Stoichiometric and Catalytic Conversion of Alkynes to Conjugated (*Z*,*Z*)-Dienes and Cyclopentadienes via Palladacyclopentadienes and 1,3-Dienylpalladium(II) Halide and Triorganopalladium(IV) Halide Compounds Containing Chelating Nitrogen Ligands†

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Palladacyclo-2,4-pentadiene compounds containing a chelating bidentate nitrogen ligand Pd{(C(E)═C(E)-C(E)═C(E)}(NN) **1a**−**f** (E = CO_2Me, NN = Ph-bip, Ar-bian, bpy, dcm-bpy, bpym) and **2a**,**b** (E = CF_3, NN = Ph-bip, (*p*-tol)-bian) have been prepared from $Pd(dba)_2$, the appropriate bidentate N-ligand, and electron-deficient acetylenes dimethyl 2-butynedioate or hexafluorobutyne. X-ray crystal structures were obtained for compounds **1a** (NN = Ph-bip) and **1d** (NN = 2,2′-bpy). In solution, an equilibrium between the monomer and a dimer exists for compounds **1d** and **1e** (NN = bipyrimidine); in the solid state, **1d** is a monomer. The dimeric form of **1d** is of the same type as the zerovalent palladium compound [(μ-3,3′-dicarbomethoxy-2,2′-bipyridine)Pd(tcne)]$_2$ in which the two bipyridine derivatives bridge between the two palladium centers, as determined from the X-ray crystal structure of this compound (**7**). The palladacycles **1** undergo oxidative addition of methyl iodide, benzyl bromide, or iodobenzene. Subsequent reductive elimination gives rise to the formation of 4-functionalized 1,3-dienylpalladium(II) halide compounds **3**−**5** (cis arrangement of the ester functions at the double bonds). In the reaction with an excess of 1,4-chloro-2-butyne, a trimerization took place forming 1-(1′-chloroethenyl)-1,2,3,4,5-pentakis(chloromethyl)-2,4-cyclopentadiene (**6**). Employing the established kinetic compatibility of the formation of the palladacycles with a successive oxidative addition/reductive elimination of organic halides and subsequent transmetalation with tetramethyltin, a catalytic cycle for the three-component synthesis of (*Z*,*Z*)-dienes of the type R−C(E)═C(E)C(E)═C(E)CH_3 (**8**, R = alkyl, aryl; E = CO_2CH_3) has been conceived, e.g., from dimethyl 2-butynedioate, an organic halide, and tetramethyltin employing 1% of **1b** as the catalyst in DMF. This constitutes the first catalytic synthesis of conjugated dienes from alkynes. Pd(phosphine) compounds do not catalyze this reaction.

Introduction

There has been considerable interest in carbon−carbon bond-forming reactions proceeding via palladium compounds.[1] Mechanistic studies have shown that the coupling of the organic fragments can occur not only from a Pd(II) species but also from Pd(IV) compounds. The chemistry of Pd(IV) compounds has been developing very rapidly lately, and studies on the oxidative addition and reductive elimination have been published together with several crystal structures of Pd(IV) species.[1c,2] In most studies involving Pd(II), phosphorus compounds were used as ligands, whereas in the Pd(IV) chemistry, mostly nitrogen ligands have been applied. The role of Pd(IV) intermediates in palladium(phosphine)-catalyzed vinylations of aryl halides (Heck reaction) has been the subject of debate,[3a−d] and a number of Pd-catalyzed

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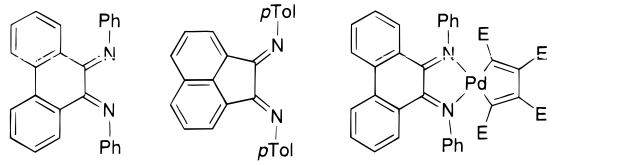
dimerization and vinylation reactions have been reported to involve Pd(IV) intermediates.[3e,f]

The use of palladium compounds containing rigid bidentate nitrogen ligands has proven to be very successful for obtaining mechanistic information concerning palladium-catalyzed carbon−carbon coupling reactions involving Pd(II) and Pd(IV) species and the formation of polyketones. The ligands could also be used for the preparation of several precatalysts which are active in carbon−carbon cross-coupling reactions and the hydrogenation of electron-deficient alkenes.[4] It was shown, for instance, that the carbon−carbon cross-coupling reaction between specific magnesium and zinc compounds with aromatic iodides proceeds exclusively via a Pd(II) intermediate. The palladium compounds containing a rigid bidentate nitrogen ligand were also good catalysts in the cross coupling of organotin, -magnesium, and -zinc compounds with a variety of organic halides,[4b,e] and a mechanistic study revealed a previously unidentified mechanism to explain homocoupling products.[4f]

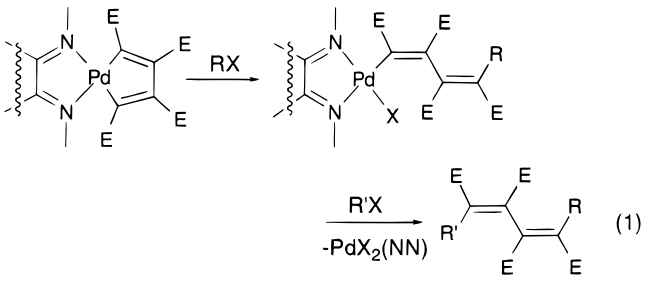
In our ongoing program dealing with the application of bidentate nitrogen ligands in catalytic and stoichiometric C−C coupling reactions, we were interested to see if palladacyclopentadiene compounds containing two mutually cis-oriented Pd−C bonds would also be amenable to carbon−carbon coupling with organic halides (or other reagents).



phenyl-bip (*p*-tolyl)-bian (phenyl-bip)palladacyclopentadiene
E = COOMe

The palladacyclopentadienes can be prepared from alkynes,[10] and by combining this reaction with the oxidative-addition/reductive-elimination sequence known from the Pd(IV) chemistry, one might achieve conversion of alkynes into dienes. Possibly, this reaction can be rendered catalytic by using dinitrogen ligands. We have, therefore, focused on palladacycles of the type (NN)Pd−C(E)=C(E)−C(E)=C(E) containing rigid bidentate nitrogen ligands (NN) such as aryl-bip[5] and aryl-bian[6] but common ligands such as bipyridine and dppe were also employed for comparison.

In reactions with suitable organic electrophiles, an oxidative addition/reductive elimination sequence may lead to the formation of σ-dienylpalladium compounds and possibly, after a second sequence of events, to dienes with a *Z,Z* configuration (see eq 1). This route is very



(1)

interesting because only a limited number of methods are available for the stereospecific preparation of dienes from acetylenes. Most of these either rely upon the use of a stoichiometric amount of metal and have a very low tolerance for the substituents present, since reactive organometallic reagents are involved,[7a,b] require more than one reaction step,[7c] or start from pure stereoisomers in a cross-coupling reaction.[8] Titanium- and zirconium-catalyzed cyclization of diynes to exocyclic conjugated dienes[9a−c] and boration of diynes[9d] are well-known. However, a selective catalytic process for the preparation of "open chain" conjugated (*Z,Z*)-dienes directly from acetylenes is not available.

The synthesis of palladacyclopentadienes bearing electron-withdrawing substituents has been reported previously.[10] These compounds were found to be intermediates in the Pd(0)-catalyzed cyclotrimerization of acetylenes, which has been extensively studied together with the cocyclotrimerizations of acetylenes with other acetylenes, alkenes, and allenes.[11] Crystal structures of a few palladacyclopentadiene compounds containing 1,5-COD,[12] 2,6-lutidine,[13] and $Ph_3PC_5H_4$ (triphenylphosphonium cyclopentadienylide)[14] as ligands are known. Recently, palladacyclopentadienes were also found to be catalysts in the metathesis of enynes.[15] However, reactions of these compounds with electrophiles have only been scarcely studied.[10c] In this paper, we report the synthesis of palladacyclopentadienes stabilized by

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various nitrogen ligands and their reaction with organic halides and small molecules such as dihydrogen, carbon monoxide, and carbon dioxide. On the basis of the results, we have designed a catalytic cycle for the synthesis of conjugated dienes from acetylenes. A preliminary report has been published.[4g]

Experimental Section

General. All reactions were performed in an atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were distilled prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AMX 300 spectrometer (300.13 and 75.48 MHz, respectively) at room temperature unless stated otherwise. Chemical shift values are in ppm relative to TMS with high-frequency shifts assigned positive. ^{19}F NMR data were collected on a Bruker AC 100 spectrometer (94.20 MHz) relative to $CFCl_3$. Exact mass determinations were obtained on a Varian MAT 711 double-focusing mass spectrometer and were performed by the Institute for Mass Spectroscopy, University of Amsterdam. GC-MS data were obtained using a HP 510 with a 80 mesh column of 12 m. The osmometric determinations were performed on a Hewlett-Packard 320B osmometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. The starting materials phenyl-bip,[5] (*p*-tolyl)-bian,[6] 3,3′-dicarbomethoxy-2,2′-bipyridine (dcm-bpy),[16] and Pd(dba)$_2$[17] were prepared according to literature procedures. Dimethyl-2-butynedioate (dmbd), methyl iodide, tetracyanoethylene (tcne), *tert*-butylisonitrile, bipyridine, bipyrimidine, and 1,3-diphenylphosphinopropane (dppp) were obtained commercially and used without further purification.

Synthesis of Pallada-2,3,4,5-tetrakis(carbomethoxy)-cyclopentadienes (1a−f) and Pallada-2,3,4,5-tetrakis-(trifluoromethyl)cyclopentadienes (2a, 2b). Typical Procedure for 1a. Method A. To a suspension of 0.50 g of Pd(dba)$_2$ (0.9 mmol) and 0.35 g of phenyl-bip (0.95 mmol) in 20 mL of acetone was added 0.3 mL of dmbd (2.4 mmol) at room temperature. After 1 h, the solvent was removed in vacuo and the product was washed with diethyl ether (2 × 20 mL). The brown product was dissolved in dichloromethane and filtered over Celite filter aid in order to remove the metallic palladium. The solvent was again removed in vacuo, yielding 0.57 mg (0.77 mmol, 85%) of light-brown product. Crystals of **1a** were obtained by slow diffusion of pentane into a dichloromethane solution of **1a** at 4 °C; crystals of **1d** were obtained by slow evaporation of the solvent of a solution of **1d** in dichloromethane. Anal. Found (Calcd) for $C_{38}H_{30}N_2O_8Pd$ (**1a**): C, 86.53 (87.12); H, 5.30 (5.06); N, 7.45 (7.82). Other data are presented in the Results.

