Rotary evaporation of solvent followed by TLC separation (SiO_2, hexane/Et_2O = 9/2) gave a yellow band of $Ru_3(CO)_8(\mu\text{-}Ph_4C_4)$ (**10**, 10 mg, 17%) followed by a yellow band of unreacted **2** (31 mg, 0.051 mmol) and a colorless band of pentaphenylpyridinone (**8**, 18 mg, 63%) which was extracted from the SiO_2 with acetone.

8: IR (KBr) ν_{CO} 1640 cm^{-1}; MS m/z (EI) calcd for $C_{35}H_{25}NO$ 475.1936, found 475.1919.

10: IR (CH_2Cl_2) ν_{CO} 2070 (m), 2026 (vs), 1975 (s), 1873 (m), 1848 (m)8 cm^{-1}; MS m/z (EI) 858 (M^+ - 1CO) plus fragments corresponding to the stepwise loss of six additional CO's.

Reaction of 5 with PhC≡CPh. A similar reaction to that described above using complex **5** gave formation of tetraphenylmethylpyridinone (**9**) in 53% yield. **9**: IR (CH_2Cl_2) ν_{CO} 1642 cm^{-1}; MS, m/z (EI) 413 (M^+).

Reaction of 2 with CO To Form 1,3,4-Triphenylmaleimide. A solution of **2**, (20 mg, 0.030 mmol) in THF (30 mL) was irradiated with a 450-W Hanovia Hg discharge lamp for 12 h under flowing CO in a quartz reaction vessel. Rotary evaporation of solvent followed by chromatographic separation (TLC, SiO_2, hexane/Et_2O, 3:1, v/v) gave only a colorless band of 1,3,4-triphenylmaleimide (**11**, 5.0 mg, 51%). **11**: IR (CH_2Cl_2) ν_{CO} 1723 cm^{-1}; MS m/z (EI) 325 (M^+).

X-ray Structural Determinations for Complexes 2, 3, and 5. Crystal, data collection, and refinement parameters are collected in Table I. All crystals were mounted for data collection on glass fibers; initial photographic screening revealed $2/m$ Laue symmetry for all and satisfactory diffraction properties. Data on **3** was limited to $2\theta \leq 42°$. Unit-cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections ($20° \leq 2\theta \leq 24°$) which included Friedel related sets to judge optical and diffractometer alignment. Systematic absences in the diffraction data provided unambiguous space group assignments. Absorption corrections were empirical (ψ-scans, 256 data, six-parameter pseudoellipsoid model).

All structures were solved by direct methods and completed by difference Fourier syntheses. Both **3** and **5** contain two chemically identical enantiomorphs as the crystallographic asymmetric unit. With the exception of the η^6-ring in **3**, all phenyl rings were treated as rigid hexagons (C-C = 1.395 Å). All nonhydrogen atoms were anisotropically refined, and hydrogen atom contributions were idealized (C-H = 0.96 Å).

SHELXTL (5.1) software (Nicolet Corp., Madison, WI) was executed on a Data General Eclipse S-30 computer. Tables of atomic coordinates, structure factors, complete bond lengths and angles, anisotropic temperature factors, and hydrogen coordinates for **2** and **3** are included as supplementary material to ref 8c. Similar data for **5** are given as supplementary material to this paper.

Acknowledgment. We thank the National Science Foundation (CHE8501548) for support of this research and for contributing funds toward the purchase of the X-ray diffractometer at the University of Delaware. Dr. G. Steinmetz and R. J. Hale at the Tennessee Eastman Co. and Dr. R. D. Minard and J. Blank at the Pennsylvania State University are acknowledged for obtaining mass spectra.

Registry No. **1**, 51185-99-0; **2**, 105121-10-6; **3**, 105121-11-7; **4**, 33310-08-6; **5**, 105102-79-2; **5'**, 110294-71-8; **8**, 62557-81-7; **9**, 110271-57-3; **10**, 94658-87-4; **11**, 5191-53-7; PhC≡CPh, 501-65-5; PhC≡CMe, 673-32-5.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen atom positions for **5** (8 pages); a listing of structure factors for **5** (30 pages). Ordering information is given on any current masthead page.

Cinnolinium Salt Synthesis from Cyclopalladated Azobenzene Complexes and Alkynes

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The reactivity of the cyclopalladated azobenzene chloro dimer is greatly enhanced when the chloro ligands are replaced by tetrafluoroborate ion. The disolvated tetrafluoroborate reacts with a variety of disubstituted alkynes under mild conditions to form 2-phenylcinnolinium tetrafluoroborates in moderate to good yields. The reaction will occur thermally with the cyclopalladated dimer, also, but only in modest yields.

Cinnolinium salts, previously, have been prepared by the alkylation of the corresponding cinnolines. The parent cinnolines were generally obtained by cyclizations of *o*-alkenyl- or similar arenediazonium salts.[1] Frequently, mixtures of 1- and 2-alkylcinnolinium salts were obtained in the alkylation with the 2-isomer predominating. The presence of large substituents at position 3 usually increased the relative amount of 1-alkylation observed.[1] 2-Arylcinnolinium salts, however, were unknown since they could not be obtained by direct arylation.

