ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2009, Vol. 54, No. 10, pp. 1590–1602. © Pleiades Publishing, Inc., 2009.
Original Russian Text © E.V. Perova, F.M. Miloserdov, M.Ya. Yakovleva, S.E. Nefedov, 2009, published in Zhurnal Neorganicheskoi Khimii, 2009, Vol. 54, No. 10, pp. 1665–1677.

COORDINATION COMPOUNDS

Formation of Binuclear Pyrazolate-Bridged Palladium Carboxylates in the Reactions of $[Pd(Hdmpz)_4](OOCR_2)$ (R = Me, Bu^t, Ph) with Heterometallic Pd–Co Acetate

E. V. Perova, F. M. Miloserdov, M. Ya. Yakovleva, and S. E. Nefedov

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia

Received October 15, 2008

Abstract—The reactions of $[Pd(Hdmpz)_4](OOCR)_2$ (R = Me, Bu^t, Ph, Hdmpz = 3,5-dimethylpyrazole) with the heterometallic acetate $Pd(\mu\text{-}OOCMe)_4Co(NCMe)$ gives pyrazolate-bridged dimers $Pd_2(\mu\text{-}dmpz)_2(Hdmpz)_2(OOCR)_2$ (R = Me, Bu^t, Ph), which were characterized by X-ray diffraction.

DOI: 10.1134/S0036023609100155

The chemistry of complexes containing coordinated molecules of pyrazole and its analogues attracts enhanced interest due to the possible deprotonation of the pyrrole nitrogen atom of the heterocycle to give pyrazolate bridges and binuclear complexes, which can be assembled into more complex polynuclear clusters up to metal-containing polymers combining bridging unsaturated organic fragments and transition metal atoms [1–6].

The present study deals with the synthesis and structure of the products of deprotonation reactions of 3,5-dimethylpyrazole (Hdmpz) coordinated to palladium(II) in the complexes $[Pd(Hdmpz)_4](OOCR)_2$ (R = Me, Bu^t, Ph) with the heterometallic lantern dimer $Pd(\mu\text{-}OOCMe)_4Co(NCMe)$ (**1**) [7]. The latter corresponds to the recently discovered type of heterometallic dimers in which the square-planar palladium(II) atom forms a Chinese lantern structure typical of binuclear carboxylates irrespective of the nature of attached nontransition, transition, or rare earth metal [8, 9]. In these heterometallic dimers, the metal atoms are located at short nonbonding metal–metal distances, which is apparently a crucial factor determining the formation of species with a 1 : 1 Pd–M stoichiometry upon the reduction with hydrogen under mild conditions (temperature up to 250°C), as was shown, for example, by the preparation of the Pd–Zn product from the complex $Pd(\mu\text{-}OOCMe)_4Zn(OH_2)$ [8, 10, 11]. Although the composition and structure of the intermediates formed in reduction of palladium(II)-based heterometallic dimers with hydrogen are unknown, nevertheless, it is quite obvious that the process involves coordination of the hydrogen molecule, electron transfer, and removal of acetic acid molecules.

EXPERIMENTAL

All operations on the synthesis and isolation of complexes were carried out under pure argon using anhydrous solvents. $[Pd(Hdmpz)_4](OOCR)_2$ (R = Me, Bu^t, Ph) and $Pd(\mu\text{-}OOCMe)_4Co(NCMe)$ were synthesized by reported procedures [7, 12].

IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets in the frequency range of 392–4000 cm^{-1}.

X-ray diffraction studies were performed by a standard procedure on a Bruker SMART Apex II automated diffractometer equipped with a CCD detector (λMo, graphite monochromator, ω scan mode). The structures were calculated using the SHELXTL PLUS program package (PC version) and refined by means of the SHELXTL-97 package [13, 14]. The crystal data and refinement details are summarized in Table 1, atomic coordinates and selected geometric parameters of the complexes are in Tables 2 to 9.

Synthesis of $Pd_2(\mu\text{-}dmpz)_2(Hdmpz)_2(OOCMe)_2$ (2). The complex $PdCo(OOCMe)_4NCMe$ (0.071 g, 0.16 mmol) in acetonitrile (5 mL) was added to $[Pd(Hdmpz)_4](OOCMe)_2$ (0.1 g, 0.16 mmol) in acetonitrile (15 mL) and the mixture was stirred for 15 min at room temperature. The solution thus formed was concentrated to 7 mL and kept for 24 h at –5°C. The precipitated crystals were separated from the mother liquor by decantation and dried in an argon flow. Yield, 0.068 g (60%).

For $Pd_2C_{26}H_{39}N_9O_4$ anal. calcd. (%): C, 41.36; H, 5.23; N, 16.69.

Found (%): C, 41.45; H, 5.38; N, 16.71.