In the case of **2a** and **2b**, the mixture of Pd(dba)$_2$ and phenyl-bip was stirred overnight in an atmosphere of perfluoro-2-butyne. The yields of the compounds **1b**−**f**, **2a**, and **2b** were 80−90%. Anal. Found (Calcd) for $C_{26}H_{24}N_2O_{12}Pd$ (**1f**): C, 46.94 (47.11); H, 3.75 (3.65); N, 4.28 (4.23). Anal. Found (Calcd) for $C_{34}H_{18}N_2F_{12}Pd$ (**2a**): C, 51.64 (51.76); H, 2.39 (2.30); N, 3.59 (3.55).

The platinum analogue of **1a** (**1′a**) was prepared similarly to **1a**, starting from Pt(dba)$_2$, by extending the reaction time to 2 weeks. Complex **1′a** was obtained in 88% yield as a dark brown solid.

Method B. To a solution of 0.5 mg of $(CH_3CN)_2Pd(dmbd)_2$ (1.1 mmol, prepared by method A) in 25 mL of dichloromethane was added 0.4 mg of phenyl-bip (1.1 mmol). After 5 min of stirring, the solvent was evaporated and the product was washed with diethyl ether (2 × 20 mL) and air-dried, yielding 0.8 mg of **1a** (1.0 mmol, 97%).

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Reactions of 1 with Organic Halides: Synthesis of Palladium (4-Alkyl/aryl-1,2,3,4-tetrakis(carbomethoxy)-1,3-butadienyl) Halides (3−5). Method A. To a solution of 80 mg of **1a** (0.11 mmol) in dichloromethane was added an excess of methyl iodide (1 mL, 16 mmol). This solution was stirred for 48 h at room temperature and then filtered through Celite filter aid (to remove the metallic palladium). The solvent was subsequently removed in vacuo, and the product was washed with diethyl ether (2 × 20 mL). The yield of **3a** was 79 mg (0.9 mmol, 81%).

The reactions with benzyl bromide were carried out in acetonitrile. For the synthesis of **4b**, the benzyl bromide was removed by extracting the solution with pentane, since the product was soluble in diethyl ether. This procedure gave similar yields for **3b**,**d** and **4b**,**d** of 80−91%. Anal. Found (Calcd) for $C_{39}H_{31}N_2O_8IPd$ (**3d**): C, 52.55 (52.69); H, 3.46 (3.51); N, 3.20 (3.15). Other data have been compiled in the Results.

Method B. A solution of 75 mg of **1a** (0.1 mmol) and 140 μL of benzyl bromide (1 mmol) in toluene was heated at 80 °C for 3 h. The solvent was then removed in vacuo, the organic products were extracted with diethyl ether (3 × 30 mL) and, after evaporation of the solvent, analyzed by GC-MS and NMR.

Trimerization of 1,4-Dichloro-2-butyne: Synthesis of 1-(1′-Chloroethenyl)-1,2,3,4,5-pentakis(chloromethyl)-2,4-cyclopentadiene (6). A solution of 15 mg of **1a** (0.02 mmol) and 250 μL of 1,4-dichloro-2-butyne (2 mmol) in 10 mL of toluene was heated at 80 °C for 3 h. The solution was evaporated to dryness, yielding **6**, a white sticky solid, in 82% yield. ^{1}H NMR (293 K, $CDCl_3$): 5.68, 5.59 (d, 2H, J = 2.9 Hz, CH_2=), 4.56 (s, 4H, 3,4-CH_2Cl), 4.40, 4.25 (d, 2 × 2H, J = 12.7 Hz, 2,5-CH_2Cl), 4.09 (s, 2H, 1-CH_2Cl). ^{13}C NMR (293 K, $CDCl_3$): 144.8, 143.4 (2 × 2C, 2/5- and 3/4-C=*C*), 137.9 (1C, Cl*C*=CH_2), 118.0 (1C, ClC=*C*H_2), 68.5 (1C, C_{quat}), 43.9 (1C, 1-*C*H_2Cl), 35.7, 35.6 (2 × 2C, 2/5- and 3/4-*C*H_2Cl). Exact mass: found m/z = 365.904 (calcd 365.907).

Synthesis of [(μ-3,3′-Dicarbomethoxy-2,2′-bipyridine)-Pd(tcne)]$_2$ (7). A mixture of 200 mg of Pd(dba)$_2$ (0.35 mmol), 100 mg of 3,3′-dicarbomethoxy-2,2′-bipyridine (0.36 mmol), and 45 mg (0.35 mmol) of tcne in 30 mL toluene was stirred for 3 h at room temperature. The suspension was filtered, and the solid product was washed subsequently with toluene (50 mL) and diethyl ether (5 × 25 mL). The product was dissolved in dichloromethane and filtered over Celite filter aid. The solvent was again removed in vacuo, yielding 151 mg (0.30 mmol, 85%) of yellow product. Crystals of **7** were obtained from dichloromethane/hexane. Anal. Found (Calcd) for $C_{20}H_{12}N_6O_4Pd$: C, 47.54 (47.43); H, 2.45(2.39); N, 16.48(16.58). ^{1}H NMR (293 K, $CDCl_3$): 9.01 (d, 2H, J = 4.5 Hz, H(6)), 8.55 (d, 2H, J = 7.9 Hz, H(4)), 7.80 (dd, 2H, H(5)), 3.83 (s, 6H, CH_3O). ^{13}C NMR (293 K, DMSO-d_6): 165.4 (1C, C=O), 155.7 (2C, C(2)), 154.9 (2C, C(6)), 141.5 (2C, C(4)), 132.2 (2C, C(3)), 127.9 (2C, C(5)), 114.4 (4C, CN), 54.0 (2C, CH_3O), 15.9 (2C, C=C).

Reactions of 1 with H_2, CO, and CO_2. All reactions were carried out using 10 mL of a 0.01 M solution of **1a**, **1b**, or **1c** in dichloromethane. Hydrogen gas was bubbled through the solution at room temperature for 2−15 min, and carbon dioxide was bubbled through the solution for 1.5 h. In the case of carbon monoxide, the solution was pressurized up to 50 bar in an autoclave and stirred for 16 h. The solvent was evaporated, and the organic products were extracted with diethyl ether, which was dried and evaporated. The remaining solids were analyzed by NMR, and the organic products were analyzed by NMR and GC-MS.

Catalytic Synthesis of Conjugated Dienes. Dimethyl-(2*Z*,4*Z*)-3,4-bis(carbomethoxy)-2,5-dimethyl-2,4-hexadien-1,6-dioate (8a). A solution of 15 mg of **1b** (0.02 mmol), 245 μL of dmbd (2 mmol), 180 mg of Me_4Sn (1 mmol), and 0.6 mL of methyl iodide (10 mmol) in 10 mL of DMF was stirred for 16 h at 65 °C. The reaction mixture was dissolved in 100 mL dichloromethane, washed with water (3 × 150 mL), and dried. The solvent was removed by evaporation, after which a sticky

Table 1. Crystallographic Data for 1a, 1d, and 7

	1a	1d	7
	Crystal Data		
formula	$C_{38}H_{30}N_2O_8Pd$	$C_{22}H_{20}N_2O_8Pd$	$C_{40}H_{24}N_{12}O_8Pd_2\cdot(C_6H_{14})_2$
mol wt	749.08	546.83	1185.90
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	*Pbcn* (No. 60)	*Pbcn* (No. 61)	*Fddd* (No. 70)
a, Å	18.4348(13)	15.4590(8)	17.7381(13)
b, Å	14.505(2)	13.5717(9)	22.2113(14)
c, Å	12.110(2)	20.4773(11)	27.600(2)
V, Å^3	3238.2(7)	4296.2(4)	10874.0(12)
D_{calc}, g cm^{-3}	1.536	1.691	1.449
Z	4	8	8
F(000)	1528	2208	4832
μ, cm^{-1}	6.2	9.2	7.2
cryst size, mm	0.30 × 0.05 × 0.05	0.13 × 0.13 × 0.18	0.50 × 0.28 × 0.25
	Data Collection		
T, K	150	150	150
θ_{min}, θ_{max}, deg	1.1, 27.5	2.0, 26.2	1.6, 27.5
λ (Mo Kα), Å (graphite monochromator)	0.71073	0.71073	0.71073
scan type	$\omega/2\theta$	ω	$\omega/2\theta$
$\Delta\omega$, deg	0.77 + 0.35 tan θ	0.70 + 0.35 tan θ	0.96 + 0.35 tan θ
horz, vert aperture, mm	3.22, 4.00	3.00 + 1.50 tan θ, 4.00	3.46, 4.00
X-ray exposure time, h	18.9	13.1	17.4
linear decay, %	4	2	2
ref reflns	6 0 2, 6 $\bar{2}$ 0, 2 0 4	2 4 0, 3 2 $\bar{3}$	$\bar{2}$ 0 10, $\bar{8}$ 2 2, 8 2 2
data set	−23:23, −18:0, 0:15	0:18, 0:17, −24:0	−23:0, −27:28, 0:35
total no. of data	8317	3940	5715
total no. of unique data	3717	3940	3129
DIFABS corr range	0.840−1.261	0.782−1.349	
	Refinement		
no. of refined params	224	302	143
final R1[a]	0.0796 [1662$F_o > 4\sigma(F_o)$]	0.0634 [2004$F_o > 4\sigma(F_o)$]	0.0318 [2265$F_o > 4\sigma(F_o)$]
final wR2[b]	0.1465 [3717 data]	0.1146 [3939 data]	0.0719 [3129 data]
goodness of fit	0.928	1.039	0.936
w^{-1} [c]	$\sigma^2(F^2) + (0.0300P)^2$	$\sigma^2(F^2) + (0.0216P)^2$	$\sigma^2(F^2) + (0.0331P)^2$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.006	0.000, 0.001	0.000, 0.000
min, max resid density, e Å^{-3}	−0.67, 0.73	−0.58, 0.70	−0.33, 0.53

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

solid remained. The organic product was then extracted with diethyl ether. After drying, evaporation of the solvents, and flash chromatography over neutral alumina with ether/hexanes 40/60 (v/v), >98% pure **8a** was isolated in 82% yield. ^{1}H NMR (293 K, $CDCl_3$): 3.82, 3.72 (s, 2 × 6H, CH_3O), 1.95 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): 170.0, 165.7 (2 × 2C, CO), 144.2, 127.7 (2 × 2C, C═C), 53.2, 53.2 (2 × 2C, CH_3O−), 16.4 (2C, CH_3−). Exact mass: found *m*/*z* = 314.102 (calcd 314.100).

