Palladium-Catalyzed Annelation of Aryl Iodides with Diphenylacetylene

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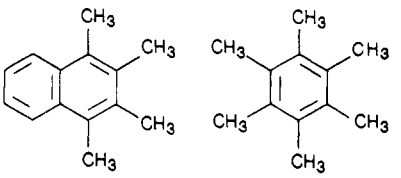
Cyclopalladated *N,N*-dimethylbenzylamine tetrafluoroborate and *N-tert*-butylbenzalimine tetrafluoroborate with 3-hexyne form 1,2,3,4-tetraethylnaphthalene derivatives. Similar reactions between aryl iodides and diphenylacetylene form 1,2,3,4-tetraphenylnaphthalene derivatives. The reactions between iodobenzene, 4-iodotoluene, and 3- or 4-iodoanisole and diphenylacetylene occur catalytically in the presence of triethylamine in 22–50% yields. 3-Hexyne and iodobenzene produce a 3:1 alkyne to aryl iodide adduct, while iodoanisole and 3-hexyne give a hexacyclic 4:2 alkyne to aryl iodide complex.

A few reports of the formation of naphthalene derivatives from aryl metal complexes have appeared in the literature. For example, Zeiss[1] reported the formation of 1,2,3,4-tetramethylnaphthalene in 38% yield (along with 58% of hexamethylbenzene) from the reaction of 2-butyne with triphenylchromium (eq 1). A mechanism involving a benzochromacyclopentadiene intermediate has been proposed.[2]

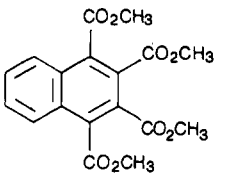
$$(C_6H_5)_3Cr \cdot 3THF + 2CH_3C{\equiv}CCH_3 \longrightarrow$$



(1)

In a more recent example, Sakakibara[3] has found that palladium promotes the annelation of a benzene–iodobenzene mixture with dimethyl acetylenedicarboxylate in the presence of *N,N*-dimethylaniline to form a 43% yield of tetramethyl 1,2,3,4-naphthalenetetracarboxylate (eq 2).

$$C_6H_5I + C_6H_6 + CH_3O_2CC{\equiv}CCO_2CH_3 \xrightarrow[4\text{-}CH_3C_6H_4NHCH_3]{Pd(OAc)_2,\ Et_3N,\ PPh_3,\ HOAc}$$



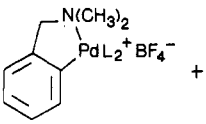
(2)

A radical mechanism was proposed.

We recently have observed[4] some related reactions between other alkynes and organopalladium derivatives, which appear to occur by a different mechanism.

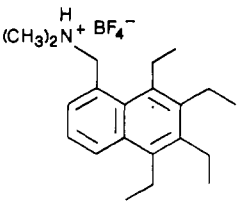
Results and Discussion

We first observed annelations to form naphthalene derivatives while studying the reactions of various cyclopalladated aromatic derivatives with disubstituted acetylenes.[4] Cyclopalladated *N,N*-dimethylbenzylamine tetrafluoroborate and 3-hexyne produce a 55% yield of 1,2,3,4-tetraethyl-5-[(dimethylammonio)methyl]-naphthalene tetrafluoroborate (eq 3).[4] The product structure was established by X-ray crystallography. Although the structure was of low quality, there is no question that it is correct since ^1H and ^{13}C NMR and analytic data are consistent with it.



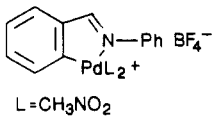
$+ 2C_2H_5C{\equiv}CC_2H_5 \xrightarrow{25\ °C}$

$L = CH_3NO_2$



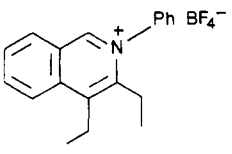
$+ Pd + 2L$ (3)

Cyclopallated benzalimine salts exhibit various behaviors depending upon the N substituent present. The *N*-methyl,[5] *N*-benzyl,[4] *N*-*o*-tolyl,[4] and *N*-phenyl[5] derivatives with 3-hexyne give predominantly monoalkyne insertion products, i.e. isoquinolinium salts (eq 4). The *N-tert*-butylbenzalimine complex, however, gave a mixture of a naphthalene derivative (22%) and a 3:1 3-hexyne to palladium complex adduct (5%) at 25 °C (eq 5). At 100 °C with slow addition of 3-hexyne, no monoalkyne insertion product was detected, but with diphenylacetylene under these conditions, a 22% yield of 3,4-diphenylisoquinoline was obtained[5] The low yield is partly due to a competitive



$+ C_2H_5C{\equiv}CC_2H_5 \xrightarrow{25\ °C}$

$L = CH_3NO_2$



$+ Pd + L_2$ (4)

80%

(1) Herwig, W.; Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 6203.
(2) Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1970**, *92*, 5625.
(3) Sakakibara, T.; Tanaka, Y.; Yamasaki, S.-I. *Chem. Lett.* **1986**, 797.
(4) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *5*, 1922.
(5) Wu, G.; Heck, R. F., unpublished results.

