994 J. Am. Chem. Soc. 1982, 104, 994-998

Synthesis, X-ray Analysis, and Chemical Properties of Binuclear Complexes with Trans Bis(palladium(II)-carbon) σ Bonds and Bridging Ligands

George R. Newkome,* Dalip K. Kohli, and Frank R. Fronczek

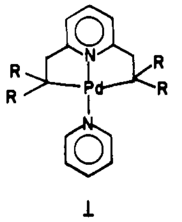
Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. *Received May 21, 1981*

Abstract: A series of binuclear palladium(II) complexes containing carbon to palladium σ bonds and bridging ligands such as pyrazine, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)acetylene, -ethene, and -ethane have been prepared. A single-crystal X-ray structure analysis on the pyrazine-bridged binuclear complex **4a** reveals that the molecule has exact C_2 symmetry, the pyrazine ring is almost orthogonal to the plane of the pyridine ring, and the palladium coordination is somewhat distorted from ideal square-planar geometry. Refinement in space group $C2/c$ fitting 2967 observed diffractometer data yielded $R = 0.030$. Cell constants are $a = 25.390$ (3) Å, $b = 14.232$ (2) Å, $c = 14.262$ (2) Å, $\beta = 111.61$ (1)°, and $Z = 4$. Bond lengths involving Pd are 2.175 (3) Å for Pd–C3, 2.143 (3) Å for Pd–C11, 2.050 (3) Å for Pd–N(pyrazine), and 1.978 (3) Å for Pd–N(pyridine). The trans-olefin-bridged complex **7b** can be photoisomerized to the cis complex **7c**, which can also be prepared by the catalytic hydrogenation of the acetylene-bridged complex **8b** over Lindlar's catalyst. The olefin and acetylene linkages in these binuclear complexes can be catalytically hydrogenated over Pd/C providing the saturated complex **7d**. These studies indicate that the carbon to palladium bonds in these complexes are stable to mild photolysis and hydrogenation conditions.

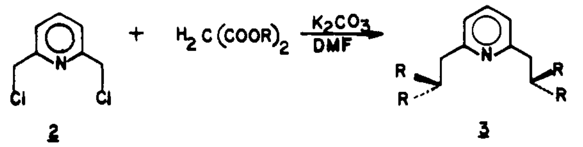
Binuclear and polynuclear complexes of transition metals with bridging ligands, such as pyrazine and 4,4′-bipyridine, are of interest due to their potential as models for intramolecular one-electron-transfer redox systems[1] and as semiconductors.[2] Although a number of these complexes with transition-metal ions have been reported,[3] limited study has been devoted to complexes of Pd(II) and Pt(II) involving bridging bidentate ligands. Our interest in these binuclear complexes arises from varied factors: (1) biological activity; (2) conformational and structural aspects; (3) potential catalytic properties; and (4) chemical and physical manipulation of the bridging ligand(s). Recently, we reported the synthesis and biological activity of a series of complexes **1**, having two Pd(II)–C σ bonds and two pyridine ligands.[4] In the present work, we report the synthesis, X-ray analysis, and preliminary physiochemical properties of binuclear Pd(II) complexes bridged by pyrazine, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)-acetylene, -ethene, and -ethane.

Ligand Synthesis. The reaction of dihalide **2**[5] with diethyl or dimethyl malonate in dry *N,N*-dimethylformamide and potassium carbonate provided the desired ligands **3a** and **3b** in 90% and 88% yields, respectively. The NMR spectrum of **3a** shows a doublet ($J = 7.5$ Hz) at δ 3.24 for pyridine CH_2 and a triplet at δ 4.0 for the methine hydrogen, which is indicative of the symmetrical, disubstituted product and confirms the absence of measurable enolization.

Complex Formation. 1. Pyrazine Bridge. An ethanolic solution of **3a** was treated with an aqueous solution of K_2PdCl_4 and KOH, which was followed by 0.5 equiv of pyrazine; dichloromethane extraction afforded, after concentration, the organic soluble binuclear Pd(II) complex **4a**. The 200-MHz NMR spectrum of **4a** shows a singlet at δ 3.80 for the pyridine methylene groups and a 16-line pattern for the ester methylene hydrogens. Double irradiation studies indicate the geminal coupling ($J = 11$ Hz) for these ester methylene groups; thus, these hydrogens appear to be in magnetically nonequivalent environments. The juxtaposed facing ethyl groups are in different environments necessary to relieve excess crowding; such a crowded orientation further transforms the anticipated (singlet) symmetrical pyrazine pattern into an AB system ($J = 2.5$ Hz).

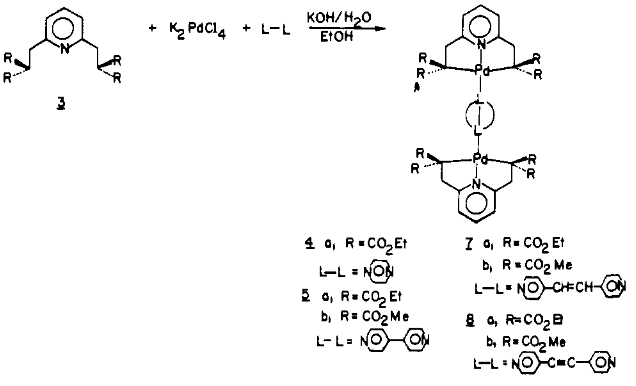


1



2

3
a; R=CO2Et
b; R=CO2Me



In view of the complex pattern exhibited in the 200-MHz NMR spectrum of **4a** and the steric crowding shown by the CPK models, the X-ray structural analysis of **4a** was conducted. Crystal Data

---

(1) Fuhrhop, J. H.; Baccouche, M.; Bunzel, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 322.

(2) Scheider, O.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 392, and references cited therein.

