.53 (dd, J = 8.7 Hz, 2 H), 5.22 (d, J = 5.7 Hz, 2 H), 3.06–3.02 (d, J = 3.1 Hz, 2H), 2.89–2.84 (dt, J = 3.1, 2.8 Hz, 2 H), 2.33–2.09 (m, 6 H), 1.95–1.86 (m, 2 H), 1.74–1.54 (m, 6 H), 1.36–1.28 (m, 2 H), 1.08 (t, J = 7.3 Hz, 6H), 0.98 (t, J = 7.4 Hz, 6 H), 0.90 (t, 7.6 Hz, 6 H), 0.58 (t, J = 7.4 Hz, 6 H)	155.4, 151.3, 140.1, 132.1, 129.2, 114.2, 73.2, 68.4, 62.2, 45.8, 26.8, 26.7, 23.5, 18.1, 15.2, 13.4, 10.5, 10.2	482.39	482.89
III, R = CH_3O, R′ = H, R″ = C_2H_5	22		see ref 1	see ref 1		
III, R = NO_2, R′ = H, R″ = C_2H_5	1.4	235	7.64 (d, J = 7.2 Hz, 1 H), 5.50 (d, J = 7.2 Hz, 1 H), 4.28 (d, J = 10.5 Hz, 1 H), 3.32 (dd, J = 8.5, 3.0 Hz, 1 H), 2.29–1.45 (m, 8 H), 1.19 (t, J = 7.1 Hz, 3 H), 1.03 (t, J = 7.6 Hz, 3 H), 0.90 (t, J = 7.7 Hz, 3 H), 0.54 (t, J = 7.3 Hz, 3 H)	167.0, 159.1, 152.1, 141.2, 135.5, 111.5, 73.7, 66.9, 64.1, 40.7, 28.0, 24.5, 21.4, 18.4, 14.9, 13.0, 10.7, 9.9	572[a]	572
III, R = CH_3CO_2, R′ = H, R″ = C_2H_5	22	200	7.17 (d, J = 6.6 Hz, 1 H), 5.44 (d, J = 6.5 Hz, 1 H), 3.82 (dd, J = 8.1, 3.0 Hz, 1 H), 3.20 (dd, J = 8.2, 3.0 Hz, 1 H), 2.18–1.40 (m, 8 H), 1.13 (t, J = 7.3 Hz, 3 H), 0.99 (t, J = 7.5 Hz, 3 H), 0.86 (t, J = 7.5 Hz, 3 H), 0.53 (t, J = 7.3 Hz, 3 H)	170.3, 162.9, 156.3, 140.6, 140.3, 131.8, 114.2, 73.3, 68.5, 63.2, 51.9, 40.9, 27.3, 24.8, 22.4, 18.4, 15.3, 13.1, 10.7, 10.0	598[a]	598

[a] Low-resolution MS.

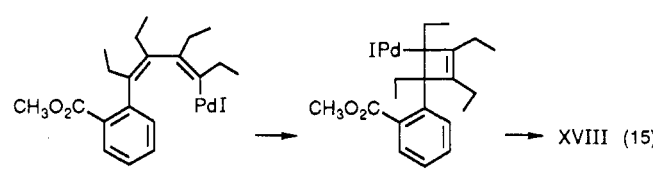
structure is based upon MS and NMR data. The last product is presumed to be the all cis isomer probably resulting from a coupling of the 3:1 alkyne to aryl halide palladium complex with *o*-iodoanisole (or its palladium derivative) (eq 13).