We have now discovered a convenient route to 2-arylcinnolinium salts in which a variety of substituents may be placed at the 3- and 4-positions.

Results and Discussion

Cyclopalladated azobenzene chloro dimers are readily available from the reaction of azobenzene or its derivatives with palladium chloride at room tempeature.[2-4] These complexes would appear to be convenient starting materials for the preparation of some heterocycles such as cinnolines, but it is known that these complexes are quite stable and generally unreactive[5] except toward carbon monoxide.[6] For example, "phenylpalladium chloride"

(1) Boulton, A. J.; McKillop, A. *Comprehensive Heterocyclic Chemistry*; Pergamon: Oxford, 1984; Vol. 3, p 18.

(2) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.

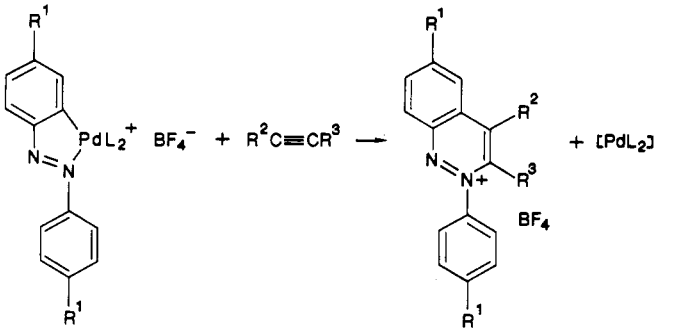
(3) Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 687.

(4) Takahashi, H.; Tsuji, J. *J. Organomet. Chem.* **1967**, *10*, 511.

(5) Hart, D. W.; Bau, R.; Chao, C. H.; Heck, R. F. *J. Organomet. Chem.* **1979**, *179*, 301.

0276-7333/87/2306-2386$01.50/0

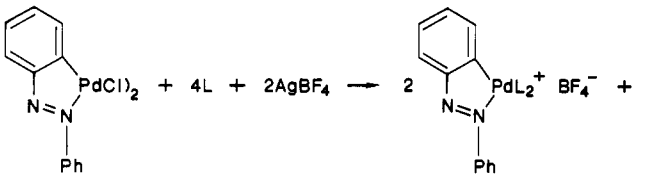
Table I. Cinnolinium Salts Prepared from Cyclopalladated Azobenzene Tetrafluoroborates and Alkynes



azobenzene complex, R^1	alkyne R^2	alkyne R^3	product R^1	product R^2	product R^3	% yield[a]
H	Ph	Ph	H	Ph	Ph	36,[b] 87
H	CO_2CH_3	CO_2CH_3	H	CO_2CH_3	CO_2CH_3	28,[b] 80
H	C_2H_5	C_2H_5	H	C_2H_5	C_2H_5	30,[b] 83
H	$C(CH_3)_2OH$	$C(CH_3)_2OH$	H	$C(CH_3)_2O$	$C(CH_3)_2$	39
H	Ph	$CH(OC_2H_5)_2$	H	$CH(OC_2H_5)_2$	Ph	71
H	$CH(OC_2H_5)_2$	$CH(OC_2H_5)_2$	H	$CH(OC_2H_5)_2$	$CH(OC_2H_5)_2$	43
H	Ph	CO_2CH_3	H	Ph	CO_2CH_3	43
CH_3	Ph	Ph	CH_3	Ph	Ph	75
CH_3	C_2H_5	C_2H_5	CH_3	C_2H_5	C_2H_5	81

[a] Alkyne added over a period of 3 h at 100 °C except where noted. [b] Alkyne all present initially.

reacts readily, below room temperature, with styrene to form stilbene,[7] while the azobenzene–palladium chloride dimer does not react even at 100 °C.[5] We have now found that removal of the strongly bound chloro ligands by reacting the azobenzene–palladium chloro dimer with silver tetrafluoroborate greatly activates the complex (eq 1).

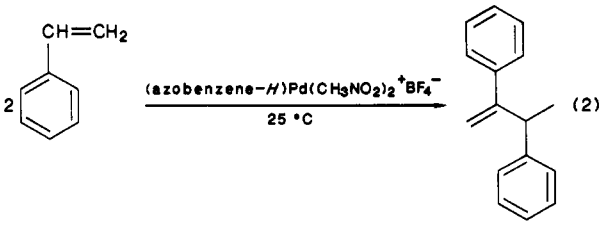


2AgCl (1)

L = CH_3CN, CH_3NO_2, CH_2Cl_2, CH_3OH

(Silver *p*-toluenesulfonate was not effective in removing the chloro ligands.) The degree of activation depends upon the solvent employed since the two chloro ligands are replaced by solvent molecules in the reaction