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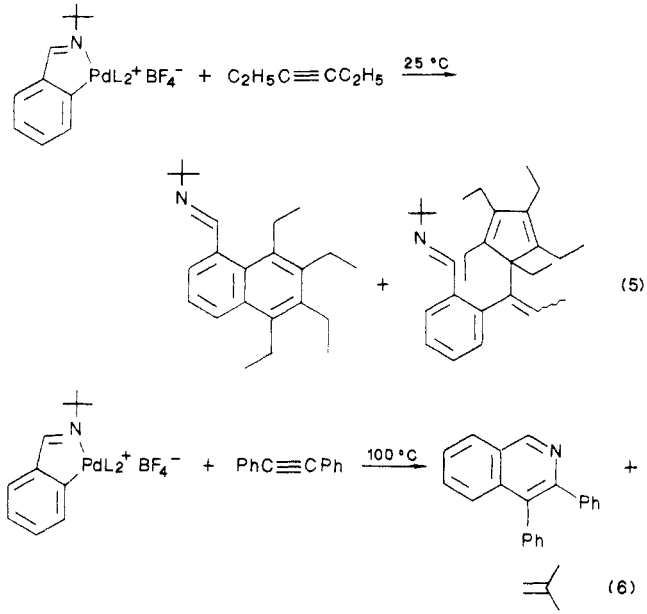


(5)

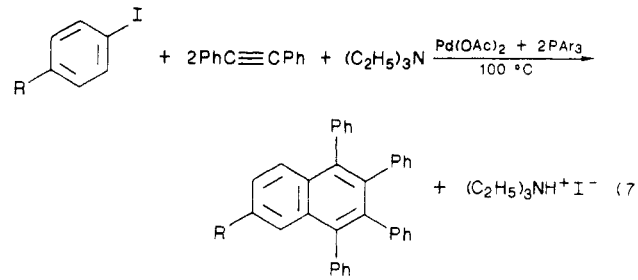
(6)

decomposition of the palladium complex under the reaction conditions. In a separate experiment, however, no pure products could be isolated from the thermal decomposition of the isolated complex.

The formation of the various alkyne adducts is readily explained on the basis of the stepwise insertion of alkyne units into the palladium–carbon bond of the complexes giving 1:1, 2:1, and 3:1 complexes (see Scheme I). Products may be formed from any of the intermediates depending upon the relative rates of further alkyne insertion compared with rates of product formation from the adducts (i.e. k_2 vs. k_1, k_4 vs. k_3 or k_6 vs. k_5). One to one and two to one alkyne to palladium complex adducts have been reported by Pfeffer[6] and Maitlis[7,8] while we have isolated a 3:1 adduct. The 3:1 adduct was obtained from cyclopalladated 8-methylquinoline tetrafluoroborate and 3-hexyne. The structure was established by X-ray crystallography.[9] Pure complexes with more than three alkyne units per palladium have not been isolated but are believed to be the major components of the amorphous side products found. The reactions believed to be involved are shown in Scheme I, illustrated with the *N,N*-dimethylbenzylamine complex. All of the reactions are not observed with any one cyclopalladated complex but are presumably possible.

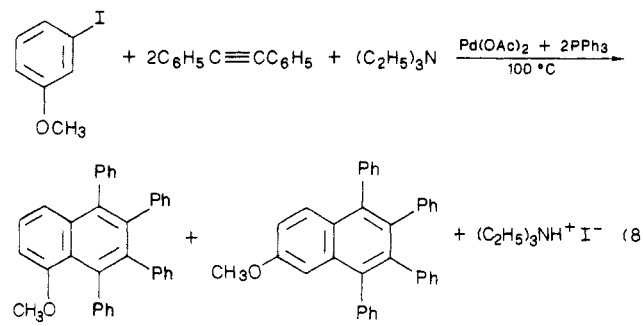
The behavior of the *N-tert*-butylimine complex is also understandable with Scheme I. The bulky *tert*-butyl group inhibits reaction k_1 so that in the presence of excess alkyne the 2:1 and 3:1 adducts are formed and both give isolable complexes. At elevated temperatures, with a limited amount of alkyne (diphenylacetylene), path k_1 can be made the main path and the 1:1 adduct is formed. Presumably, the *N-tert*-butyl group (cation) is lost to relieve the strain resulting from interaction of the *N-tert*-butyl group with the 3-phenyl substituent.

The next question to be answered was whether the formation of the 2:1 naphthalene product could be achieved without the chelating group being present as had been achieved, as noted above, by Zeiss[1] and Sakakibara (by probably different mechanisms). We found that the chelating group was not necessary for the formation of naphthalene derivatives from iodobenzene, 4-iodotoluene, 3- and 4-iodoanisoles, and diphenylacetylene. In the presence of triethylamine at 100 °C the reactions were catalytic with respect to bis(acetato)bis(triarylphosphine)palladium (eq 7). Yields of the tetraphenylnaphthalene products were 22–50%. The results are summarized in Table I.



(7)

3-Iodoanisole gave 34% of a 2:3 mixture of 5-methoxy- and 6-methoxy-1,2,3,4-tetraphenylnaphthalenes resulting from ring closure at the para and at the ortho positions, respectively (eq 8).



(8)

The naphthalene products were most easily purified when they were formed in nitromethane. We normally did our reactions in capped Pyrex tubes. This procedure proved to be convenient on a small scale but not completely safe since after about 24 h at 100 °C the mixtures began to evolve gas and build up pressure. Since most of our reactions were complete in about 24 h, this generally was not a problem. However, we suggest employing open systems if possible. In the case of 4-iodotoluene, similar yields were obtained in an open system and in a capped tube.

Our results suggest that tri-*o*-tolylphosphine gives higher product yields than triphenylphosphine and that yields increase as the catalyst concentrations are increased from 2% to at least 10%. *p*-Nitroiodobenzene, *o*-iodoaniline, *p*-iodo-*N,N*-dimethylaniline, and 2-iodo-1,4-dimethoxybenzene with diphenylacetylene gave complex product mixtures and we were unable to isolate pure products from any of these. Likewise, 2-iodothiophene and benzyl bromide gave intractable product mixtures. Aryl bromides were very unreactive toward diphenylacetylene. *cis*-2-Bromostyrene, on the other hand, gave a different type of product.

