cyclohepta-1,2,4,6-tetraene (**15**). The cyclization model and the ring expansion model thus make strikingly different predictions.[15] Irradiation of (*o*-deuteriophenyl)diazomethane gives first (*o*-deuteriophenyl)methylene (**11**, two rotamers) and then **14** and **15**. Subtraction of the infrared spectrum of **14** from the infrared spectrum of the mixture of **14** and **15** gives the spectrum of **15**.[16] The identity of **15** is established by independent synthesis. Irradiation of (*p*-deuteriophenyl)diazomethane gives (*p*-deuteriophenyl)methylene (**16**) and then 5-deuteriocyclohepta-1,2,4,6-tetraene (**17**). The infrared spectrum of **17** is different from that of either **14** or **15**. Irradiation of (*m*-deuteriophenyl)diazomethane gives (*m*-deuteriophenyl)methylene (**18**) and then simultaneously **15** and **17**. Subtraction of the infrared spectrum of **17** from that of the mixture of **15** and **17** gives an infrared spectrum of **15** identical with that from **11**. The observation of a common product from **16** and **18** and from **11** and **18** again illustrates the point that cyclization of the aryl methylenes to the bicycloheptatrienes is inconsistent with the results.

The data presented above make it clear that the product formed in the thermolysis and photolysis of phenylmethylene is cyclohepta-1,2,4,6-tetraene.

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(15) A ring-expansion, cyclization mechanism leading to bicycloheptatrienes can also be considered. This mechanism has been excluded for 1-naphthylmethylene and 2-naphthylmethylene, which form bicycloheptatrienes by cyclization.[5] The deuterium-labeling data require ring expansion as a first step.

(16) The subtraction of infrared spectra was accomplished with a Perkin-Elmer Data Station coupled to a 580-B spectrometer.

Acute Bonding Deviation in Square-Planar d8 Palladium(II) Complexes[1]

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The square-planar coordination of d8 palladium(II) complexes has been well documented;[3] further, it has been assumed that with bidentate 2,2′-bipyridine ligands, coordination is restricted to the orthogonal N electrons.[4] In the case of dichloro(2,2′-bipyridine)palladium(II), these assumptions are quite valid;[5] however, with 6,6′-disubstitution on bipyridine, herein described, drastic deviation from an overall planar configuration is established.

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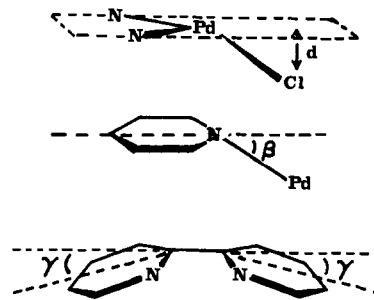(5) Kelly, E. A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1977**, 289.

Figure 1. Molecular distortions for (bipyridine)palladium(II) complexes.

Table I. Critical Measurements for the Complexes

	2	3	4
Pd–Cl(1), Å	2.283 (1)	2.287 (1)	2.299 (1)
Pd–Cl(2), Å	2.286 (1)	2.292 (2)	2.299 (1)
Pd–N(1), Å	2.048 (2)	2.062 (4)	2.063 (2)
Pd–N(2), Å	2.040 (2)	2.050 (4)	2.023 (2)
Cl(1)–Pd–Cl(2), deg	87.90 (3)	86.32 (5)	88.54 (3)
N(1)–Pd–N(2), deg	79.88 (9)	80.0 (2)	80.1 (2)
N(1)–Pd–Cl(1), deg	96.15 (7)	95.9 (1)	98.17 (6)
N(1)–Pd–Cl(2), deg	168.87 (7)	167.0 (1)	173.19 (6)
N(2)–Pd–Cl(1), deg	171.16 (7)	172.0 (1)	166.39 (7)
N(2)–Pd–Cl(2), deg	94.62 (7)	96.2 (1)	93.70 (6)
d_1, Å	0.315 (1)	0.277 (2)	0.538 (1)
d_2, Å	0.386 (1)	0.496 (1)	−0.110 (1)
β_1, deg	18.5	18.8	7.3
β_2, deg	18.7	16.8	15.2
γ_1, deg	10.2	7.5	6.9
γ_2, deg	10.1	8.5	6.7

Recently we reported the preparation of mono-[6] and dinuclear[7] complexes of bipyridine macrocycles as well as the synthesis and biochemical studies of a novel series of stable palladium(II) complexes (**1**) containing two *cis*-carbon–metal σ bonds.[8] In light
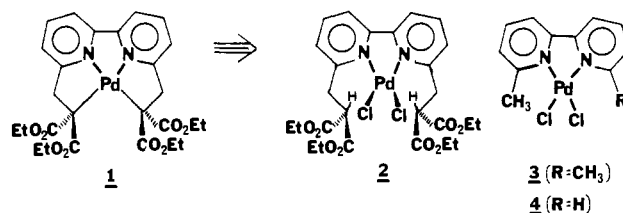
of the high activity of **1** toward in vitro nicking and binding events in DNA,[9] we needed to acquire a better molecular picture of not only **1** but also its immediate precursors. The synthesis of **1** proceeds via a stepwise bond-making sequence initiated by complexation of the ligand with either PdCl2 or PdCl2(C6H5CN)2.