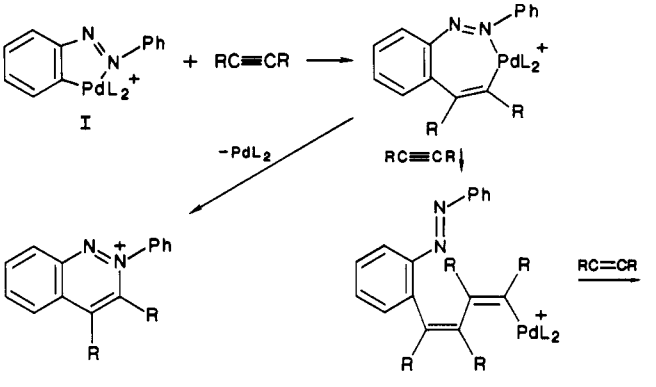
The bis(acetonitrile) complex, for example, is a yellow crystalline solid of intermediate reactivity while the viscous red liquid nitromethane and methylene chloride derivatives are reactive toward styrene even at room temperature. The styrene does not insert into the Pd–C bond, however, as it does with nonchelated arylpalladium derivatives, but it dimerizes to 2,3-diphenyl-1-butene in 90% yield (eq 2).



This dimer has not been observed previously. Other palladium catalysts, however, are known to dimerize styrene to 1,3-diphenyl-1-butene.[8] The difference between the azobenzene catalyst and the previously known catalysts appears to be due to the size of the azobenzene ligand. The results may be readily explained on the basis of catalysis by palladium hydride species, as has been proposed previously.[8] The cationic styrene dimerization mechanism suggested by Sen[9] cannot explain the ligand effect on the dimer structure.

3-Phenyl-1-propene is isomerized to 1-phenyl-1-propene by the azobenzene tetrafluoroborate catalyst while methyl acrylate (at 50 °C) and phenylacetylene (at 25 °C) are polymerized by it.

Disubstituted alkynes react differently than phenylacetylene with cyclopalladated azobenzene salts (eq 3).



oligomers (3)

R = Ph–, C_2H_5–, CH_3O_2C–, $(C_2H_5O)_2CH$–; L = CH_3NO_2

The tetrafluoroborate salts in nitromethane solution react at room temperature to form cinnolinium tetrafluoroborates and alkyne oligomers.[10] Better yields of cinnolinium salts are obtained by slow addition of the disubstituted alkyne to the azobenzene complex at elevated temperatures (100 °C). This procedure favors ring closure of the monoalkyne insertion product over addition to an-

(6) Thompson, J. M.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 2667.
(7) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518.
(8) Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *Organometallics* **1984**, *3*, 1130.
(9) Sen, A.; Lai, T.-W. *Organometallics* **1983**, *2*, 1059.
(10) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *5*, 1922.