Dimethyl-(2*Z*,4*Z*)-2-benzyl-3,4-bis(carbomethoxy)-5-methyl-2,4-hexadien-1,6-dioate (8b). The procedure is similar to that for **8a**, but 50 equiv of benzyl bromide was added and the reaction temperature was kept at 85 °C. The yield of **8b** was 75%. ^{1}H NMR (293 K, $CDCl_3$): 7.4−7.1 (m, 5H, C_6H_5), 3.61, 3.70, 3.66, 3.60 (s, 4 × 3H, CH_3O). ^{13}C NMR (293 K, $CDCl_3$): 168.0, 167.7, 164.7, 164.5 (4 × C, C═O), 145.3, 143.5 (2 × C, C═*C*−*C*═C), 135.2 (1C, C_{ipso}), 129.0, 128.1 (2 × 2C, C_m and C_o), 127.6, 126.6 (2 × C, *C*═C−C═*C*), 126.5 (1C, C_p), 52.4, 52.3, 52.1, 51.8 (4 × 1C, CH_3O), 36.0 (1C, −CH_2−), 17.6 (1C, CH_3). Exact mass: found *m*/*z* = 390.132 (calcd 390.130).

Dimethyl-(2*Z*,4*Z*)-3,4-bis(carbomethoxy)-2-methyl-5-phenyl-2,4-hexadien-1,6-dioate (8c). The procedure is similar to that for **8a**, but 50 equiv of iodobenzene was added and the reaction temperature was kept at 85 °C. The yield of **8c** was 76%. ^{1}H NMR (293 K, $CDCl_3$): 7.3−7.4 (m, 5H, C_6H_5), 3.86, 3.76, 3.74, 3.70 (s, 4 × 3H, CH_3O), 1.57 (s, 3H, CH_3). ^{13}C NMR (293 K, $CDCl_3$): 170.1, 169.0, 166.2, 166.0 (4 × C, C═O), 148.6, 143.9 (2 × C, C═*C*−*C*═C), 134.3 (1C, C_{ipso}), 130.5 (1C, C_p), 129.2, 128.5 (C_m and C_o), 127.6, 126.7 (2 × C, *C*═C−C═*C*), 54.1, 53.4, 53.2, 53.0 (4 × 1C, CH_3O), 18.8 (1C, CH_3). Exact mass: found *m*/*z* = 376.115 (calcd 376.116).

X-ray Structure Determinations of 1a, 1d, and 7. When appropriate, data of **1a**, **1d**, and **7** are given in that order. Suitable crystals for X-ray determination were mounted on a Lindemann-glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined from the setting angles of 25 reflections (SET4[18]) in the ranges 9.9° < θ < 13.8°, 10.0° < θ < 13.9°, and 11.6° < θ < 14.1°. Reduced-cell calculations did not indicate higher lattice symmetry.[19] Crystal data and details on data collection and refinement are presented in Table 1. Data were corrected for *Lp* effects and for the observed linear decay of the reference reflections. On **1a** and **1d**, an empirical absorption/extinction correction was applied (DIFABS[20] as implemented in PLATON[21]). The structures **1a** and **1d** were solved by automated Patterson methods and subsequent difference Fourier techniques DIRDIF-92.[22] The structure of **7** was solved by automated direct methods (SHELXS86[23]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93[24]); no observance criterion was applied during refinement.

All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were calculated riding

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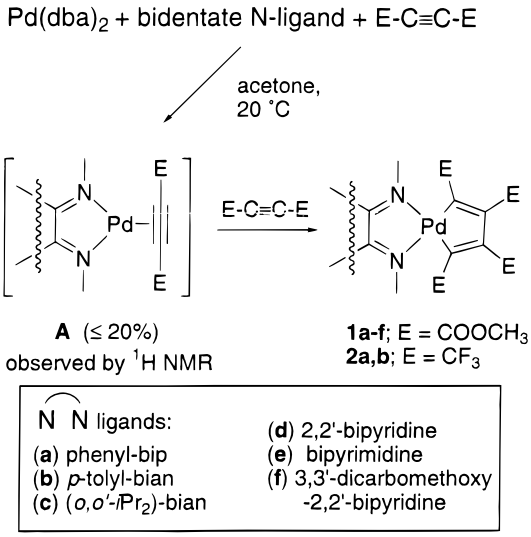
Scheme 1. Synthesis of Palladacycles 1 and 2 with Various (Rigid) Bidentate N-Ligands



on their carrier atoms. The hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.5 or 1.2 times the value of the equivalent isotropic thermal parameter of their carrier atoms for the methyl hydrogen atoms and all other hydrogen atoms, respectively. Compound **7** contains a *n*-hexane disordered over an inversion center for which no satisfactory model could be refined. The SQUEEZE[25] procedure from PLATON[21] was used to take this electron density into account. Weights were optimized in the final refinement cycles. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 26.

Results and Discussion

Synthesis of Palladacyclopentadienes. The palladacycles **1a**−**f** and **2a**,**b** were synthesized in good yields (82−97%) from either $Pd(dba)_2$ or $(CH_3CN)_2Pd(dmbd)_2$ (Scheme 1). The new compounds, air-stable solids which are very soluble in chloroform and dichloromethane, were analyzed by elemental analysis or mass spectroscopy and by ^1H and ^{13}C NMR in solution, while new data of earlier reported compounds have also been included (see tables). Crystal structure determinations were performed on (phenyl-bip)pallada-2,3,4,5-tetrakis(carbomethoxy)-2,4-cyclopentadiene (**1a**) and its bipyridine analogue (**1d**).

The formation of **1** was usually instantaneous, and no intermediates could be observed. When phenyl-bip was used in the synthesis of **1a** by method A, the formation of an intermediate (phenyl-bip)Pd(dmbd) compound (**A**, up to maximum 20%) was observed by ^1H and ^{13}C NMR. It could, however, not be isolated. This acetylene complex exhibited signals at 4.12 (methyl protons) and 69.5 (acetylenic carbons) ppm characteristic of a π-coordinated dmbd molecule. Since (i) no acetylene complex could be observed for (*p*-tolyl)-bian and (ii) it has been reported that (ligand)$Pd^0(\eta^2$-alkyne) compounds become more stable with an increasing π-accepting capacity of the bidentate nitrogen ligand,[10d] we believe that the relative stability of the acetylene complex is most likely caused by the more pronounced π-accepting capacity of phenyl-bip as compared to the other ligands of similar type.[5b] In other cases, the steric demands of the ligand stabilizes the acetylene complex, but for the very bulky *tert*-butyl-dab,[27] for instance, no formation of the palladacyle was possible due to the steric crowding.

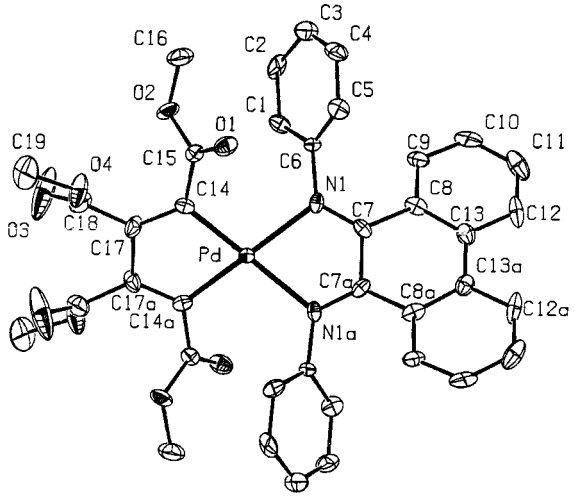


Figure 1. ORTEP plot of **1a** at the 50% probability level; hydrogen atoms were omitted for clarity.

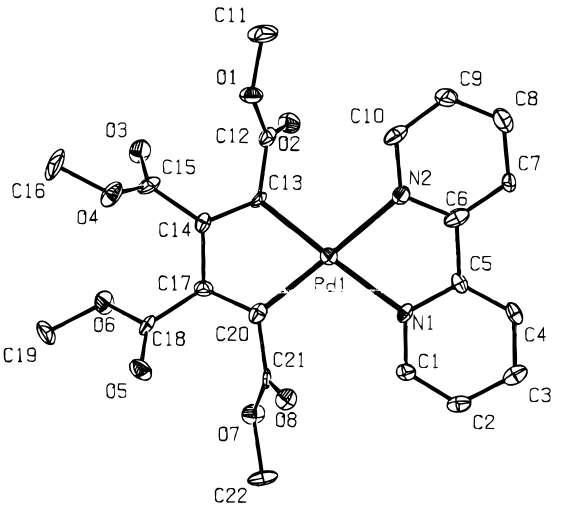


Figure 2. ORTEP plot of **1d** at the 50% probability level; hydrogen atoms were omitted for clarity.

The platinum analogue **1′a** could be prepared in high yield (88%) when the reaction time was extended to 2 weeks. It was isolated as a dark brown solid, which was only moderately soluble in dichloromethane or chloroform.

The incorporation of other acetylenes, besides dimethyl butynedioate and perfluoro-2-butyne, has also been attempted. Unfortunately, employing diphenylacetylene, 1,4-dihydroxy-2-butyne, methyl propiolate, phenylacetylene, 4-octyne, or 2-methyl-3-pentyne did not lead to the formation of palladacycles. In the cases of 1,4-dihydroxy-2-butyne, methyl propiolate, and phenylacetylene, only the formation of metallic palladium was observed. In these cases, decomposition of the product is probably facilitated due to the formation of intermediate palladium hydride compounds.

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Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 1a

Pd−N(1)	2.130(6)	N(1)−C(6)	1.430(9)	C(17)−C(17a)	1.488(10)	O(2)−C(15)	1.328(10)
Pd−C(14)	2.008(7)	C(7)−C(7a)	1.495(10)	O(1)−C(15)	1.215(10)	O(4)−C(18)	1.299(14)
N(1)−C(7)	1.285(9)	C(14)−C(17)	1.347(10)	O(3)−C(18)	1.177(14)		

N(1)−Pd−N(1a)	76.6(2)	C(14)−Pd−C(14a)	79.4(3)	Pd−C(14)−C(17)	116.7(6)
N(1)−Pd−C(14)	103.9(3)	Pd−N(1)−C(7)	113.9(5)	N(1)−C(7)−C(7a)	114.9(6)
N(1)−Pd−C(14a)	165.4(3)	Pd−N(1)−C(6)	122.3(5)	C(14)−C(17)−C(17a)	113.5(6)

N(1)−C(7)−C(7a)−N(1a)	28.6(9)	C(8)−C(13)−N(13a)−C(8a)	7.0(11)	C(14)−C(17)−C(17a)−C(14a)	7.0(16)
C(8)−C(7)−N(7a)−C(8a)	33.7(9)	C(1)−C(6)−N(1)−C(7)	115.4(8)	O(1)−C(15)−C(14)−C(17)	126.9(11)
C(12)−C(13)−C(13a)−C(12a)	12.6(12)	C(5)−C(6)−N(1)−C(7)	−67.6(10)	O(3)−C(18)−C(17)−C(14)	123.5(13)

