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## Formazanylpalladium Compounds. Synthesis and Structure of Bis(1,3,5-tri-*p*-tolylformazanyl)palladium

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Bis(1,3,5-triarylfornazanyl)palladium and (1,3,5-triarylfornazanyl)palladium hexafluoroacetylacetonate chelates have been prepared from the corresponding formazan and palladium bis(hexafluoroacetylacetonate). The structure of bis-(1,3,5-tri-*p*-tolylformazanyl)palladium has been determined by X-ray diffraction techniques. Crystal data: monoclinic,  $P2_1/a$ ,  $a = 12.797$  (4) Å,  $b = 14.703$  (4) Å,  $c = 10.729$  (3) Å,  $\beta = 104.94$  (2)°,  $V = 1951$  Å<sup>3</sup>, and  $Z = 2$ .  $R$  and  $R_w$  converged at the final values of 0.056 and 0.069, respectively. The molecule consists of two six-membered  $CN_4Pd$  rings which share a common palladium atom. There is a significant puckering along the N(1)-N(4) vector in each ring. The *p*-tolyl groups attached to these nitrogens are twisted out of the  $PdN_4$  plane, and no short intermolecular contacts are observed. The ring carbon atoms and nitrogen atoms are effectively  $sp^3$  hybridized. Despite the nonplanarity, there is considerable electron delocalization in the spiro  $(CN_4)_2Pd$  system.

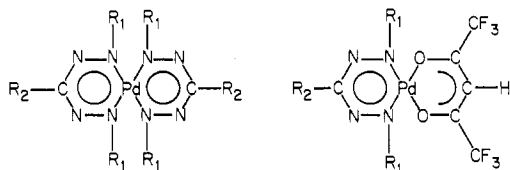
### Introduction

Transition-metal complexes of polyazo ligands have recently attracted considerable attention. Crystallographic studies have delineated bonding in triazenido,<sup>1,2</sup> tetrazolyl,<sup>3,4</sup> tetrazene,<sup>5,6</sup> triazido,<sup>7</sup> and benzotriazenido<sup>8,9</sup> complexes. Metal derivatives of di- and triarylfornazans are highly colored and are of interest as pigments and analytical reagents.<sup>10</sup> Coordination compounds of neutral formazans with tin tetrachloride and titanium tetrachloride are known,<sup>11</sup> and a crystal structure of [(1,5-diphenylformazan)<sub>2</sub>Cu]ClO<sub>4</sub> has been reported.<sup>12</sup>

Formazanyl chelates of cobalt, nickel, and copper have been prepared by combining an arylformazan with the appropriate metal salt.<sup>13,14</sup> This strategy is unsuccessful when applied to the halo ions  $PdCl_4^{2-}$  and  $PtCl_4^{2-}$ , probably because of the low nucleophilicity of the hydrogen-bonded formazan or its conjugate base. The charge on hexafluoroacetylacetonate(1-) is extensively delocalized, and this anion is weakly bound. We report the preparation of a series of formazanylpalladium chelates from palladium bis(hexafluoroacetylacetonate) (1) and *N*-arylfornazans<sup>15</sup> and the crystal structure of one of these, bis(1,3,5-tri-*p*-tolylformazanyl)palladium.

### Results and Discussion

Displacement of hexafluoroacetylacetonate(1-) from 1 by *N*-arylfornazans proceeds readily in such solvents as acetonitrile or butanone. The bis(formazanyl)palladium compounds



- 2a,  $R_1 = R_2 = C_6H_5$   
 b,  $R_1 = R_2 = p-CH_3 C_6H_4$   
 c,  $R_1 = R_2 = p-ClC_6H_4$   
 d,  $R_1 = R_2 = p-CH_3 OC_6H_4$   
 e,  $R_1 = C_6H_5$ ,  $R_2 = CN$   
 f,  $R_1 = C_6H_5$ ,  $R_2 = NO_2$
- 3a,  $R_1 = R_2 = C_6H_5$   
 b,  $R_1 = R_2 = p-CH_3 C_6H_4$   
 c,  $R_1 = R_2 = p-ClC_6H_4$   
 d,  $R_1 = R_2 = p-CH_3 OC_6H_4$

2 precipitate from solution. The deeply colored crystalline materials can be recrystallized from hot pyridine or acetonitrile although they usually separate in analytically pure form. The unsymmetrical chelates 3 are formed as byproducts. The remaining hexafluoroacetylacetonate group leads to high solubility in organic solvents. These compounds are obtained by evaporating the mother liquor from which 2 has been

Table I. Analytical Data

compd	% C		% H		% N	
	calcd	found	calcd	found	calcd	found
2a	64.6	64.7	4.5	4.7	15.9	16.3
2b	67.0	66.6	5.3	5.4	14.2	14.2
2c	50.0	49.8	2.6	2.5	12.3	12.1
2d	59.7	59.5	4.8	4.7	12.7	12.6
2e	55.8	56.3	3.3	3.4	23.3	22.9
2f	48.6	49.0	3.1	3.5	21.8	20.2
3a	47.1	47.4	2.6	2.8	9.2	9.1
3b	49.5	50.0	3.5	3.6	8.5	8.8
3c	40.3	40.6	1.8	2.0	7.8	8.1
3d	46.2	46.1	3.1	3.4	8.0	8.5

isolated and extracting with hot hexane. The mixed chelate 3d is the major product formed from tri-*p*-anisylformazan, and forcing conditions are required to displace the remaining hexafluoroacetylacetonate group to form 2d. Analytical data for these compounds are given in Table I.