IR (KBr, ν, cm^{-1}): 3424 m br., 3172 w, 3076 w, 3024 w, 2960 m, 2868 w, 2732 w, 1604 s, 1564 s, 1480 m, 1396 s,

Table 1. Crystallographic parameters and structure refinement details for **2–4**

	2 · MeCN	**3 · MeCN**	**3 · C_6H_{14}**	**4**
Molecular formula	$C_{26}H_{39}N_9O_4Pd_2$	$C_{32}H_{51}N_9O_4Pd_2$	$C_{33}H_{55}N_8O_4Pd_2$	$C_{34}H_{40}N_8O_4Pd_2$
M	754.46	838.62	840.65	837.54
Temperature, K	160(2)	296(2)	120(2)	100(2)
Color	Ligth beige	Ligth beige	Ligth beige	Ligth beige
System	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	*P*-1	*P*2(1)/*c*	*P*-1
Unit cell parameters				
a, Å	9.5344(7)	10.059(6)	12.7140(16)	8.6137(6)
b, Å	10.7589(8)	11.560(7)	19.576(3)	13.0828(9)
c, Å	16.267(1)	18.165(9)	16.862(2)	16.5597(12)
α, deg	6.978(1)	95.02(1)	90	81.2300(10)
β, deg	92.918(1)	101.38(1)	108.115(2)	88.4420(10)
γ, deg	103.405(1)	104.09(1)	90	72.3680(10)
V, Å^3	1605.8(2)	1988(2)	3988.8(9)	1757.3(2)
Z	2	2	4	2
ρ_{calcd}, mg/m^3	1.560	1.401	1.400	1.583
μ, mm^{-1}	1.164	0.948	0.945	1.072
F(000)	764	860	1732	848
Crystal dimensions, mm	0.10 × 0.08 × 0.06	0.14 × 0.12 × 0.10	0.14 × 0.12 × 0.10	0.16 × 0.14 × 0.12
Scanning θ range, deg	1.96 –28.00	1.84–25.00	1.69–26.00	2.21–27.00
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-21 \le l \le 21$	$-11 \le h \le 11$, $-13 \le k \le 13$, $-20 \le l \le 21$	$-15 \le h \le 15$, $-24 \le k \le 24$, $-20 \le l \le 20$	$-11 \le h \le 10$, $-16 \le k \le 16$, $-21 \le l \le 21$
Number of reflections	16576	12097	26983	16666
Number of unique reflections	7702 [*R*(int) = 0.0548]	6896 [*R*(int) = 0.1025]	7721 [*R*(int) = 0.0762]	7602 [*R*(int) = 0.0413]
GOOF	0.998	0.995	1.169	1.018
R [$I > 2\sigma(I)$]	*R*1 = 0.0299, *wR*2 = 0.0620	*R*1 = 0.0597, *wR*2 = 0.1539	*R*1 = 0.0541, *wR*2 = 0.1358	*R*1 = 0.0345, *wR*2 = 0.0815
R (for all reflections)	*R*1 = 0.0399, *wR*2 = 0.0648	*R*1 = 0.0925, *wR*2 = 0.1737	*R*1 = 0.1189, *wR*2 = 0.1842	*R*1 = 0.0486, *wR*2 = 0.0884
Electron density peaks (min/max), e Å^{-3}	1.052 and –0.460	1.268 and –1.360	1.670 and –0.652	1.620 and –0.682

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic factors ($Å^2$, $\times 10^3$) for complex **2**

Atom	*x*	*y*	*z*	U_{eq}
Pd(1)	8583(1)	7723(1)	1561(1)	21(1)
Pd(2)	9976(1)	10583(1)	2573(1)	21(1)
O(1)	9692(2)	6337(2)	1475(1)	31(1)
O(2)	11512(3)	7432(2)	2380(2)	56(1)
O(3)	9252(2)	11145(2)	3671(1)	30(1)
O(4)	8460(2)	9098(2)	3891(1)	37(1)
N(1)	7396(2)	9038(2)	1602(1)	23(1)
N(2)	8003(2)	10242(2)	2003(1)	24(1)
N(3)	10137(2)	8900(2)	1060(1)	22(1)
N(4)	10719(2)	10100(2)	1486(1)	22(1)
N(5)	7082(2)	6580(2)	2144(1)	25(1)
N(6)	6817(2)	6981(2)	2927(1)	28(1)
N(7)	11964(2)	10866(2)	3142(1)	25(1)
N(8)	12691(2)	9924(2)	3061(1)	27(1)
N(9)	12272(4)	15777(3)	5371(2)	78(1)
C(1)	6042(3)	9004(3)	1301(2)	29(1)
C(2)	5064(3)	7815(3)	823(2)	42(1)
C(3)	5793(3)	10212(3)	1508(2)	33(1)
C(4)	7046(3)	10972(3)	1958(2)	30(1)
C(5)	7404(3)	12346(3)	2357(2)	43(1)
C(6)	10877(3)	8739(2)	390(1)	26(1)
C(7)	10507(3)	7537(3)	–214(2)	37(1)
C(8)	11950(3)	9858(2)	386(2)	27(1)
C(9)	11823(3)	10690(2)	1082(2)	26(1)
C(10)	12692(3)	12027(3)	1398(2)	35(1)
C(11)	6238(3)	5396(2)	1926(2)	29(1)
C(12)	6247(3)	4676(3)	1085(2)	41(1)
C(13)	5418(3)	5048(3)	2588(2)	33(1)
C(14)	5819(3)	6075(3)	3216(2)	32(1)
C(15)	5361(4)	6289(3)	4077(2)	47(1)
C(16)	12857(3)	11892(3)	3590(2)	31(1)
C(17)	12385(3)	13116(3)	3794(2)	45(1)
C(18)	14172(3)	11588(3)	3790(2)	38(1)
C(19)	14029(3)	10327(3)	3454(2)	33(1)
C(20)	14994(3)	9429(3)	3484(2)	48(1)
C(21)	10914(3)	6495(3)	1879(2)	34(1)
C(22)	11623(4)	5379(3)	1708(2)	58(1)
C(23)	8677(3)	10279(3)	4104(2)	29(1)
C(24)	8271(3)	10791(3)	4943(2)	42(1)
C(25)	11512(5)	15155(4)	5763(2)	63(1)
C(26)	10525(5)	14338(5)	6251(3)	91(2)