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 1d

Pd−N(1)	2.127(6)	C(5)−C(6)	1.474(12)	O(2)−C(12)	1.210(11)	O(1)−C(12)	1.363(11)
Pd−N(2)	2.113(7)	C(13)−C(14)	1.352(12)	O(3)−C(15)	1.205(11)	O(4)−C(15)	1.332(11)
Pd−C(13)	2.003(8)	C(14)−C(17)	1.473(12)	O(5)−C(18)	1.205(10)	O(6)−C(18)	1.351(11)
Pd−C(20)	2.024(9)	C(17)−C(20)	1.329(13)	O(8)−C(21)	1.203(11)	O(7)−C(21)	1.360(10)

N(1)−Pd−N(2)	77.6(3)	N(2)−Pd−C(13)	101.3(3)	Pd−C(13)−C(14)	117.8(6)
C(13)−Pd−C(20)	78.5(3)	N(2)−Pd−C(20)	169.7(3)	Pd−C(20)−C(17)	116.3(6)
N(1)−Pd−C(13)	170.4(3)	Pd−N(1)−C(5)	113.9(5)	C(13)−C(14)−C(17)	112.1(8)
N(1)−Pd−C(20)	104.4(3)	Pd−N(2)−C(6)	115.8(5)	C(20)−C(17)−C(14)	115.1(8)

N(1)−C(5)−C(6)−N(2)	1.4(11)	O(2)−C(12)−C(13)−C(14)	−111.0(10)	O(5)−C(18)−C(17)−C(20)	37.3(15)
C(4)−C(5)−N(6)−C(7)	−1.6(14)	O(3)−C(15)−C(14)−C(13)	49.8(13)	O(8)−C(21)−C(20)−C(17)	−104.8(11)
C(13)−C(14)−C(17)−C(20)	−1.9(12)				

Using 1,4-dichloro-2-butyne, the palladacyclic compound was also probably formed under the conditions described in the Experimental Section (method A), but this could not be ascertained due to the extremely low solubility of the product. The formation of the intermediate palladacycle in this case was inferred from the reaction products obtained when the compound was reacted with bromine. In analogy to the reaction of poly[pallada-2,3,4,5-tetrakis(carbomethoxy)cyclopentadiene] with bromine,[10a] this reaction was expected to yield 1,4-dibromo-1,2,3,4-tetrakis(chloromethyl)-1,3-butadiene. In the present case, however, products with more than two bromine atoms were observed by GC-MS, which have arisen from a further addition reaction of bromine to the double bonds of the initially formed 1,4-dibromobutadiene, yielding tetrabromo and hexabromo compounds.

X-ray Crystal Structures of 1a and 1d. The adopted numbering schemes of the molecular structures of **1a** and **1d** are depicted in Figures 1 and 2, and selected bond distances, bond angles, and torsion angles have been compiled in Tables 2 and 3. The crystallographic symmetry of the molecule **1a** is C_2. The geometry around the palladium center in **1a** is distorted square planar. The palladacycle itself and the chelate ring Pd−N(1)−C(7)−C(7a)−N(1a) are essentially planar, as indicated by the small deviations from the least-squares planes, which are 0.033(13) and 0.125(7) Å for C(17) and C(7), respectively. The distortion from square planarity is reflected by the dihedral angle between these planes of 27.1(4)°. The nitrogen atoms are located 0.539(6) Å beneath and above the plane of the palladacyle, and C(14) and C(14a) are located 0.568(9) Å above the coordination plane. The bite angle N(1)−Pd(1)−N(1a) of 76.6(2)° is normal for chelating dinitrogen ligands, e.g., for $PdCl_2$(phenyl-bip),[5b] (bpy)Pd(C(O)Me)Cl, and (2-(*N*-2-propanecarbaldimine)pyridyl)Pd(Me)Cl[28] it was 78.8(4)°, 77.8(4)°, and 78.1(1)°, respectively.

The Pd(1)−N(7) distance of 2.130(6) Å is somewhat longer than the similar bonds in the palladium dichloride coordination compound $PdCl_2$(phenyl-bip)[5b] (2.016(9) and 2.032(9) Å), probably due to a slightly stronger trans influence of the carbon atoms with respect to the chlorides, since almost the same values were observed for **1d** (vide infra). The C(7)−N(1) bond length (1.285(9) Å) is of the same order as the bond distance in $PdCl_2$(phenyl-bip) (1.305(16) and 1.269(14) Å) and in the free phenyl-bip ligand (1.278(4) and 1.280(5) Å). The amount of puckering of the backbone in the phenyl-bip ligand lies between that of the free ligand (which has the *Z*,*Z* configuration in stead of the *E*,*E*) and the palladium dichloride compound.[5b] This is illustrated by comparison of the different torsion angles. The N(1)−C(7)−C(7a)−N(1a) angle is 28.6(9)° in the palladacycle containing phenyl-bip, whereas it is 21.3(15)° in its coordination compound with $PdCl_2$ and 44.7(5)° and 51.3(4)° in the free ligand (the latter has two independent molecules in the unit cell). The higher degree of puckering of **1a** is probably the result of a combination of the longer Pd−N bonds and the interaction of the *N*-phenyl rings with the ester groups on the α-position (relative to palladium, see Figure 1).

The features of the palladacyclopentadiene part of the molecule are very similar to other reported analogous structures[12,13] and also resemble the features of **1d**. However, in this compound (**1d**), the distortion of the square-planar coordination around palladium is less than that for **1a**: the dihedral angle between the coordination plane and the palladacycle is 27.1° in the latter and 15.6(4)° in **1d**. This is caused by a diminished steric interaction of the bpy, as compared to the phenyl-bip, with the ester groups on the palladacycle. The dihedral angle (N(1)−C(5)−C(6)−N(2)) of bipyridine is only 1.4(11)°. The other features of bpy are as expected (vide supra), viz. Pd−N(1) = 2.127(6) Å, Pd−N(2) = 2.113(7) Å, N(2)−C(6)−C(5) = 116.2(7)°, N(1)−C(5)−C(6) = 116.3(7)°, and the bite angle N(1)−Pd−N(2) = 77.6(3)°, which is only slightly larger than in the case of **1a** (76.6(2)°).

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Table 4. ^{1}H NMR Data of Palladacyclopentadienes 1 and 2[a,g]

	ligand	E	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)	H(11)	R″
1a	phenyl-bip	3.69, 2.93	6.7 d, 7.7	7.00 t, 7.8	7.5 m	7.8 d, 7.9			7.91 d, 7.8	7.22 m	7.33 t, 7.3	7.5 m	6.76 t, 7.6	
1′a	phenyl-bip	3.64, 2.98	6.64 d, 8.1	7.00 t, 7.8	7.56 t, 7.8	7.82 d, 7.9			8.08 d, 7.2	6.89 t, 7.2	7.38 t, 7.2	*c*	*c*	
2a	phenyl-bip		6.90 t, 7.8	7.07 t, 7.4	7.55 t, 7.3	7.86 d, 7.7			8.06 b	6.74 b	7.34 t, 7.2	*c*	*c*	
1b	(*p*-tolyl)-bian	3.58, 2.99	6.52 d, 7.3	7.41 t, 7.8	8.02 d, 8.3				7.13 d, 8.2	7.31 d, 8.2		(=8)	(=7)	2.49 (CH_3)
2b	(*p*-tolyl)-bian[e]		6.90 d, 7.3	7.50 t, 8.0	8.04 d, 8.3				7.28 d, 7.6	7.35 d, 7.6		(=8)	(=7)	2.49 (CH_3)
1c	(*o,o′-i*Pr-phenyl)-bian	3.51, 2.79	5.76 d, 7.2	7.44 t, 7.8	8.02 d, 8.2					7.35 m	7.35 m	(=8)	(=7)	3.25 (CH−), 1.41, 0.66 (CH_3) d, 6.4, 6.7
1d	bpy[f]	3.73 (2×)			8.17 d, 8.0	7.99 pst	7.46 pst	8.37 d, 4.7						
1e	bipyrimidine	3.74, 3.73				9.13 b	7.71 b	(=4)						
1f	dcm-bpy	3.77, 3.75				8.44 d, 7.9	7.66 dd	8.97 d, 5.3						3.72 ($COOCH_3$)

[a] Recorded at 300.13 MHz in $CDCl_3$ at 293 K. For atomic-numbering scheme, see structural formula below. Coupling constants (Hz) are given after the chemical shifts, except for E. Abbreviations used: s = singlet, d = doublet, pst = pseudotriplet, m = multiplet, b = broad. [b] Recorded at 233 K. [c] Masked. [d] ^{19}F NMR: aa′bb′ pattern, −54.24 and −59.27 ppm. [e] ^{19}F NMR: aa′bb′ pattern, −54.36 and −59.60 ppm. [f] Recorded at low concentration. [g] Selected data for Pd-cycles with ancillary P-ligands: dppp ^{1}H NMR 7.8 (m, H_o), 7.4 (m, H_p and H_m), 3.56, 2.59 (CH_3O), ^{31}P{^{1}H} 6.16 ppm; PPh_3 ^{1}H NMR 7.34 (b), 7.26 (t, H_p), 7.14 (t, H_m), 3.64 2.37 (CH_3O), ^{31}P 20.19 ppm.

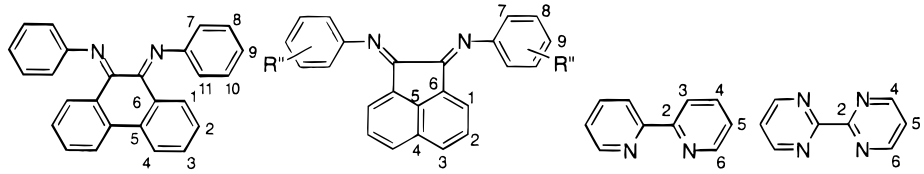


Table 5. ^{13}C NMR Data of Palladacyclopentadienes 1 and 2[a]

	ligand	OMe	C=O	C=C	C=N	C−N	C(1)	C(2)	C(3)	C(4)	C(5/6)	C(7)	C(8)	C(9)	R″
1a	phenyl-BIP[e]	52.1 51.6	171.3, 168.6	165.3, 147.1	163.7	148.3	131.6	128.8	134.6	126.1	126.4, 137.4	122.3[b]	130.6[c]	128.1	
2a	phenyl-BIP[e]			n.o.	168.2	149.2	131.8	129.1	134.8	126.2	126.1, 137.7	121.9[b]	130.5[c]	128.4	
1′a	phenyl-BIP[e]	52.0, 51.7	171.6, 169.0	166.6, 146.3	165.7	148.3	131.2	129.1	134.5	126.3	127.2, 137.5	120.3	n.o.	128.6	
1b	(*p*-tolyl)-bian[e]	51.8, 51.4	171.5, 172.5	164.7, 145.9	163.1	144.7	126.4	129.0	132.1	131.7	145.7, 126.4	121.8	130.6	138.0	21.8 (CH_3)
2b	(*p*-tolyl)-bian[e]			n.o.	168.2	145.2	126.7	129.1	132.0	132.0	139.8, 126.3	121.8	130.7	138.3	21.6 (CH_3)
1c	(*o,o′-i*Pr-phenyl)-bian[e]	51.7, 51.3	173.6, 171.4	164.5, 145.5	163.3	143.5	126.8	123.2	132.5	131.5	144.9, 127.4	140.1	125.3	128.5	29.97 (CH), 25.1, 23.4 (CH_3)
1d	bpy[d]	52.3, 51.1	174.3, 165.2	163.3, 146.0				155.5	123.6	140.6	151.3, 127.2				
1f	dcm-bipy	52.3, 52.2	173.2, 165.7	162.4, 146.8				156.7	130.7	140.2	153.7, 126.4				134.8 (C=O), 53.7 ($COOCH_3$)

[a] Recorded at 75.48 MHz in $CDCl_3$ at 293 K. For atomic-numbering scheme, see structural formula in Table 4. [b] Broad signal. [c] Very broad signal. [d] Low concentration sample. [e] For C(10) see C(8), and for C(11) see C(7).

