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MOLECULAR STRUCTURE OF 2,2'-BIPYRIDYLDIBENZYLIDENEACETONEPALLADIUM(0)

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Summary

The molecular structure of the complex 2,2'-bipyridyldibenzylideneacetonepalladium has been determined crystallographically. The crystal structure is composed of two weakly associated Pd(bipy)(DBA) molecules and a benzene solvate. Metals in both complex molecules are three coordinate with each Pd bound to one bipyridyl and one dibenzylideneacetone olefin. Palladium—carbon distances in both molecules indicate a Pd—olefin bond of intermediate strength. Structural differences between the two molecules suggest slight bonding dissimilarities.

Introduction

The organometallic chemistry of zerovalent palladium has developed far more slowly than that of nickel and platinum. Routes to Pd(0) complexes have been plagued by formation of metallic Pd at room temperature. Recent use of atomic metals as synthetic reagents has produced a number of interesting organopalladium(0) complexes, among these the elusive bis(cycloocta-1,5-diene)palladium complex, tris(bicyclo[2.2.1]heptene)palladium and tris(ethylene)palladium [1]. These compounds, however, are only stable under thermal conditions well below room temperature. The synthetic advantages afforded by such complexes as the bis(1,5-COD) complexes of Ni(0) and Pt(0) have been absent in the case of zerovalent palladium [2,3].

This problem has been offset by the discovery of a remarkably stable series of Pd(0) complexes with dibenzylideneacetone (DBA) [4]. Ishii and coworkers have reported synthetic routes to $Pd_2(DBA)_3$ which may further form $Pd(DBA)_3$ with excess DBA [5]. The metals in these molecules are ostensibly tris(olefin)

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systems, similar to two of the examples above [5,6,7]. Unlike many complexes of nucleophilic Group VIII metals, $Pd_2(DBA)_3$ is easily prepared and does not require inert atmospheric conditions for preparation or storage. Structural investigations appear to indicate that metal encapsulation by the bulky DBA ligands contributes to their stability and low reactivity in solid.

The Pd—DBA complexes have proven to be useful precursors to other Pd(0) complexes with phosphine, isocyanide and nitrogen donor ligands [5,8,9]. Reactive patterns of Pd(0) complexes indicate a relative low nucleophilicity for the metal. Addition of the ligands 2,2'-bipyridyl, 9,10-phenanthroline or pyridine to $Pd_2(DBA)_3$ yields Pd(N—N)(DBA) with activity of the metal greatly enhanced. In the presence of molecular oxygen Pd(N—N)(O_2) forms which reverts to a dihydroxo species in protic solvents [8]. The bipyridyl complex Pd(bipy)(DBA) also reacts with organic azides forming an amido complex under related conditions [10].

In the interest of comparing Pd—DBA coordination in Pd(bipy)(DBA) to other Pd—DBA complexes and to Pt—olefin bonding in the $Pt(PPh_3)_2$(olefin) systems we have determined the molecular structure of the complex. We now report the results of this investigation.