Table II. Physical Properties and Microanalyses for Cinnolinium Salts

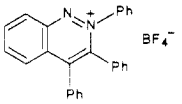
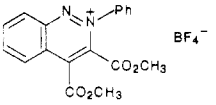
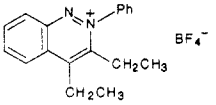
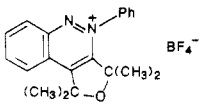
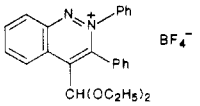
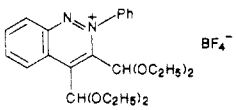
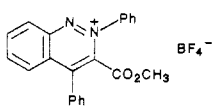
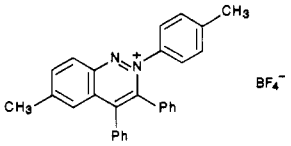
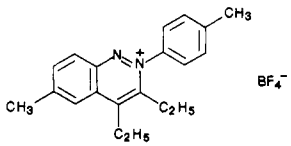
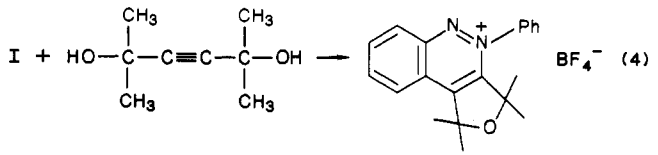
structure	mp, °C (color)	found (calcd) C	H	N	^{1}H NMR ($CDCl_3$, ppm)	^{13}C NMR ($CDCl_3$, ppm)
	277–278 (yellow)	69.79 (69.86)	4.30 (4.26)	6.07 (6.26)	8.58 (d, J = 8.6 Hz, 1 H), 8.20–8.07 (m, 2 H), 7.91 (d, J = 7.9 Hz, 2 H), 7.63–7.06 (m, 14 H)	
	189–190 (yellow)	52.67 (52.38)	3.66 (3.69)	6.83 (6.69)	(CD_3OD) 8.86 (b s, 1 H), 8.57 (b s, 1 H), 7.84–7.76 (m, 7 H), 4.20 (s, 3 H, CH_3), 3.84 (s, 3 H, CH_3)	
	216–217 (colorless)	61.71 (61.68)	5.43 (5.41)	8.09 (7.87)	8.34 (d, J = 8.0 Hz, 2 H), 8.06–8.22 (m, 2 H), 7.74–7.64 (m, 6 H), 3.44 (q, J = 7.7 Hz, 2 H, CH_2), 3.24 (q, J = 7.6 Hz, 2 H, CH_2), 1.51 (t, J = 7.7 Hz, 3 H, CH_3), 1.24 (t, J = 7.6 Hz, 3 H, CH_3)	155.7, 150.4, 147.5, 144.0, 137.9, 134.8, 131.4, 130.7, 130.6, 130.0, 125.4, 123.8, 24.6, 22.4, 14.7, 13.1
	276–278 (green)	61.02 (61.25)	5.40 (5.40)	7.14 (6.88)	(CD_3OD) 8.68–8.60 (m, 1 H), 8.47–8.34 (m, 2 H), 7.86–7.66 (m, 6 H), 1.96 (s, 6 H, $2CH_3$), 1.47 (s, 6 H, $2CH_3$)	155.7, 151.6, 148.0, 141.5, 139.3, 136.1, 132.1, 130.4, 129.2, 126.4, 123.3, 83.9, 83.7, 28.7, 28.5
	253–254 (yellow)	63.38 (63.58)	2.29 (2.30)	5.75 (5.93)	9.21–9.17 (d, 1 H), 8.53 (d, 1 H), 8.25–8.17 (m, 2 H), 7.57–7.31 (m, 1/ H), 5.38 (s, 1 H, $CH(OEt)_2$), 3.64 (qd, J_1 = 7.0 Hz, J_2 = 2.4 Hz), 3.49 (qd, J_1 = 7.0 Hz, J_2 = 2.4 Hz, H), 1.15 (t, J = 7.0 Hz, $2CH_3$)	150.9, 149.3, 144.4, 143.1, 138.4, 135.4, 131.1, 131.0, 130.7, 130.6, 129.2, 129.1, 128.9, 128.8, 127.2, 126.5, 100.9, 64.8, 14.9
	183–184 (yellow)	58.04 (57.86)	6.41 (6.27)	5.68 (5.62)	9.21 (d, J = 9.8 Hz, 1 H), 8.55 (m, 1 H), 8.25 (m, 2 H), 7.82–7.75 (m, 5 H), 6.77 (s, 1 H, $CH(OEt)_2$), 5.62 (s, 1 H), 4.00 (qd, J = 7.0 Hz, 2.3 Hz, 2 H), 3.78–3.65 (m, 4 H), 3.51 (qd, J = 7.0, 2.2 Hz, CH_2), 1.26 (t, J = 7.0 Hz, 6 H, $2CH_3$), 1.20 (t, J = 7.0 Hz, 6 H, $2CH_3$)	149.3 (s), 147.4 (s), 145.3 (s), 143.1 (s), 138.1 (d), 136.1 (d), 132.3 (d), 130.6 (d), 130.5 (s), 130.3 (d), 128.5 (d), 125.7 (d), 100.5 (d), 99.4 (d), 65.9 (t), 65.4 (t), 15.2 (q), 14.8 (q)
	211–212 (colorless)	61.96 (61.71)	3.98 (3.97)	6.51 (6.54)	8.69 (d, J = 7.8 Hz, 1 H), 8.33–8.21 (m, 2 H), 8.03 (d, J = 7.9 Hz, 1 H), 7.91 (d, J = 7.8 Hz, 2 H), 7.72–7.62 (m, 8 H), 3.46 (s, 3 H, CH_3)	160.2 (s, CO), 148.9 (s), 146.3 (s), 144.0 (s), 142.8 (s), 140.0 (d), 136.8 (d), 132.4 (d), 131.3 (d), 131.0 (d), 130.4 (s), 130.0 (d), 129.7 (d), 129.4 (s), 129.1 (d), 126.4 (d), 125.7 (d), 54.1 (q, CH_3)

Table II (Continued)

structure	mp, °C (color)	found (calcd) C	H	N	^{1}H NMR ($CDCl_3$, ppm)	^{13}C NMR ($CDCl_3$, ppm)
	285–287 (pale yellow)	70.76 (70.91)	4.93 (4.85)	5.70 (5.91)	8.37 (d, J = 8.9 Hz, 1 H), 7.90 (d, J = 8.9 Hz, H), 7.53 (s, H), 7.44 (d, J = 8.3 Hz, 2 H), 7.37–7.26 (m, 5 H), 7.24 (d, J = 8.3 Hz, 2 H), 7.06–7.01 (m, 5 H), 2.56 (s, CH_3), 2.28 (s, CH_3)	151.7 (s), 151.1 (s), 147.6 (s), 146.5 (s), 142.7 (s), 140.7 (s), 137.8 (d), 131.6 (s), 131.0 (d), 130.5 (s), 130.2 (d), 129.5 (d), 129.3 (d), 128.4 (d), 128.0 (d), 126.4 (d), 23.4 (q), 21.2 (q)
	181–182 (colorless)	63.23 (63.36)	6.38 (6.33)	7.12 (7.39)	8.20 (d, J = 8.9 Hz, 1 H), 8.07 (s, 1 H), 7.92 (d, J = 8.9 Hz, 1 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.4 Hz, 2 H), 3.38 (q, J = 7.5 Hz, 2 H, CH_2), 3.21 (q, J = 7.6 Hz, 2 H, CH_2), 2.74 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 1.48 (t, J = 7.5 Hz, 3 H, CH_3), 1.21 (t, J = 7.6 Hz, 3 H, CH_3)	155.2 (s), 150.8 (s), 148.3 (s), 146.1 (s), 141.8 (s), 141.5 (s), 137.6 (d), 130.6 (s), 130.4 (d), 130.1 (d), 125.2 (d), 122.0 (d), 24.4, 23.4, 22.1, 21.3, 14.5 (q), 13.1 (q)