The reaction of *cis*-2-bromostyrene (85% cis) with diphenylacetylene and triethylamine with a catalytic amount (2%) of the palladium acetate–triphenylphosphine catalyst at 100 °C produced 27% of 1,2,3,4,6-pentaphenylfulvene (45% based on alkyne consumed) as the only isolatable product. The structure was established by X-ray crystallography.[9] A mechanism involving insertion of two alkyne units into the styrylpalladium bromide followed by an internal addition of the vinylpalladium group to the styrene double bond and a final palladium hydride elimination explains the formation of the product (eq 9 and

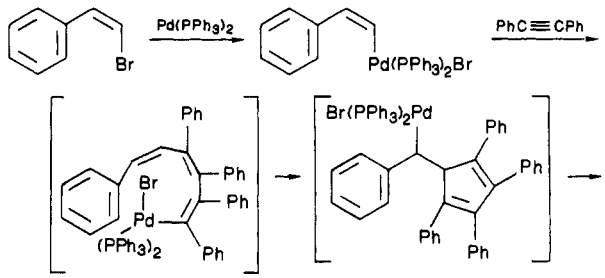
(6) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.
(7) Calvo, C.; Hosokawa, T.; Reinheimer, H.; Maitlis, P. M. *J. Am. Chem. Soc.* **1973**, *95*, 4914.
(8) Hosokawa, T.; Calvo, C.; Lee, H. B.; Maitlis, P. M. *J. Am. Chem. Soc.* **1973**, *95*, 4924.
(9) Rheingold, A. L., manuscript in preparation.

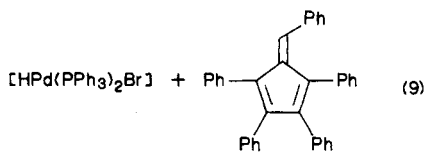
Table I. Formation of 1,2,3,4-Tetraphenylnaphthalene Derivatives from Aryl Iodides[a]

aryl iodide	catalyst	solvent	conditions	product (% yield)
C_6H_5I	2% $Pd(OAc)_2$, 4% PPh_3	CH_3NO_2	41 h, 100 °C	1,2,3,4-tetraphenylnaphthalene (47)
4-$CH_3C_6H_4I$	2% $Pd(OAc)_2$, 4% PPh_3	CH_3NO_2	22 h, 100 °C	6-methyl-1,2,3,4-tetraphenylnaphthalene (22)
4-$CH_3C_6H_4I$	4% $Pd(OAc)_2$, 8% P(*o*-tol)$_3$	CH_3NO_2	30 h, 100 °C	6-methyl-1,2,3,4-tetraphenylnaphthalene (36)[b]
4-$CH_3C_6H_4I$	4% $Pd(OAc)_2$, 8% P(*o*-tol)$_3$	CH_3NO_2	72 h, ~95 °C[c]	6-methyl-1,2,3,4-tetraphenylnaphthalene (29)[d]
3-$CH_3OC_6H_4I$	2% $Pd(OAc)_2$, 4% PPh_3	CH_3NO_2	28 h, 100 °C	5-methoxy-1,2,3,4-tetraphenylnaphthalene (13) 6-methoxy-1,2,3,4-tetraphenylnaphthalene (21)
4-$CH_3OC_6H_4I$	2% $Pd(OAc)_2$, 4% PPh_3	CH_3NO_2	45 h, 100 °C	6-methoxy-1,2,3,4-tetraphenylnaphthalene (30)
4-$CH_3OC_6H_4I$	2% $Pd(OAc)_2$, 4% PPh_3	CH_3CN	17 h, 100 °C	6-methoxy-1,2,3,4-tetraphenylnaphthalene (12)
4-$CH_3OC_6H_4I$	2% $Pd(OAc)_2$, 4% P(*o*-tol)$_3$	CH_3CN	18 h, 100 °C	6-methoxy-1,2,3,4-tetraphenylnaphthalene (26)
4-$CH_3OC_6H_4I$	10% $Pd(OAc)_2$, 20% P(*o*-tol)$_3$	$(C_2H_5)_3N$	18 h, 100 °C	6-methoxy-1,2,3,4-tetraphenylnaphthalene (50)
4-$CH_3OC_6H_4I$	5% $Pd(OAc)_2$, 10% P(*o*-tol)$_3$	CH_3NO_2	24 h, 100 °C	6-methoxy-1,2,3,4-tetraphenylnaphthalene (38)

[a] Carried out with 5 mm of aryl iodide, 11 mm of diphenylacetylene, 14 mm of triethylamine, and 3 mL of solvent in capped Pyrex tubes. [b] The yield was 52% based upon the 4-iodotoluene which reacted. [c] Solution was heated at reflux temperature in an oil bath. [d] The yield was 48% based upon reacted 4-iodotoluene.

10). This may be a useful synthesis of some fulvene derivatives since in this case, at least, the synthesis is much shorter than a recently reported method.[10]



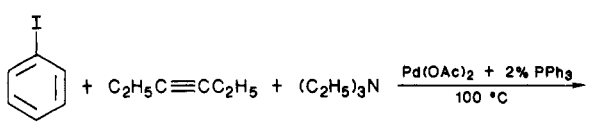


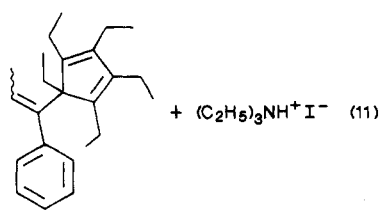
(9)

$$HPd(PPh_3)_2Br + (C_2H_5)_3N \rightarrow Pd(PPh_3)_2 + (C_2H_5)_3NH^+Br^- \quad (10)$$

Attempts to form naphthalene derivatives from aryl iodides and acetylenes other than diphenylacetylene were not successful. Dimethyl acetylenedicarboxylate polymerized under the reaction conditions. 3-Phenylpropargyl aldehyde diethyl acetal gave complex mixtures of products while 3-hexyne gave different products.