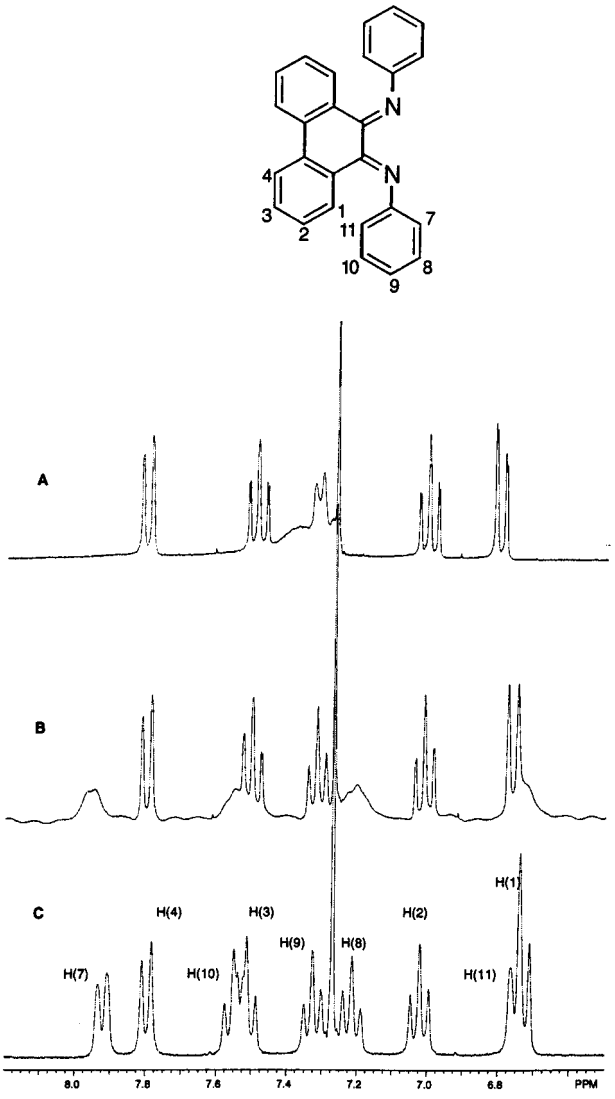


Figure 3. Variable-temperature ^{1}H NMR (at 300.13 MHz) of compound **1a**: (A) at 323 K, (B) at 283 K, (C) at 243 K.

NMR Spectroscopy of Palladacyclopentadienes. The most characteristic chemical shifts of all compounds (except for **2**) are the ones that correspond to the methoxycarbonyl groups; they act as a probe for the compounds' geometry, i.e., symmetric compounds show two and asymmetric show four resonance signals. The signals due to the methoxycarbonyl groups are observed around 3.7 ppm in the ^{1}H NMR spectra, but the ones at the α-positions (relative to palladium) show, in some cases, a low-frequency shift of about 0.7 ppm (Table 4) due to anisotropic shielding by the phenyl group of the nitrogen ligand. This phenomenon is observed for compounds containing phenyl-bip (**1a**), (*p*-tolyl)-bian (**1b**), and (*o,o′-i*Pr$_2$-phenyl)-bian (**1c**) as well as for compounds containing dppp and triphenylphosphine. When bipyridines or bipyrimidines were used as the chelating ligands (**1d** and **1f**), both ester signals were close together around 3.7 ppm. Another common feature of all palladacycles concerns the chemical shifts of the alkene in the ^{13}C NMR (Table 5) at approximately 165 and 145 ppm, of which the latter is assigned to the α-carbon atom attached to palladium. It is worth mentioning that for compound **1a** the increase in conjugation of the backbone of phenyl-bip compared to the free phenyl-bip ligand, i.e., the molecule becomes more planar upon coordination, is clearly reflected in the ^{13}C NMR spectrum. As a result, the peak due to the quaternary aromatic carbon C(13) is shifted from 135 ppm in the free ligand to 126 ppm in **1a**.

Table 6. Activation Energies for Fluxional Processes[a]

compound	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^{\ddagger}$ (kJ/mol)
1a	344	303	57.5 (±0.5)
1a[b]	16	270	57.9 (±0.6)
1′a (Pt analogue)	359	298	56.4 (±0.5)
2a	384	306	57.8 (±0.5)
1e	90	233	48.4 (±1)

[a] ^{1}H NMR recorded at 300.13 MHz unless stated otherwise. [b] ^{13}C NMR recorded at 75.48 MHz.

The protons of the nitrogen ligands in **2a** and **2b** have almost the same chemical shift in the ^{1}H NMR spectra as compared to their analogues **1a** and **1b**. This is also the case for the carbon atoms in their ^{13}C NMR spectra, but the alkenic carbon atoms of the palladacycle are of too low intensity to be observed due to coupling with the fluorine nuclei.

Fluxional Behavior of 1a, 2a, 1d, and 1e in Solution. The palladacycles containing phenyl-bip (**1a**, **1′a**, and **2a**) show fluxional behavior on the NMR time scale involving the atoms on the ortho and meta positions of the phenyl rings, as observed in the ^{1}H (see Figure 3) and ^{13}C NMR spectra at 300.1 and 75.5 MHz, respectively. Coalescence was reached at temperatures between 300 and 270 K in all cases.

This fluxional process of the compounds containing phenyl-bip can be ascribed to an inversion of the conformation of the phenyl-bip ligand, by which process the diastereotopic ortho (and meta) atoms interconvert.[29] Such behavior is not observed in the compound containing the rigid and flat (*p*-tolyl)-bian ligand (**1b**). The free enthalpy of activation ($\Delta G^{\ddagger}_{303}$) estimated for **1a** was 57.7 kJ/mol (see Table 6).[30] For the analogous platinum compound (**1′a**), $\Delta G^{\ddagger}_{298}$ was estimated to be 56.4 kJ/mol, and for **2a** the $\Delta G^{\ddagger}_{306}$ was 57.8 kJ/mol. The activation energies for this exchange process are approximately the same for all three cases and are significantly higher than that of the free phenyl-bip ligand ($\Delta G^{\ddagger}_{193}$ = 36 kJ/mol[5b]), which must be ascribed to the coordination of the ligand to the metal center. This can be understood by taking into account that upon coordination the angle N(1)−C(7)−C(7a) of the diimine moiety of 114.9(6)° is much smaller than that of the free ligand (the smallest one is 126.4(3)° [5b]). This will result in more ring strain in the planar transition state for the coordination compound as compared to the free ligand.

For the compound containing bipyridine (**1d**), both a concentration and temperature dependence of the chemical shifts of the bipyridine ligand was observed. All protons were shifted, but H(6) was influenced most in both cases. The chemical shift difference for the temperature-dependent process was only about 0.1 ppm for H(6), whereas a chemical shift difference of 0.4 ppm was observed for the concentration-dependent process. The

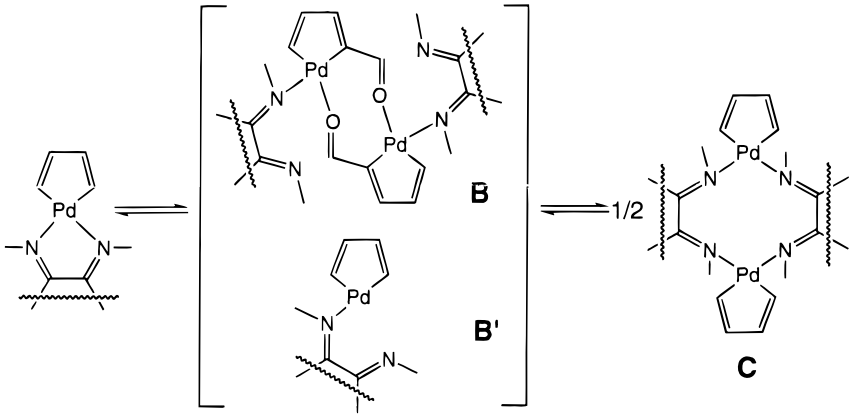
(29) Due to the twisted biphenyl backbone, the phenyl-BIP ligand is C_2 symmetric (the dihedral angle C(7)−N(1)−C(6)−C(5) is −67.6-(10)° in the crystal structure, see Figure 1).

(30) Although doublets are involved, the coalescence temperature could be reasonably well-established because of the relatively large difference in the chemical shift between the diastereotopic *ortho*-protons in this case.

Table 7. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for 7

Pd(1)−N(1)	2.123(2)	C(8)−C(8b)	1.457(4)	C(4)−C(5)	1.391(4)
Pd(1)−C(8)	2.047(3)	C(8)−C(9)	1.442(4)	C(4)−C(6)	1.500(4)
N(1)−C(1)	1.352(3)	C(8)−C(10)	1.448(4)	C(6)−O(1)	1.191(4)
N(1)−C(5)	1.345(4)	C(1)−C(2)	1.377(4)	C(6)−O(2)	1.335(3)
N(2)−C(9)	1.140(4)	C(2)−C(3)	1.383(4)	O(2)−C(7)	1.446(5)
N(3)−C(10)	1.143(4)	C(3)−C(4)	1.396(4)	C(5)−C(5c)	1.494(3)
N(1)−Pd(1)−N(1b)	100.50(7)	Pd(1)−C(8)−C(9)	112.5(2)	C(2)−C(3)−C(4)	119.5(3)
C(8)−Pd(1)−C(8b)	41.70(11)	Pd(1)−C(8)−C(10)	114.4(2)	C(4)−C(5)−N(1)	121.5(2)
N(1)−Pd(1)−C(8)	108.92(8)	Pd(1)−C(8)−C(8b)	69.15(19)	C(4)−C(6)−O(1)	123.2(3)
N(1)−Pd(1)−C(8b)	100.50(7)	N(1)−C(1)−C(2)	118.8(2)	C(9)−C(8)−C(20)	114.6(3)
N(1)−C(5)−C(5c)−N(1c)	91.5(3)	C(8b)−Pd(1)−N(1)−C(1)	−51.7(3)	O(2)−C(6)−C(4)−C(5)	−1.5(4)
C(4)−C(5)−C(5c)−C(4c)	93.2(4)	O(1)−C(6)−C(4)−C(5)	−179.6(3)	C(7)−O(2)−C(6)−C(4)	−174.8(3)
C(8)−Pd(1)−N(1)−C(1)	−54.8(2)				

Scheme 2. Formation of a Dimer of 1



process involved can be explained by taking recourse to the similar palladacylic compound containing bipyrimidine as the ancillary ligand (**1e**). Bipyrimidine closely resembles bpy in its coordination behavior,[31] and it has been shown that protons H(4) and H(6) of **1e** are averaged at room temperature and decoalesce at low temperature. The free enthalpy of activation ($\Delta G^{\ddagger}_{233}$) for **1e** amounts to 48.4 (±1) kJ/mol, which is of the same order of magnitude observed for a similar process involving chelate dissociation, rearrangement, and chelate association.[32] It is likely, therefore, that the temperature-dependent process observed for **1d** similarly involves rotation of the bipyridine after dissociation of one N-donor atom. Recently, N-ligands such as 4,5-diazafluoren-9-one and 4,5-diazafluorene,[33] (*p*-anisyl)-bian,[34] and 2,9-dimethyl-1,10-phenanthroline[35] were found to coordinate in a monodentate fashion.