1348 s, 1308 m, 1260 s, 1220 s, 1176 w, 1152 w, 1092 s, 1028 s, 800 s, 640 w, 612 w, 480 w, 384 m, 312 w.

Synthesis of $Pd_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCBu^t)_2$ (3). The complex $[Pd(Hdmpz)_4](OOCBu^t)_2$ (0.1 g, 0.14 mmol) was dissolved in acetonitrile (10 mL). A solution of $PdCo(OOCMe)_4NCMe$ (0.062 g, 0.14 mmol) in acetonitrile (5 mL) was added to the resulting solution. The reaction mixture was stirred for 30 min at room temperature, concentrated to 7 mL, and kept for 24 h at –5°C. The precipitated crystals were separated from the mother liquor by decantation and dried in an argon flow. Yield, 0.073 g (65%)

For $Pd_2C_{32}H_{51}N_9O_4$ anal calcd. (%): C, 45.85; H, 6.10; N, 15.66.

Found (%): C, 45.76; H, 6.08; N, 15.03.

IR (KBr, ν, cm^{-1}): 3424 m br., 3175 w, 3080 m, 3020 m, 2960 m, 2732 w, 1602 s, 1564 s, 1483 m, 1391 s, 1344 s, 1302 m, 1265 s, 1219 s, 1178 w, 1093 s, 1027 s, 800 s, 640 w, 480 w, 384 m, 312 w.

Synthesis of $Pd_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCPh)_2$ (4). A solution of $PdCo(OOCMe)_4NCMe$ (0.062 g, 0.14 mmol) in acetonitrile (5 mL) was added to a solution of $[Pd(Hdmpz)_4](OOCPh)_2$ (0.1 g, 0.14 mmol) in acetonitrile (10 mL). The resulting solution was stirred for 30 min at room temperature, concentrated to 5 mL, and kept for 24 h at –5°C. The precipitated crystals were separated from the mother liquor by decantation and dried in an argon flow. Yield, 0.088 g (75%)

For $Pd_2C_{34}H_{40}N_8O_4$ anal calcd. (%): C, 48.79; H, 4.78; N, 13.35.

Found (%): C, 48.71; H, 4.91; N, 13.38.

IR (KBr, ν, cm^{-1}): 3430 m br., 3177 w, 3085 m, 3028 m, 2925 m, 2782 w, 1608 s, 1569 s, 1420 m, 1362 s, 1303 m, 1173 m, 1065 m, 1025 m, 814 m, 758 w, 715 s, 685 m, 591 w, 517 w, 455 w.

RESULTS AND DISCUSSION

Previously, it was found that the heterometallic dimer $Pd(\mu\text{-}OOCMe)_4Co(NCMe)$ (**1**)) containing a labile acetonitrile molecule reacts with bidentate N-donors (phenanthroline or bipyridine) to give complexes in which the ligand is bound to the added metal atom and the three-bridged binuclear fragment is retained [15]. Unlike bidentate donors, monodentate pyridine destroys the binuclear complex yielding the pentanuclear complex $\{[Pd(\mu\text{-}OOCMe)_4]Co\}_2(OOCMe)_2Pdpy_2$, which was also obtained in a quantitative yield by an independent synthetic route starting from mononuclear $Pd(py)_2(OOCMe)_2$ and **1** [16].

It was expected that complex **1** would react with compounds $(PdL_4)^{2+}(OOCR^-)_2$ containing an outer-sphere two-electron carboxylate anion to give the anions $Pd(\mu$-