(3) (a) Haddad, M. S.; Hendrickson, D. N.; Cannady, J. P.; Drago, R. S.; Bieksza, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 898. (b) Taube, H. In "Bioinorganic Chemistry-II"; American Chemical Society: Washington, D.C., 1977, Adv. Chem. Ser. No. 162. (c) Sulikowska, C.; Maria, D.; Radwanska, J. D. *Pol. J. Chem.* **1979**, *53*, 2439.

(4) Newkome, G. R.; Kawato, T.; Kohli, D. K.; Puckett, W.; Olivier, B. D.; Chiari, G.; Fronczek, F. R.; Deutsch, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 3423.

(5) Baker, W.; Buggle, K. M.; McOmie, J. F. W.; Watkins, D. A. M. *J. Chem. Soc.* **1958**, 3594.

0002-7863/82/1504-0994$01.25/0

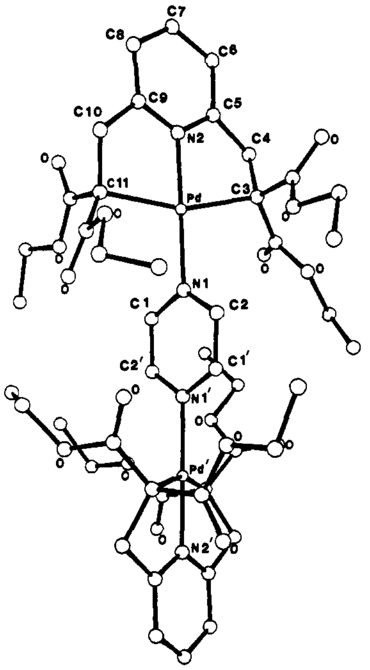


Figure 1. Perspective drawing of the μ-pyrazine dimer **4a**. The atoms designated by primes are related to the unprimed atoms by $-x, y, ^1/_2 - z$.

Table I. Deviations from the Best Planes

atom	deviations, Å	atom	deviations, Å
	Coordination Plane		
Pd	0.010 (1)	C3	−0.040 (3)
N1	0.028 (3)	C11	−0.041 (3)
N2	0.043 (3)		
	Pyridine Plane[a]		
N2	−0.001 (3)	C7	−0.002 (4)
C5	−0.008 (3)	C8	−0.007 (4)
C6	0.009 (4)	C9	0.008 (3)
C3	0.574 (3)	C11	−0.625 (3)
C4	−0.100 (4)	Pd	0.029 (1)
C10	0.059		
	Pyrazine Plane		
N1	0.000 (3)	N1′	0.000 (3)
C1	0.012 (4)	C1′	0.011 (4)
C2	−0.011 (4)	C2′	−0.012 (4)

[a] Defined by N2 and C5 through C9.

for $Pd_2C_{46}H_{58}N_4O_{16}$ (**4a**): M_r, 1135.8, monoclinic, $C2/c$, a = 25.390 (3) Å, b = 14.232 (2) Å, c = 14.262 (2) Å, β = 111.61 (1)°, $Z = 4$, d_{calcd} = 1.574 g cm^{-3}, μ(Mo Kα) = 8.16 cm^{-1}, R = 0.030 for 2967 independent reflections with $I > 3\sigma(I)$.

Table II. Selected Bond Distances in Complex 4a

atoms	distance, Å	atoms	distance, Å
Pd-N1	2.050 (3)	C11-C18	1.485 (5)
Pd-N2	1.978 (3)	C11-C21	1.487 (5)
Pd-C3	2.175 (3)	C12-O1	1.183 (4)
Pd-C11	2.143 (3)	C12-O2	1.326 (4)
N1-C1	1.346 (4)	O2-C13	1.452 (4)
N1-C2	1.334 (4)	C13-C14	1.449 (7)
C1-C2′	1.368 (5)	C15-O3	1.204 (4)
N2-C5	1.332 (4)	C15-O4	1.349 (4)
N2-C9	1.351 (4)	O4-C16	1.442 (5)
C3-C12	1.486 (5)	C16-C17	1.432 (6)
C3-C15	1.486 (5)	C18-O5	1.207 (5)
C3-C4	1.558 (4)	C18-O6	1.326 (5)
C4-C5	1.486 (5)	O6-C19	1.433 (5)
C5-C6	1.383 (5)	C19-C20	1.391 (8)
C6-C7	1.386 (5)	C21-O7	1.204 (4)
C7-C8	1.372 (6)	C21-O8	1.337 (4)
C8-C9	1.382 (5)	O8-C22	1.443 (4)
C9-C10	1.492 (5)	C22-C23	1.484 (6)
C10-C11	1.539 (5)		

Table III. Selected Bond Angles in Complex 4a

atoms	angle, deg	atoms	angle, deg
N1-Pd-N2	178.5 (1)	Pd-C11-C21	108.5 (1)
C3-Pd-C11	161.1 (1)	C12-C3-C4	115.0 (3)
N1-Pd-C3	99.6 (1)	C4-C3-C15	109.2 (3)
N1-Pd-C11	99.6 (1)	C12-C3-C15	117.0 (3)
N2-Pd-C3	80.9 (1)	C10-C11-C18	111.6 (3)
N2-Pd-C11	80.5 (1)	C10-C11-C21	109.5 (3)
Pd-N1-C1	121.4 (1)	C18-C11-C21	112.7 (3)
Pd-N1-C2	122.8 (1)	C3-C4-C5	111.1 (3)
C1-N1-C2	115.7 (3)	C4-C5-N2	114.2 (3)
N1-C1-C2′	122.1 (3)	C4-C5-C6	126.1 (3)
N1-C2-C1′	122.1 (3)	N2-C5-C6	119.6 (3)
Pd-N2-C5	118.8 (1)	C5-C6-C7	118.4 (4)
Pd-N2-C9	117.8 (1)	C6-C7-C8	120.8 (3)
C5-N2-C9	123.3 (3)	C7-C8-C9	119.3 (3)
Pd-C3-C4	101.8 (1)	N2-C9-C8	118.6 (3)
Pd-C3-C12	106.7 (1)	N2-C9-C10	118.6 (3)
Pd-C3-C15	105.4 (1)	C8-C9-C10	127.9 (3)
Pd-C11-C10	102.5 (1)	C9-C10-C11	110.4 (3)
Pd-C11-C18	111.6 (1)		