Methyl *o*-iodobenzoate and 3-hexyne yield three products in addition to 5% of methyl 5,6,7,8-tetraethyl-1-naphthalenecarboxylate. The major product (26%) XVI again is a 4:2 alkyne to aryl halide product probably with a structure similar to that of XIV. Other products formed from methyl *o*-iodobenzoate and 3-hexyne included 4-(*o*-methoxycarbonyl)phenyl-2,3-hexadiene, XVII (4%), and 3-[*o*-(methoxycarbonyl)phenyl]-1,2,3-triethyl-4-ethylidenecyclobutene, XVIII (1%) (eq 14). The struc-



tures of the liquids XVII and XVIII are again based upon MS and NMR spectra. Their relatively low molecular weight limit the possibilities. The allene structure for XVII is based upon the ^{1}H NMR which shows the presence of an isolated ethyl group, a doublet methyl, and a singlet methyl. There is the expected long-range coupling between the methylene and the vinyl hydrogen as observed in other allenes. The ^{1}H NMR spectrum of XVIII shows three ethyl groups, one at higher field than the others, a vinyl-H quartet coupled with a doublet methyl, and an ester methyl. The allene product XVII probably arises from a palladium hydride elimination from the initial 1:1 aryl-palladium complex–3-hexyne adduct. This appears to be the first observed instance of a palladium hydride elimination from a vinylpalladium compound to form an allene. The ethylidene cyclobutene product XVIII must be produced by a cyclization of the 2-alkyne to one aryl halide adduct (eq 15). A possibly related cyclization of two



diphenylacetylenes by palladium chloride to a π-tetraphenylcyclobutadienepalladium complex has been reported.[6] The products prepared, yields, and physical data are given in Tables II, III, and IV. X-ray structures for III (R = CH_3O, R″ = H[1]) and for III (R = R″ = H (Figure 5, supplementary material) have been obtained.

Chelated complex VI (X = BF_4) and 3-hexyne react to yield mainly the naphthalene and a little 3:1 complex. The naphthalene product is probably being formed by the same mechanism as in the aryl iodide–diphenylacetylene reaction. In the absence of major steric effects, the initial cis,cis two-hexyne insertion product must retain its structure long

(6) Hüttel, R.; Neugebauer, H. *Tetrahedron Lett.* **1964**, *47*, 3541.

Table IV. Properties of Products from the Reactions of 3-Hexyne with Ortho-Substituted Aryl Iodides