The orange crystalline complex **2** was characterized by an X-ray crystal structure determination.[10] The geometry of **2** is most unique in that the best plane of the four donor atoms surrounding

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(10) Crystal data for **2**: C26H32N2O8PdCl2; mw 677.85; monoclinic; space group *P*2₁/*n*; *a* = 12.246 (2), *b* = 19.644 (13), *c* = 12.340 (2) Å; β = 97.56 (2)°; *Z* = 4, *d_c* = 1.530 g cm⁻³; μ (Mo Kα) 8.52 cm⁻¹; intensities were recorded on an Enraf-Nonius CAD-4 diffractometer and merged to give 3091 unique observed reflections [*F* > 3σ(*F*)], R = 0.031. This structure, as well as the others, were solved by the heavy-atom method and refined by full-matrix least-squares methods.
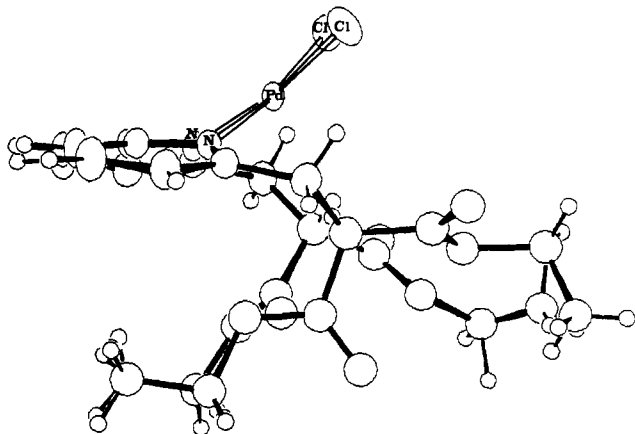
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Figure 2. ORTEP drawing of the side view of dichloro-[6,6'-bis[1''-(2'',2''-dicarbethoxy)ethyl]-2,2'-bipyridine]palladium(II) (**2**).
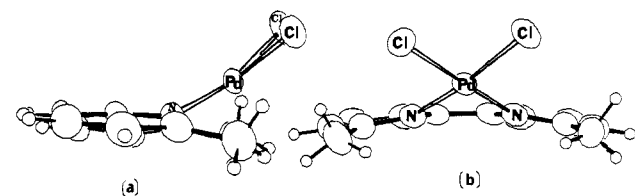

Figure 3. ORTEP drawing of the side (a) and front (b) views of dichloro(6,6'-dimethyl-2,2'-bipyridine)palladium(II) (**3**).

the metal is acutely bent by ca. 40° out of the best plane of the bipyridine ligand. This complex also exhibits other unexpected molecular distortions. These can be described by the following definitions: (1) the *out-of-plane distortions of the coordination plane* (d_1 and d_2) can be quantified by the perpendicular distances of the two chloride atoms from the plane defined by Pd and the two N-donor atoms (Figure 1). A positive sign for d is chosen to be a distortion that *increases* the distance between the chlorine atoms and the substituent atom at the 6 position on each pyridine ring. If $d_1 = d_2$, a pure pyramidal distortion of the metal would be indicated. (2) *The angle β for each aromatic ring is a measure of the acute tilt of the ring away from the expected coordination geometry.* It is defined as the acute angle that the Pd–N bond makes with its orthogonal projection upon the plane. (3) *The angle γ is a measure of the distortion of the bipyridine ligand itself from its expected planar geometry.* It is defined for each pyridine ring as the acute angle formed by the connecting bipyridine C–C bond and its orthogonal projection onto the plane of the ring. Table I lists these quantities as well as other structural features of importance for complex **2**.

In complex **2**, the metal is distorted toward pyramidal coordination, as specified by the similar positive values of d_1 and d_2, the aromatic rings are tilted by an average 18.6° away from their expected geometries, and the bipyridine ligand itself is "bowed" away from perfect planarity by a total angle of 20.3° ($γ_1 + γ_2$).[11] Furthermore, neither ring is strictly planar in that each has a slight pucker [av deviation from a best plane; 0.026 (2) and 0.032 (2) Å for rings 1 and 2, respectively] in a pseudochair fashion (Figure 2). In order to gain better insight into these unexpected distortions, less cumbersome Pd(II) complexes were prepared.