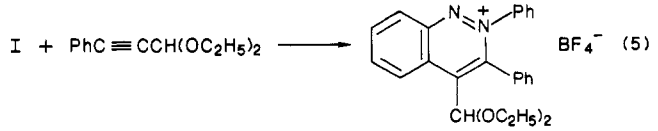
other alkyne and oligomer formation. A crystal structure for 2,3,4-triphenylcinnolinium tetrafluoroborate, obtained from azobenzene and diphenylacetylene, has been obtained.

A variety of alkynes have been employed in the reaction with the azobenzene and 4-azotoluene tetrafluoroborate complexes. The results are summarized in Table I. Diphenylacetylene, 3-hexyne, and dimethyl acetylenedicarboxylate gave 75–90% yields of cinnolinium salts by the slow addition method at 100 °C while only 28–35% yields were obtained when all of the alkyne was added initially and the reaction was carried out at room temperature (eq 4). Butynedial tetraethyl diacetal[11] reacted less well, giving only 43% cinnolinium salt. Even the very bulky alkyne 2,5-dimethyl-3-butyne-2,5-diol reacted to give a cinnolinium salt in 39% yield, but the neighboring diol groups formed an ether with loss of water.



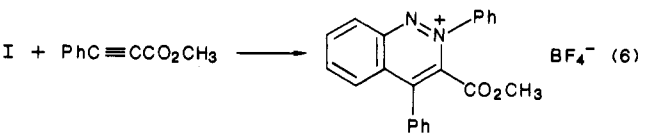
(4)

Some unsymmetrically substituted alkynes reacted selectively. 3-Phenylpropargyl aldehyde diethyl acetal gave 71% of the 2,3-diphenyl-4-formyl diethyl acetal derivative (eq 5). The structure was determined by X-ray crystal-



(5)

lography. The 2,4-diphenyl isomer might have been expected from this reaction since the palladium-catalyzed addition of iodobenzene to methyl cinnamate yields only the 3,3-diphenylacrylate ester.[12] Therefore, we carried out the addition of methyl 3-phenylpropiolate to the azobenzene salt (eq 6). We obtained in 43% yield the 2,4-



(6)

diphenyl isomer in this case as determined by X-ray crystallography. Thus, we are able to obtain either the 2,3- or the 2,4-diaryl isomers depending upon whether we add the arylpropynal acetal or the arylpropiolate ester. The conjugating effect of the ester group apparently exerts more influence on the direction of the addition than the aryl group does.

While yields in our reaction have usually been good, we were concerned as to why they were low in some instances. Steric problems probably were responsible for the low yield in the 2,5-dimethyl-3-hexyne-2,5-diol reaction causing oligomer formation to be more favorable than ring closure. This is clearly not the cause of the 43% yield in the addition of the methyl propiolate, however, since addition of the alkyne to the tetrafluoroborate salt I over a period of 1 h gave exactly the same yield of product as did addition in 3 h. The remaining material from these reactions is a viscous intractable substance, and we have not discovered how it is formed.

Reactions were carried out in four solvents: methanol, acetonitrile, methylene chloride, and nitromethane. The last solvent gave the highest yields and cleanest products.

Attempts to prepare *N*-methylcinnolinium salts from cyclopalladated phenylazomethane[13] failed because the cyclopalladated complex (chloride or acetate) was unstable. The reaction also failed when bis(trimethylsilyl)acetylene was reacted with I or its 4,4′-dimethyl derivative. We also failed in an attempt to react complex I with benzyne generated in situ from isoamyl nitrite and anthranilic acid or with isolated benzene diazonium carboxylate.

(11) Wohl, A. *Chem. Ber.* **1912**, *45*, 340.
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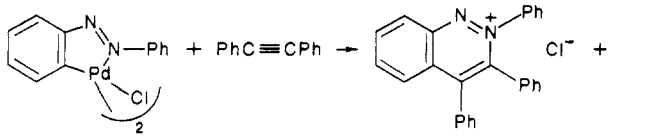
The alkyne addition to cyclopalladated azobenzene derivatives occurs best with the tetrafluoroborate salts; however, the reaction also will occur thermally with the cyclopalladated chloro dimers. The azobenzene chloro dimer and diphenylacetylene at 100 °C overnight in nitromethane solution, for example, gave 30% of 2,3,4-triphenylcinnolinium chloride when all of both reactants were present initially (eq 7). Slow addition of the alkyne at



Pd (7)

100 °C also gave a 30% yield in nitromethane solution but a 41% yield in DMF solution. This method avoids the use of the silver salt but with a significant loss in yield.