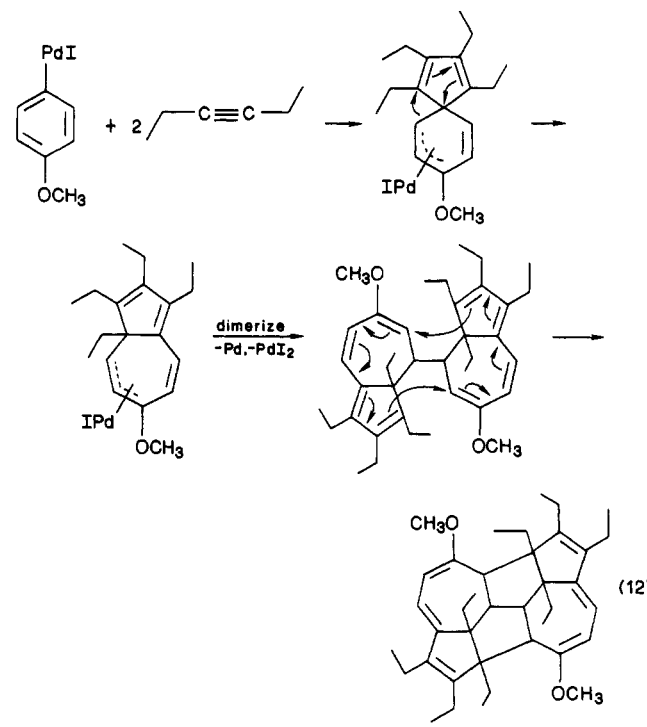
Iodobenzene, 3-hexyne, and triethylamine with a palladium acetate–triphenylphosphine catalyst at 100 °C gave 47% of a 3:1 alkyne to palladium complex which proved to be analogous to the 3:1 product from the *N-tert*-butylbenzalimine complex–3-hexyne reaction described above (eq 11).





(11)

A more complex reaction occurred when 4-iodoanisole was reacted with 3-hexyne under the above conditions. A 5% yield of a crystalline, hexane-soluble, four alkyne to two anisole unit product was isolated. The structure of the product, shown in Figure 1 (supplementary material), was established by X-ray crystallography[9] and NMR. The formation of this product may be explained by a mechanism involving an initial insertion of two alkyne units into the carbon palladium bond of the 4-anisylpalladium iodide complex. A ring closure to the spiro-π-allylic palladium complex follows. In this case, however, the spiro complex apparently rearranges to a [5.3.0]bicyclodecane rather than a substituted naphthalene as seen in other examples. The bicyclic palladium complex then forms a symmetrical dimer by loss of palladium iodide, and finally the dimer undergoes an electrocyclization to produce the observed product (eq 12).



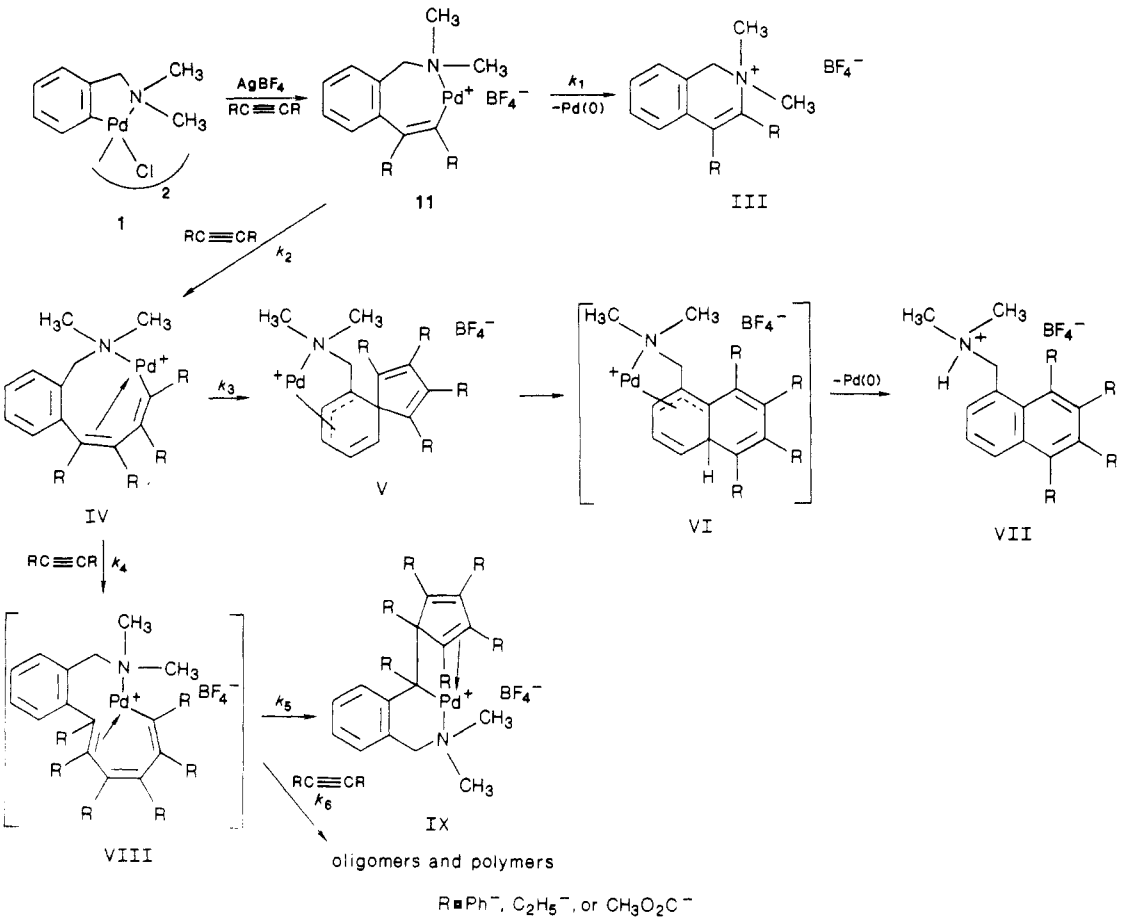
(12)

The low isolated yield of this product is at least partly due to its high solubility in organic solvents causing losses in the purification. Major side products are amorphous oligomers as are found in all of our reactions involving alkynes.