**Spectroscopic Properties.** The infrared spectra of the new formazanylpalladium compounds are given in Table II. Absorption maxima for the bis(formazanyl) complexes agree, in general, with those of the bis(formazanyl)nickel analogues which were interpreted before the conformation of the  $CN_4$  (metal) ring was established.<sup>16</sup> Two bands at ca. 1300  $cm^{-1}$  are associated with aryl C-N groups. Bands at about 1260 and 1280  $cm^{-1}$  are associated with ring N-N and C-N stretching, respectively. In addition, the unsymmetrical chelates 3a-d show absorptions between 1100 and 1300  $cm^{-1}$  due to the  $CF_3$  group and a strong 1630- $cm^{-1}$  band which is a

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Table II. Infrared Absorption Maxima

compd	$\lambda_{\max}$ , $\text{cm}^{-1}$
2a	3060 (w), 1645 (w), 1595 (w), 1495 (w), 1480 (m), 1455 (s), 1340 (m), 1305 (m), 1295 (m), 1275 (s), 1200 (s), 1160 (w), 985 (m), 760 (m), 750 (s), 680 (s), 675 (s), 640 (w), 620 (w), 580 (w), 540 (w)
2b	3050 (w), 1600 (w), 1515 (m), 1500 (s), 1455 (m), 1385 (w), 1310 (s), 1300 (m), 1280 (s), 1265 (s), 1200 (m), 1180 (w), 980 (w), 810 (s), 755 (m), 650 (m), 630 (w), 615 (m), 550 (m), 530 (m), 505 (m)
2c	3045 (w), 1630 (w), 1535 (w), 1495 (w), 1480 (s), 1460 (s), 1415 (w), 1380 (m), 1305 (s), 1300 (s), 1275 (s), 1260 (s), 1225 (m), 1200 (m), 1155 (s), 1145 (s), 1090 (s), 1010 (w), 985 (w), 830 (s), 500 (w)
2d	3050 (w), 1615 (m), 1600 (s), 1585 (s), 1515 (s), 1500 (s), 1470 (s), 1450 (m), 1445 (m), 1425 (m), 1340 (m), 1315 (s), 1295 (s), 1245 (s), 1205 (m), 1180 (s), 1160 (s), 1110 (s), 1030 (s), 990 (m), 960 (w), 885 (s), 875 (s), 750 (m), 660 (m), 650 (m), 640 (m), 620 (w), 610 (s), 560 (m), 540 (w), 525 (m)
2e	3045 (w), 2230 (s), 1710 (w), 1585 (w), 1485 (w), 1460 (s), 1360 (s), 1315 (s), 1280 (s), 1205 (m), 1020 (s), 760 (s), 690 (s), 675 (m), 630 (w), 620 (m), 605 (w), 545 (m)
2f	3030 (w), 1530 (s), 1460 (s), 1375 (s), 1320 (w), 1280 (s), 1035 (m), 1025 (w), 1010 (m), 1000 (w), 865 (w), 775 (s), 760 (s), 735 (m), 685 (s)
3a	3020 (w), 1670 (w), 1630 (s), 1600 (m), 1555 (w), 1525 (w), 1470 (s), 1455 (m), 1345 (s), 1305 (s), 1285 (s), 1260 (s), 1220 (s), 1190 (m), 1140 (s), 1105 (m), 980 (m), 905 (w), 795 (m), 750 (s), 670 (s), 630 (w)
3b	3010 (w), 1630 (s), 1600 (w), 1555 (w), 1515 (w), 1475 (s), 1350 (sh), 1345 (m), 1315 (s), 1280 (s), 1265 (s), 1215 (s), 1205 (s), 1155 (s), 1140 (s), 1105 (m), 815 (s), 795 (m), 685 (w), 500 (w)
3c	3020 (w), 1630 (s), 1610 (m), 1495 (m), 1480 (s), 1450 (s), 1415 (w), 1350 (m), 1310 (s), 1275 (s), 1265 (s), 1225 (s), 1155 (s), 1140 (s), 1105 (w), 1090 (s), 1010 (m), 1005 (w), 985 (w), 830 (s), 800 (w), 500 (w)
3d	3010 (w), 1635 (s), 1600 (s), 1585 (s), 1520 (s), 1495 (s), 1440 (m), 1315 (m), 1295 (m), 1245 (s), 1215 (m), 1160 (m), 1150 (m), 1140 (m), 1030 (s), 825 (s), 745 (w)

Table III. NMR Data

compd	solvent	$\sigma$ (assignment)
2d	acetone- $d_6$	3.85 (OCH <sub>3</sub> ), 6.9, 7.55 (H <sub>m</sub> ), 7.95 (H <sub>o</sub> )
3a	CCl <sub>4</sub>	6.00 (methine CH), 7.35 (H <sub>m,p</sub> ), 8.0 (H <sub>o</sub> )
3b	CCl <sub>4</sub>	2.41 (CH <sub>3</sub> ), 5.96 (methine CH), 7.18 (H <sub>m</sub> ), 7.87 (H <sub>o</sub> )
3c	CCl <sub>4</sub>	6.00 (methine CH), 7.3 (H <sub>m</sub> ), 7.85 (H <sub>o</sub> )
3d	CDCl <sub>3</sub>	3.87 (OCH <sub>3</sub> ), 6.01 (methine CH), 6.96 (H <sub>m</sub> ), 7.98 (H <sub>o</sub> )