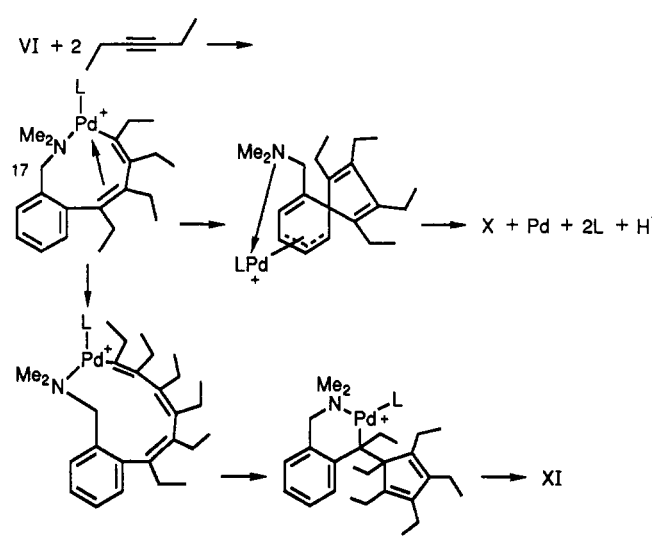
product	% yield	^{1}H NMR ($CDCl_3$), ppm	^{13}C NMR ($CDCl_3$), ppm	mol wt (HRMS) found	mol wt (HRMS) calcd
XIV	26	6.84 (d, J = 9.7 Hz, 1 H), 6.02 (s, 1 H), 4.84 (d, J = 9.8 Hz, 1 H), 3.59 (s, 3 H), 2.29–2.10 (m, 8 H), 1.07 (t, J = 7.5 Hz, 6 H), 0.96 (t, J = 7.5 Hz, 6 H)	145.5 (d), 142.8 (s), 131.6 (s), 130.5 (d), 123.7 (s), 123.6 (s), 122.9 (d), 122.7 (s), 97.1 (d), 65.6 (s), 53.8 (q), 19.3 (t), 19.2 (t), 14.9 (q), 14.7 (q)	540.40	540.39
5-methoxy-1,2,3,4-tetraethylnaphthalene	5	7.64 (d, J = 7.3 Hz, 1 H), 7.31 (t, J = 7.2 Hz, 1 H), 6.79 (d, J = 7.2 Hz, 1 H), 3.93 (s, 3 H), 3.11–2.80 (m, 8 H), 1.33–1.20 (m, 12 H)		270.20	270.20
XV	4	8.05 (d, J = 7.3 Hz, 1 H), 7.30 (t, J = 7.2 Hz, 1 H), 6.72 (t, J = 7.2 Hz, 1 H), 6.65 (d, J = 7.3 Hz, 1 H), 4.05 (s, 3 H), 2.15 (q, J = 6.3 Hz, 2 H), 3.00 (q, J = 6.2 Hz, 2 H), 2.85 (q, J = 6.3 Hz, 2 H), 1.30–1.21 (m, 9 H)	149.1 (s), 147.8 (s), 133.9 (d), 131.7 (d), 130 (s), 128.7 (s), 124.6 (s), 116.3 (d), 106.6 (d), 55.9 (q), 21.5 (t), 19.8 (t), 18.6 (t), 17.5 (q) 16.9 (q), 16.0 (q)	460[a]	460.
XVI	26	7.17 (s, 1 H), 5.74 (d, J = 10 Hz, 1 H), 4.76 (d, J = 8.3 Hz, 1 H), 3.50 (s, 3 H), 2.29–2.05 (m, 8 H), 1.05 (t, J = 7.6 Hz, 6 H), 0.94–0.85 (2t, J = 7.6 Hz, 6 H)	166.5 (s), 154.0 (s), 147.4 (s), 145.9 (s), 142.7 (s), 142.6 (s), 140.5 (d), 132.9 (d), 132.2 (s), 126.0 (s), 124.0 (d), 50.7 (q), 19.1 (t), 18.9 (q), 14.8 (t), 14.7 (q)	596[a]	596.
methyl 5,6,7,8-tetraethylnaphthalene-1-carboxylate	5	8.13 (d, J = 7.3 Hz, 1 H), 7.45–7.35 (m, 2 H), 3.95 (s, 3 H), 3.15–2.81 (m, 8 H), 1.33–1.12 (m, 12 H)		298.20	298.20
XVII	4	7.70–7.25 (m, 4 H), 5.32–5.18 (m, 1 H), 3.85 (s, 3 H), 2.37–2.28 (m, 2 H), 1.67 (d, J = 7.6 Hz, 3 H), 1.08 (t, J = 7.2 Hz, 3 H)	140.0 (s), 131.1 (d), 130.2 (s), 129.6 (d), 129.4 (d), 126.5 (d), 107.5 (s), 87.6 (d), 51.9 (q), 26.5 (t), 14.4 (q), 12.6 (q)	216[a]	216.
XVIII	1	7.51–7.09 (m, 4 H), 6.29 (q, J = 7.6 Hz, 1 H), 3.73 (s, 3 H), 2.58 (q, J = 7.6 Hz, 2 H), 2.15 (q, J = 7.7 Hz, 2 H), 1.92 (q, J = 7.4 Hz, 2 H), 1.72 (d, J = 7.7 Hz, 3 H), 1.16 (t, J = 7.4 Hz, 3 H), 1.04 (t, J = 7.5 Hz, 3 H), 0.67 (t, J = 7.5 Hz, 3 H)	177.0 (s), 142.3 (s), 136.2 (s), 135.0 (s), 134.2 (s), 133.5 (s), 131.6 (s), 127.3 (d), 126.9 (d), 123.8 (d), 123.6 (d), 123.3 (d), 52.0 (q), 29.5 (t), 22.0 (t), 21.0 (t), 14.5 (q), 14.3 (q), 13.7 (q), 8.43 (q)	298[a]	298.