The μ-pyrazine dimer **4a** has exact C_2 symmetry in the crystal, as illustrated in Figure 1, with the 2-fold axis normal to the pyrazine plane. The pyrazine bridge deviates slightly from linearity, as the two Pd–N vectors related by the symmetry axis form an angle of 172.0°. Both linear and slightly nonlinear bridges are known for μ-pyrazine complexes.[6–10] The conformation of **4a** may be summarized by the relative orientations of three planes: the coordination plane, the pyrazine plane, and the pyridine portion of the tridentate ligand. Of the three, both aromatic rings are perfectly planar within experimental uncertainty, but the coordination "plane" exhibits small but significant deviations from planarity (Table I). The pyrazine and pyridine planes form a 70.9° dihedral angle, and the pyridine and coordination planes form a 16.4° angle. Comparable values of 89.5° and 14.1°, respectively, are found in the monomeric pyridine analogue. Distances and angles involved in the metal ion coordination are given in Tables II and III, respectively. Complex **4a** exhibits a slight deviation from square-planar geometry, with the Pd–C bonds bent an average of 9.3° from perpendicular to the Pd–N bonds. The two Pd–C bonds differ by 0.032 (4) Å, but both fall well within the range typical of Pd(II)–C(sp^3) bonds.[11–13] The shorter of the two, 2.143 (3) Å, is identical with that found in the monomeric pyridine analogue,[4] 2.140 (5) Å. Both Pd–N distances are experimentally indistinguishable from those of the monomeric complex, with Pd–N(pyridino) shorter by 0.072 (4) Å than Pd–N(pyrazino) as a result of the steric demands of the tridentate ligand. The latter distance is typical of those found in Pd(II) pyridine complexes.[13–16] The two five-membered chelate rings are decidedly nonplanar; that involving C3 has $\sum|\omega|$ (torsion angles) of 115°, and that involving C11, 116°. The aromatic rings

---

(6) Belford, R. C. E.; Fenton, D. E.; Truter, M. R. *J. Chem. Sec., Dalton Trans.* **1974**, 17.

(7) Baker, E. C.; Raymond, K. N. *Inorg. Chem.* **1977**, *16*, 2710.

(8) Beattie, J. K.; Hush, N. S.; Taylor, P. R.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1977**, 1121.

(9) Carreck, P. W.; Goldstein, M.; McPartlin, E. M.; Unsworth, W. D. *Chem. Commun.* **1971**, 1634.

(10) Morosin, B.; Hughes, R. C; Soos, Z. G. *Acta Crystallogr., Sect. B* **1975**, *B31*, 762.

(11) Roe, D. M.; Calvo, C.; Krishnamachari, N.; Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1973**, 436.

(12) Alyea, E. C.; Dias, S. A.; Ferguson, G.; McAlees, A. J.; McCrindle, R.; Roberts, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 4985.

(13) Horike, M.; Kai, Y.; Yosuoka, N.; Kasai, N. *J. Organomet. Chem.* **1975**, *86*, 269.

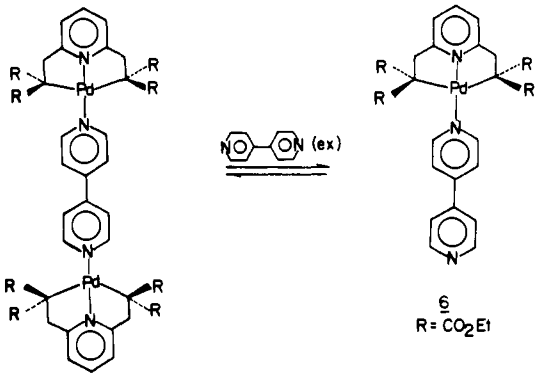
(14) Okeya, S.; Kawaguchi, S.; Yasuoka, N.; Kai, Y.; Kasai, N. *Chem. Lett.* **1976**, 53.

(15) Goddard, R.; Green, M.; Hughes, R. P.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1890.

(16) Kobayashi, Y.; Ohsawa, A.; Iitaka, Y. *Tetrahedron Lett.* **1973**, *2643*.

exhibit normal geometries: the C–C distances average 1.378 (4) Å, and the C–N distances average 1.341 (5) Å. Distances and angles within the four carbethoxy groups show excellent internal agreement as well as agreement with accepted values, except for the ethyl C–C distances, which range 1.391 (8)–1.484 (6) Å, and appear to be rendered inaccurate by the high thermal motion present in these molecular termini.

2. 4,4′-Bipyridine Bridge. Treatment of ligands **3a** and **3b** with K_2PdCl_4, potassium hydroxide, and 4,4′-bipyridine provided the binuclear complexes **5a** and **5b**, respectively, as yellow crystalline solids. The symmetrical structure of **5a** can be shown by NMR spectroscopy, in which the α-methylene hydrogens appear as a singlet at δ 3.86, indicative of a symmetry plane through the nitrogen–nitrogen axis. The upfield shift of the doublet of doublets for the 2,6-bipyridine bridge hydrogens is similar to that observed in the case of pyridine *N*-oxide.[17] The singlet at δ 3.40 for the methyl ester (**5b**) suggests that all methyl groups are in magnetically equivalent surrounding on the NMR time frame. The infrared spectra of **5** shows very strong carboxyl absorptions at approximately 1650 cm^{-1}; the 50–80-cm^{-1} shift for the carbonyl stretching vibration upon complexation is supportive of the palladium–carbon σ bond formation.