Table IV. Mass Spectral Data

compd	$m/e$ (assignment)
2a	704 (M <sup>+</sup> ), 299 (Ph <sub>3</sub> CN <sub>4</sub> <sup>+</sup> )
2b	788 (M <sup>+</sup> ), 447 (M <sup>+</sup> - (C <sub>7</sub> H <sub>7</sub> ) <sub>3</sub> CN <sub>4</sub> ), 341 ((C <sub>7</sub> H <sub>7</sub> ) <sub>3</sub> CN <sub>4</sub> <sup>+</sup> )
2c	715 (M <sup>+</sup> ), 401 ((C <sub>6</sub> H <sub>5</sub> Cl) <sub>3</sub> CN <sub>4</sub> <sup>+</sup> )
2d	884 (M <sup>+</sup> ), 495 (M <sup>+</sup> - (C <sub>7</sub> H <sub>7</sub> O) <sub>3</sub> CN <sub>4</sub> ), 389 ((C <sub>7</sub> H <sub>7</sub> O) <sub>3</sub> CN <sub>4</sub> <sup>+</sup> )
2e	602 (M <sup>+</sup> ), 248 (CNPh <sub>2</sub> CN <sub>4</sub> <sup>+</sup> )
2f	642 (M <sup>+</sup> ), 268 (NO <sub>2</sub> Ph <sub>2</sub> CN <sub>4</sub> <sup>+</sup> )
3a	612 (M <sup>+</sup> ), 543 (M <sup>+</sup> - CF <sub>3</sub> ), 405 (M <sup>+</sup> - C <sub>5</sub> HF <sub>6</sub> O <sub>2</sub> ), 299 (Ph <sub>3</sub> CN <sub>4</sub> <sup>+</sup> )
3b	654 (M <sup>+</sup> ), 447 (M <sup>+</sup> - C <sub>5</sub> HF <sub>6</sub> O <sub>2</sub> ), 341 ((C <sub>7</sub> H <sub>7</sub> ) <sub>3</sub> CN <sub>4</sub> <sup>+</sup> ), 314 (M <sup>+</sup> - (C <sub>7</sub> H <sub>7</sub> ) <sub>3</sub> CN <sub>4</sub> )
3c	714 (M <sup>+</sup> ), 508 (M <sup>+</sup> - C <sub>5</sub> HF <sub>6</sub> O <sub>2</sub> ), 401 ((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CN <sub>4</sub> <sup>+</sup> )
3d	702 (M <sup>+</sup> ), 389 ((C <sub>7</sub> H <sub>7</sub> O) <sub>3</sub> CN <sub>4</sub> <sup>+</sup> )

group mode due to hexafluoroacetylacetonate covalently bonded through the oxygen atoms to palladium.

Proton NMR spectral data are given in Table III and show peaks typical for para-substituted phenyl rings. In addition, the unsymmetrical chelates display a sharp peak at about  $\delta$  6 due to the methine CH protons and single <sup>19</sup>F resonances at  $\delta$  76 upfield from internal CFCl<sub>3</sub>.

The mass spectra, Table IV, all show molecular ion peaks as well as peaks due to the stable tetrazolium ion (aryl)<sub>3</sub>CN<sub>4</sub><sup>+</sup>. In the case of the *p*-tolyl and *p*-anisyl compounds **2b** and **2d**, ions resulting from loss of one tetrazolium fragment were observed.

The electronic spectra of the para-substituted bis(triarylformazanyl)palladium compounds are summarized in Table V. They all show long-wavelength absorptions at 750–810 nm which, in general, move to higher energy as the substituent becomes more electron releasing. This transition cannot be reliably assigned without a detailed investigation of the (C-

Table V. Electronic Spectral Data

compd	medium	$\lambda_{\max}$ (log $\epsilon$ ), nm
2a	Nujol	300, 355, 480, 790
2b	Nujol	305, 360, 535, 800
2c	Nujol	295, 335 (sh), 365 (sh), 520, 810
2d	Nujol	285, 315, 370, 485, 750
2d	CHCl <sub>3</sub>	280 (4.61), 330 (sh), 360 (sh), 500 (4.81), 720 (4.09)
2e	Nujol	330, 400, 610 (sh), 645
2f	Nujol	270, 375, 450, 630
3a	C <sub>6</sub> H <sub>12</sub>	253 (4.62), 312 (4.32), 605 (3.93)
3b	C <sub>6</sub> H <sub>12</sub>	255 (4.65), 315 (4.30), 600 (3.86)
3c	C <sub>6</sub> H <sub>12</sub>	260 (4.61), 320 (4.40), 560 (sh), 620 (3.97)
3d	C <sub>6</sub> H <sub>12</sub>	265 (4.60), 295 (4.36), 585 (sh), 630 (3.40)

N<sub>4</sub>)<sub>2</sub>Pd chromophore. It is, however, associated with a molecular orbital which includes both C-aryl rings and the (CN<sub>4</sub>)<sub>2</sub>Pd system since no similar band is seen in the [(aryl)<sub>3</sub>CN<sub>4</sub>]Pd(F<sub>6</sub>acac) compounds **3a–d** or in the C-nitro and C-cyano compounds **2e** and **2f**. These data suggest that, despite the puckering in the formazanylpalladium ring (vide infra), there is still significant overlap between the C-aryl and PdCN<sub>4</sub>  $\pi$  systems.

The longest wavelength absorption in the palladium formazanyl hexafluoroacetylacetonates, which occurs between 600 and 630 nm, is likely associated with transitions in an isolated CN<sub>4</sub>Pd ring as they are not observed in **2a–d**. Bands in the 500-nm region occur both in the palladium chelates and in neutral formazans and therefore are associated with the (aryl)<sub>3</sub>CN<sub>4</sub> ring itself.