[a] Low-resolution MS.

enough to cyclize to the naphthalene. The restraining effect of the chelating group is necessary, however, to cause this reaction. It seems probable that the cis,cis complex is also an intermediate in the 3:1 product synthesis, since the trans,cis complex XII with 3-hexyne gives the 3:1 complex in only low yield (~7%) (Scheme V). The formation of 3:1 products from aryl iodides and 3-hexyne must follow a similar course (Scheme V). The formation of the 3:1 isomer XIII from aryl iodides may be explained as a result of a palladium hydride elimination from XIX, followed by a reverse readdition and a final elimination to form the terminal alkene. The last compound then undergoes a palladium(II)-catalyzed [3,3] sigmatropic rearrangement[7] to the less strained isomer XIII (Scheme VI) (eq 12).

The 4:2 product III is obtained in the best yields when a 10:20 palladium acetate–triphenylphosphine catalyst is used. This observation is consistent with the bimolecular mechanism proposed, previously.[1] This product is not seen in reactions of the chelated complexes presumably because the chelating group sterically inhibits the dimerization. A competition between cyclization of the cis,cis two 3-hexyne insertion product to a spiro[5.4]decatetraenyl palladium complex and insertion of another 3-hexyne determines the relative yields of the 4:2 and 3:1 products, respectively. The spiro compound then rearranges to a bicyclo[5.3.0]-decatetraenylpalladium complex, dimerizes, and does an

Scheme V

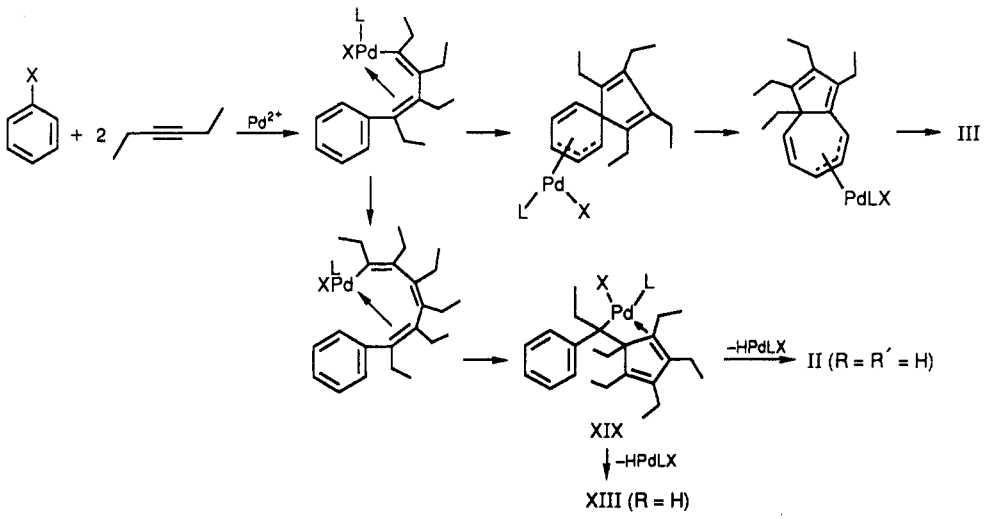


electrocyclic reaction to form the 4:2 complex as proposed before.[1] The 3:1 product is likely formed by the intramolecular addition of the vinylpalladium group in a cis,-cis,cis three-alkyne insertion product with the double bond next to the aromatic ring (Scheme VI).

2-Butyne, also, reacts easily with aryl iodides yielding only 3:1 type products (II) in high yield. Maitlis has reported the reaction of "phenylpalladium chloride" with 2-butyne at room temperature and obtained an interme-

(7) Heck, R. F. *Palladium Reagents in Organic Synthesis*, Academic Press: New York, 1985; pp 24–25.