Experimental Section

General Data. Palladium chloride, palladium acetate, and silver tetrafluoroborate were purchased from Strem Chemical Inc. and were used without further purification. Phenylpropiolic acid, *p*-nitrotoluene, phenylacetylene, diphenylacetylene, dimethyl acetylenedicarboxylate, 2,5-dimethyl-3-hexyne-2,5-diol, and styrene were obtained from the Aldrich Chemical Co. 3-Hexyne (Chem Samples Co.), 3-phenyl-2-propynyl aldehyde diethyl acetal (Farchan Labs, Inc.), acetonitrile (Fisher), and triethylamine (Fisher) were, also, commercial samples. The last two chemicals were dried over 4A molecular sieves before use. Methyl phenylpropiolate was prepared from phenylpropiolic acid by way of the acid chloride.

Bis(μ-chloro)bis(azobenzne-C^2,N)dipalladium(II). This complex was prepared in 90% yield by the method of Cope.[2]

Bis(μ-acetato)bis(azobenzene-C^2,N)dipalladium(II). This complex was prepared in 76% yield by the reported method.[6]

Bis(μ-chloro)bis(azotoluene-C^2,N)dipalladium(II). Azotoluene was prepared in 48% yield by the method of Cook.[14] The palladium complex was prepared in 84% yield by the method of Cope;[2] mp 259–261 °C dec; ^{1}H NMR ($CDCl_3$, ppm) 7.73 (d, J = 8.3 Hz, 2 H), 7.68 (d, J = 7.9 Hz, 1 H), 7.26 (d, J = 8.3 Hz, 2 H), 7.15 (b s, 1 H), 7.03 (d, J = 7.9 Hz, 1 H), 2.45 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3). Anal. Calcd for $C_{28}H_{28}N_4Cl_2Pd_2$: C, 47.75; H, 4.01; N, 7.95. Found: C, 47.61; H, 3.92; N, 7.91.

(Azobenzene-C^2,N)bis(acetonitrile)palladium(II) Tetrafluoroborate. A mixture of 4.55 g (6.9 mmol) of bis(μ-chloro)-bis(azobenzene-C^2,N)dipalladium(II) and 2.70 g (13.9 mmol) of silver tetrafluoroborate in 125 mL of acetonitrile contained in a 250-mL round-bottom flask was stirred magnetically overnight. The reaction mixture was filtered to give 2.00 g of gray silver chloride. The filtrate was concentrated and allowed to stand at room temperature for 4 h. The crystals formed were filtered and washed with ethyl ether. Addition of more ether to the filtrate gave more product. The two portions of the product were dried in vacuo to give 5.76 g (91%) of yellow crystals: mp 170–171 °C; ^{1}H NMR (acetone-d_6, ppm) 8.09–7.31 (m, 9 H), 2.27 (s, 6 H, $2CH_3$). Anal. Calcd for $C_{16}H_{15}H_4BF_4Pd$: C, 42.09; H, 3.31; N, 12.26. Found; C, 41.94; H, 3.41; N, 12.15.

Dimerization of Styrene. A solution of 0.46 g (1.0 mmol) of (azobenzene-C^2,N)bis(acetonitrile)palladium(II) tetrafluoroborate and 10.9 g (105 mmol) of styrene in a 50-mL flask attached to a condenser was refluxed for 22 h. The cooled reaction mixture was filtered through Celite to remove the palladium formed, and the Celite was washed with ethyl acetate. After removal of solvent from the filtrate, the residue was chromatographed on silica gel. Elution with ether gave 9.8 g (90% based on styrene and 720% on the catalyst) of the product 2,3-diphenyl-1-butene; HRMS calcd for $C_{16}H_{16}$ m/z 208.125, found m/z 208.124; ^{1}H NMR (CDCl, ppm) 7.40–7.14 (m, 10 H), 6.39 (d, J = 4.0 Hz, 2 H, C=CH_2), 3.62 (dd, J = 4.0, 7.0 Hz, 1 H), 1.45 (d, J = 7.0 H, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, ppm) 145.6 (s), 137.5 (s), 135.2 (s), 128.5 (d), 128.4 (d), 127.3 (d), 127.0 (d), 126.5 (d), 126.1 (t), 42.5 (d), 21.2 (q).

When styrene was dimerized by bis(μ-chloro)bis(azobenzene-C^2,N)dipalladium(II) in the presence of silver tetrafluoroborate in methylene chloride at room temperature, the yield was also 90%.