#### Single-Crystal X-ray Structure of [(*p*-tolyl)<sub>3</sub>CN<sub>4</sub>]<sub>2</sub>Pd (**2b**).

The crystal consists of well-separated molecules (shortest intermolecular contact is 2.96 Å between H5A and H7B). An ORTEP drawing of the bis(1,3,5-tri-*p*-tolylformazanyl)palladium molecule is shown in Figure 1. The PdN<sub>4</sub> coordination core geometry is planar as required by the inversion center at the palladium atom. Figure 2 presents an ORTEP drawing of the coordination core and vicinity along with selected distances and angles. Table VI presents positional and thermal parameters, Table VII the interatomic distances and angles and Table VIII a listing of selected least-squares planes.

The variation among the N–Pd–N angles is large, reflecting the distortions imposed by the CN<sub>4</sub> chelate. Thus, N(1)–Pd–N(4) is 80.4 (2)° and N(1)–Pd–N(4') is 99.6 (2)°. The dihedral angle between the PdN<sub>4</sub> plane and the one defined by N(1), N(2), N(3), and N(4) is 43.2° (cf. Table VIII).

Table VI. Positional and Thermal Parameters and Their Estimated Standard Deviations<sup>a</sup>

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Pd	0.0000 (0)	0.0000 (0)	0.0000 (0)	0.00451 (3)	0.00297 (3)	0.00592 (5)	0.0009 (1)	0.00441 (6)	0.0014 (1)
N1	-0.0316 (4)	-0.0637 (4)	0.1540 (5)	0.0059 (4)	0.0032 (3)	0.0062 (5)	0.0000 (5)	0.0055 (6)	0.0012 (6)
N2	0.0469 (4)	-0.0772 (4)	0.2580 (5)	0.0061 (4)	0.0041 (3)	0.0070 (5)	0.0002 (6)	0.0043 (7)	0.0009 (7)
N3	0.1831 (4)	-0.1028 (4)	0.1483 (5)	0.0055 (4)	0.0034 (3)	0.0078 (5)	0.0013 (6)	0.0036 (7)	0.0014 (7)
N4	0.1180 (4)	-0.0949 (4)	0.0333 (5)	0.0053 (3)	0.0040 (3)	0.0061 (5)	0.0014 (6)	0.0033 (7)	0.0007 (7)
C	0.1513 (5)	-0.0794 (5)	0.2529 (6)	0.0053 (4)	0.0034 (3)	0.0067 (6)	0.0002 (6)	0.0042 (8)	0.0007 (8)
C1A	-0.1338 (5)	-0.0947 (4)	0.1623 (6)	0.0055 (4)	0.0029 (3)	0.0066 (5)	0.0012 (6)	0.0064 (7)	0.0007 (7)
C2A	-0.1475 (6)	-0.1433 (6)	0.2691 (7)	0.0066 (5)	0.0057 (4)	0.0075 (6)	0.0006 (8)	0.0056 (9)	0.0031 (9)
C3A	-0.2493 (6)	-0.1717 (6)	0.2725 (8)	0.0088 (5)	0.0056 (5)	0.0122 (8)	0.0011 (9)	0.0121 (9)	0.0046 (10)
C4A	-0.3394 (5)	-0.1550 (5)	0.1757 (7)	0.0062 (5)	0.0037 (4)	0.0130 (8)	-0.0000 (7)	0.0087 (9)	-0.0006 (10)
C5A	-0.3244 (6)	-0.1094 (6)	0.0676 (8)	0.0051 (5)	0.0058 (4)	0.0106 (8)	-0.0020 (8)	-0.0003 (11)	-0.0000 (11)
C6A	-0.2227 (6)	-0.0796 (5)	0.0614 (7)	0.0066 (5)	0.0044 (4)	0.0089 (7)	-0.0002 (8)	0.0045 (9)	0.0013 (10)
C7A	-0.4531 (6)	-0.1869 (7)	0.1806 (10)	0.0067 (5)	0.0067 (5)	0.0232 (12)	-0.0038 (9)	0.0151 (11)	0.0000 (15)
C1B	0.2347 (5)	-0.0749 (5)	0.3779 (6)	0.0056 (4)	0.0037 (3)	0.0074 (6)	0.0005 (7)	0.0032 (9)	0.0008 (9)
C2B	0.2084 (6)	-0.0483 (6)	0.4891 (7)	0.0064 (5)	0.0054 (4)	0.0081 (7)	0.0024 (8)	0.0034 (10)	0.0010 (10)
C3B	0.2859 (6)	-0.0475 (6)	0.6055 (7)	0.0081 (6)	0.0046 (4)	0.0080 (7)	0.0007 (9)	0.0024 (11)	-0.0012 (10)
C4B	0.3907 (6)	-0.0730 (5)	0.6158 (8)	0.0079 (6)	0.0042 (4)	0.0088 (8)	0.0007 (8)	0.0004 (11)	0.0003 (10)
C5B	0.4168 (6)	-0.0966 (6)	0.5026 (8)	0.0052 (5)	0.0069 (5)	0.0111 (9)	0.0014 (9)	-0.0011 (11)	-0.0009 (12)
C6B	0.3408 (6)	-0.0991 (6)	0.3857 (7)	0.0059 (5)	0.0062 (5)	0.0095 (7)	0.0003 (8)	0.0052 (9)	0.0007 (11)
C7B	0.4744 (7)	-0.0740 (7)	0.7456 (9)	0.0084 (7)	0.0073 (6)	0.0098 (9)	0.0004 (11)	-0.0050 (14)	-0.0009 (13)
C1C	0.1489 (5)	-0.1441 (5)	-0.0653 (6)	0.0063 (4)	0.0031 (3)	0.0078 (6)	0.0010 (7)	0.0064 (8)	0.0011 (8)
C2C	0.2481 (6)	-0.1872 (6)	-0.0450 (7)	0.0077 (5)	0.0067 (5)	0.0086 (7)	0.0038 (9)	0.0071 (9)	0.0003 (11)
C3C	0.2739 (7)	-0.2327 (6)	-0.1440 (8)	0.0100 (6)	0.0045 (4)	0.0151 (10)	0.0038 (9)	0.0119 (11)	-0.0002 (11)
C4C	0.2038 (6)	-0.2416 (6)	-0.2631 (8)	0.0096 (5)	0.0044 (4)	0.0140 (8)	-0.0032 (8)	0.0145 (9)	-0.0044 (10)
C5C	0.1032 (7)	-0.1996 (6)	-0.2833 (8)	0.0100 (7)	0.0052 (4)	0.0108 (8)	-0.0035 (9)	0.0059 (12)	-0.0041 (11)
C6C	-0.0758 (6)	0.1509 (5)	0.1846 (7)	0.0070 (5)	0.0051 (4)	0.0087 (7)	-0.0000 (8)	0.0054 (9)	-0.0015 (10)
C7C	0.2319 (8)	-0.2940 (8)	-0.3743 (9)	0.0166 (8)	0.0090 (6)	0.0181 (10)	-0.0045 (13)	0.0222 (13)	-0.0131 (13)