Complex **3**[12] is unencumbered by large ester substituents but

Figure 4. ORTEP drawing of the side view of dichloro(6-methyl-2,2'-bipyridine)palladium(II) (**4**).

is strikingly similar to **2** (see Table I, Figure 3). The aromatic rings exhibit a similar slight puckering as well with average deviations of 0.027 (2) and 0.023 (2) Å. In complex **4**,[13] an obvious difference from **2** and **3** exists (Table I, Figure 4) in that d_1 and d_2 have opposite signs, indicative of a distortion toward a tetrahedral geometry. Also, the β angle is over twice as large for the substituted as for the unsubstituted ring, and the substituted pyridine ring is slightly puckered [av deviation 0.018 (2) Å], while the unsubstituted ring is nearly planar.

In general, Pd(II) and Pt(II) bipyridine complexes are *not* appreciably distorted, although packing forces may cause small distortions.[14,15] The red form of bpyPtCl₂ is perfectly planar, lying on a mirror plane in the crystal.[16] This favored bonding mode is accomplished by σ donation of the N-lone-pair electrons with metal-to-ligand π bonding as a stabilizing factor.

It is clear that the methyl–chloro interaction is in part responsible for the large acute angle β but is not alone sufficient to explain the large distortions.[17] The unique pyramidal distortion of **2** and **3** demands that the N lone pair cannot overlap optimally with the Pd d orbitals. However, the Pd–N bond distances are the same as or shorter than those found in relatively undistorted complexes.[14] Chemically, **2–4** are stable indefinitely in solution and undergo oxidative addition of Cl₂ in CHCl₃ without loss of the dipyridine moiety.

Studies are currently in progress[19] to delineate the mode of bonding and to ascertain the stereochemical significance of these distortions in binuclear complexes.

Supplementary Material Available: Listings of fractional coordinates for nonhydrogen atoms of complexes **2**, **3**, and **4** and of deviations from the best planes of the pyridine rings are available (4 pages). Ordering information is given on any current masthead page.

(11) The bowing of a dipyridine moiety by $γ_1 = γ_2 = 8°$ takes ca. 1.85 kcal/mol as calculated by the ab initio method (STO-3G): Baker, G. R. Louisiana State University, unpublished results.

(12) Crystal data for **3**: C₁₂H₁₂N₂PdCl₂; mw 361.54; monoclinic; space group P2₁/n; a = 10.928 (2), b = 8.794 (2), c = 13.630 (2) Å; $β$ = 94.70 (2)°; Z = 4, d_c = 1.872 g cm⁻³, μ (Mo Kα) 20.3 cm⁻¹; intensities were recorded on an Enraf-Nonius CAD-4 diffractometer and merged to give 1663 unique observed reflections [$F > 3σ(F)$], R = 0.034. The sample crystal contained a small (ca. 8%) substitutional disorder involving the compound with a bromo substituent at C9.
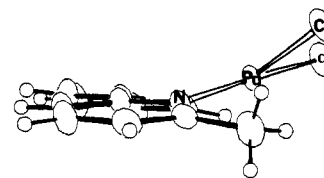
(13) Crystal data for **4**: C₁₁H₁₀N₂PdCl₂; mw 347.51; monoclinic; space group P2₁/n; a = 9.126 (2), b = 7.673 (3), c = 16.882 (4) Å; $β$ = 97.91 (2)°; Z = 4, d_c = 1.971 g cm⁻³, μ (Mo Kα) 19.8 cm⁻¹; intensities were recorded on an Enraf Nonius CAD-4 diffractometer and merged to give 1712 unique observed reflections [$F > 3σ(F)$], R = 0.023.

(14) Distortions in related complexes[15] can be correlated by calculating the dihedral angles of the central, metal-containing, five-membered ring. Average dihedral angles are less than 5° for these complexes, which denotes relatively inconsequential distortions. Average Pd–N bond distances range from 2.0–2.1 Å: S. F. Watkins, Louisiana State University, unpublished results.

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(16) Osborn, R. S.; Rogers, D. *J. Chem. Soc., Dalton Trans.* **1974**, 1002.

(17) Slight distortions ($β$ = ca 2.5°) have been reported[18] for dinitro-(2,9-dimethyl-1,10-phenanthroline)palladium(II).

(18) Fridrichson, J.; Mathieson, A. M.; Power, L. F. *J. Cryst. Mol. Struct.* **1971**, *1*, 333.

(19) The X-ray crystal structure of dichloro(2,9-dimethyl-1,10-phenthroline)palladium(II) has been completed and shown to have the same degree of acute distortion: Kiefer, G. E.; Fronczek, F. R. Louisiana State University, unpublished results.