Isomerization of 3-Phenyl-1-propene. A pressure tube containing a mixture of 0.323 g (0.5 mmol) of bis(μ-chloro)bis-(azobenzene-C^2,N)dipalladium, 0.20 g (1.0 mmol) of silver tetrafluoroborate, and 0.135 g (1.1 mmol) of diisopropylethylamine was sealed under nitrogen. To this was added 0.12 g (1.0 mmol) of 3-phenyl-1-propene by syringe. The mixture was magnetically stirred for overnight at ambient temperature. Then quantitative GLC was carried out, and 12% of the isomerization product 1-phenyl-1-propene was detected. A sample was collected by GLC: ^{1}H NMR ($CDCl_3$, ppm) 7.35–7.15 (m, 5 H), 6.40 (dq, J = 15.7, 1.4 Hz, 1 H), 6.25 (dq, J = 15.7, 6.3 Hz, 1 H), 1.88 (dd, J = 6.3, 1.4 Hz, 3 H, CH_3).

General Procedure for the Reaction of Cyclopalladated Azobenzene Complexes with Alkynes. 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 is 0.1 M). The mixture was magnetically stirred for 2–4 h at ambient temperature. The precipitated silver chloride was removed by filtration through Celite, and the residue was washed with nitromethane until the filtrate was colorless. The filtrate was concentrated under reduced pressure until the tetrafluoroborate complex was 0.2 M. To 10 mL of this solution at 100 °C was added dropwise the alkyne (2.4–4.4 equiv) in 5 mL of nitromethane over a period of 1.5–3.5 h and the mixture 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 are recrystallized from methylene chloride–ether. The ^{1}H NMR and ^{13}C NMR of the products prepared and other data are listed in Table II.

Thermal Reaction of Bis(μ-chloro)bis(azobenzene-C^2,N)dipalladium(II) with Diphenylacetylene. A three-necked flask attached to a condenser was charged with 0.65 g (1.0 mmol) of bis(μ-chlorobis(azobenzene-C^2,N)dipalladium(II) and 0.72 g (4.0 mmol) of diphenylacetylene in 10 mL of nitromethane. The mixture was refluxed for overnight. After cooling, the mixture was filtered through Celite. The solvent was evaporated, and the residue was chromatographed on silica gel, eluting with CH_2Cl_2–CH_3OH. Recrystallization from methylene chloride–ether gave 0.24 g (30% based upon the palladium complex) of yellow crystals: mp >330 °C; ^{1}H NMR ($CDCl_3$, ppm) 8.60 (d, J = 8.5 Hz, 1 H), 8.17 (t, 1 H), 8.09 (t, 1 H), 7.90 (d, J = 8.0 Hz, 2 H), 7.61–7.36 (m, 11 H), 7.11 (m, 2 H). Anal. Calcd for $C_{26}H_{19}N_2Cl\cdot{}^3/_2H_2O$: C, 74.02, H, 4.74; N, 6.64. Found: C, 74.18; H, 4.70; N, 6.89.

When this reaction was carried out in *N*,*N*-dimethylformamide, at 135 °C with slow addition of diphenylacetylene, the yield of product was 41%.

Reaction of Cyclopalladated Azobenzene Tetrafluoroborate with Benzyne. The benzyne precursor benzenediazonium carboxylate was prepared in 17% yield by the method of Stiles.[17] To 10 mL of a nitromethane solution of the cyclopalladated azobenzene tetrafluoroborate (0.2 M) was added at 50 °C 0.32 g (2.2 mmol) of the diazonium carboxylate in 5 mL of nitromethane over a period of 1 h. The reaction mixture was further heated at 50 °C overnight. After removal of solvent, the residue was chromatographed on silica gel to give a dark brown solid which did not crystallize and was not a pure material judging by its ^{1}H NMR. Little if any of the desired product could have been present in the brown material judging from the spectrum.

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financial support of this project.