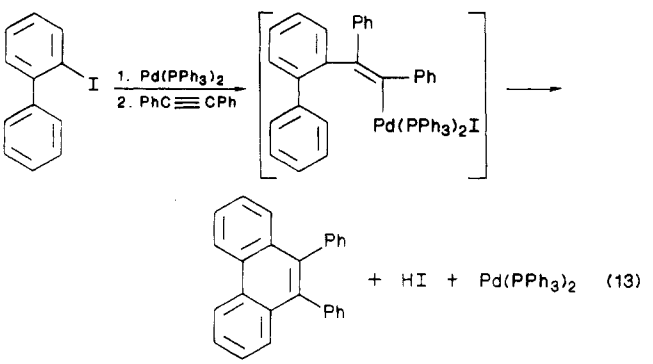
It occurred to us that if our mechanism of cyclization to the naphthalene derivatives is correct that similar cyclizations might occur if other 4-arylbutadienyl or butenyl type palladium derivatives were formed. As noted above, however, *cis*-β-bromostyrene preferred to form a 2:1 alkyne to Pd complex, a fulvene with diphenylacetylene rather

(10) Sekiguchi, A.; Tanikawa, H.; Ando, W. *Organometallics* **1985**, *4*, 584.

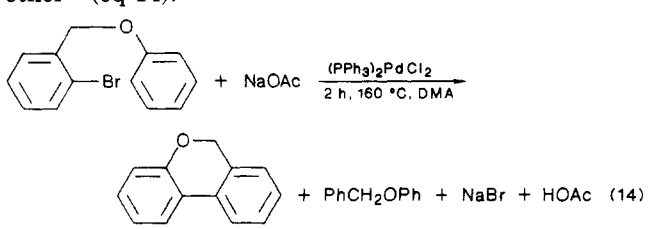
Scheme I. Possible Reactions of Alkynes with Cyclopalladated Complexes



than the cyclized 1:1 adduct, 1,2-diphenylnaphthalene. 2-Iodobiphenyl and diphenylacetylene did form the 1:1 product 9,10-diphenylphenanthrene but only in 14% yield (eq 13).



Several examples of the (presumed similar) cyclization of *o*-bromobenzyl and *o*-bromoaryl phenyl ethers as well as related amines with palladium catalysts have been reported.[11] For example, *o*-bromophenyl phenyl ether gives 36% of the cyclic product along with 35% of benzyl phenyl ether[11] (eq 14).



(11) Ames, D. E.; Opalko, A. *Tetrahedron* **1984**, *40*, 1919.

Unfortunately, the yields of tetraphenylnaphthalenes by our procedure are only modest and the reaction appears to be limited to a few simple aryl iodides. The procedure, however, is simple and may be of synthetic value in cases where the benzyne–tetraphenylcyclopentadienone method is not convenient or not successful.[12]

Experimental Section

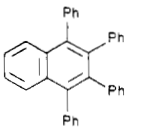
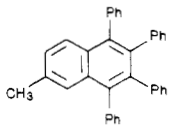
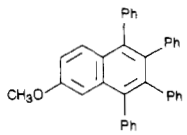
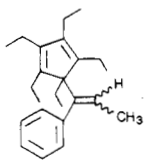
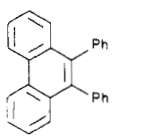
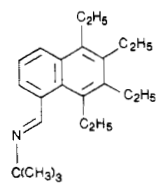
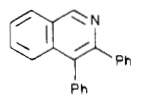
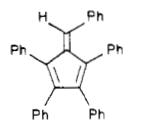
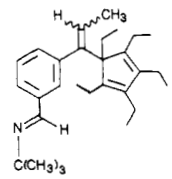
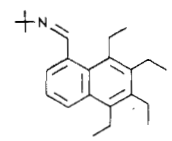
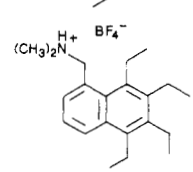
Chemical Sources. Palladium chloride, palladium acetate and silver tetrafluoroborate were purchased from Strem Chemical, Inc., and were used without further purification. Triphenylphosphine, 4-iodoanisole, 3-iodoanisole, 4-iodotoluene, iodobenzene, diphenylacetylene, benzaldehyde, methylamine, dimethylamine, and *N-tert*-butylamine were obtained from the Aldrich Chemical Co. 3-Hexyne (Chem Samp Co.), 2-iodobiphenyl (Pfaltz & Bauer, Inc.), acetonitrile (Baker), nitromethane (Fisher), and triethylamine (Fisher) were, also, commercial samples used as received, except for the last three chemicals which were dried over 4-Å molecular sieves before use.

Bis(μ-chloro)bis[α-(dimethylamino)-*o*-tolyl]dipalladium-(II) was prepared (97%) as described by Cope.[13]

Reaction of Bis(μ-chloro)bis[2-(dimethylamino)-*o*-tolyl]dipalladium(II) with 3-Hexyne. A 15-mL pressure tube was charged with 0.569 g (1.0 mm) of the palladium complex and 0.429 g (2.1 mmol) of silver tetrafluoroborate. A magnetic stirring bar was added and the tube was capped under nitrogen with a rubber-lined metal cap with a small hole in it through which syringe needles could be injected. Then 3 mL of dry nitromethane was injected into the tube. The color of the solution changed from yellow to brown. The addition of 0.44 g (5.0 mmol) of 3-hexyne

(12) Friedman, L.; Logullo, F. *J. Am. Chem. Soc.* **1963**, *85*, 1549; *J. Org. Chem.* **1969**, *34*, 3089.
(13) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