Experimental section

The complex Pd(bipy)(DBA) was prepared by addition of a slight excess of 2,2'-bipyridine to a benzene solution of $Pd_2(DBA)_3 \cdot CH_2Cl_2$ under nitrogen [5]. Slow evaporation of the solvent gave orange-red crystals. Chemical analyses indicated the presence of a hemibenzene solvate. Precession and Weissenberg photographs indicated monoclinic symmetry with extinctions $0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$ consistent with space group $P2_1/n$. A crystal of the complex was mounted, coated with an amorphous resin to retard decomposition in air and aligned on a Picker four-circle automated diffractometer. The angular settings of 18 strong, independent reflections with 2θ values greater than 20° were centered using Mo-K_α radiation ($\lambda = 0.7107$ Å) and used to give refined lattice constants of $a = 13.926$ (3), $b = 13.935$ (3), $c = 25.565$ (5) and $\beta = 94.36$ (5)°. An experimental density of 1.44 (1) g cm^{-3} is in agreement with a calculated value of 1.435 g cm^{-3} for four bimolecular units of composition $[Pd(N_2C_{10}H_8)(C_{17}H_{14}O)]_2 \cdot C_6H_6$ per unit cell. The mosaic spread of the crystal was determined using the narrow-source open-counter ω-scan technique and was found to be acceptable at 0.08°. An independent set of intensity data was collected by the θ-2θ scan technique using Zr filtered Mo-K_α radiation and allowances for the $K_{\alpha_1} - K_{\alpha_2}$ separation at higher 2θ values. The data set was collected within the angular range $4 \leqslant 2\theta \leqslant 45°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded 9000 counts/sec during scan. During data collection the intensities of four standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these reflections showed more than statistical deviations in intensity during the time required to collect data. Data were processed in the usual way with values of I and σ(I) corrected for Lorentz and polarization effects. No significant variations in transmission coefficients were found for the data set ($\mu = 7.63$ cm^{-1}) so no correction for absorption was applied. The intensities of 7052

(continued on p. 107)

TABLE 1

FINAL ATOMIC AND GROUP PARAMETERS FOR $[Pd(bipy)(DBA)]_2 \cdot C_6H_6$ [a]