The concentration-dependent dynamic behavior observed for **1d** indicates an equilibrium between a mono- and a binuclear species. This has been corroborated by osmometric measurements, which revealed a molecular weight for **1d** in solution of 674 (monomer, 547). The formation of a dimeric species in which the bipyridine coordinates in a monodentate fashion and one ester carbonyl coordinates (**B** in Scheme 2), as known for substituted pyridines,[13] is not likely since the N-ligand and the palladacycle remain symmetric (even at −60 °C no broadening was observed in the 300 MHz ^{1}H NMR spectrum). The existence of an equilibrium between compounds containing a chelating (left-hand in Scheme 2) and a bridging bipyridine (**C** in Scheme 2) is more likely. Compounds containing bridging bipyridines may arise from the starting chelate compound via a monocoordinated intermediate (**B′** in Scheme 2, the same intermediate that plays a role in the pyridine rotation) or via the dimeric form with a bridging C═O (**B** in Scheme 2), which has been described above. Circumstantial evidence for the viability of a species such as **C** was gained from a single-crystal X-ray study (see below) of [(μ-3,3′-dicarbomethoxy-2,2′-bipyridine)Pd(tcne)]$_2$ (**7**), exemplifying the bridging coordination mode for 2,2′-bipyridine and similar ligands. Moreover, **7** showed a concentration dependence (in DMSO) similar to **1d** in the ^{1}H NMR spectrum, and molecular weight determinations in dichloromethane gave similar results to those of **1d** (found 663, monomer 504), indicating that for **7** an equilibrium also exists between the monomer and the dimer.

X-ray Crystal Structure of [(μ-3,3′-dcm-2,2′-bipyridine)Pd(tcne)]$_2$ (7). The molecular structure and the adopted numbering scheme are depicted in Figure 4, selected bond distances, bond angles, and torsion angles are compiled in Table 7. In this D_2-symmetric compound, two 3,3′-dicarbomethoxy-2,2′-bipyridine molecules bridge between two palladium atoms, each have one molecule of tcne coordinated to it. The bridging

(31) Winslow, L. N.; Rillema, D. P.; Welch, J. H.; Singh, P. *Inorg. Chem.* **1989**, *28*, 1596.
(32) Gogoll, A.; Örnebrom, J.; Grennberg, H.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.
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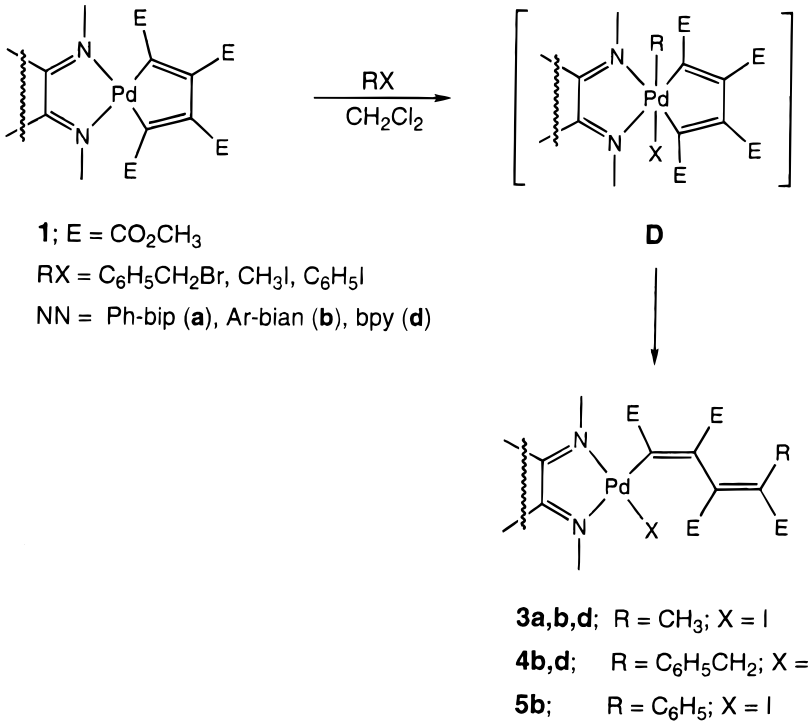
Scheme 3. Stoichiometric Reactions of Palladacyclopentadienes 1 with Organic Halides



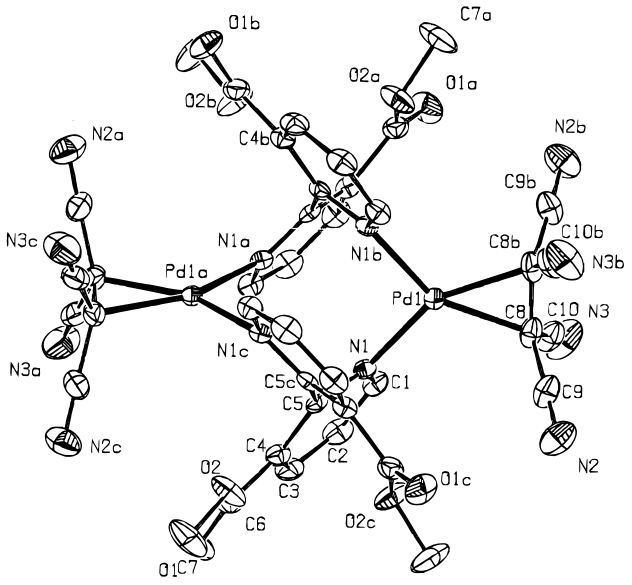


Figure 4. ORTEP plot of **7** at the 50% probability level; hydrogen atoms were omitted for clarity.

mode is accessible because the two pyridyl units of each dcm-bpy ligand are almost perpendicular to each other, i.e., the dihedral angle N(1)−C(5)−C(5c)−N(1c) is 91.5-(3)°. However, in its coordination compound with palladium dichloride, 3,3′-dicarbomethoxy-2,2′-bipyridine forms a chelate.[36]

There is no interaction between the two palladium atoms in **7**, and the intermetallic separation amounts to 4.777(4) Å. The coordination around the palladium centers can be considered trigonal planar, as expected for zerovalent compounds of the type PdL_2(alkene).[37] However, the long alkene bond length C(8)−C(8b) of 1.457(4) Å and the large angles Pd(1)−C(8)−C(10) and Pd(1)−C(8)−C(9) of 114.4(2)° and 112.5(2)°, respectively, indicate that a strong rehybridization toward sp^3 has occurred, and therefore, the geometry around palladium can also be considered square planar (as for a palladacyclopropane).[38] The alkene moiety is positioned in the coordination plane (C(5) is 0.082(2) Å above this plane).

The Pd(1)−N(1) distance of 2.123(2) Å is comparable to other Pd−bpy systems, i.e., 2.164(8) Å in Pd(bpy)-(dba)[39] and 2.127(6) and 2.113(7) Å in **1d**. The Pd(1)−C(8) bond of 2.047(3) Å, however, is relatively short compared to other Pd(alkene) compounds but is almost the same as in Pd(*o*,*o*′-*i*Pr_2-bian)(maleic anhydride) where this Pd−C distance is 2.064(8) Å.[34] Since the bipyridine is not chelating, the bite angle N(1)−Pd(1)−N(1b) in **7** is relatively large, 100.50(7)°. The other distances and angles showed no anomalies.

Some examples of bridging bipyridines in compounds of the type $L_3M(\mu\text{-bpy})ML_3$ have been reported, but most of these are based on indirect evidence.[40] Only a few crystal structures, i.e., a Cr[41] and a Pt[42] compound, are known. There have been no reports of palladium compounds of the type shown at the right-hand of Scheme 2.

Reactions with Dihydrogen, Carbon Monoxide, and Carbon Dioxide. Upon reaction of **1a**, **1b**, or **1c**

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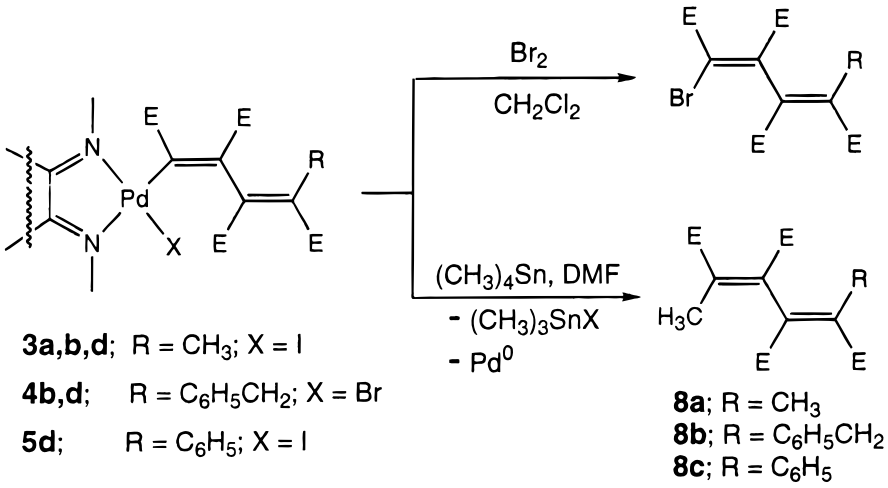
(42) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Fortuño, C. *Polyhedron* **1989**, *8*, 2209.

Scheme 4. Stoichiometric Reactions of Dienylpalladium(II) Compounds 3−5 with Br_2 and Tetramethyltin



with dihydrogen at 20 or 0 °C in dichloromethane, only small amounts (<10%) of 1,2,3,4-tetrakis(carbomethoxy)-1,3-butadiene were formed, even when the reaction was carried out at 0 °C. Under these conditions a mixture of hydrogenated products was also obtained, due to a heterogeneous conversion catalyzed by the metallic palladium which precipitated during the reaction. All palladacycles were unreactive toward CO and CO_2 in dichloromethane solutions at room temperature and pressures up to 50 bar.