Registry No. PhC≡CPh, 501-65-5; $CH_3O_2CC{\equiv}CCO_2CH_3$, 762-42-5; $C_2H_5C{\equiv}CC_2H_5$, 928-49-4; $HO(CH_3)_2CC{\equiv}CCCH_3)_2OH$, 142-30-3; $PhC{\equiv}CCH(OC_2H_5)_2$, 6142-95-6; $(C_2H_5O)_2CHC{\equiv}CCH(OC_2H_5)_2$, 3975-08-4; $PhC{\equiv}CCO_2CH_3$, 4891-38-7; (azobenzene-C^2,N)Pd$(CH_3CN)_2^+BF_4^-$, 110294-93-4; (azotoluene-C^2,N)Pd$(CH_3NO_2)_2^+BF_4'$, 110294-95-6; 2,3,4-triphenylcinolinium tetrafluorobroate, 103905-36-8; 3,4-bis(methoxycarbonyl)-2-phenylcinolinium tetrafluoroborate, 103905-40-4; 3,4-diethyl-2-phenylcinolinium tetrafluoroborate, 103905-38-0; 2-phenyl-3,4-(1,1,3,3-tetramethyl-2-oxa-1,3-propanediyl)cinolinium tetrafluoroborate, 110294-97-8; 4-(diethoxymethyl)-2,3-diphenylcinolinium tetrafluoroborate, 110313-44-5; 3,4-bis(diethoxymethyl)-2-phenylcinolinium tetrafluoroborate, 110294-99-0; 2,4-diphenyl-3-(methoxycarbonyl)cinolinium tetrafluoroborate, 110295-01-7; 3,4-diphenyl-6-methyl-2-(4-methylphenyl)cinolinium tetrafluoroborate, 110295-03-9; 3,4-diethyl-6-methyl-2-(4-methylphenyl)cinolinium tetrafluoroborate, 110295-05-1; bis(μ-chloro)bis(azobenzene-C^2,N)dipalladium (II), 14873-53-1; (azobenzene-C^2,N)PdnCH$_3$NO$_2$)$_2^+BF_4^-$, 110295-07-3; 2,3-diphenyl-1-butene, 22875-84-9; 3-phenyl-1-propene, 300-57-2; 1-phenyl-1-propene, 637-50-3; styrene, 100-42-5; methylacrylate, 96-33-3; phenylacetylene, 536-74-3; bis(trimethylsilyl)acetylene, 14630-40-1; benzenediazoniumcarboxylate, 1608-42-0.

Supplementary Material Available: Figures 1, 2, and 3 showing the structures of 1,2,3-triphenylcinnolinium tetrafluoroborate (I), 2,3-diphenyl-3-(diethoxymethyl)cinnolium tetrafluoroborate (II), and methyl 2,4-diphenylcinnolinium-3-carboxylate tetrafluoroforate (III), respectively, crystallographic data for compounds I–III, tables containing atomic coordinates and isotropic thermal parameters (Tables 1s, 7s, and 13s), bond lengths (Tables 2s, 8s, and 14s), bond angles (Tables 3s, 9s, and 15s), and hydrogen atom coordinates (Tables 5s, 11s, and 16s) for compounds I–III, and tables of anisotropic thermal parameters (Tables 4s and 10s) for compounds I and II (18 pages); listings of observed and calculated structure factors for compounds I–III (Tables 6s, 12s, and 17s) (31 pages). Ordering information is given on any current masthead page.

Conversion of Primary Amines to Carbamate Esters Using Palladium Chloride and Di-*tert*-butyl Peroxide. Double Carbonylation of Secondary Amines

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Primary aliphatic and aromatic amines react with carbon monoxide and di-*tert*-butyl peroxide in alcohol, catalyzed by palladium and copper chlorides, to give carbamate esters in good yields; double carbonylation to oxamate esters, using the peroxide or oxygen, resulted in the case of secondary amines.

In 1985, we described the reaction of primary aromatic amines with carbon monoxide, oxygen, alcohol, hydrochloric acid, cupric chloride, and palladium chloride as the catalyst to give the carbamate ester in 16–99% yield.[2] While this reaction occurs at room temperature and atmospheric pressure, it is too slow to be commercially viable, while the use of elevated pressures is unsafe due to the explosive nature of mixtures of carbon monoxide and oxygen. Also, an undesirable side reaction, associated with the coproduction of water, is the conversion of carbon monoxide to carbon dioxide. Therefore, an effort was made to utilize a substitute for oxygen in this process. Recently, di-*tert*-butyl peroxide was found to be effective for the palladium- and copper-catalyzed oxidative carbonylation of methanol to dimethyl oxalate and dimethyl carbonate.[3] We now wish to report (i) that this peroxide is very useful, as an oxygen substitute, in the conversion of both aliphatic and aromatic primary amines to carbamate esters, (ii) that ureas are the principal products at elevated temperatures and pressures, and (iii) that with either oxygen or di-*tert*-butyl peroxide, secondary amines afford products resulting from a novel double as well as monocarbonylation reaction.

Methyl cyclohexylcarbamate (**2**, R = C_6H_{11}, R′ = H, R″ = CH_3) was obtained in 86% yield when cyclohexylamine was carbonylated in methanol by using palladium chloride as the catalyst, hydrochloric acid, di-*tert*-butyl peroxide, and copper(II) chloride at room temperature and 1-atm pressure.

$$\underset{\mathbf{1}}{RR'NH} + CO + R''OH \xrightarrow[[(CH_3)_3CO]_2,\ \text{acid, room temp, 1 atm}]{PdCl_2,\ CuCl_2} \underset{\mathbf{2}}{RR'NCOOR''} + \underset{\mathbf{3}}{RR'NCOCOOR''}$$

The yield of ester was 17% when the reaction was repeated in the absence of the peroxide while 18% carbamate ester resulted in the absence of acid (but the peroxide was present). Another effective acid was tetrafluoroboric acid, and even the Lewis acid born trifluoride could be used in this reaction. The optimum ratio of substrate/$[(CH_3)_3CO]_2$/$CuCl_2$/$PdCl_2$ for these reactions is 5.0/5.0/1.0/0.5, and 1–2 drops of acid were used in all cases.

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