Atom	x	y	z	β_{11} [b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd(1)	0.27459(7)	0.18867(8)	0.34135(4)	0.00550(7)	0.00555(8)	0.00146(2)	−0.00007(7)	0.00102(3)	−0.00022(3)
Pd(2)	−0.08831(7)	0.26346(8)	0.44049(4)	0.00570(7)	0.00611(9)	0.00125(2)	−0.00033(7)	0.00101(3)	−0.00030(3)
N(1)	0.2268(7)	0.2723(7)	0.4064(4)	0.0073(9)	0.0066(9)	0.0010(2)	−0.0014(8)	0.0008(4)	−0.0008(4)
C(1)	0.1547(8)	0.3365(8)	0.3951(5)	0.0046(10)	0.0029(10)	0.0018(3)	−0.0001(8)	0.0001(5)	0.0005(5)
C(2)	0.1127(9)	0.3893(10)	0.4326(5)	0.0068(11)	0.0068(12)	0.0016(3)	−0.0017(9)	0.0021(5)	−0.0008(5)
C(3)	0.1514(10)	0.3753(10)	0.4847(5)	0.0077(13)	0.0065(13)	0.0017(4)	−0.0022(10)	0.0014(6)	−0.0005(5)
C(4)	0.2258(10)	0.3102(11)	0.4970(5)	0.0081(13)	0.0080(14)	0.0017(3)	−0.0020(12)	0.0014(6)	−0.0003(6)
C(5)	0.2647(9)	0.2572(10)	0.4556(5)	0.0056(10)	0.0090(13)	0.0014(3)	−0.0024(10)	0.0010(5)	−0.0014(6)
N(2)	0.1716(7)	0.2849(7)	0.3047(4)	0.0068(9)	0.0064(10)	0.0019(3)	−0.0010(7)	0.0013(4)	0.0004(4)
C(6)	0.1215(9)	0.3430(9)	0.3375(5)	0.0048(10)	0.0043(11)	0.0017(3)	−0.0001(9)	0.0011(5)	0.0004(5)
C(7)	0.0510(9)	0.4052(9)	0.3206(5)	0.0052(11)	0.0054(12)	0.0020(3)	0.0006(9)	0.0011(5)	0.0012(5)
C(8)	0.0250(10)	0.4139(11)	0.2657(6)	0.0059(12)	0.0078(14)	0.0032(5)	−0.0010(10)	0.0012(6)	0.0009(7)
C(9)	0.0763(10)	0.3530(11)	0.2313(5)	0.0072(12)	0.0080(14)	0.0020(4)	−0.0010(11)	0.0005(6)	0.0014(6)
C(10)	0.1472(10)	0.2905(10)	0.2516(5)	0.0072(12)	0.0076(14)	0.0012(3)	−0.0026(10)	0.0004(5)	0.0009(5)
N(3)	0.0192(7)	0.1562(7)	0.4600(4)	0.0070(9)	0.0047(8)	0.0018(2)	−0.0007(6)	0.0009(4)	−0.0002(4)
C(11)	0.0503(9)	0.1002(10)	0.4192(5)	0.0056(10)	0.0066(12)	0.0013(3)	−0.0020(9)	0.0003(5)	0.0002(5)
C(12)	0.1152(9)	0.0260(10)	0.4259(6)	0.0046(10)	0.0077(13)	0.0024(4)	0.0021(10)	0.0008(5)	0.0010(6)
C(13)	0.1559(11)	0.0059(12)	0.4747(6)	0.0089(14)	0.0102(15)	0.0023(4)	0.0006(11)	0.0014(6)	0.0000(7)
C(14)	0.1238(10)	0.0599(11)	0.5183(6)	0.0073(13)	0.0088(14)	0.0025(4)	0.0006(11)	0.0003(6)	0.0014(6)
C(15)	0.0561(10)	0.1373(11)	0.5098(5)	0.0068(11)	0.0096(14)	0.0014(3)	−0.0011(10)	0.0000(5)	0.0013(5)
N(4)	−0.0723(7)	0.1900(7)	0.3654(4)	0.0064(8)	0.0056(8)	0.0015(2)	−0.0016(7)	0.0007(4)	−0.0006(4)
C(16)	0.0031(9)	0.1283(9)	0.3662(5)	0.0042(9)	0.0045(10)	0.0023(4)	0.0006(8)	0.0007(5)	−0.0003(5)
C(17)	0.0336(9)	0.0892(10)	0.3192(5)	0.0063(10)	0.0074(12)	0.0016(3)	−0.0015(9)	0.0011(5)	−0.0010(5)
C(18)	−0.0168(10)	0.1173(10)	0.2724(5)	0.0065(11)	0.0078(13)	0.0016(3)	−0.0012(10)	0.0014(5)	0.0002(5)
C(19)	−0.0919(10)	0.1820(11)	0.2716(5)	0.0075(12)	0.0078(12)	0.0016(3)	−0.0009(10)	0.0011(5)	−0.0008(5)
C(20)	−0.1198(10)	0.2173(10)	0.3200(5)	0.0075(11)	0.0081(13)	0.0010(3)	−0.0024(9)	0.0000(5)	0.0000(5)
C(21)	0.3715(9)	0.0789(9)	0.3599(5)	0.0067(12)	0.0062(12)	0.0010(3)	0.0010(10)	0.0006(5)	−0.0006(5)
C(22)	0.3442(9)	0.0777(9)	0.3059(5)	0.0050(11)	0.0034(11)	0.0020(4)	0.0008(9)	0.0006(5)	−0.0004(5)
C(23)	0.2635(9)	0.0180(9)	0.2855(5)	0.0057(12)	0.0033(11)	0.0022(5)	0.0011(9)	0.0006(6)	−0.0002(6)
C(24)	0.2351(9)	0.0255(9)	0.2271(4)	0.0054(12)	0.0061(13)	0.0008(3)	0.0001(10)	0.0006(4)	−0.0009(5)
C(25)	0.1686(9)	−0.0369(10)	0.2083(5)	0.0059(11)	0.0078(12)	0.0014(3)	0.0019(9)	0.0007(5)	−0.0004(5)
O(2)	−0.1042(6)	0.4924(6)	0.4118(3)	0.0070(8)	0.0068(8)	0.0015(2)	−0.0013(7)	0.0012(3)	−0.0002(3)
C(26)	−0.1143(9)	0.3639(9)	0.4993(4)	0.0078(13)	0.0059(12)	0.0009(3)	0.0005(10)	0.0018(5)	−0.0009(5)