Table II. The ^1H NMR and ^{13}C NMR Spectra of the Compounds Prepared

structure	^1H NMR ($CDCl_3$, ppm)	^{13}C NMR ($CDCl_3$, ppm)
	7.64 (dd, J = 6.50, 3.4 Hz, 2 H), 7.37 (dd, J = 6.5, 3.4 Hz, 2 H), 7.23–7.18 (m, 10 H), 6.85–6.82 (m, 8)	140.5 (s), 139.6 (s), 138.8 (s), 138.4 (s), 132.0 (s), 131.3 (d, 2C), 127.5 (d), 126.9 (d), 126.5 (d), 126.4 (d), 125.8 (d), 125.3 (d)
	7.54 (d, J = 8.6 Hz, 1 H), 7.40 (bs, 1 H), 7.27–7.14 (m, 12 H), 7.07 (d, J = 8.6 Hz, 1 H), 6.89–6.75 (m, 8 H), 2.37 (s, 3 H, CH_3)	140.6, 140.5, 138.7, 138.9, 138.4, 138.2, 137.9, 137.7, 136.4, 135.7, 135.5, 132.1, 131.9, 131.3, 131.26, 131.24, 131.1, 130.3, 128.2, 128.0, 127.5, 126.9, 126.5, 126.3, 125.8, 125.2, 21.8 (CH_3)
	7.55 (d, J = 9.2 Hz, 1 H), 7.24–7.16 (m, 12 H), 7.06 (dd, J = 9.2, 2.6 Hz, 1 H), 6.95 (d, J = 2.6 Hz, 1 H), 6.83 (m, 8 H), 3.68 (s, 3 H, CH_3O)	157.5 (s), 140.7 (s), 140.5 (s), 139.8 (s), 139.7 (s), 139.4 (s), 139.3 (s), 137.2 (s), 136.7 (s), 133.2 (d), 131.4 (d), 131.2 (d), 131.1 (d), 128.6 (d), 127.6 (d), 127.4 (d), 126.4 (d), 126.3 (d), 125.2 (d), 125.1 (d), 117.9 (d), 105.6 (d), 55.1 (q)
	7.07–7.02 (m, 3 H), 6.81–6.77 (m, 2 H), 5.73 (q, J = 6.7 Hz, 1 H, CH=C), 2.18–2.00 (m, 8 H, $4CH_2$), 1.83 (q, J = 7.2 Hz, CH_2), 1.44 (d, J = 6.7 Hz, 3 H, CH_3CH=C), 1.04 (t, J = 7.6 Hz, 6 H, $2CH_3$), 0.71 (t, J = 7.5 Hz, 6 H, $2CH_3$), 0.71 (t, J = 7.5 Hz, 6 H, $2CH_3$), 0.52 (t, J = 7.2 Hz, CH_3)	144.3 (s), 144.0 (s), 142.0 (s), 139.5 (s), 128.5 (d), 126.3 (d), 125.7 (d), 121.5 (d), 67.5 (s), 22.5 (t), 19.5 (t), 18.7 (t), 15.2 (q), 14.1 (q), 13.6 (q), 0.8 (q)
	8.79 (d, J = 8.2 Hz, 2 H), 7.65 (ddd, J = 8.3, 6.7, 1.6 Hz, 2 H), 7.56 (dd, J = 8.2, 1.2 Hz, 2 H), 7.47 (ddd, J = 8.3, 6.7, 1.2 Hz, 2 H), 7.27–7.13 (m, 10 H)	139.5 (s), 137.2 (s), 131.8 (d), 131.0 (d), 129.9 (s), 127.8 (d), 127.6 (d), 126.6 (d), 126.4 (d), 126.3 (d), 122.5 (d)
	9.29 (s, 1 H, CH=N), 8.38 (d, J = 8.3 Hz, 1 H), 7.95 (d, J = 7.3 Hz, 1 H), 7.56 (dd, J = 8.3, 7.3 Hz, 1 H), 3.11 (q, J = 7.4 Hz, 2 H, CH_2), 2.90 (m, J = 7.5 Hz, 6 H, $3CH_2$), 1.70 (s, 9 H, $(CH_3)_3N$), 1.42 (t, J = 7.4 Hz, 3 H, CH_3), 1.35–1.20 (m, 9 H, $3CH_3$)	143.8 (s), 140.3 (s), 138.3 (s), 133.9 (d), 133.2 (s), 132.4 (d), 130.6 (s), 124.2 (s), 125.0 (d), 61.9 (s), 27.8 (q), 26.2 (t), 23.0 (t), 22.8 (t), 22.2 (t), 16.8 (q), 16.5 (q), 16.4 (q), 16.2 (q)
	9.37 (d, J = 0.7 Hz, 1 H, CH=N), 8.05–8.00 (m, 1 H), 7.69–7.55 (m, 3 H), 7.41–7.28 (m, 5 H), 7.27–7.14 (m, 5 H)	151.8 (d, CH=N), 150.7 (s), 140.8 (s), 137.3 (s), 135.9 (s), 131.2 (d), 130.6 (s), 130.5 (d), 130.3 (d), 128.3 (d), 127.6 (d), 127.5 (d), 127.4 (s), 127.3 (d), 127.0 (d), 126.8 (d), 125.6 (d)
	7.42 (s, 1 H, C=CHPh), 7.28–7.23 (m, 3 H), 7.04–6.77 (m, 22 H)	145.9, 144.3, 141.7, 141.3, 141.2, 136.6, 136.1, 135.6, 135.3, 135.2, 131.6, 131.1, 130.8, 130.5, 130.4, 130.3, 127.7, 127.6, 127.3, 127.2, 127.1, 127.0, 126.5, 126.3, 126.2, 125.4
	7.70 (d, 1 H), 7.10–7.09 (m, 3 H), 4.72 (bs, 1 H), 2.50 (bs, 3 H, CH_3), 2.45–2.28 (m, 4 H, $2CH_2$), 2.26–1.85 (m, 6 H, $3CH_2$), 1.32 (s, 9 H, $(CH_3)_3N$), 1.18 (t, J = 7.4 Hz, 3 H, CH_3), 1.09 (t, J = 7.6 Hz, 3 H, CH_3), 0.87 (t, J = 7.6 Hz, 3 H, CH_3), 0.63 (t, J = 7.6 Hz, 3 H, CH_3), 0.42 (t, J = 6.9 Hz, 3 H, CH_3)	144.8, 144.0, 143.9, 143.8, 143.4, 142.4, 135.7, 133.7, 128.9, 125.5, 123.6, 123.5, 66.2, 65.3, 62.4, 28.1 (q), 25.9 (q), 19.5 (t), 19.3 (t), 19.0 (t), 18.8 (t), 15.5 (t), 14.5 (q), 14.2 (q), 13.5 (q), 13.3 (q), 6.6 (q)
	9.29 (s, 1 H, CH=N), 8.38 (d, J = 8.3 Hz, 1 H), 7.95 (d, J = 7.3 Hz, 1 H), 7.56 (dd, J = 8.3, 7.3 Hz, 1 H), 3.11 (q, J = 7.4 Hz, 2 H, CH_2), 2.90 (m, J = 7.5 Hz, 6 H, $3CH_2$), 1.70 (s, 9 H, $3CH_3$), 1.42 (t, J = 7.4 Hz, 3 H, CH_3), 1.35–1.20 (m, 9 H, $3CH_3$)	143.8 (s), 143.0 (s), 138.3 (s), 133.9 (d), 133.2 (s), 132.4 (d), 130.6 (s), 124.2 (s), 125.0 (d), 61.9 (s), 27.8 (q), 26.2 (t), 23.0 (t), 22.8 (t), 22.2 (t), 16.8, 16.5 (q), 16.4 (q), 16.2 (q)
	8.18 (d, J = 8.7 Hz, 1 H), 7.56–7.39 (m, 3 H), 4.85 (bs, 2 H, CH_2–N), 3.14–3.05 (m, 4 H, $2CH_2$), 2.94–2.80 (m, 4 H, $2CH_2$), 2.73 (s, 6 H, $(CH_3)_2N$), 1.34–1.16 (m, 12 H, $4CH_3$)	142.3, 139.1, 137.0, 133.8, 132.8, 131.7, 130.5, 128.2, 124.6, 124.0, 63.9 (t, CH_2N), 43.2 (q, $(CH_3)_2N$), 24.4, 23.2, 23.1, 22.3 (t, $4CH_2$), 16.0, 15.55, 15.50 (q, $4CH_3$)