Table 3. Bond lengths (*d*) and bond angles (ω) for complex **2**

Bond	*d*, Å	Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Pd(1)–N(3)	1.9919(19)	Pd(1)–N(1)	2.0044(19)	N(2)Pd(2)Pd(1)	61.79(6)	N(4)Pd(2)Pd(1)	61.55(6)
Pd(1)–O(1)	2.0145(17)	Pd(1)–N(5)	2.0158(19)	N(7)Pd(2)Pd(1)	116.35(6)	O(3)Pd(2)Pd(1)	120.51(5)
Pd(1)–Pd(2)	3.2549(3)	Pd(2)–N(2)	1.988(2)	C(21)O(1)Pd(1)	121.51(17)	C(23)O(3)Pd(2)	118.34(16)
Pd(2)–N(4)	1.9935(19)	Pd(2)–N(7)	2.007(2)	C(1)N(1)N(2)	108.6(2)	C(1)N(1)Pd(1)	133.26(18)
Pd(2)–O(3)	2.0216(16)	O(1)–C(21)	1.273(3)	N(2)N(1)Pd(1)	118.11(14)	C(4)N(2)N(1)	109.0(2)
O(2)–C(21)	1.221(3)	O(3)–C(23)	1.275(3)	C(4)N(2)Pd(2)	132.37(18)	N(1)N(2)Pd(2)	118.55(14)
O(4)–C(23)	1.242(3)	N(1)–C(1)	1.348(3)	C(6)N(3)N(4)	108.59(19)	C(6)N(3)Pd(1)	133.16(17)
N(1)–N(2)	1.359(3)	N(2)–C(4)	1.340(3)	N(4)N(3)Pd(1)	117.96(14)	C(9)N(4)N(3)	108.47(19)
N(3)–C(6)	1.344(3)	N(3)–N(4)	1.366(3)	C(9)N(4)Pd(2)	132.64(17)	N(3)N(4)Pd(2)	118.61(14)
N(4)–C(9)	1.344(3)	N(5)–C(11)	1.335(3)	C(11)N(5)N(6)	107.0(2)	C(11)N(5)Pd(1)	133.06(17)
N(5)–N(6)	1.350(3)	N(6)–C(14)	1.343(3)	N(6)N(5)Pd(1)	119.87(15)	C(14)N(6)N(5)	111.1(2)
N(7)–C(16)	1.335(3)	N(7)–N(8)	1.351(3)	C(16)N(7)N(8)	106.6(2)	C(16)N(7)Pd(2)	132.71(18)
N(8)–C(19)	1.349(3)	N(9)–C(25)	1.143(5)	N(8)N(7)Pd(2)	120.56(15)	C(19)N(8)N(7)	111.3(2)
C(1)–C(3)	1.379(4)	C(1)–C(2)	1.498(4)	N(1)C(1)C(3)	108.0(2)	N(1)C(1)C(2)	122.6(2)
C(3)–C(4)	1.395(4)	C(4)–C(5)	1.494(4)	C(3)C(1)C(2)	129.4(2)	C(1)C(3)C(4)	106.6(2)
C(6)–C(8)	1.388(3)	C(6)–C(7)	1.486(4)	N(2)C(4)C(3)	107.7(2)	N(2)C(4)C(5)	121.2(2)
C(8)–C(9)	1.385(3)	C(9)–C(10)	1.498(4)	C(3)C(4)C(5)	131.1(2)	N(3)C(6)C(8)	108.2(2)
C(11)–C(13)	1.400(4)	C(11)–C(12)	1.490(4)	N(3)C(6)C(7)	122.3(2)	C(8)C(6)C(7)	129.6(2)
C(13)–C(14)	1.379(4)	C(14)–C(15)	1.495(4)	C(6)C(8)C(9)	106.4(2)	N(4)C(9)C(8)	108.3(2)
C(16)–C(18)	1.399(4)	C(16)–C(17)	1.494(4)	N(4)C(9)C(10)	121.5(2)	C(8)C(9)C(10)	130.2(2)
C(18)–C(19)	1.373(4)	C(19)–C(20)	1.484(4)	N(5)C(11)C(13)	108.9(2)	N(5)C(11)C(12)	120.9(2)
C(21)–C(22)	1.514(4)	C(23)–C(24)	1.513(4)	C(13)C(11)C(12)	130.2(2)	C(14)C(13)C(11)	106.3(2)
C(25)–C(26)	1.467(6)			N(6)C(14)C(13)	106.7(2)	N(6)C(14)C(15)	121.0(2)
Angle	ω, deg	Angle	ω, deg	C(13)C(14)C(15)	132.3(2)	N(7)C(16)C(18)	109.1(2)
N(3)Pd(1)N(1)	90.21(8)	N(3)Pd(1)O(1)	91.12(7)	N(7)C(16)C(17)	120.4(2)	C(18)C(16)C(17)	130.4(3)
N(1)Pd(1)O(1)	176.84(8)	N(3)Pd(1)N(5)	176.18(8)	C(19)C(18)C(16)	106.6(2)	N(8)C(19)C(18)	106.4(2)
N(1)Pd(1)N(5)	90.04(8)	O(1)Pd(1)N(5)	88.82(8)	N(8)C(19)C(20)	120.6(3)	C(18)C(19)C(20)	133.0(3)
N(3)Pd(1)Pd(2)	61.88(6)	N(1)Pd(1)Pd(2)	61.47(6)	O(2)C(21)O(1)	126.0(3)	O(2)C(21)C(22)	119.7(3)
O(1)Pd(1)Pd(2)	121.66(5)	N(5)Pd(1)Pd(2)	115.04(6)	O(1)C(21)C(22)	114.3(3)	O(4)C(23)O(3)	125.3(2)
N(2)Pd(2)N(4)	89.13(8)	N(2)Pd(2)N(7)	178.12(8)	O(4)C(23)C(24)	120.0(2)	O(3)C(23)C(24)	114.7(2)
N(4)Pd(2)N(7)	90.16(8)	N(2)Pd(2)O(3)	91.31(8)	N(9)C(25)C(26)	178.8(5)		
N(4)Pd(2)O(3)	177.80(7)	N(7)Pd(2)O(3)	89.47(8)				