TABLE 1 (continued)

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(27)	−0.1883(9)	0.3699(9)	0.4562(4)	0.0085(13)	0.0042(11)	0.0008(3)	0.0014(9)	0.0001(5)	0.0001(4)
C(28)	−0.1692(9)	0.4323(9)	0.4123(5)	0.0050(12)	0.0052(12)	0.0014(3)	−0.0008(10)	0.0011(5)	−0.0010(5)
C(29)	−0.2399(9)	0.4163(9)	0.3668(5)	0.0053(11)	0.0061(12)	0.0013(3)	0.0023(9)	0.0000(5)	0.0000(5)
C(30)	−0.2245(9)	0.4602(9)	0.3198(5)	0.0068(12)	0.0051(11)	0.0015(3)	0.0031(9)	0.0006(5)	−0.0001(5)

Group[c]	x_c	y_c	z_c	ϕ	θ	ρ
R(1)	0.5659(5)	0.1250(4)	0.0402(3)	2.402(16)	−1.954(6)	−0.978(16)
R(2)	0.1018(4)	−0.0570(5)	0.0975(3)	3.012(25)	−1.816(6)	2.216(25)
R(3)	−0.1439(4)	0.2828(4)	0.6011(2)	2.123(6)	2.824(6)	−1.302(6)
R(4)	−0.3373(5)	0.4226(5)	0.2225(3)	−0.809(8)	2.594(7)	1.345(7)
Bz	−0.0824(6)	0.2497(6)	0.7887(4)	−0.788(15)	−2.873(9)	−0.462(17)

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ [c] x_c, y_c, z_c are the fractional coordinates of the rigid group centers The angles ϕ θ ρ are in radians and have been defined by Eisenberg and Ibers [19]

reflections were measured of which 3379 were observed to be greater than 2σ and used in the refinement

The structure was solved using conventional Patterson and Fourier techniques [11] In all calculations phenyl rings associated with the dibenzylideneacetone ligands and the solvate were treated as rigid groups (d(C—C) = 1 392 Å) During all cycles of refinement the function minimized was $\Sigma w(|Fo| - |Fc|)^2$ and weights taken as $4\ Fo^2/\sigma^2(Fo^2)$ Standard deviations, $\sigma(F^2)$, were calculated as described previously [12] Scattering factors used were taken from conventional sources [13] Final refinement of the structure including fixed contributions for all hydrogen atoms converged with R = 0 059 and R_ω = 0.063 ($R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $R_w = (\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2)^{1/2}$). The final positional and thermal parameters of the structure are given in Table 1 Derived positional and isotropic thermal parameters of the group atoms are given in Table 2 A table of the final Fo and |Fc| values ×10 for the 3379 reflections used in the refinement is available *

TABLE 2

DERIVED POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR GROUP CARBON ATOMS