5 a, R=CO_2Et

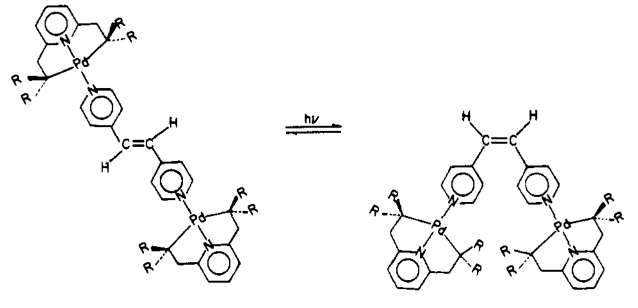
6
R= CO_2Et

If during the complexation, an excess (more than 1 equiv) of the bridging ligand is used, only formation of a 1:1 complex (**6**) is observed. The 1:1 complex **6** can arise either through an incomplete reaction or by external ligand exchange due to the excess of bridging ligand. Ligand exchange in similar systems has been previously demonstrated by warming **1** (R = CO_2Et) in the presence of excess 4-methylpyridine; albeit slow, the reaction will proceed to completion.[4]

On the basis of spectral data, the conformation of **5** is expected to be such that the external pyridine (L–L) is orthogonal to the plane of the tridentate ligand. On the further basis of the preferred conformation of 4,4′-bipyridine, this bridging ligand is most probably also orthogonal; thus the alternating rings are coplanar.

3. 1,2-Bis(4-pyridyl)ethylene Bridges. Ligands **3a** and **3b** were treated with potassium tetrachloropalladate, and potassium hydroxide in the presence of 0.5 equiv of *trans*-1,2-bis(4-pyridyl)ethylene to give the olefin-bridged complexes **7a** and **7b**, respectively. In both complexes **7**, the olefinic hydrogens appear as a singlet at δ 7.25, indicating the trans double bond remained intact and quite similar to position (δ 7.21) for the free ligand.

These trans olefinic complexes (**7**) present a unique possibility of studying the photoinduced trans to cis isomerization and of determining the photostability of these palladium complexes. When a methanol solution of *trans*-**7b** was photolyzed in the presence of benzil as the photosensitizer, under argon, a greater than 50% conversion to the cis isomer **7c** was observed. The NMR spectrum of **7c** confirmed the cis olefin linkage by the upfield shift of the olefin hydrogen position to δ 6.80 and the upfield shift of doublet for the 3,5-bipyridine hydrogens. The singlet for the olefin hydrogen in *cis*-1,2-bis(4-pyridyl)ethylene appears at δ 6.75; a similar upfield shift was also observed for the 3,5-hydrogens. It is interesting to note that during this photoisomerization, *no decomposition of the palladium complex was observed*; thus, the palladium–carbon bonds are stable to these photolysis conditions.

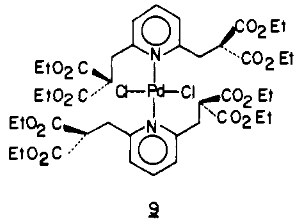


7b
R= CO_2Me

7c
R= CO_2Me

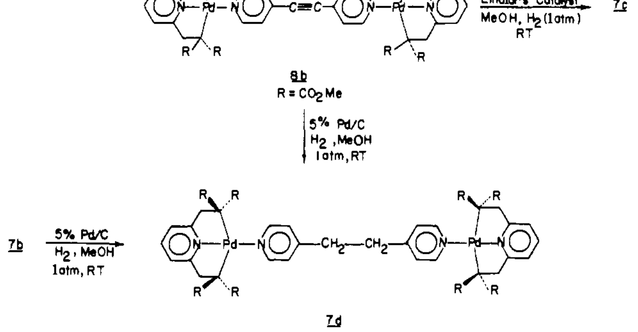
4. 1,2-Bis(4-pyridyl)acetylene Bridge. In a manner analogous to olefin-bridge formation, the introduction of 1,2-bis(4-pyridyl)acetylene during the reaction gave complexes **8a** and **8b**. The bridging 2,6-pyridine hydrogens are shifted slightly upfield in **8a** (δ 8.68) and more so in **8b** (δ 8.55) as compared to the free ligand (δ 8.72). No such change is observed for the (L–L) 3,5-hydrogens, which appear at the same frequency (δ 7.45) as that in the free ligand.

During the synthesis of **8a**, the sterically crowded complex **9** was isolated as a major side product. The structure of **9** was confirmed by spectral and analytical analyses. The infrared spectrum showed a carbonyl absorption at 1725 cm^{-1}, indicating the absence of a carbon to metal bond. The NMR spectrum of **9** in $DCCl_3$ showed a triplet at δ 4.49 (*J* = 7.0 Hz) for the methine hydrogen and a doublet at δ 4.96 (*J* = 7.0 Hz) for the α-methylenes. The tremendous downfield shift for these hydrogens (δ 1.72 and 0.49 ppm, respectively), when compared to the free ligand (**3a**), suggests that the ethyl malonate moieties are facing out from the palladium core; thus the methylene hydrogens are thrust directly into the metal's environment.



9

5. 1,2-Bis(4-pyridyl)ethane Bridge. The unsaturated bridges in **7** and **8** were catalytically reduced to the etheno and ethano bridges, respectively. Hydrogenation of the *trans*-**7b** in the presence of 5% Pd/C in methanol under 1 atm of hydrogen gave the saturated complex **7d** in quantitative yield. Ideally, one might expect to carry out the hydrogenation of the internal double bond in **7b** using the complexed Pd(II) present in the binuclear complex.



7d
R= CO_2Me

---

[17] Hamm, P.; Philipsborn, W. v. *Helv. Chim. Acta* **1971**, *54*, 2363, and references cited therein.