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic factors ($Å^2, \times 10^3$) for complex **3 · MeCN**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
Pd(1)	6627(1)	8259(1)	1934(1)	44(1)	C(10)	4241(11)	10038(8)	1797(6)	93(3)
Pd(2)	5834(1)	6486(1)	3170(1)	49(1)	C(11)	8896(9)	8584(7)	973(4)	57(2)
O(1)	5407(5)	7989(5)	880(3)	57(1)	C(12)	8432(10)	9608(8)	643(6)	89(3)
O(2)	4206(7)	6168(5)	969(3)	79(2)	C(13)	9981(9)	8098(8)	884(5)	67(2)
O(3)	6920(6)	5295(5)	3468(3)	63(1)	C(14)	9965(8)	7204(7)	1337(5)	56(2)
O(4)	8101(8)	5496(6)	2556(4)	94(2)	C(15)	10887(10)	6361(8)	1476(6)	87(3)
N(1)	7589(6)	7843(5)	3493(3)	49(2)	C(16)	3553(10)	4108(8)	3115(6)	75(3)
N(2)	7897(6)	8600(5)	2961(3)	49(2)	C(17)	4027(12)	4128(11)	3957(6)	110(4)
N(3)	4704(7)	7659(5)	2926(4)	55(2)	C(18)	2584(11)	3301(8)	2571(7)	90(3)
N(4)	5026(6)	8405(5)	2408(3)	49(2)	C(19)	2521(9)	3724(7)	1886(6)	71(3)
N(5)	8220(7)	8025(5)	1471(3)	50(2)	C(20)	1647(11)	3233(9)	1111(6)	100(4)
N(6)	8902(6)	7188(5)	1691(3)	51(2)	C(21)	4490(8)	6996(7)	606(4)	50(2)
N(7)	4113(7)	5055(5)	2788(4)	55(2)	C(22)	3802(10)	6885(9)	–233(5)	77(2)
N(8)	3497(6)	4806(5)	2046(4)	53(2)	C(23)	3245(12)	7950(10)	–387(6)	104(3)
N(9)	6627(14)	10411(11)	4240(7)	145(4)	C(24)	2604(13)	5737(11)	–483(6)	122(4)
C(1)	8644(10)	8161(7)	4110(5)	65(2)	C(25)	4873(11)	6827(11)	–684(6)	101(3)
C(2)	8577(12)	7529(9)	4798(5)	93(3)	C(26)	7774(9)	5028(7)	3100(5)	63(1)
C(3)	9671(9)	9133(8)	3993(5)	70(2)	C(27)	8366(15)	4002(12)	3331(10)	134(4)
C(4)	9192(8)	9365(6)	3273(5)	55(2)	C(28)	7440(16)	2829(12)	2902(9)	157(5)
C(5)	9868(9)	10314(8)	2856(6)	78(3)	C(29)	8252(15)	3788(13)	4161(9)	155(5)
C(6)	3623(9)	7907(8)	3186(5)	68(2)	C(30)	9759(16)	4217(14)	3373(10)	174(5)
C(7)	3022(11)	7235(10)	3761(7)	101(4)	C(31)	6460(20)	9553(17)	4888(12)	168(7)
C(8)	3263(9)	8808(8)	2818(6)	79(3)	C(32)	6160(20)	8954(16)	5461(11)	176(7)
C(9)	4167(9)	9124(7)	2347(5)	65(2)					