Reactions of 1 with Organic Halides. Attempts to synthesize symmetric 1,4-disubstituted 1,3-dienes from palladacycles (**1a**,**b**,**d**) employing excess methyl iodide or benzyl bromide (see eq 1) in toluene, acetonitrile, or dichloromethane were not successful. Relatively high temperatures had to be applied to obtain any conversion at all in toluene, and as shown by GC-MS, only a very low yield of diene was obtained. Instead, reaction of **1a**,**b**,**d** with methyl iodide in dichloromethane or acetonitrile at room temperature resulted in the clean formation of the palladium-1,2,3,4-tetrakis(carbomethoxy)-1,3-pentadienyl compounds **3a**,**b**,**d**, **4b**,**d**, and **5b** (Scheme 3).

The reaction time required for the formation of **3** depended strongly on the ligand involved: the compounds containing the diimines (**1a**,**b**) and bipyridine (**1d**) gave complete conversion with a 200-fold excess of methyl iodide in 72 h at room temperature, whereas the phosphine compounds gave no conversion under these conditions. When reacted with benzyl bromide, **1b** and **1d** gave complete conversion to a single product only in acetonitrile solution in 48 h. Due to side reactions in the reaction with **1a**, the benzyl bromide adduct (**4a**) could not be isolated in pure form. These results and the known occurrence of triorgano(NN)palladium(IV) halide compounds in C−C bond-formation reactions[2−4] point to the intermediacy of high-valent palladium compounds **D**.

The dienyl compounds do not (or only very sluggishly, vide supra) react with excess organic halides but they do react with an additional equivalent of dihalogen, in the case of **3** yielding an asymmetric diene of the type 1-halo-1,2,3,4-tetrakis(carbomethoxy)-1,3-pentadiene (Scheme 4).[4g]

Competition experiments involving a Pd(NN)(alkene) complex, 2 equiv of alkyne (dmbda), and alkyl halide revealed that the palladacyclic compounds **1** are formed much more rapidly than the concurrent oxidative addition of alkyl halide. Furthermore, adding excess alkyl halide to solutions of **1** resulted in the formation of **3**−**5**, but no 1,4-dialkyl-1,3-dienes due to successive addition−elimination sequences were formed. The lack of formation of these dienes in the reaction of **1** with organic halides is most probably due to the low nucleophilicity of the σ-dienylpalladium(II) compounds **3**−**5**, which is even lower than that for the parent palladacyclic compounds. Oxidative addition of organic halides to divalent palladium compounds seems to be a facile process only in the case of dialkylpalladium(II) species.[43] It cannot be excluded that steric factors play a role, i.e., the position of the dienyl fragment with respect to the coordination plane might hinder the addition.

Transmetalation of the dienylpalladium halides **3**−**5** appeared to be feasible; whereas Grignard and organozinc regagents resulted in competitive addition to the carbonyl moieties, the use of tetramethyltin in DMF at 50−70 °C resulted in clean conversion into the dienes **8**. In the presence of alkene, Pd(NN)(alkene) compounds were formed, and with dmbda, the palladacycles **1** were formed as the other product. The above-mentioned successful stoichiometric single steps open a perspective for rendering an overall *catalytic* reaction of alkynes with organic halides and tetramethyltin to give conjugated dienes that are functionalized in the 1- and 4-positions. This aspect will be dealt with below.

The ^1H and ^{13}C NMR data of selected compounds **3**−**5** are listed in Tables 8 and 9. The data are in agreement with the expected inequivalence of both halves the N-ligand and of all positions in the dienyl moiety. Furthermore, from the inequivalence of the protons of the *N*-phenyl group in the bip compounds and the *N*-*p*-tolyl group in the bian compounds (in some cases only at low temperature), it is concluded that the dienyl fragment is positioned perpendicularly to the plane of coordination (Figure 5).[44]

Catalytic Coupling of Alkynes. Trimerization of 1,4-Dichloro-2-butyne: Synthesis of 1-(1′-Chloro-

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Table 8. ^{1}H NMR Data of Dienylpalladium(II) Compounds 3, 4, and 5[a]

	ligand	E	R	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	R″
3a	phenyl-BIP[d]	3.88, 3.72, 3.67, 3.59	1.02 (CH_3)	*b*	*b*	7.49 t, 7.1	7.81 d, 7.7			6.98 b	7.31 b	
3b	(*p*-tolyl)-bian[d]	3.91, 3.71, 3.68, 3.56	1.16 (CH_3)	6.73, 6.69 d, 7.3	7.43 t, 7.8	8.01 d, 8.2				7.12 b	7.34 b	2.46, 2.45 (CH_3)
4b	(*p*-tolyl)-bian[d]	3.86, 3.71, 3.63, 3.01	3.26, 3.21 ($-CH_2-$), 7.10[b] (t, $J = 7.0$)	6.71, 6.86 d, 7.2	*b*	8.03 dd				6.96 d, 7.1	7.31 d, 7.1	2.55, 2.47 (CH_3)
5b	(*p*-tolyl)-bian[d]	3.92, 3.79, 3.57, 2.82	7.59[b] (b, C_o)	6.70, 6.37 d, 7.1	*b*	8.01 d, 8.2				6.50 d, 7.2	b	2.48, 2.36 (CH_3)
3d	bpy	3.85, 3.73, 3.69, 3.16	2.03 (CH_3)			*c*	*c*	7.60, 7.48 m	9.67, 8.95 d, 5.3			
4d	bpy	3.89, 3.63, 3.46, 3.24	3.62 ($-CH_2-$), 7.2 (m, phenyl)			*c*	*c*	7.5 m	9.36, 8.98 d, 5.3			

[a] Recorded at 300.13 MHz in $CDCl_3$ at 293 K. For atomic-numbering scheme, see structural formula in Table 4. [b] Signals (multiplets from 6.9−7.5 ppm) cannot be assigned. [c] Multiplet 7.9−8.1 ppm. [d] For H(10) see H(7), and for H(11) see H(8).

Table 9. ^{13}C NMR Data of Dienylpalladium(II) Complexes 3, 4, and 5[a]

	E	R	C═O	C═C	C═N	C−N	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	R″
3a[b]	53.7, 53.2, 52.4 (2×)		172.6, 169.7, 167.6, 166.9	164.3, 142.3, 133.7, 127.4	167.0, 164.2	148.7, 146.9	132.4, 132.0	128.5, 128.2	134.9, 134.7	126.1, 125.9	126.3	137.1	123.6 b	129.1, 128.9	129.9, 129.8	
3b[b]	54.0, 52.8, 52.5, 52.1	18.0 (CH_3)	173.2, 170.2, 169.3, 163.7	158.2, 146.2, 138.1, 133.8	173.5, 171.9	145.1, 144.8	126.1	129.1	131.8	131.7	138.5	126.5	123.3, 122.3	130.6, 130.1	138.5, 138.0	22.0 (CH_3)
4b[b]	53.8, 52.8, 52.3, 51.9	36.7, 127.4, 128.7, 129.1, 139.1 (benzyl)	172.7, 170.2, 169.5, 164.1	159.0, 146.3, 137.6, 131.9	174.2, 171.5	145.0, 143.8	126.2, 126.1	128.7	132.1, 132.0	130.8	138.2	126.5, 126.0	123.6, 122.2	130.8, 130.3	138.1, 137.5	22.0 (CH_3)
5b[b]	54.1, 53.2, 51.9, 51.6	129.1, 128.5, 131.3, 136.9 (phenyl)	172.8, 171.1, 169.9, 162.5	156.2, 146.3, 134.9, 132.8	174.3, 172.0	145.9, 145.2	126.5, 126.0	128.0	131.9	131.8	138.9	126.4	122.9, 122.3	130.1	138.9, 138.0	22.0 (CH_3)
3d	52.8, 52.7, 52.5, 52.0	19.8 (CH_3)	174.0, 170.3, 168.4, 165.4	162.8, 139.8, 135.0, 128.8				154.8, 153.9	122.4, 122.3	139.7, 139.6	127.7, 127.0	156.2, 155.0				
4d	52.7, 52.6, 52.5, 52.3	39.8, 137.7, 129.9, 128.7, 127.4 (benzyl)	174.0, 169.7, 168.2, 167.7	162.1, 144.0, 133.8, 128.2				154.3, 151.6	122.8, 122.6	140.4, 139.9	127.1, 126.9	156.4, 154.5				

[a] Recorded at 75.48 MHz in $CDCl_3$ at 293 K. For atomic-numbering scheme, see structural formula in Table 4. [b] For C(10) see C(7), and for C(11) see C(8).

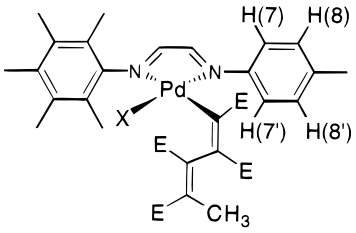


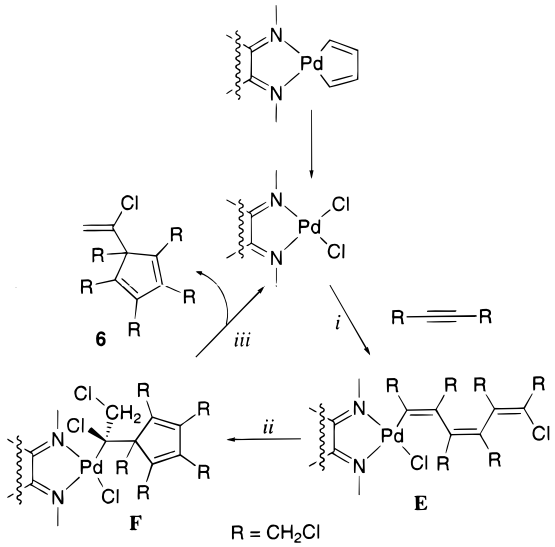
Figure 5. Schematic representation of a (NN)Pd−dienyl complex, showing the inequivalent protons of the *N*-aryl group.

ethenyl)-1,2,3,4,5-pentakis(chloromethyl)-2,4-cyclopentadiene (6). When 1,4-dichloro-2-butyne was used as an electrophile (in a 100-fold excess) with any of the palladacycles (**1a**−**f**), the catalytic formation of a cyclopentadiene derivative (**6**) was observed. This conversion only occurred for palladacycles containing nitrogen ligands and did not take place when palladacycles containing PPh_3 or dppp were employed. The formation of **6** was found to be catalyzed by a palladium dichloride compound and not by a zerovalent palladium species, as known for the trimerization of electron-deficient acetylenes. The palladium dichloride compound can be formed in toluene at 80−100 °C from the palladacyclopentadiene by two successive sequences of oxidative addition of 1,4-dichloro-2-butyne and reductive elimination, yielding 1% of diene. The trimerization also takes place in dichloromethane at room temperature when (NN)$PdCl_2$ (NN = nitrogen ligand) is used as the catalyst.