Scheme VI



diate complex in which palladium hydride elimination has not occurred.[8] Pfeffer has reported a similar complex more recently.[9] Our variation causes decomposition of the palladium complex, and with an amine present the reaction becomes catalytic (eq 2, R″ = CH_3; III not formed).

Experimental Section

General Data. Palladium acetate and silver tetrafluoroborate were obtained from Strem Chemicals, Inc. Silver trifluoromethanesulfonate, dimethyl acetylenedicarboxylate, diphenylacetylene, and 2-butyne were products of Aldrich, while 3-hexyne was obtained from the Chem Samples Co. All were used as received.

Preparation of Product VIII (X = CF_3SO_3). A solution of 0.55 g (1 mmol) of IV (X = Cl, Z = H, Q = CH_3) in 25 mL of methylene chloride was added with stirring to a solution of 0.51 g (2 mmol) of silver trifluoromethanesulfonate dissolved in a mixture of 1.5 mL of acetonitrile and 15 mL of methylene chloride under nitrogen. After the solution was stirred for a few minutes, the precipitate of silver chloride was removed by filtration through Celite, the pale yellow filtrate was concentrated under reduced pressure to about 2 mL, and 30 mL of pentane was added. The green precipitate was separated by filtration and air-dried. The yield of green solid was 0.86 g (91%).

A solution of 0.47 g (1 mmol) of the above product and 0.40 g (2.2 mmol) of diphenylacetylene in 100 mL of chlorobenzene was stirred magnetically and heated to reflux for 3 h. After cooling, the solution was filtered throuth Celite to remove precipitated palladium metal and the filtrate was concentrated under reduced pressure. The residue was stirred with pentane; the precipitate was separated by filtration and recrystallized from methylene chloride by adding pentane. The product VIII [X = CF_3SO_3; 0.29 g (46%)], was obtained as yellow-orange needles, mp 120 °C dec. ^1H NMR ($CDCl_3$): δ 7.93–6.78 (m, 23 H), 5.86 (d, J = 7.7 Hz, 1 H), 4.20 (d, J = 13.6 Hz, 1 H), 3.90 (d, J = 13.6 Hz, 1 H), 2.66 (s, 3 H), 1.74 (s, 3 H).

The free base was obtained from VIII by dissolving 50 mg of the salt in a solution of 0.4 g of sodium acetate in 20 mL of methanol. After the solution was stirred for several minutes, the methanol was evaporated under reduced pressure and water was added to the residue. The insoluble product was separated by filtration and recrystallized from methylene chloride–hexane. The product [0.030 g (79%); mp 130–132 °C] was obtained as orange prisms. ^1H NMR ($CDCl_3$): δ 7.70–6.65 (m, 22 H), 6.18 (d, J = 7.7 Hz, 1 H), 3.32 (d, J = 14.2 Hz, 1 H), 3.23 (d, J = 14.2 Hz, 1 H), 2.02 (s, 6 H).

Complex V (X = Cl, Z = 5-CH_3O, R = CH_3O_2C). A solution of 0.22 g (0.40 mmol) of cyclopalladated *N,N*-dimethyl-3-methoxybenzylamine chloro dimer and 0.24 g (1.7 mmol) of dimethyl acetylenedicarboxylate in 60 mol of methylene chloride was stirred magnetically and heated at reflux temperature for 24 h. The solvent was then evaporated, and the crude product was chromatographed on silica gel. Ethyl acetate eluted the product. Recrystallization from acetone–pentane gave 0.16 g (62%) of yellow crystals of the product, mp 220 °C dec. The NMR spectrum appears in Table I.

Anal. Calcd for $C_{22}H_{26}NO_9ClPd$: C, 46.61; H, 4.85; N, 2.26. Found: C, 46.26; H, 4.83; N, 2.08.