Table 5. Bond lengths (*d*) and bond angles (ω) for complex **3 · MeCN**

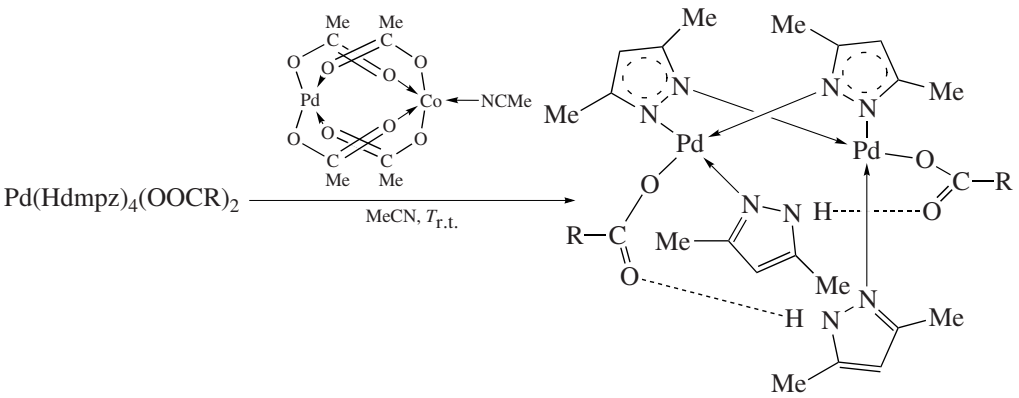
Bond	*d*, Å	Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Pd(1)–N(2)	1.988(6)	Pd(1)–N(4)	2.005(6)	O(3)Pd(2)Pd(1)	121.57(16)	N(7)Pd(2)Pd(1)	115.79(18)
Pd(1)–O(1)	2.013(5)	Pd(1)–N(5)	2.013(6)	C(21)O(1)Pd(1)	121.9(5)	C(26)O(3)Pd(2)	122.4(5)
Pd(1)–Pd(2)	3.2547(15)	Pd(2)–N(3)	1.996(6)	C(1)N(1)N(2)	109.1(6)	C(1)N(1)Pd(2)	134.0(5)
Pd(2)–N(1)	2.000(6)	Pd(2)–O(3)	2.002(5)	N(2)N(1)Pd(2)	116.7(4)	C(4)N(2)N(1)	106.2(6)
Pd(2)–N(7)	2.036(6)	O(1)–C(21)	1.273(9)	C(4)N(2)Pd(1)	134.0(5)	N(1)N(2)Pd(1)	119.1(4)
O(2)–C(21)	1.219(9)	O(3)–C(26)	1.264(10)	C(6)N(3)N(4)	108.6(7)	C(6)N(3)Pd(2)	132.6(6)
O(4)–C(26)	1.230(10)	N(1)–C(1)	1.337(10)	N(4)N(3)Pd(2)	118.8(5)	C(9)N(4)N(3)	108.7(6)
N(1)–N(2)	1.389(8)	N(2)–C(4)	1.364(9)	C(9)N(4)Pd(1)	133.7(6)	N(3)N(4)Pd(1)	117.6(4)
N(3)–C(6)	1.348(10)	N(3)–N(4)	1.364(8)	C(11)N(5)N(6)	105.7(6)	C(11)N(5)Pd(1)	134.1(5)
N(4)–C(9)	1.333(9)	N(5)–C(11)	1.351(9)	N(6)N(5)Pd(1)	120.1(4)	C(14)N(6)N(5)	110.9(6)
N(5)–N(6)	1.360(8)	N(6)–C(14)	1.349(9)	N(8)N(7)C(16)	107.1(7)	N(8)N(7)Pd(2)	119.8(4)
N(7)–N(8)	1.341(8)	N(7)–C(16)	1.347(10)	C(16)N(7)Pd(2)	131.9(6)	N(7)N(8)C(19)	111.0(7)
N(8)–C(19)	1.356(10)	N(9)–C(31)	1.61(2)	N(1)C(1)C(3)	108.8(7)	N(1)C(1)C(2)	121.1(8)
C(1)–C(3)	1.392(12)	C(1)–C(2)	1.506(12)	C(3)C(1)C(2)	130.0(8)	C(4)C(3)C(1)	106.0(7)
C(3)–C(4)	1.374(11)	C(4)–C(5)	1.493(11)	N(2)C(4)C(3)	109.8(7)	N(2)C(4)C(5)	121.2(7)
C(6)–C(8)	1.369(13)	C(6)–C(7)	1.491(13)	C(3)C(4)C(5)	129.0(8)	N(3)C(6)C(8)	107.1(8)
C(8)–C(9)	1.376(13)	C(9)–C(10)	1.515(13)	N(3)C(6)C(7)	121.5(9)	C(8)C(6)C(7)	131.4(9)
C(11)–C(13)	1.373(11)	C(11)–C(12)	1.504(11)	C(6)C(8)C(9)	108.0(8)	N(4)C(9)C(8)	107.6(8)
C(13)–C(14)	1.376(12)	C(14)–C(15)	1.505(11)	N(4)C(9)C(10)	121.2(8)	C(8)C(9)C(10)	131.1(8)
C(16)–C(18)	1.346(13)	C(16)–C(17)	1.506(13)	N(5)C(11)C(13)	109.8(7)	N(5)C(11)C(12)	119.2(8)
C(18)–C(19)	1.372(13)	C(19)–C(20)	1.485(13)	C(13)C(11)C(12)	130.9(8)	C(11)C(13)C(14)	106.9(8)
C(21)–C(22)	1.526(11)	C(22)–C(25)	1.485(13)	N(6)C(14)C(13)	106.6(7)	N(6)C(14)C(15)	121.9(8)
C(22)–C(23)	1.498(12)	C(22)–C(24)	1.523(14)	C(13)C(14)C(15)	131.5(8)	C(18)C(16)N(7)	107.8(8)
C(26)–C(27)	1.507(13)	C(27)–C(30)	1.348(17)	C(18)C(16)C(17)	132.5(9)	N(7)C(16)C(17)	119.7(9)
C(27)–C(28)	1.493(19)	C(27)–C(29)	1.57(2)	C(16)C(18)C(19)	109.8(8)	N(8)C(19)C(18)	104.3(8)
C(31)–C(32)	1.34(3)			N(8)C(19)C(20)	122.7(9)	C(18)C(19)C(20)	133.0(9)
Angle	ω, deg	Angle	ω, deg	O(2)C(21)O(1)	123.5(7)	O(2)C(21)C(22)	121.5(8)
N(2)Pd(1)N(4)	89.5(2)	N(2)Pd(1)O(1)	177.0(2)	O(1)C(21)C(22)	114.9(7)	C(25)C(22)C(23)	109.3(9)
N(4)Pd(1)O(1)	92.1(2)	N(2)Pd(1)N(5)	90.0(2)	C(25)C(22)C(24)	108.2(9)	C(23)C(22)C(24)	109.3(9)
N(4)Pd(1)N(5)	177.1(2)	O(1)Pd(1)N(5)	88.6(2)	C(25)C(22)C(21)	108.8(8)	C(23)C(22)C(21)	110.4(7)
N(2)Pd(1)Pd(2)	61.77(17)	N(4)Pd(1)Pd(2)	61.93(17)	C(24)C(22)C(21)	110.9(8)	O(4)C(26)O(3)	125.5(8)
O(1)Pd(1)Pd(2)	121.22(14)	N(5)Pd(1)Pd(2)	115.37(16)	O(4)C(26)C(27)	118.2(10)	O(3)C(26)C(27)	116.2(9)
N(3)Pd(2)N(1)	90.1(3)	N(3)Pd(2)O(3)	176.7(2)	C(30)C(27)C(28)	117.4(15)	C(30)C(27)C(26)	113.6(12)
N(1)Pd(2)O(3)	90.9(2)	N(3)Pd(2)N(7)	92.0(3)	C(28)C(27)C(26)	110.6(12)	C(30)C(27)C(29)	102.6(14)
N(1)Pd(2)N(7)	176.0(2)	O(3)Pd(2)N(7)	87.2(2)	C(28)C(27)C(29)	100.0(12)	C(26)C(27)C(29)	111.3(12)
N(3)Pd(2)Pd(1)	61.67(19)	N(1)Pd(2)Pd(1)	62.44(17)				