atom	x	y	z	atom	x	y	z
H2A	-0.087 (5)	-0.136 (5)	0.351 (6)	H5B	0.481 (5)	-0.119 (5)	0.502 (6)
H3A	-0.249 (5)	-0.205 (5)	0.328 (6)	H6B	0.362 (5)	-0.115 (5)	0.319 (6)
H5A	-0.385 (5)	-0.105 (5)	0.008 (6)	H2C	0.277 (5)	-0.188 (5)	0.021 (6)
H6A	-0.200 (5)	-0.055 (5)	-0.016 (6)	H3C	0.347 (5)	-0.262 (5)	-0.109 (6)
H2B	0.148 (5)	-0.031 (5)	0.492 (7)	H5C	0.052 (5)	-0.199 (4)	-0.371 (6)
H3B	0.263 (5)	-0.038 (5)	0.671 (7)	H6C	0.010 (5)	-0.122 (5)	-0.202 (6)

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$ . For all H atoms  $B = 4.0 \text{ \AA}^2$ .

Table VII. Selected Interatomic Distances and Angles<sup>a</sup>

Distances, \AA							
Pd-N1	2.028 (5)	C1A-C2A	1.400 (9)	C1B-C2B	1.378 (9)	C1C-C2C	1.385 (10)
Pd-N4	2.019 (5)	C2A-C3A	1.377 (10)	C2B-C3B	1.380 (10)	C2C-C3C	1.365 (11)
N1-N2	1.310 (7)	C3A-C4A	1.361 (11)	C3B-C4B	1.368 (10)	C3C-C4C	1.366 (12)
N4-N3	1.304 (7)	C4A-C5A	1.395 (10)	C4B-C5B	1.384 (11)	C4C-C5C	1.394 (12)
N2-C	1.351 (8)	C5A-C6A	1.391 (10)	C5B-C6B	1.375 (11)	C5C-C6C	1.397 (10)
N3-C	1.334 (8)	C6A-C1A	1.371 (9)	C6B-C1B	1.385 (9)	C6C-C1C	1.382 (10)
N1-N4	2.613 (7)	C4A-C7A	1.542 (9)	C4B-C7B	1.522 (10)	C4C-C7C	1.537 (10)
N1-N4'	3.091 (7)	N1-C1A	1.409 (7)	C-C1B	1.485 (9)	N4-C1C	1.420 (8)

Angles, Deg					
N1-Pd-N4	80.4 (2)	Pd-N1-C1A	125.7 (4)	N1-C1A-C2A	122.1 (6)
N1-Pd-N4'	99.6 (2)	Pd-N4-C1C	124.0 (4)	N1-C1A-C6A	119.5 (6)
Pd-N1-N2	119.6 (4)	N2-N1-C1A	114.7 (5)	C-C1B-C2B	121.0 (6)
Pd-N4-N3	119.7 (4)	N3-N4-C1C	115.2 (5)	C-C1B-C6B	120.6 (6)
N1-N2-C	121.2 (5)	N2-C-C1B	116.8 (6)	N4-C1C-C2C	122.5 (6)
N4-N3-C	120.9 (5)	N3-C-C1B	117.8 (6)	N4-C1C-C6C	118.3 (6)
N2-C-N3	124.1 (6)				

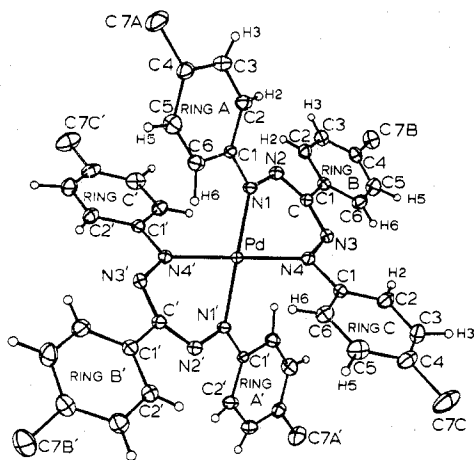
<sup>a</sup> The numbers in parentheses are the estimated standard deviations of the last significant figure.