Preparation of IX. A solution of 0.14 g (0.18 mmol) of cyclopalladated [(dimethylamino)methyl]ferrocene[10] and 60 mg (0.73 mmol) of 3-hexyne in 30 mL of methylene chloride was stirred and heated at reflux temperature for 24 h. Evaporation of the solvent and chromatography of the residue on silica gel gave 0.17 g (86%) of the product as orange crystals, mp 135–136 °C. The crystal structure of the complex is shown in Figure 2, and its NMR spectrum is given in Table I.

Reaction of VI with 3-Hexyne. A 50-mL stainless-steel bomb was charged with 0.50 g (1.2 mmol) of VI (X = BF_4), 0.22 g (2.8 mmol) of 3-hexyne, and 30 mL of chlorobenzene. The bomb was sealed, and the contents were stirred and heated to 150 °C for 24 h. After cooling, the bomb was opened and the reaction mixture was filtered through Celite to remove metallic palladium. The filtrate was evaporated to dryness under reduced pressure, and the residue was chromatographed on silica gel. Methylene chloride eluted the naphthalene derivative [0.088 g (20%)], and methylene chloride–methanol (98:2) eluted the 3:1 alkyne to ligand product: 0.044 g (11%); mp 125–126 °C. The ^1H NMR spectrum and melting point of the naphthalene salt were the same as reported previously.[1] The ^1H NMR spectrum of the 3:1 adduct in $CDCl_3$ was as follows: δ 7.3–6.9 (m, 4 H), 6.01 (q, J = 7.6 Hz, 1 H), 4.08 (d, J = 13.6 Hz, 1 H), 3.77 (d, J = 13.6 Hz, 1 H), 2.78 (s, 6 H), 2.20–1.78 (m, 10 H), 1.47 (d, J = 7.2, 3 H), 1.12 (t, J = 7.3 Hz, 3 H), 0.93 (t, J = 7.3 Hz, 3 H), 0.85 (t, J = 7 Hz, 3 H), 0.74 (t, J = 7.3 Hz, 3 H), 0.50 (t, J = 7.3 Hz, 3 H).

Addition of Carbon Monoxide to V. In a 50-mL stainless-steel bomb were placed 0.56 g (1.27 mmol) of V (R = C_2H_5, Q = CH_3, X = Cl, Z = H) and 20 mL of methanol. The bomb was sealed, flushed with carbon monoxide, and finally pressured to 25 psi with carbon monoxide. The solution was then stirred at 50 °C for 20 h. After cooling, the bomb was opened and the solution was filtered to remove some palladium metal. The filtrate was concentrated under reduced pressure. The residue was dissolved in a minimum of methylene chloride, and pentane was added. After standing overnight yellow crystals separated. The crystals were removed by filtration and air-dried to give 0.19 g (32%) of product, mp 170 °C dec. Anal. Calcd for $C_{22}H_{32}NOClPd$:

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C, 56.42; H, 6.89; N, 2.99. Found: C, 56.55; H, 6.95; N, 2.90.

The crystal structure of this complex is shown Figure 3. Heating the carbonyl complex to 100 °C under 100 psi of carbon monoxide resulted in decomposition of the complex into at least three new products. These were not investigated further.

Methyl 5,6,7,8-Tetraphenyl-2-naphthalenecarboxylate. In a 20-mL heavy-walled Pyrex tube were placed a magnetic stirring bar, 1.31 g (5 mmol) of methyl *p*-iodobenzoate, 1.96 g (11 mmol) of diphenylacetylene, 0.023 g (0.10 mmol) of palladium acetate, 0.032 g (0.02 mmol) of triphenylphosphine, 2 mL of triethylamine, and 3 mL of nitromethane. The tube was capped and the contents were warmed and shaken until the solution was homogeneous. The yellow solution was then heated with stirring at 100 °C (steam bath) for 26 h at which time GLC of the reaction mixture indicated that all of the methyl *o*-iodobenzoate had reacted. After cooling, the tube was opened and the contents were rinsed into a flask with methylene chloride. The mixture was evaporated to dryness under reduced pressure, and the residue was chromatographed on silica gel. Methylene chloride–hexane (1:20) eluted the product. Two recrystallizations from methylene chloride–hexane gave 33% of colorless crystals: mp 291–292 °C; mol wt calcd for $C_{36}H_{26}O_2$, 490.193, found (HRMS) 490.191.