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic factors ($Å^2, \times 10^3$) for complex $\mathbf{3 \cdot C_6H_{14}}$

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
Pd(1)	4428(1)	6661(1)	6165(1)	39(1)	C(11)	3338(6)	6307(4)	7508(5)	49(2)
Pd(2)	6973(1)	6668(1)	6140(1)	43(1)	C(12)	2210(6)	6415(5)	6935(6)	74(3)
O(1)	3590(4)	7529(3)	6192(3)	50(1)	C(13)	3670(7)	6123(4)	8334(5)	58(2)
O(2)	5075(5)	8172(3)	6519(5)	97(3)	C(14)	4808(7)	6092(4)	8592(5)	55(2)
O(3)	8241(4)	6378(3)	7133(3)	55(1)	C(15)	5648(9)	5969(5)	9424(6)	85(3)
O(4)	7269(5)	6322(4)	8009(4)	85(2)	C(16)	8668(6)	7826(5)	6269(6)	64(2)
N(1)	4707(5)	6935(3)	5113(4)	43(2)	C(17)	9505(7)	7352(5)	6121(7)	89(3)
N(2)	5775(5)	6932(3)	5100(4)	44(2)	C(18)	8727(7)	8517(5)	6418(7)	75(3)
N(3)	5171(5)	5773(3)	6123(3)	39(1)	C(19)	7749(8)	8718(5)	6495(6)	70(3)
N(4)	6219(5)	5773(3)	6098(4)	48(2)	C(20)	7307(9)	9387(5)	6672(8)	103(4)
N(5)	4226(5)	6388(3)	7257(4)	45(2)	C(21)	4082(7)	8086(4)	6356(5)	53(2)
N(6)	5112(5)	6253(3)	7928(4)	48(2)	C(22)	3338(8)	8719(5)	6324(6)	70(2)
N(7)	7669(5)	7596(3)	6236(4)	51(2)	C(23)	4018(9)	9319(5)	6781(7)	97(3)
N(8)	7128(6)	8146(3)	6384(4)	57(2)	C(24)	2835(9)	8913(5)	5411(6)	101(3)
C(1)	4059(6)	7115(4)	4347(5)	46(2)	C(25)	2467(10)	8560(6)	6730(8)	103(3)
C(2)	2826(6)	7155(5)	4153(5)	63(2)	C(26)	8145(6)	6275(4)	7842(5)	54(2)
C(3)	4704(7)	7226(4)	3851(5)	50(2)	C(27)	9169(9)	6067(8)	8520(8)	109(3)
C(4)	5780(7)	7109(4)	4331(5)	51(2)	C(28)	9014(10)	5937(8)	9320(8)	143(4)
C(5)	6839(8)	7153(5)	4125(6)	76(3)	C(29)	9845(10)	5606(8)	8294(8)	150(4)
C(6)	4833(6)	5123(4)	6112(4)	47(2)	C(30)	9868(13)	6710(8)	8702(10)	169(5)
C(7)	3719(7)	4952(5)	6152(6)	68(2)	C(31)	9962(15)	4648(7)	5100(12)	167(6)
C(8)	5697(7)	4704(4)	6078(5)	59(2)	C(32)	10486(15)	4381(11)	5862(12)	192(8)
C(9)	6549(7)	5121(4)	6070(5)	51(2)	C(33)	10322(15)	3707(11)	6069(12)	202(8)
C(10)	7688(8)	4960(5)	6059(6)	82(3)					

$OOCMe)_4Co(OOCR)^-$ in which it would be possible to follow the effect of electronic and steric features of the substituent R on the structure of the resulting compounds.