Atom	x	y	z	B (A)
R1C(1)	0 4726(7)	0 1059(22)	0 3794(4)	4 5(3)
R1C(2)	0 5411(7)	0 1393(10)	0 3470(3)	4 8(3)
R1C(3)	0 4974(8)	0 0916(14)	0 4326(4)	5 4(3)
R1C(4)	0 6593(7)	0 1442(22)	0 4209(4)	5 9(4)
R1C(5)	0 5908(7)	0 1108(11)	0 4534(3)	6 4(4)
R1C(6)	0 6345(8)	0 1585(14)	0 3677(4)	5 3(4)
R2C(1)	0 1717(25)	0 0120(24)	0 1109(4)	4 6(3)
R2C(2)	0 1395(17)	−0 0017(14)	0 0586(3)	5 1(4)
R2C(3)	0 1340(10)	−0 0433(14)	0 1498(3)	4 2(3)
R2C(4)	0 0319(25)	−0 1259(24)	0 0840(4)	6 9(4)
R2C(5)	0 0641(17)	−0 1123(14)	0 1364(3)	4 5(3)
R2C(6)	0 0696(11)	−0 0796(14)	0 0451(3)	5.7(4)
R3C(1)	−0 1322(7)	0 3212(6)	0 5518(3)	3.3(3)
R3C(2)	−0 0679(6)	0 3451(6)	0 5941(4)	4 1(3)
R3C(2)	−0 2082(6)	0 2589(6)	0 5589(3)	4 5(3)
R3C(4)	−0 1556(8)	0 2445(7)	0 6506(3)	5 5(4)
R3C(5)	−0 2199(6)	0 2206(7)	0 6083(4)	5 6(4)
R3C(6)	−0 0796(6)	0 3068(7)	0 6435(3)	5 7(4)
R4C(1)	−0 2849(7)	0 4414(9)	0 2699(3)	4 8(3)
R4C(2)	−0 3647(7)	0 3810(7)	0 2685(4)	6 1(4)
R4C(3)	−0 2575(7)	0 4829(8)	0 2239(4)	5 1(3)
R4C(4)	−0 3896(8)	0 4039(9)	0 1750(3)	6 1(4)
R4C(5)	−0 3098(7)	0 4642(7)	0 1764(3)	5 6(4)
R4C(6)	−0 4171(7)	0 3623(8)	0 2211(5)	7 6(5)
BzC(1)	−0 0276(24)	0 3215(19)	0 0875(11)	9 3(8)
BzC(2)	0 0044(20)	0.2268(22)	0 0880(13)	9 6(8)
BzC(3)	−0 1144(27)	0 3443(14)	0 1081(11)	8 4(7)
BzC(4)	−0 1372(18)	0 1779(18)	0 1297(10)	7 2(7)
BzC(5)	−0 1692(20)	0 2726(20)	0 1292(14)	7 9(7)
BzC(6)	−0 0505(21)	0 1551(19)	0.1091(12)	8.1(7)

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* The table of structure factors has been deposited as NAPS Document No. 02919. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016 A copy may be secured by citing the document number.

Description of the structure

The structure consists of two weakly interacting Pd(bipy)(DBA) molecules and a well separated benzene solvate. A stereoview showing both complex molecules is presented in Fig 1 Views of the inner coordination geometries of the two molecules are presented in Fig. 2 and 3. Bond distances and angles for both molecules are contained in Table 3

The DBA ligand is remarkably diverse in its coordination properties It may bond as a diclefin to one [14] or two [5,7] metal centers, as a single olefin [6] or as an oxygen donor [15] It exists in three conformational forms all of which have been observed in various DBA complexes. Gross structural features of both Pd(bipy)(DBA) molecules are similar The metals are three coordinate with DBA ligands bonding through one olefin in the "W" conformational form Palladium-carbon distances in the two Pd(bipy)(DBA) molecules are substantially shorter than values found in $Pd_2(DBA)_3$ CH_2Cl_2, $Pd_2(DBA)_3$ $CHCl_2$ or $Pd(DBA)_3$ all of which fall in the 2.25 Å range Distances found in molecule 1 (containing Pd(1)) average to 2.074 (9) while similar distances in the second molecule average to 2.100 (9) Å.

In drawing comparisons to Pt—olefin bonding in the $Pt(PPh_3)_2$—(olefin) systems it should be pointed out that while the metallic radii of Pd and Pt are comparable (Pt is about 0.01 Å larger) contraction of the nitrogen—palladium—nitrogen angle to 76.4 (4)° in the Pd(bipy)(DBA) molecules compared with P—Pt—P angles of 100—105° in the $Pt(PPh_3)_2$(olefin) systems may alter bonding properties at the olefin coordination site. However, major differences between the two types of complexes would most likely relate to the strong donor nature of the bipyridyl ligand with enhanced Pd—olefin bonding Platinum—carbon distances in the $Pt(PPh_3)_2$(olefin) series range from 2.11 (3) Å for ethylene [16] to 2.00 (1) Å for C_2F_4 [17]. The present values, therefore, reflect a Pd—olefin interaction of only intermediate strength with the enhanced nucleophilicity expected with the nitrogen donors moderated by the low affinity for π-acceptor ligands of zerovalent palladium.