in nitromethane (3 mL) caused the color of the solution to change back to yellow. The mixture was magnetically stirred for 6 days at 25 °C during which time palladium metal precipitated slowly. After removal of the solvent in vacuo, the residue was chromatography on 15 g of silica gel, eluting with ether. Recrystallization of the product from ether gave 0.42 g (55% based on the palladium complex) of 1,2,3,4-tetraethyl-5-[(dimethylammonio)methyl]-naphthalene tetrafluoroborate, as colorless crystals, mp 178–179 °C. Anal. Calcd for $C_{21}H_{32}NBF_4$: C, 65.48; H, 8.31; N, 3.64. Found: C, 65.16; H, 8.66; N, 3.14. NMR spectra are given in Table II.

Bis(μ-chloro)bis[*o*-(*N*-*tert*-butyliminomethyl)phenyl]-dipalladium(II) was prepared (73%) as described by Widdowson:[14] mp 243–245 °C (with dec); ^1H NMR ($CDCl_3$, ppm) 7.87 (bs, 1 H, CH=N), 7.47 (dd, J = 6.8, 1.9 Hz, 1 H), 7.21 (dd, J =

(14) Widdowson, D. A.; Girling, I. R. *Tetrahedron Lett.* **1982**, *23*, 4281.

6.8, 2.3 Hz, 1 H), 7.08–6.97 (m, 2 H), 1.54 (s, 9 H, 3 CH_3).

General Procedure for the Reaction of the Chloro-Bridged Complexes with Acetylenes. A Pyrex pressure tube was charged with the palladium complex (1 equiv) and silver tetrafluoroborate (2.4–2.6 equiv). A magnetic stirring bar was added and the tube was sealed under nitrogen. To this mixture was added nitromethane by syringe through the cap (concentration of the palladium complex was 0.1 M). The mixture was stirred for 2–4 h at 25 °C. The precipitated silver chloride was removed through Celite and the residue washed with nitromethane until the filtrate was colorless. The filtrate was concentrated under reduced pressure until the tetrafluoroborate was ~0.2 M. To 10 mL of this solution at 100 °C was added dropwise the acetylene (2.4–4.4 equiv) in a 5 mL of nitromethane over a period of 1.5–3.5 h by means of a constant rate addition funnel. The mixture was allowed to cool and then filtered through Celite to remove the precipitated palladium metal. The residue was washed with methylene chloride and methanol. The filtrate was concentrated under reduced pressure and the residue was chromatographed on 25 g of silica gel. The products were recrystallized from methylene chloride–ether. The ^1H NMR and ^{13}C NMR are listed in Table II and other data are given below.

3,4-Diphenylisoquinoline was obtained (27%) from cyclopalladated *N-tert*-butylbenzaldimine tetrafluoroborate and diphenylacetylene, mp 155–156 °C (lit.[15] 155–156 °C[15]).

Reaction of bis(μ-chloro)bis[*o*-(*N-tert*-butyliminomethyl)phenyl]dipalladium(II) with 3-hexyne was carried out by using the same procedure as in the reaction of bis(μ-chloro)bis[2-(dimethylamino)-*o*-tolyl]dipalladium(**II**) with 3-hexyne described above. The crude product was chromatographed on silica gel. Elution with methylene chloride gave two fractions: 0.14 g (22%) of 5,6,7,8-tetraethylnaphthalenecarboxaldehyde *N-tert*-butylimine [mol wt (high resolution mass spectrometry) 323.262 (calcd 323.261); mp 177–179 °C) and 0.05 g (5%) of the 3-alkyne insertion product (mp 140–142 °C; molecular weight (HRMS) 405.343 (calcd for $C_{29}H_{43}N$ 405.340)]. NMR spectra are given in Table II.