Table IV. Coordinates and Their Standard Deviations for Nonhydrogen Atoms in 4a

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pd	0.12440 (1)	0.20129 (2)	0.20515 (2)	C7	0.2892 (1)	0.2082 (3)	0.1312 (3)
O1	0.0332 (1)	0.4098 (3)	0.1541 (3)	C8	0.2711 (1)	0.1249 (3)	0.1573 (3)
O2	0.1170 (1)	0.4314 (2)	0.2713 (2)	C9	0.2222 (1)	0.1235 (3)	0.1786 (3)
O3	0.1109 (1)	0.3148 (2)	−0.0317 (2)	C10	0.1942 (1)	0.0406 (3)	0.2043 (3)
O4	0.0287 (1)	0.3110 (2)	−0.0084 (2)	C11	0.1616 (1)	0.0705 (3)	0.2716 (3)
O5	0.0912 (1)	−0.0460 (3)	0.1961 (2)	C12	0.0828 (1)	0.3979 (3)	0.1831 (3)
O6	0.1096 (1)	−0.0057 (2)	0.3555 (2)	C13	0.0917 (2)	0.4828 (4)	0.3321 (3)
O7	0.2510 (1)	0.0636 (3)	0.4072 (3)	C14	0.1068 (2)	0.4393 (4)	0.4304 (4)
O8	0.1822 (1)	0.1415 (2)	0.4327 (2)	C15	0.0855 (1)	0.3213 (3)	0.0245 (3)
N1	0.0507 (1)	0.1959 (2)	0.2328 (2)	C16	−0.0007 (2)	0.3109 (4)	−0.1163 (3)
N2	0.1944 (1)	0.2052 (2)	0.1750 (2)	C17	−0.0603 (2)	0.2998 (5)	−0.1399 (4)
C1	0.0002 (1)	0.1966 (3)	0.3430 (3)	C18	0.1178 (2)	0.0004 (3)	0.2691 (3)
C2	0.0498 (1)	0.1950 (3)	0.3257 (3)	C19	0.0705 (2)	−0.0741 (4)	0.3649 (5)
C3	0.1138 (1)	0.3390 (3)	0.1344 (3)	C20	0.0573 (2)	−0.0602 (4)	0.4503 (4)
C4	0.1764 (1)	0.3688 (3)	0.1575 (3)	C21	0.2024 (1)	0.0893 (3)	0.3755 (3)
C5	0.2113 (1)	0.2871 (3)	0.1507 (2)	C22	0.2168 (2)	0.1486 (3)	0.5384 (3)
C6	0.2593 (1)	0.2906 (3)	0.1266 (3)	C23	0.1836 (2)	0.2018 (4)	0.5873 (3)

However, a stirred solution of **7b** in methanol under hydrogen (1 atm) does not take up hydrogen—*a quantitative recovery of starting material was realized.* Thus, these palladium complexes are stable to mild catalytic hydrogenation conditions.

The hydrogenation of acetylene **8b** with Lindlar's catalyst in methanol at 26 °C at 1 atm of hydrogen gave *cis*-**7c** in 70% yield whereas the reduction of **8b** in the presence of 5% Pd/C afforded the ethano-bridges complex **7d** in quantitative yield.

Due to the stability of the carbon–palladium bonds in these bipyridine-bridged binuclear complexes, the use of **5b** as a homogeneous hydrogenation catalyst is currently being explored and will be reported elsewhere.

Experimental Section

General Comments. All melting points were taken in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. NMR spectra were determined on a Bruker WP-200 NMR spectrophotometer on $CDCl_3$ solutions, except where noted, with tetramethylsilane as the internal standard. IR spectra were recorded on a Perkin-Elmer 621 grating-infrared spectrophotometer. Mass spectral (MS) data were determined by D. Patterson on a Hewlett-Packard HP 5992 GC/mass spectrometer. X-ray diffraction data were collected with graphite-monochromatized Mo Kα radiation on an Enraf-Nonius CAD-4 diffractometer.

Reported R_f values were ascertained by a standardized thin-layer chromatography (TLC) procedure: 0.25-mm Brinkmann silica gel 60 HF-254-366 plates eluting with the stipulated solvents. For preparative thick-layer chromatography (ThLC) 2-mm silica gel PF-254-366 plates were used. Elemental analyses were performed by R. Seab in these laboratories.

2,6-Bis[2,2′-bis(carbethoxy)ethyl]pyridine (3a) was prepared (90%) from 2,6-bis(chloromethyl)pyridine (**2**), diethyl malonate, and potassium carbonate in anhydrous DMF by a previously described procedure:[4] bp 170–173 °C (0.35 mm).

2,6-Bis[2,2′-bis(carbomethoxy)ethyl]pyridine (3b) was synthesized (88%) in an identical manner except for the substitution of dimethyl malonate: NMR δ 3.32 (d, py CH_2, J = 7.5 Hz, 4 H), 3.71 (s, OCH_3, 12 H), 4.15 [t, $CH(CO_2CH_3)_2$, J = 7.5 Hz, 2 H), 6.99 (d, 3,5-py H, J = 7.5 Hz, 2 H), 7.47 (t, 4-py H, J = 7.5 Hz, 1 H); IR (KBr) 1736 (C═O), 1590, 1572, 1150, 1027 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_8$: C, 55.58; H, 5.76; N, 3.81. Found: C, 55.42; H, 5.93; N, 3.67.

General Procedure for Complexation. To a stirred solution of ligand **3** (0.335 mmol) in absolute ethanol (2 mL) was added a solution of K_2PdCl_4 (0.336 mmol) in water (10 mL). After stirring for 1 h at 25 °C, potassium hydroxide (1.398 mmol) in water was added, followed after 2 h by addition of the bridging ligand (0.167 mmol) in ethanol (1 mL). The mixture was stirred an additional 4–8 h and then extracted with dichloromethane (4 × 20 mL). The combined extract was dried over anhydrous magnesium sulfate and concentrated in vacuo to give the crude product, which was analyzed by TLC and purified by either column chromatography or ThLC eluting with the stipulated solvent system.