Thus, the six-membered rings are not planar but significantly folded along the N(1)-N(4) vector. This folding is best seen in the ORTEP stereoview shown in Figure 3.

The plane of the aromatic ring B is twisted  $10.6^\circ$  out of the plane formed by N(2), N(3), C, and C(1B). This presumably reduces nonbonded repulsions between the ortho hydrogens and N(2,3). Here  $d(\text{H}_{2\text{B}}-\text{N}(2))$  and  $d(\text{H}_{6\text{B}}-\text{N}(3))$  are 2.59 and 2.55 \AA, respectively. The planes formed by the *p*-tolyl groups (rings A and C) attached to N(1) and N(4) make dihedral angles of  $47.0^\circ$  and  $55.5^\circ$ , respectively, with the PdN<sub>4</sub> plane. This is probably caused by a combination of maximizing conjugation between the *p*-tolyl rings and the adjacent nitrogens and minimizing steric repulsions between tolyl rings A and C'.

The ring carbon atom C is effectively  $sp^2$  hybridized. The sum of the angles about C is  $358.7^\circ$ , and the displacement of C from the C, N(2), N(3), C(1B) least-squares plane is 0.07 \AA. Similarly, N(1) and N(4) are  $sp^2$  hybridized as well; the sums of the angles about these atoms are 360.0 and  $358.9^\circ$ , respectively. The positioning of the *p*-tolyl rings is such as to maximize conjugation with the CN<sub>4</sub>Pd ring system. Thus the dihedral angles between *p*-tolyl rings A and C and the planes formed by Pd, N(1), N(2), and C(1A) and Pd, N(3), N(4), and C(1C) are 3.8 and  $16.3^\circ$ , respectively.

The bond lengths in the heterocyclic CN<sub>4</sub>Pd rings are rather similar:  $d(\text{N}-\text{N})_{\text{av}}$  is 1.307 (7) \AA and  $d(\text{C}-\text{N})_{\text{av}}$  is 1.343 (8) \AA which indicates significant double-bond character. The average N-C<sub>tolyl</sub> separation, 1.415 (7) \AA, is considerably



**Figure 1.** ORTEP drawing of bis(1,3,5-tri-*p*-tolylformazanil)palladium(II) showing the labeling scheme. The Pd is on an inversion center, and primed atoms are related to unprimed atoms by the inversion symmetry operation.

shorter than the 1.485 (9) Å distance between the chelate ring carbon C and C(1B) of the *p*-tolyl group. These trends parallel those observed by Dale<sup>17</sup> in a disordered crystal of bis(1-phenyl-4-*p*-tolylformazanil)nickel(II) and indicate that considerable electron delocalization occurs in the spiro (CN<sub>4</sub>)<sub>2</sub>Pd system despite the significant deviations from planarity.

The reasons for the puckering of the CN<sub>4</sub>Pd ring are not completely clear. The folding along the N(1)–N(4) vector is required to accommodate a square-planar metal in the ring. The angles about N(1), N(2), C, N(3), and N(4) are all close to 120°, and, if the palladium were coplanar with these atoms, a comparable N(1)–Pd–N(4) angle would be required. This can be neatly avoided when the palladium atom is located out of the CN<sub>4</sub> plane. It may be that a MCN<sub>4</sub> ring in which the metal has a tetrahedral coordination geometry will have a different, more nearly planar ring conformation.

A unique explanation for the slight folding which is apparent along the N(2)–N(3) vector has not been obtained thus far. In any event, the deformation is not sufficient, as judged from the optical spectra, to prevent conjugation between the C-aryl group and the CN<sub>4</sub>Pd ring.

The average Pd–N bonding distance is 2.024 (5) Å, in good agreement with other values such as 2.032 Å in (en)<sub>2</sub>PdCl<sub>2</sub>,<sup>18</sup> 2.038 Å in [(bpy)<sub>2</sub>Pd(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>,<sup>19</sup> 2.033 Å in Pd(NH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>H<sub>2</sub>N<sub>2</sub>(CO<sub>2</sub>)<sub>2</sub>,<sup>20</sup> 1.978 Å in *cis*-(en)PdCl<sub>2</sub>,<sup>21</sup> and 1.996 Å in palladium 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetraaza[14]annulene.<sup>22</sup>

Phenyl rings A, B, and C are each planar within experimental error. The 18 carbon–carbon bands within the phenyl rings vary from 1.36 (1) to 1.40 (1) Å and average 1.38 Å, a value which is in good agreement with the accepted C–C (aromatic) distance of 1.394 ± 0.005 Å. The 12 C(phenyl)–H distances vary from 0.71 (7) to 1.02 (7) Å, and average 0.89 Å, in good agreement with accepted values. The three C(phenyl)–C(methyl) distances average 1.5 Å, and the *p*-tolyl carbons are within experimental error of their respective phenyl planes.