A similar reaction carried out with 3 mL of triethylamine in place of the nitromethane (5 mL total) yielded 26% of the product. ^1H NMR spectrum ($CDCl_3$): δ 8.42 (d, J = 1.7 Hz, 1 H), 7.97 (dd, J = 1.7, 8.4 Hz, 1 H), 7.70 (d, J = 8.4 Hz, 1 H), 7.2–7.3 (m, 10 H), 6.81–6.87 (m, 10 H), 3.85 (s, 3 H).

3,4-Diphenylisocoumarin. A mixture of 0.011 g (0.05 mmol) of palladium acetate, 0.0265 g (0.1 mmol) of tri-*o*-tolylphosphine, 0.98 g (5.5 mmol) of diphenylacetylene, 0.615 g (2.5 mmol) of methyl *o*-iodobenzoate, 0.01 mL (0.73 mmol) of triethylamine, 0.21 g (2.5 mmol) of anhydrous sodium acetate, and 5 mL of dimethylformamide (dried with molecular sieves) was prepared in a 20-mL, heavy-walled Pyrex tube. A magnetic stirring bar was added, and the tube was capped. The mixture was shaken until homogeneous and then heated in an oil bath at 100 °C with magnetic stirring. After 40 h the mixture was cooled and rinsed into a separatory funnel with ether and water. The ether extracts were separated, washed three times with water, dried over $MgSO_4$, and concentrated to an oil under reduced pressure. The residue was chromatographed on 30 g of alumina. The product was recrystallized from hexane–ethyl acetate. The yield of yellow needles [mp 168.5–170 °C (reported 169 °C[11])] was 56%. ^1H NMR: 8.4 (dd, J = 7.9, 1.2 Hz, 1 H), 7.65 (t, J = 7.6 Hz, 1 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.44–7.04 ppm (m, 11 H). ^{13}C-NMR: 162.2, 150.9, 138.8, 134.6, 134.3, 132.9, 131.2, 130.0, 129.5, 129.2, 129.0, 128.9, 128.8, 128.5, 128.1, 128.05, 127.8, 125.3, 120.5, 116.9 ppm. HRMS: found, 298.10; calcd, 298.10.

Also prepared by the same procedure were the following: 3,4-di-*p*-anisylisocoumarin (HRMS: found, 358.12; calcd 358.12), pink needles, mp 156.5–158 °C; 3-*n*-butyl-4-phenylisocoumarin (HRMS: found, 278.13; calcd, 278.13), yellow liquid; and 7-nitro-3,4-diphenylisocoumarin (HRMS: found, 343.08; calcd, 343.08), bright yellow needles, mp 192–193 °C.

General Procedure for the Prepration of Type II and III Products. A mixture of 5.0 mmol of the aryl iodide (or bromide), 1.40 g (17 mmol) of 3-hexyne, 0.11 g (0.5 mmol) of palladium acetate, 0.30 g (1 mmol) of tri-*o*-tolylphosphine, and 5 mL of triethylamine was placed in a 20-mL heavy-walled Pyrex tube with a magnetic stirring bar. The tube was capped and shaken with warming until it was homogeneous. It was then stirred and heated at 100° (steam bath) until GLC analyses of the reaction mixture showed that the aryl iodide had all reacted. The mixture was cooled, the tube was opened, and the products were rinsed into a separatory funnel with water and methylene chloride. The organic layer was separated, washed twice with water, and dried with anhydrous magnesium sulfate. The solution was filtered and concentrated under reduced pressure, and the residue was chromatographed on silica gel. Hexane or hexane–methylene chloride (4:1) eluted the products. The solvent was removed under reduced pressure, the residue was dissolved in a few milliliters of methanol, and the solution was placed in a freezer overnight. The colorless crystals of III that formed were separated by filtration. Concentration of the mother liquor and cooling again in the freezer gave II. The rearranged isomers of II (eq 11) remained in the mother liquors and could be separated by preparative GLC.