4,4′-Bipyridine-Bridged Complexes. Complex 5a was purified (ThLC) on silica gel, eluting with 7.5% methanol in ethyl acetate to give (40%) yellow crystals: mp 228–230 °C; NMR δ 1.00 (t, OCH_2CH_3, J = 8.5 Hz, 24 H), 3.68, 3.74 (2q, $OCH_2{}^A$, J = 8.5 Hz, 8 H), 3.86 (s, py CH_2, 8 H), 3.98, 4.04 (2q, $OCH_2{}^B$, J = 8.5 Hz, 8 H), 7.15 (d, 3,5-py H, J = 8.0 Hz, 4 H), 7.60 (d, 3,5-bpy H, J = 7.0 Hz, 4 H), 7.65 (t, 4-py H, J = 8.0 Hz, 2 H), 8.80 (d, 2,6-bpy H, J = 7.0 Hz, 4 H); IR (KBr) [1710, 1670, 1645 (C═O)], 1062 (C–O) cm^{-1}. Anal. Calcd for $C_{52}H_{62}N_4O_{16}Pd_2 \cdot 2H_2O$: C, 50.04; H, 5.32; N, 4.48. Found: C, 49.79; H, 5.10; N, 4.33.

Complex 5b was purified (column chromatography) on silica gel eluting with 9% methanol in ethyl acetate to yield (48%) a yellow solid: mp 226–227 °C (CH_2Cl_2); NMR δ 3.40 (s, OCH_3, 24 H), 3.87 (s, py CH_2, 8 H), 7.15 (d, 3,5-py H, J = 8.0 Hz, 4 H), 7.62 (t, 4-py H, J = 8.0 Hz, 2 H), 7.68 (d, 3,5-bpy H, J = 7.0 Hz, 4 H), 8.67 (d, 2,6-bpy H, J = 7.0 Hz, 4 H); IR (KBr) [1705, 1665 (C═O)], 1092, 1060 (C–O) cm^{-1}. Anal. Calcd for $C_{44}H_{46}N_4O_{16}Pd_2$: C, 48.05; H, 4.21; N, 5.09. Found: C, 47.74; H, 4.25; N, 5.13.

Complex 6a was obtained when an excess of 4,4′-bipyridine (0.50 mmol) was used. Purification (ThLC) gave (58%) **6a** as a yellow solid: mp 149–151 °C dec; NMR δ 0.99 (t, OCH_2CH_3, J = 7.0 Hz, 12 H), 3.65, 3.72 (2q, $OCH_2{}^A$, J = 7.0 Hz, 4 H), 3.86 (s, py CH_2, 4 H), 3.95, 4.02 (2q, $OCH_2{}^B$, J = 7.0 Hz, 4 H), 7.11 (d, 3,5-py H, J = 8.0 Hz, 2 H), 7.52 (d, 3,5-bpy H, J = 6.0 Hz, 2 H), 7.57 (d, 3′,5′-bpy H, J = 6.0 Hz, 2 H), 7.62 (t, 4-py H, J = 8.0 Hz, 1 H), 8.72 (d, 2,6-bpy H, J = 6.0 Hz, 2 H), 8.77 (d, 2′,6′-bpy H, J = 6.0 Hz, 2 H); IR (KBr) [1708, 1672 (C═O)], [1094, 1052 (C–O)] cm^{-1}. Anal. Calcd for $C_{31}H_{35}N_3O_8Pd$: C, 54.43; H, 5.16; N, 6.14. Found: C, 54.66; H, 5.48; N, 5.89.

Pyrazine-Bridged Complexes. Complex 4a was isolated (ThLC) on silica gel eluting with 3% methanol in ethyl acetate to give (10%) yellow microcrystals: mp 168–172 °C (ether); NMR δ 0.93 (t, OCH_2CH_3, J = 7.0 Hz, 18 H), 1.10 (t, OCH_2CH_3, J = 7.0 Hz, 6 H), 3.61, 3.67 (2q, $OCH_2{}^A$, J = 7.0 Hz, 8 H), 3.80, (s, py CH_2, 8 H), 3.91, 3.96, (2q, $OCH_2{}^B$, J = 7.0 Hz, 8 H), 7.10 (d, 3,5-py H, J = 7.5 Hz, 4 H), 7.62 (t, 4-py H, J = 7.5 Hz, 2 H), 8.65 (2d, pyrazine H, J = 2.5 Hz, 4 H); (IR) (KBr) [1715, 1692(C═O)], 1060 (C–O) cm^{-1}. Anal. Calcd for $C_{46}H_{56}N_4O_{16}Pd_2 \cdot {}^1/_2(Et_2O)$: C, 49.25; H, 5.25; N, 4.78. Found: C, 49.23; H, 5.70; N, 4.53.

***trans*-1,2-Bis(4′-pyridyl)ethylene-Bridged Complexes. Complex 7a** was isolated (ThLC) eluting with 1% methanol in ethyl acetate to give (7%) yellow microcrystals: mp 180–190 °C dec; NMR δ 1.01 (t, OCH_2CH_3, J = 7 Hz, 24 H), 3.96, 3.75 (2q, $OCH_2{}^A$, J = 7.0 Hz, 8 H), 3.85 (s, py CH_2, 8 H), 3.98, 4.04 (2q, $OCH_2{}^B$, J = 7.0 Hz, 8 H), 7.13 (d, 3,5-py H, J = 7.5 Hz, 4 H), 7.25 (s, CH═CH, 2 H), 7.45 (d, 3′,5′-py H, J = 7.0 Hz, 4 H), 7.63 (t, 4-py H, J = 7.5 Hz, 2 H), 8.63 (d, 2′,6′-py H, J = 7.0 Hz, 4 H); IR (KBr) [1665, 1640(C═O)] [1095, 1062 (C-O)] cm^{-1}. Anal. Calcd for $C_{54}H_{64}N_4O_{16}Pd_2$: C, 52.39; H, 5.21; N, 4.52. Found: C, 52.17; H, 5.31; N, 3.87.