### Experimental Section

Infrared spectra were obtained on Nujol mulls by using a spec-

**Table VIII.** Least-Squares Planes

plane no. <sup>b</sup>	atoms		dist from plane, Å
	forming the plane <sup>a</sup>	other	
1	Pd		0
	N1		0
	N4		0
2	N1		–0.01
	N2		0.01
	N3		–0.01
	N4		0.01
		C	–0.23
		Pd	–1.06
3	C1B		–0.01
	C2B		0.01
	C3B		0.01
	C4B		–0.02
	C5B		–0.01
	C6B		0.00
		C	–0.06
	C7B	–0.05	
4	C1A		0.00
	N1		0.01
	N2		0.00
	Pd		0.00
5	C1B		–0.02
	C		0.07
	N2		–0.02
	N3		–0.03
6	C1C		0.02
	N4		–0.07
	N3		0.03
	Pd		0.02
7	C1A		–0.02
	C2A		0.01
	C3A		0.01
	C4A		–0.02
	C5A		0.01
	C6A		0.01
	N1	–0.02	
	C7A	–0.02	
8	C1C		0.01
	C2C		–0.01
	C3C		0.01
	C4C		0.00
	C5C		0.00
	C6C		0.00
		N4	0.00
	C7C	0.01	

<sup>a</sup> Planes calculated by using unit weights. <sup>b</sup> Dihedral angles between planes: 1 and 2, 43.2°; 3 and 5, 10.6°; 4 and 7, 3.8°; 6 and 8, 16.3°; 1 and 5, 56.1°; 1 and 3, 51.1°.

trometer with grating optics. Electronic spectra were obtained on a Cary 14 instrument. Mass spectra were run in the electron-impact mode using 70-eV electrons. Triphenylformazan was obtained from the Aldrich Chemical Co. Other triarylformazans were prepared by literature methods.<sup>1</sup> 3-Nitro- and 3-cyano-1,5-diphenylformazan were gifts from Dr. Gil Eian. <sup>1</sup>H and <sup>19</sup>F NMR spectra were obtained at 60 and 94.6 MHz, respectively.

**Reaction of 1 with Triphenylformazan.** Triphenylformazan, 0.60 g (2 mmol), was dissolved in 75 mL of boiling Spectrograde acetonitrile. The solution was filtered, and to it was added 0.52 g (1 mmol) of palladium bis(hexafluoroacetylacetonate) in 5 mL of acetonitrile. After the mixture was allowed to stand for 6 h, the product, **2a**, was collected on a filter and washed with acetonitrile. The yield of reflective purple crystals was 0.48 g (68%). Recrystallization from pyridine did not change the elemental analysis.

The above filtrate was evaporated to dryness under reduced pressure and the residue extracted with hot hexane. The extract was concentrated and cooled in a dry-ice bath to give 0.07 g (11%) of **3a** as violet microcrystals, mp 189 °C.

**(Tri-*p*-anisylformazanil)palladium Hexafluoroacetylacetonate (3d).** A solution of 0.52 g of palladium bis(hexafluoroacetylacetonate) in 5 mL of carbon tetrachloride was added to 0.39 g (1 mmol) of tri-*p*-anisylformazan in 70 mL of CCl<sub>4</sub>. The reaction mixture was

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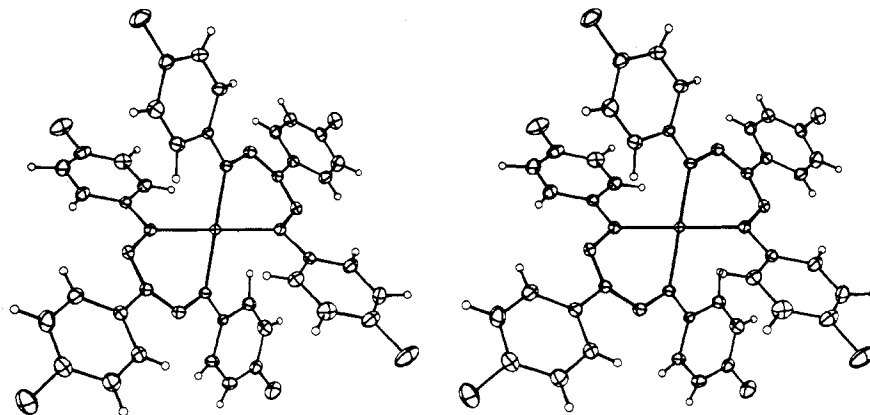


Figure 2. ORTEP stereoview of the molecule using 20% probability ellipsoids.

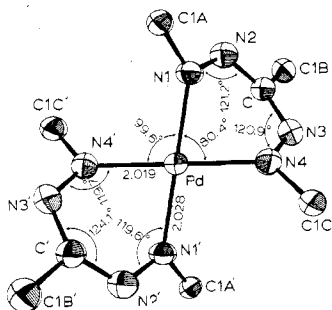


Figure 3. ORTEP drawing of the coordination core using 50% probability ellipsoids.

filtered, and, on cooling, 0.60 g (85%) of product separated as fibrous purple needles. Recrystallization from  $\text{CCl}_4$  afforded the analytical sample. When this reaction was carried out by using twice the amount of formazan, the product was predominantly **3d** contaminated with some **2d** (NMR analysis).

**Bis(tri-*p*-anisylformazanyl)palladium (2d).** A mixture of 0.52 g of **1**, 2 mmol of tri-*p*-anisylformazan, and 50 mL of butanone was stirred and refluxed overnight. The hot reaction mixture was filtered and the solid product washed with warm butanone. The yield of black microcrystals was 0.17 g (19%). On standing, the mother liquor deposited 0.25 g of **3d**.