Reaction of Methyl *o*-Iodobenzoate with 3-Hexyne. A mixture of 1.31 g (5 mmol) of methyl *o*-iodobenzoate, 1.54 g (18 mmol) of 3-hexyne, 0.115 g (0.50 mmol) of palladium acetate, 0.30 g (1.00 mmol) of tri-*o*-tolylphosphine, and 8 mL of triethylamine was placed in a 20-mL heavy-walled Pyrex tube with a magnetic stirring bar. The tube was capped and stirred in a 100 °C bath for 2 days. After the tube was cooled, the contents of the tube were rinsed into a separatory funnel with water and methylene chloride. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated under reduced pressure. The residue was chromatographed an silica gel. The naphthalenecarboxylate product, the allene XVII, and the ethylidenecyclobutene product XVIII were eluted together with hexane–methylene chloride (9:1), and they were separated by preparative GLC. Yields were estimated by use of an internal standard. The approximate yields were 5%, 4%, and 1%, respectively. The dimeric diester XVI was eluted from the chromatography column with hexane–methylene chloride (1:1). Concentration of the elutate gave XVI as a viscous red liquid. The NMR spectra and observed molecular weights of these products appear in Table IV.

Reaction of *o*-Iodoanisole with 3-Hexyne. This reaction was carried out as in the methyl *o*-iodobenzoate example above employing *o*-iodoanisole in place of the benzoate ester. Chromatography of the products on silica gel separated the naphthalene product and the triene XV from the tetracyclic compound XIV. The yields of the three (liquid) products were 5%, 4%, and 26%, respectively. The NMR spectra and other physical data are given in Table IV.

Reaction of Aryl Iodides with 2-Butyne. A 60-mL stainless-steel bomb was charged with 0.11 g (0.5 mmol) of palladium acetate, 0.30 g (1.0 mmol) of tri-*o*-tolylphosphine, and 5.0 mmol of the aryl iodide. A magnetic stirring bar was added; the bomb was stoppered and cooled in a dry ice–acetone bath. Then, 5 mL of precooled triethylamine was added followed by 1.3 mL (0.92 g, 17 mmol) of cold 2-butyne, and the bomb was sealed. The contents were stirred at room temperature for a few minutes and at 100 °C in a steam bath for 30 h. The bomb was cooled, vented, and opened. The residue was rinsed into a separatory funnel with the aid of some ether. The organic phase was separated, washed twice with water, and dried ($MgSO_4$). The solution was filtered, concentrated, and chromatographed on silica gel. Hexane eluted tri-*o*-tolylphosphine first and then the 3:1 products II (R = OCH_3 or CO_2CH_3, R = H, R′ = CH_3, R″ = H). The liquid products were quite pure as isolated judging by their ^1H NMR spectra. The data are given in Table II. No other products could be removed from the chromatography columns.

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Supplementary Material Available: Figures 4 and 5 showing structures of 6-methyl-1,2,3,4-tetraphenylnaphthalene and the "2:4 iodobenzene to 3-hexynes product", respectively, Table V giving crystallographic data for the five structures reported in this paper, and Tables 1a–6a, 1b–6b, 1c–6c, and 1d–6d giving atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates, respectively, for the five structures (35 pages); Tables 1e–6e giving observed and calculated structure factors for the five structures (81 pages). Ordering information is given on any current masthead page.

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