Complex 7b was isolated (35%) by column chromatography on silica gel eluting first with ethyl acetate to remove **3a** and then with 20% methanol in ethyl acetate to give yellow crystals: mp 234–235 °C; NMR δ 3.41 (s, OCH_3, 24 H), 3.88 (s, py CH_2, 8 H), 7.13 (d, 3,5-py H, J = 8.0 Hz, 4 H), 7.28 (s, CH═CH, 2 H), 7.49 (d, 3′,5′-py H, J = 7.0 Hz, 4 H); IR (KBr) 1662 (C═O), [1095, 1015(C–O)] cm^{-1}. Anal. Calcd for $C_{46}H_{48}N_4O_{16}Pd_2$: C, 49.08; H, 4.29; N, 4.97. Found: C, 48.29; H, 4.18; N, 4.77.

4,4′-Bipyridine Acetylene Bridged Complexes. In the reaction of **3a**, K_2PdCl_4, KOH, and 4,4′-bipyridine, two complexes were isolated from column chromatography of the reaction mixture on silica gel, eluting first with ethyl acetate and then with an increasing ratio of methanol in ethyl acetate.

Fraction 1 was obtained from the initial ethyl acetate elution. Upon concentration in vacuo, the bis complex **9a** was isolated (10%) as a yellow crystalline solid: mp 168–169 °C; NMR δ 1.22 (t, OCH_2CH_3, J = 7.5 Hz, 24 H), 4.2 (m, OCH_2CH_3, 16 H), 4.49 [t, $CH(CO_2Et)_2$, J = 7.0 Hz, 4 H], 4.96 (d, py CH_2, J = 7.0 Hz, 8 H), 7.22 (d, 3,5-py H, J = 7.5 Hz, 4 H), 7.58 (t, 4-py H, J = 7.5 Hz, 2 H); IR (KBr) 1725 (C=O) 1592, 1451, 1360, 1285, 1150, 1025 cm^{-1}. Anal. Calcd for $C_{42}H_{58}N_2O_{16}PdCl_2$: C, 49.25; H, 5.90; N, 2.73. Found: C, 49.08; H, 5.61; N, 2.51.

Fraction 2 was eluted with 30% methanol in ethyl acetate and upon concentration in vacuo afforded (12%) **8a** as yellow microcrystals: mp 185–190 °C; NMR δ 1.0 (t, OCH_2CH_3, J = 7.0 Hz, 24 H), 3.71–3.77 (2q, OCH_2^B, J = 7.0 Hz, 8 H), 3.85 (s, py CH_2, 8 H), 3.98–4.04 (2q, OCH_2^B, J = 7.0 Hz, 8 H), 7.13 (d, 3,5-py H, J = 8.0 Hz, 4 H), 7.45 (d, 3′,5′-py H, J = 6.5 Hz, 4 H), 7.63 (t, 4-py H, J = 8.0 Hz, 2 H), 8.68 (d, 2′,6′-py H, J = 6.5 Hz, 4 H); IR (KBr) 1673 (C=O), 1600, 1085 (C–O), 1050 cm^{-1}. Anal. Calcd for $C_{54}H_{62}N_4O_{16}Pd_2$: C, 52.48; H, 5.05; N, 4.53. Found: C, 52.30; H, 5.09; N, 4.44.

Complex 8b was synthesized in a similar manner from **3b**. Chromatography (ThLC) of the reaction mixture on silica gel eluting with 20% methanol in ethyl acetate afforded (40%) **8b** as yellow crystals: mp 236–238 °C; NMR δ 3.37 (s, OCH_3, 24 H), 3.82 (s, py CH_2, 8 H), 7.08 (d, 3,5-py H, J = 7.5 Hz, 4 H), 7.43 (d, 3′,5′-py H, J = 6.5 Hz, 4 H), 7.60 (t, 4-py H, J = 7.5 Hz, 2 H), 8.55 (d, 2′,6′-py H, J = 6.5 Hz, 4 H); IR (KBr) 1660 (C=O), 1422, 1282, 1172, 1062 cm^{-1}. Anal. Calcd for $C_{46}H_{46}N_4O_{16}Pd_2$: C, 49.17; H, 4.12; N, 4.98. Found: C, 49.33; H, 4.08; N, 4.81.

Photolysis of *trans*-7b. A degassed solution of *trans*-**7b** (50 mg) in methanol (200 mL) was photolyzed in the presence of benzil (10 mg) in a Pyrex vessel under argon for 8 h. The solvent was removed and the residue chromatographed (ThLC), eluting with 40% methanol in ethyl acetate, to give a slower moving fraction (R_f 0.28), which was identified as the yellow crystalline *cis*-**7b**: mp 224–225 °C; NMR δ 3.43 (s, OCH_3, 24 H), 3.81 (s, py CH_2, 8 H), 6.72 (s, olefinic H, 2 H), 7.07 (d, 3,5-py H, J = 8.0 Hz, 4 H), 7.20 (d, 3′,5′-py H, J = 6.5 Hz, 4 H), 7.58 (t, 4-py H, J = 8.0 Hz, 2 H), 8.39 (d, 2′,6′-py H, J = 6.5 Hz, 4 H); IR (KBr) [1720, 1680, 1650 (C=O)], 1180, 1070 (C–O), 846 cm^{-1}. Anal. Calcd for $C_{46}H_{48}N_4O_{16}Pd$: C, 49.08; H, 4.29; N, 4.97. Found: C, 49.19; H, 4.24; N, 4.74.