General Procedure for the Reaction of Aromatic Iodides with Diphenylacetylene Catalyzed by Palladium Acetate. A solution of 5 mmol of the aromatic iodide, 11 mmol of diphenylacetylene, 0.023 g (0.1 mmol, 2%) of palladium acetate, and 0.053 g (0.2 mmol, 4%) of triphenylphosphine in 2 mL (14 mmol) of triethylamine and 3 mL of nitromethane was prepared in a 15-mL pressure tube. After the tube was capped, the mixture was heated to 100 °C for 1 or 2 days until GLC indicated that the iodide had all reacted or had stopped reacting. Then the mixture was allowed to cool and was concentrated under reduced pressure. The residue was chromatographed on silica gel. This procedure was also employed for the palladium-catalyzed reaction of 2-iodobiphenyl or β-bromostyrene with diphenylacetylene. The ^1H NMR and ^{13}C NMR spectra of the products produced are listed in Table II, and the yields, mass spectra, or microanalyses and melting points are given below.

1,2,3,4-Tetraphenylnaphthalene, mp 203–204 °C (reported mp 205 °C[11]) was obtained in 45% yield based upon iodobenzene. The molecular weight (HRMS) was 432.1882 (calcd 432.1877).

1,2,3,4-Tetraphenyl-8-methylnaphthalene, mp 212–213 °C, was obtained from 4-iodotoluene and was isolated in 22% yield based on the iodide and 1200% yield based on palladium. The molecular weight (HRMS) was 446.2039 (calcd 446.2034).

5,6,7,8-Tetraphenyl-2-methoxynaphthalene. The yield of this compound, mp 272–273 °C, obtained from 4-iodoanisole was 30% based on the iodide and 1500% on palladium. The molecular weight (HRMS) was found to be 462.1977 (calcd 462.1983).

1-Pentaethylcyclopentadienyl-1-phenyl-1-propene. After chromatography of the iodobenzene-3-hexyne reaction mixture, this product was isolated by bulb to bulb distillation. The yield of product, mp 45–46 °C, was 47% based upon iodobenzene and 2350% based upon palladium. The molecular weight (HRMS) was 322.266 (calcd 322.266). NMR spectra are shown in Table II.

9,10-Diphenylphenanthrene. The product, mp 236–237 °C (lit.[16] 241–242 °C), was obtained in 13% yield based upon 2-iodobiphenyl and 450% based upon palladium.

1,2,3,4,6-Pentaphenylfulvene. This product, mp 201–202 °C (lit.[10] 200–201 **C**), was isolated in 27% yield based on *cis*-β-bromostyrene and 45% based upon the diphenylacetylene consumed. NMR spectra are listed in Table II.

Product from 4-iodoanisole and 3-hexyne (structure shown in Figure 1), mp 198–200 °C (dec), was isolated in 5% yield based upon 4-iodoanisole. Anal. Calcd for $C_{38}H_{54}O_2$: C, 84.13; H, 9.96. Found: C, 84.32; H, 9.92. ^1H NMR ($CDCl_3$, ppm) 5.10 (d, J = 6.5 Hz, 2 H), 4.81 (d, J = 6.5 Hz, 2 H), 3.42 (s, 6 H, $2CH_3$), 3.05 (m, 2 H), 2.86 (m, 2 H), 2.18–2.03 (m, 6 H), 1.96–1.82 (m, 2 H), 1.80–1.52 (m, 6 H), 1.45–1.28 (m, 2 H), 1.07 (t, J = 7.4 Hz, 6 H, $2CH_3$), 0.98 (t, J = 7.4 Hz, 6 H, $2CH_3$), 0.87 (t, J = 7.5 Hz, 6 H, $2CH_3$), 0.58 (t, J = 7.3 Hz, 6 H, $2CH_3$). ^{13}C NMR ($CDCl_3$, ppm) 160.1, 150.1, 147.8, 139.8, 110.8, 98.6, 72.1, 66.6, 60.7, 53.8, 49.0, 26.7, 26.4, 20.2, 18.3, 15.5, 13.5, 10.4, 10.2.

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Registry No. I, 18987-59-2; IV (R = Et), 109284-48-2; C_6H_5I, 591-50-4; 4-$CH_3C_6H_4I$, 624-31-7; 3-$CH_3OC_6H_4I$, 625-95-6; 3-hexyne, 928-49-4; bis(μ-chloro)bis[*O*-(*N-tert*-butyliminomethyl)phenyl]-dipalladium(II), 39046-09-8; 5-*tert*-butyliminomethyl-1,2,3,4-tetraethylnaphthalene, 109306-52-7; 1-pentaethylcyclopentadienyl-1-[(2-*tert*-butyliminomethyl)phenyl]-1-propene, 109306-53-8; 3,4-diphenylisoquinoline, 52839-45-9; 6-methyl-1,2,3,4-tetraphenylnaphthalene, 21991-42-4; *cis*-2-bromostyrene, 588-73-8; 1,2,3,4,6-pentaphenylfulvene, 6937-59-3; diphenylacetylene, 501-65-5; 1,2,3,4-tetraphenylnaphthalene, 751-38-2; 5-methoxy-1,2,3,4-tetraphenylnaphthalene, 38382-51-3; 6-methoxy-1,2,3,4-tetraphenylnaphthalene, 38382-52-4.

Supplementary Material Available: Figures 1, 2, and 3 showing structures of the 2:4 iodoanisole to 3-hexyne product, 1,2,3,4,6-pentaphenylfulvene, and the 1:2 cyclopalladated *N,N*-dimethylbenzylamine tetrafluoroborate to 3-hexyne product, respectively, and tables containing the crystallographic data, atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters for these compounds (19 pages); tables of calculated and observed structure factors (38 pages). Ordering information is given on any current masthead page.

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