Subtle but consistent structural disparities between the two Pd(bipy)(DBA) molecules suggest differences in Pd—DBA coordination within the molecular

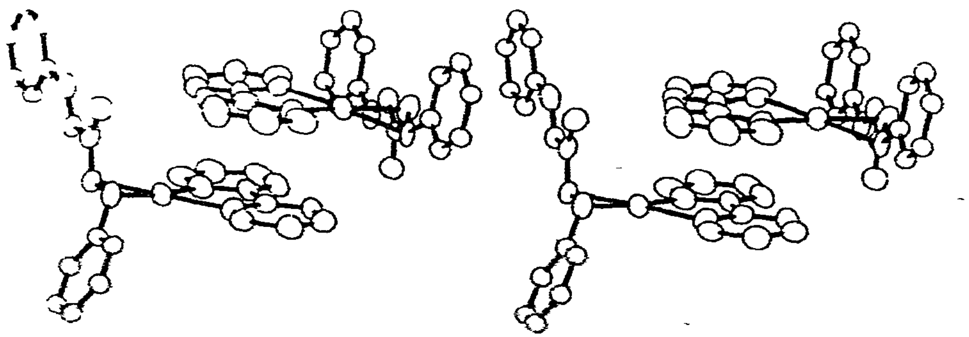

Fig. 1 Stereoview showing the two independent Pd(bipy)(DBA) molecules. Molecule 1 is at the lower left of the view.

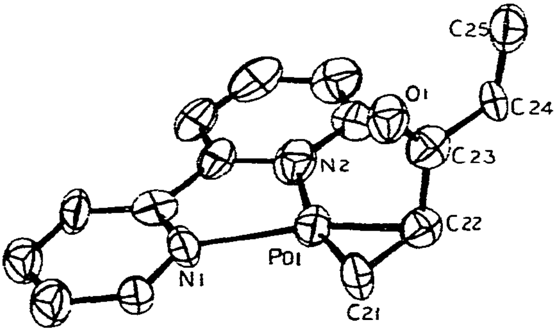

Fig 2 View of the inner coordination geometry of molecule 1

pair. Palladium—carbon distances are shorter in molecule 1 than molecule 2 In both molecules Pd—N lengths are approximately 0.05 Å longer on the side containing the uncoordinated portion of the pentadienone moiety. This may be due to an interaction with the bipyridyl ring proton at the 6 position as further indicated by bond angles about both Pd atoms. However, related Pd—N lengths within the two molecules are 0 02 to 0 03 Å shorter in molecule 1 While this difference is of marginal statistical significance stronger donor bonding in this molecule is consistent with the stronger Pd—olefin bond

Other features of the structure have bearing on this observation. Theoretical treatments on trigonal olefin complexes of d^{10} metals indicate that π bonding is most effective with the olefin contained in the molecular plane [18] The dihedral angles between PdN_2 and Pd—olefin planes are 4 4 (5)° in molecule 1 and 16 7 (5)° in molecule 2 (Table 4) An additional feature associated with strong metal—olefin coordination is distortion of substituents out of the olefin plane, away from the metal. Dibenzylideneacetone ligands of the $Pd_2(DBA)_3$ and $Pd(DBA)_3$ molecules have been found to be planar, including phenyl substituents In the present structure the DBA associated with Pd(2) also exhibits no substantial deviation from planarity However the phenyl ring associated with the coordinated olefin in molecule 1 is 31° from the plane of the pentadienone

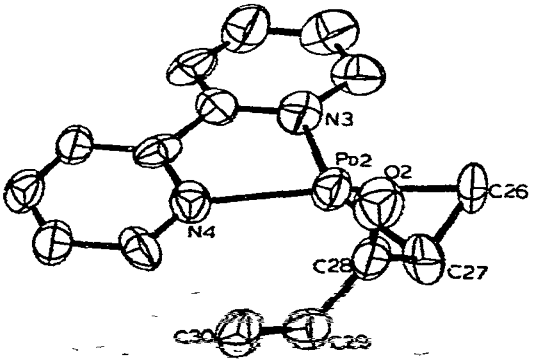

Fig. 3. View of the inner coordination geometry of molecule 2.