Catalytic Hydrogenation of 7b. A solution of **7b** (20 mg, 0.017 mmol) in methanol (50 mL) was hydrogenated in the presence of 5% Pd/C under 1 atm of hydrogen at 26 °C. After 1 equiv of hydrogen was consumed, the reaction was stopped by filtration of the catalyst. Upon concentration, the residue was shown to be the saturated complex **7d** as a yellow solid: mp 229–230 °C; 100%; NMR δ 3.01 [s, $(py\ CH_2)_2$, 4 H], 3.41 (s, OCH_3, 24 H), 3.87 (s, py CH_2, 8 H), 7.12 (d, 3,5-py H, J = 7.5 Hz, 4 H), 7.25 (d, 3′,5′-py H, J = 6.0 Hz, 4 H), 7.64 (t, 4-py H, J = 7.5 Hz, 2 H), 8.45 (d, 2′,6′-py H, J = 6.0 Hz, 4 H); IR (KBr) 1670 (b, C=O), 1618, 1170, 1060 (C–O), 835 cm^{-1}. Anal. Calcd for $C_{46}H_{50}N_4O_{16}Pd_2$: C, 48.99; H, 4.43; N, 4.96. Found: C, 49.04; H, 4.35; N, 4.68.

Selective Hydrogenation of 8b with Lindlar Catalyst. A solution of **8b** (20 mg, 0.017 mmol) in methanol (50 mL) was hydrogenated in the presence of Lindlar catalyst (10 mg) under 1 atm of hydrogen at 25 °C. After 1 equiv of hydrogen was consumed, the catalyst was removed by filtration. Upon concentration of the solvent, the yellow crystalline residue was shown to be identical with *cis*-**7b**: mp 224–225 °C, 15 mg (75%); NMR and IR spectra were superimposable with *trans* ⇄ *cis*-**7b** sample.

X-ray Data Collection. An orange crystal of dimensions 0.22 × 0.32 × 0.44 mm was mounted in random orientation on an Enraf-Nonius CAD-4 automatic diffractometer equipped with a graphite monochromator and Mo Kα radiation (λ = 0.71073 Å). Lattice constants and crystal orientation were determined from the setting angles of 25 precisely centered reflections having 40° ≤ 2θ ≤ 47°. The space group is $C2/c$ (by systematic absences hkl with $h + k$ odd, $h0l$ with l odd, and successful refinement in the centrosymmetric space group). Intensity data were collected by the θ–2θ scan method using variable scan rates designed to yield $I \simeq 25\sigma(I)$ for all observable reflections. Scan speeds, determined during a 10.0 deg min^{-1} prescan of each reflection, varied from 0.39 to 10.0 deg min^{-1}. Reflections having $I < \sigma(I)$ during the prescan were considered unobserved, and the maximum time spent on a weak reflection was limited to 120 s. Scan angles varied as $\Delta\theta = 0.5 + 0.35 \tan\theta$ and were extended at each extreme by 25% to provide background measurements. All data in one quadrant having 2° ≤ 2θ ≤ 50° were measured in this fashion. During data collection, two reflections were recentered every 200 measurements as a check of crystal orientation, and the intensities of three standards were remeasured periodically, but no significant changes were noted in either test.

During data reduction, Lorentz, polarization, and background corrections were applied. Empirical absorption corrections, based upon ψ scans of two reflections at $\chi \simeq 90°$ with differing θ values, were applied to the data; the minimum relative transmission factor was 92%. Of the 4226 unique data measured, 2964 had $I > 3\sigma(I)$ and were used in the structure solution and refinement.

Structure Solution and Refinement. The structure was solved by heavy-atom methods. Refinement was accomplished by full matrix least squares with unit weights. All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package programs. All nonhydrogen atoms were treated anisotropically; hydrogen atoms were placed in calculated positions with isotropic B = 4.0 Å^2 and were not refined. In calculation of H atom positions, the C–H distance was taken to be 0.95 Å, and a staggered configuration for ethyl groups was assumed. At convergence, R = 0.030 for 2964 data and 307 variables. A final difference map exhibited peaks of density less than 0.60 e Å^{-3}, associated with the Pd position, as its only significant features. Refined coordinates for nonhydrogen atoms are listed in Table IV.

Acknowledgment. We are grateful to the National Science Foundation and Dow Chemical USA for partial support of this work.

Registry No. 3a, 77502-99-9; **3b**, 80317-58-4; **4a**, 80327-86-2; **5a**, 80327-87-3; **5b**, 80327-88-4; **6a**, 80327-89-5; **7a**, 80327-90-8; **7b**, 80374-71-6; **7c**, 80327-91-9; **7d**, 80327-92-0; **8a**, 80327-93-1; **8b**, 80327-94-2; **9a**, 80327-95-3.

Supplementary Material Available: Anisotropic thermal parameters, assigned hydrogen atom coordinates, and structure factors (15 pages). Ordering information is given on any current masthead page.

Copper(I) Catalysis of Olefin Photoreactions. 9. Photobicyclization of α-, β-, and γ-Alkenylallyl Alcohols[1]

Robert G. Salomon,* Daniel J. Coughlin, Subrata Ghosh, and Michael G. Zagorski

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received April 20, 1981

Abstract: Cyclobutylcarbinyl alcohols of the bicyclo[3.2.0]heptane ring system are produced by UV irradiation of α-, β-, and γ-alkenylallyl alcohols in the presence of copper(I) trifluoromethanesulfonate (CuOTf). *endo*-2-Hydroxy epimers of bicyclo[3.2.0]heptan-2-ols are generated stereoselectively. This result as well as the effect of CuOTf on the ^{1}H NMR spectrum of 4,4-dimethyl-1,6-heptadien-3-ol suggests that coordination of two C=C bonds and the hydroxyl group with a single copper(I) is important. The derived bicyclo[3.2.0]heptan-2-ones fragment cleanly at 580 °C to afford cyclopent-2-en-1-ones. Geometric isomerization competes with photobicyclization of (E)- and (Z)-octa-2,7-dien-1-ols.

To enhance the utility of 2π + 2π photocycloadditions for organic synthesis, we are exploring copper(I)-catalyzed photochemistry[2] of olefins which bear functional substituents. Allylic substituents are of special interest since they can facilitate useful

0002-7863/82/1504-0998$01.25/0 © 1982 American Chemical Society