Variation of the nitrogen ligand in the palladium compound has only a limited influence on the reaction, i.e., only the amount of byproducts decreases from 5% to 1% when diimine ligands were used instead of bis(benzonitrile)palladium dichloride or even neat palladium chloride. However, for the diimine compounds, some (up to 5%) hexa(chloromethyl)benzene was also formed as a byproduct. Importantly, when compounds containing *phosphines* (PPh_3 or dppe) were used as the catalyst, *no conversion* whatsoever took place.

The trimerization is catalyzed by a $PdCl_2$ compound (Scheme 5) and starts with three successive acetylene insertions, the first one in a Pd−Cl bond and the following in the Pd−C bond.[45] Subsequently, a 5-*exo*-dig cyclization (i.e., addition of the Pd−C bond to the terminal alkene moiety in the intermediate trienylpalladium compound **E** (Scheme 5)) takes place, yielding palladium compound **F** containing a cyclopentadiene moiety.[46] The first steps in this mechanism are similar to the ones that are proposed for the formation of a stable iridium compound with 1-(2′,2′-difluoroethenyl)-1,2,3,4,5-pentakis(trifluoromethyl)-2,4-cyclopentadiene as a trimerization product of perfluoro-2-butyne,[47] the formation of a cyclopentadienylpalladium compound as a trimerization product of dmbd,[45a] and the formation of 1,2,3,4,6-pentaphenylfulvene from bromostyrene and diphenylacetylene.[48] The product 1-(1′-chloroethenyl)-1,2,3,4,5-pentakis(chloromethyl)-2,4-cyclopentadiene (**6**) is released in the last step via a β-Cl elimination in which the palladium dichloride compound is regenerated. If the intramolecular addition would result in a 6-*endo*-dig cyclization, a benzene species would be formed after the β-Cl elimination. The preference for the 5-*exo*-dig cyclization mode is most likely dictated by the steric demands within the trienylpalladium compound, since it was only in the case of the diimine ligands that some hexa(chloromethyl)benzene was formed.

Scheme 5. Catalytic Cycle for the Formation of 1-(1′-Chloroethenyl)-1,2,3,4,5-pentakis(chloromethyl)-2,4-cyclopentadiene (6)



Catalytic Formation of Conjugated Alkyl- and Aryl-Substituted Tetrakis(carbomethoxy)dienes. On the basis of the relative stability of the dienylpalladium compounds **3**−**5**, i.e., their lack of reactivity toward organic halides (vide supra), a catalytic cycle was designed for the synthesis of conjugated dienes. In the envisaged cycle, the formation of the σ-dienylpalladium compound is followed by a transmetalation step with formation of a diorganopalladium compound **G** (see Scheme 6). After reductive elimination, the zerovalent palladium species **A**, necessary to regenerate the palladacycle, would be formed together with the diene. This catalytic cycle closely resembles the one proposed for the cross-coupling reaction of organic halides with organotin compounds, except for the additional formation of the palladacycle.

As a logical consequence of our observations regarding the feasibility of the required single stoichiometric steps and that (i) in the synthesis of palladacycles **1** from Pd(dba)$_2$ and electron-deficient alkynes, the formation of the palladacycle is a much faster reaction than oxidative addition of benzyl bromide to zerovalent Pd species and (ii) the insertion of a third molecule of acetylene in **1** is slow compared to reaction of the organic halide with **1**, we anticipated the feasibility of such a catalytic procedure for the synthesis of dienes **8**, as outlined in Scheme 6. Indeed, employing **1a**−**e** as the precatalyst (or Pd-

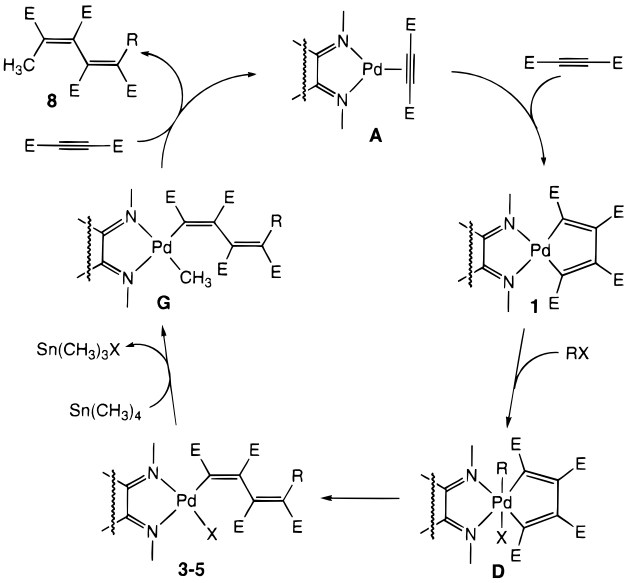
(45) Kelly, E. A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1977**, 289.

(46) (a) Roe, D. M.; Calvo, C.; Krishnamachari, N.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1975**, 125. (b) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161. (c) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *J. Chem. Soc., Chem. Commun.* **1986**, 1922. (d) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567. (e) Reingold, A. L.; Wu, G.; Heck, R. F. *Inorg. Chim. Acta* **1987**, *122*, 147.

(47) Corrigan, P. A.; Dickson, R. S. *Aust. J. Chem.* **1979**, *32*, 2147.

(48) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. In this example the fulvene was formed by means of a β-H elimination.

Scheme 6. Proposed Cycle for the Pd(NN)-Catalyzed Three-Component Synthesis of Conjugated Dienes 8 from Alkynes, an Organic Halide, and Tetramethyltin



E = CO_2CH_3; RX = $C_6H_5CH_2Br$, CH_3I, C_6H_5I

$(dba)_2$ together with an equimolar amount of Ar-bian or Ar-bip) in the presence of 100 equiv of dimethyl butynedioate, 50 equiv of tetramethyltin, and 50−200 equiv of benzyl bromide, methyl iodide, or iodobenzene resulted, after 8−16 h in DMF at 65 °C, in the complete conversion of the alkyne into (*Z*,*Z*)-2,3-hexadien-1,6-dioates **8a**−**c**. By doing so, the first catalytic three-component synthesis of conjugated open chain dienes has been achieved.[4g,49]

As a complication, an addition reaction of dmbd with the solvent DMF occurred, generating 1-(dimethylamino)-1,2-di(carbomethoxy)ethene. This side reaction does not take place in the absence of the catalyst, and the relative amount of this alkene depended on the type of catalyst used. The necessity of the presence of palladium compounds for the formation of byproducts suggests that a palladium-catalyzed decarbonylative addition of dimethylamine, originating from DMF, takes place. On the other hand, some dissociated N-ligand may also promote the decomposition of DMF.

The best results for coupling of dmbd with the organic halides employed (methyl iodide, benzyl bromide, and iodobenzene) were obtained with catalyst **1b**. In this case, complete conversion of the alkyne was observed. There was about 10% of 1-(dimethylamino)-1,2-di(carbomethoxy)ethene present in the crude product in these cases. The reaction with iodobenzene yielded a small amount of the alkyne trimer (hexa(carbomethoxy)-benzene) together with another byproduct, i.e., 1-phenyl-1,2-di(carbomethoxy)-1-propene (in a ratio of 71:14:4:7 for diene/alkene/trimer/propene).

It was found that when β-hydrogens were present in the electrophile, as is the case for ethyl iodide and phenethyl bromide, two dienes were formed in a 25:75 ratio, viz. the expected products 2,3,4,5-tetrakis(carbomethoxy)-2,4-heptadiene and 1,2,3,4-tetrakis(carbomethoxy)-1,3-pentadiene. The latter probably arises from β-hydrogen elimination. No conversion was observed under the described conditions when diphenyl acetylene was used or when using 4-chlorotoluene or chlorocyclohexane as the organic halides.

The successful catalytic diene syntheses resulted in the formation of the conjugated dimethyl-(2*Z*,4*Z*)-3,4-bis(carbomethoxy)-2-methyl-5-R-2,4-hexadien-1,6-dioates (R = methyl, benzyl, phenyl; Scheme 6). The configuration around the double bonds could only be ascertained in the case of **8a**. Assuming that reductive eliminations in similar compounds also occur with retention of configuration around the alkene bonds, we have tentatively attributed the *Z*,*Z*-configuration to **8b** and **8c** as well.[44,50]

Conclusion

After having established the stoichiometric reactions of Pd(0) compounds with alkynes and organic halides and of the resulting alkadienyl−Pd(II) compounds with tetramethyltin, we have arrived at a new three-component *catalytic* synthesis of conjugated dienes from two molecules of an electron-deficient alkyne, an organic halide, and tetramethyltin. This reaction protocol constitutes the first catalytic synthesis of conjugated dienes from alkynes. One may envisage the modification and further elaboration of these dienes by transformation of the esters or the halide functionalities. By doing so, the method can be useful for obtaining building blocks for further applications in synthetic chemistry.

In the reactions mentioned above, the role of the ligand is very important. Both in the catalytic diene formation and the trimerization of 1,4-dichloro-2-butyne, the best results for activity and selectivity are obtained for palladium compounds containing the rigid bidentate nitrogen ligand (*p*-tolyl)-bian. Phosphines are not suitable as ligands in any of the catalytic reactions discussed, because they either react with the reagents (acetylenes) or the palladium−phosphine compound exhibits no catalytic activity whatsoever toward alkynes.

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Supporting Information Available: Further details of the structure determination, including tables of atomic coordinates, bond distances and angles, and thermal parameters for **1a**, **1d**, and **7** (15 pages). Ordering information is given on a current masthead page.

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(49) An alternative sequence consisting of an oxidative addition to the zerovalent palladium intermediate, a double alkyne insertion, transmetalation, and a reductive elimination could a priori also be considered. Our observations during catalytic experiments were as follows, however, rendering this alternative highly unlikely: (i) addition of carbon monoxide to the reacting mixture has no influence on the reaction, whereas it has been reported that Pd(Me)Cl(bian) readily inserts CO,[4c,d] and (ii) no reaction was observed for diphenylacetylene, which is known to insert into Pd−C bonds, see: (a) Beydoun, N.; Pfeffer, M.; DeCian, A.; Fischer, J. *Organometallics* **1991**, *10*, 3693. (b) Vicente, J.; Saura-Llamas, I.; Ramirez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1995**, 2529.

(50) One must bear in mind that *E*/*Z*-isomerizations of dienyl fragments in σ-dienylpalladium compounds have been reported, see: Ryabov, A. D.; van Eldik, R.; Le Borgne, G.; Pfeffer, M. *Organometallics* **1993**, *12*, 1386.