TABLE 3

PRINCIPAL INTRAMOLECULAR BOND DISTANCES AND ANGLES IN $[\mathrm{Pd(Bipy)(DBA)}]_2\ C_6H_6$

Atom	Distances (Å)	Atoms	Angles (deg)
Complex molecule I			
Pd(1)—N(1)	2 177(8)	N(1)—Pd(1)—N(2)	76 3(4)
Pd(1)—N(2)	2 129(8)	N(1)—Pd(1)—C(21)	116 9(4)
Pd(1)—C(21)	2 071(9)	N(1)—Pd(1)—C(22)	156 6(4)
Pd(1)—C(22)	2 077(9)	N(2)—Pd(1)—C(21)	166 4(4)
N(1)—C(1)	1 35(1)	N(2)—Pd(1)—C(22)	126 5(5)
C(1)—C(2)	1 38(1)	Pd(1)—N(1)—C(1)	116 8(8)
C(2)—C(3)	1 41(1)	Pd(1)—N(1)—C(5)	120 7(9)
C(3)—C(4)	1 40(1)	Pd(1)—N(2)—C(6)	116 9(8)
C(4)—C(5)	1 43(1)	Pd(1)—N(2)—C(10)	125 3(9)
C(5)—N(1)	1 34(1)	N(1)—C(1)—C(2)	123(1)
C(1)—C(6)	1 51(1)	N(1)—C(1)—C(6)	115(1)
N(2)—C(6)	1 39(1)	N(2)—C(6)—C(7)	124(1)
C(6)—C(7)	1 36(1)	N(2)—C(6)—C(1)	115(1)
C(7)—C(8)	1 43(1)	C(21)—Pd(1)—C(22)	40 0(4)
C(8)—C(9)	1 45(1)	Pd(1)—C(21)—C(22)	70 2(7)
C(9)—C(10)	1 39(1)	Pd(1)—C(22)—C(21)	69 7(7)
C(10)—N(2)	1 38(1)	C(21)—C(22)—C(23)	120(1)
C(21)—C(22)	1 42(1)	C(22)—C(23)—C(24)	116(1)
C(22)—C(23)	1 46(1)	C(22)—C(23)—O(1)	123(1)
C(23)—O(1)	1 22(1)	C(24)—C(23)—O(1)	120(1)
C(23)—C(24)	1 52(1)	C(23)—C(24)—C(25)	115(1)
C(24)—C(25)	1 33(1)		
C(21)—R1C(1)	1 51(2)		
C(25)—R2C(1)	1 52(2)		
Complex molecule II			
Pd(2)—N(3)	2 147(8)	N(3)—Pd(2)—N(4)	76 4(4)
Pd(2)—N(4)	2 203(8)	N(3)—Pd(2)—C(26)	116 8(4)
Pd(2)—C(26)	2.106(9)	N(3)—Pd(2)—C(27)	155 6(4)
Pd(2)—C(27)	2.095(9)	N(4)—Pd(2)—C(26)	165 0(4)
N(3)—C(11)	1 40(1)	N(4)—Pd(2)—C(27)	127 5(4)
C(11)—C(12)	1 38(1)	Pd(2)—N(3)—C(11)	117 7(9)
C(12)—C(13)	1 36(1)	Pd(2)—N(3)—C(15)	123 9(9)
C(13)—C(14)	[illegible] 4(1)	Pd(2)—N(4)—C(16)	114 2(8)
C(14)—C(15)	[illegible](1)	Pd(2)—N(4)—C(20)	123 0(9)
C(15)—N(3)	1 36(1)	N(3)—C(11)—C(12)	124(1)
C(11)—C(16)	1 51(1)	N(3)—C(11)—C(16)	113(1)
N(4)—C(16)	1 36(1)	N(4)—C(16)—C(17)	121(1)
C(16)—C(17)	1 41(1)	N(4)—C(16)—C(11)	117(1)
C(17)—C(18)	1 40(1)	C(26)—Pd(2)—C(27)	40 5(4)
C(18)—C(19)	1 38(1)	Pd(2)—C(26)—C(27)	69 3(6)
C(19)—C(20)	1 41(1)	Pd(2)—C(27)—C(26)	70 2(7)
C(20)—N(4)	1 35(1)	C(26)—C(27)—C(28)	117(1)
C(26)—C(27)	1 45(1)	C(27)—C(28)—C(29)	111(1)
C(27)—C(28)	1 46(1)	C(27)—C(28)—O(2)	126(1)
C(28)—O(2)	1 23(1)	C(29)—C(28)—O(2)	122(1)
C(28)—C(29)	1 48(1)	C(28)—C(29)—C(30)	119(1)
C(29)—C(30)	1 37(1)		
C(26)—R3C(1)	1.51(2)		
C(30)—R4C(1)	1 50(2)		