**Bis(tri-*p*-tolylformazanyl)palladium (2b).** To a filtered solution of 0.68 g of tri-*p*-tolylformazan in 50 mL of butanone was added 0.52 g of **1** in 5 mL of the same solvent. After the mixture was allowed to stand for 12 h, the product was collected on a filter and washed with fresh solvent. The yield of chunky black needles was 0.55 g (70%). These were used for the X-ray structure determination.

The mother liquor was evaporated and extracted with hexane. The extracts yielded 0.05 g of **3b** after recrystallization from methylcyclohexane (8%).

**Structure Determination.** A good-quality crystal of bis(1,3,5-tri-*p*-tolylformazanyl)palladium(II),  $\text{PdN}_8\text{C}_{44}\text{H}_{42}$ , of dimensions  $0.30 \times 0.20 \times 0.20$  mm was selected and used in the structure determination. The crystal belonged to the monoclinic crystal class which was later shown to be  $P2_1/a$  by the systematic absences in the data ( $h0l$ ,  $h = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ ). Successful solution and refinement were achieved by using this space group (vide infra). Equivalent positions for this nonstandard space group are  $\pm(x, y, z; 1/2 + x, 1/2 - y, z)$ . The unit cell dimensions were determined by least-squares refinement of the angular settings of 25 peaks centered on the diffractometer at ambient temperature and are  $a = 12.797$  (4) Å,  $b = 14.703$  (4) Å,  $c = 10.729$  (3) Å,  $\beta = 104.94$  (2)°, and  $V = 1951$  Å<sup>3</sup>. The density is calculated to be 1.344 g/cm<sup>3</sup> by assuming  $Z = 2$  and agrees with measured density of 1.34 g/cm<sup>3</sup> (by flotation).

A total of 3612 unique reflections were measured in the scan range  $2\theta = 0$ – $50^\circ$  on an Enraf-Nonius CAD4 automatic diffractometer using graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) and employing a variable rate  $\omega$ - $2\theta$  scan technique. No decay was noted in the intensity of three check reflections measured at intervals of 200 sequential reflections. After correction for Lorentz, polarization, and background effects,<sup>23</sup> 2201 reflections were judged observed [ $F_o^2$

$\geq 2.0\sigma(F_o^2)$ ] and were used in all subsequent calculations.<sup>24</sup>

The data were not corrected for absorption ( $\mu = 5.13$  cm<sup>-1</sup>) since, with maximum and minimum transmission factors of 0.90 and 0.84, such a correction would not have a significant effect on the data. Conventional heavy-atom techniques were used to solve the structure, and refinement, with all nonhydrogen atoms thermally anisotropic and the hydrogen atoms isotropic but with fixed temperature parameters by full-matrix least-squares methods (277 variables), converged  $R$  and  $R_w$  to their final values of 0.056 and 0.069, respectively.<sup>25</sup> The error in an observation of unit weight was determined to be 1.28 by using a value of 0.06 for  $p$  in the  $\sigma(I)$  equation.<sup>23</sup> In the final difference Fourier map, the highest peak not within 1 Å of the palladium atom was  $0.56$  e Å<sup>-3</sup> and was located near C7A. The methyl hydrogen atoms were not located in this map and therefore were not included in the refinement. All other hydrogen atoms were located by difference Fourier analysis, and their positional parameters were refined. The palladium atom is on an inversion center, and therefore the asymmetric unit contains half of the molecular formula.

The final atomic coordinates with their estimated standard deviations and the final thermal parameters are given in Table VI. Tables of observed and calculated structure factor amplitudes and general anisotropic temperature factor expressions are available (supplementary material). Figure 1 presents an ORTEP perspective of the molecular structure and shows the labeling scheme.

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**Registry No.** **1**, 64916-48-9; **2a**, 73496-90-9; **2b**, 73496-89-6; **2c**, 73497-07-1; **2d**, 73497-06-0; **2e**, 73497-05-9; **2f**, 73497-04-8; **3a**, 73497-03-7; **3b**, 73497-02-6; **3c**, 73497-01-5; **3d**, 73497-00-4.

**Supplementary Material Available:** Structure factor table (10 pages). Ordering information is given on any current masthead page.

- (23) The intensity data were processed as described in the "CAD4 and SDP Users Manual", Enraf-Nonius, Delft, Holland, 1978. The net intensity  $I$  is given as  $I = (K/NPI)(C - 2B)$ , where  $K = 20.1166$  (attenuator factor),  $NPI =$  ratio of fastest possible scan rate to scan rate for the measurement,  $C =$  total count, and  $B =$  total background count. The standard deviation in the net intensity is given by  $\sigma^2(I) = (K/NPI)^2[C + 4B + (pI)^2]$ , where  $p$  is a factor used to downweight intense reflections. The observed structure factor amplitude  $F_o$  is given by  $F_o = (I/Lp)^{1/2}$ , where  $Lp =$  Lorentz and polarization factors. The  $\sigma(I)$ 's were converted to the estimated errors in the relative structure factors  $\sigma(F_o)$  by  $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$ .
- (24) All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP programs. This crystallographic computing package is described by B. A. Frenz in "Computing in Crystallography", H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G. C. Bassi, Eds., Delft University Press, Delft, Holland, 1978, pp 64–71.
- (25) The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(F_o)$ . The unweighted and weighted residuals are defined as  $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$  and  $R_w = [(\sum w(|F_o| - |F_c|)^2) / (\sum w|F_o|^2)]^{1/2}$ . The error in an observation of unit weight is  $[\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$ , where NO and NV are the number of observations and variables, respectively. Atomic scattering factors were taken from the "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962. Anomalous dispersion corrections from the same source were used for palladium.