portion of the ligand These features are all consistent with stronger bipyridyl and DBA coordination to Pd(1) than to Pd(2).

The two independent Pd(bipy)(DBA) molecules are oriented in the crystal structure such that atoms of the bipyridyl ligand of one are superimposed on

TABLE 4

DIHEDRAL ANGLES AND LEAST-SQUARES PLANES IN [Pd(bipy)(DBA)]$_2$ C_6H_6

Dihedral angles

Plane 1	Plane 2	Angle (°)
N(1) C(2) C(4)	N(2) C(7) C(9)	2 4(6)
N(3) C(12) C(14)	N(4) C(17) C(19)	10 4(6)
C(22) C(23) C(24)	C(27) C(28) C(29)	10 4(6)
Pd(1) N(1) N(2)	Pd(1) C(21) C(22)	4 4(5)
Pd(2) N(3) N(4)	Pd(2) C(26) C(27)	16 7(5)
C(22) C(23) C(24)	Group R(1)	31
C(22) C(23) C(24)	Group R(2)	5
C(27) C(28) C(29)	Group R(3)	4
C(27) C(28) C(29)	Group R(4)	7

Least Squares Planes [a]

Compound	Atom	Distance (Å)
Dibenzylideneacetone I	Pd(1)	1 92
$-9\ 51x + 9\ 92y + 5\ 52z = 0\ 77$	O(1)	0 00(1)
	C(21)	0 01(1)
	C(22)	−0 04(1)
	C(23)	0 02(1)
	C(24)	0 04(1)
	C(25)	−0 04(1)
Dibenzylideneacetone II	Pd(2)	1 95
$-9\ 06x + 9\ 31y + 10\ 48z = -9\ 82$	O(2)	−0 02(1)
	C(26)	0 16(1)
	C(27)	−0 11(1)
	C(28)	−0 06(1)
	C(29)	−0 07(1)
	C(30)	0 15(1)

[a] Least-squares planes calculated according to [20] Equations given in monoclinic coordinates

the bipyridyl ligand of the adjacent molecule Shortest interatomic separations between ligands range from 3.40 to 3.62 Å with interplanar separations of 3 51 and 3 55 Å between isolated pairs of pyridine rings. This particular feature is normally associated with donor—acceptor behavior between electronically dissimilar species. If such an intermolecular interaction is responsible for the pairing of Pd(bipy)(DBA) molecules it is extremely weak but consistent with the structural differences between molecules

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