However, unexpectedly, the reactions of **1** with mononuclear complexes $[Pd(Hdmpz)_4](OOCR)_2$ in acetonitrile at room temperature resulted in deprotonation of palladium-coordinated Hdmpz to give binuclear pyrazolate-bridged complexes $Pd_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCR)_2$ (R = Me (**2**), Bu^t (**3**), and Ph (**4**)) in high yield:



R = Me (**2**), Bu^t (**3**), Ph (**4**)

According to X-ray diffraction data, the Pd(II) atoms in 2 · MeCN are located at a non-bonding distance (Pd(1)···Pd(2) 3.2549(3) Å) and have a square planar environment composed of two nitrogen atoms of the bridging deprotonated pyrazole molecules (Pd(1)–N(1), 2.004(2); Pd(1)–N(3), 1.992(2); Pd(2)–N(2), 1.988(2) Å; Pd(2)–N(4), 1.993(2) Å), the pyridine nitrogen atom of the Hdmpz molecule (Pd(1)–N(5),

Table 7. Bond lengths (*d*) and bond angles (ω) for complex **3 · C_6H_{14}**

Bond	*d*, Å	Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Pd(1)–N(1)	1.988(6)	Pd(1)–N(3)	1.990(6)	N(7)Pd(2)Pd(1)	114.77(17)	O(3)Pd(2)Pd(1)	122.15(15)
Pd(1)–N(5)	2.009(6)	Pd(1)–O(1)	2.014(5)	C(21)O(1)Pd(1)	120.8(5)	C(26)O(3)Pd(2)	123.2(5)
Pd(1)–Pd(2)	3.2488(8)	Pd(2)–N(4)	1.987(6)	C(1)N(1)N(2)	107.5(6)	C(1)N(1)Pd(1)	134.5(5)
Pd(2)–N(2)	2.001(6)	Pd(2)–N(7)	2.006(6)	N(2)N(1)Pd(1)	117.9(5)	C(4)N(2)N(1)	108.5(6)
Pd(2)–O(3)	2.011(5)	O(1)–C(21)	1.245(9)	C(4)N(2)Pd(2)	133.0(5)	N(1)N(2)Pd(2)	118.5(5)
O(2)–C(21)	1.217(10)	O(3)–C(26)	1.256(9)	C(6)N(3)N(4)	108.4(6)	C(6)N(3)Pd(1)	132.5(5)
O(4)–C(26)	1.234(9)	N(1)–C(1)	1.345(9)	N(4)N(3)Pd(1)	119.1(4)	N(3)N(4)C(9)	108.8(6)
N(1)–N(2)	1.365(7)	N(2)–C(4)	1.344(9)	N(3)N(4)Pd(2)	118.0(4)	C(9)N(4)Pd(2)	133.1(6)
N(3)–C(6)	1.340(9)	N(3)–N(4)	1.347(8)	C(11)N(5)N(6)	106.2(6)	C(11)N(5)Pd(1)	133.2(5)
N(4)–C(9)	1.349(9)	N(5)–C(11)	1.332(8)	N(6)N(5)Pd(1)	120.6(4)	C(14)N(6)N(5)	111.5(6)
N(5)–N(6)	1.351(8)	N(6)–C(14)	1.332(9)	C(16)N(7)N(8)	104.9(7)	C(16)N(7)Pd(2)	134.5(6)
N(7)–C(16)	1.332(9)	N(7)–N(8)	1.342(8)	N(8)N(7)Pd(2)	120.2(5)	N(7)N(8)C(19)	112.3(7)
N(8)–C(19)	1.349(11)	C(1)–C(3)	1.360(10)	N(1)C(1)C(3)	109.0(7)	N(1)C(1)C(2)	120.6(7)
C(1)–C(2)	1.501(10)	C(3)–C(4)	1.375(11)	C(3)C(1)C(2)	130.3(8)	C(1)C(3)C(4)	106.9(7)
C(4)–C(5)	1.494(11)	C(6)–C(8)	1.387(10)	N(2)C(4)C(3)	108.0(7)	N(2)C(4)C(5)	120.9(8)
C(6)–C(7)	1.477(11)	C(8)–C(9)	1.359(11)	C(3)C(4)C(5)	131.1(8)	N(3)C(6)C(8)	107.9(7)
C(9)–C(10)	1.487(11)	C(11)–C(13)	1.373(11)	N(3)C(6)C(7)	121.5(7)	C(8)C(6)C(7)	130.6(8)
C(11)–C(12)	1.474(11)	C(13)–C(14)	1.377(11)	C(9)C(8)C(6)	106.8(8)	N(4)C(9)C(8)	108.1(7)
C(14)–C(15)	1.495(12)	C(16)–C(18)	1.374(12)	N(4)C(9)C(10)	121.0(8)	C(8)C(9)C(10)	130.9(8)
C(16)–C(17)	1.491(12)	C(18)–C(19)	1.347(12)	N(5)C(11)C(13)	109.3(7)	N(5)C(11)C(12)	121.6(7)
C(19)–C(20)	1.492(12)	C(21)–C(22)	1.549(11)	C(13)C(11)C(12)	129.1(7)	C(11)C(13)C(14)	107.1(7)
C(22)–C(25)	1.506(13)	C(22)–C(23)	1.518(13)	N(6)C(14)C(13)	106.0(7)	N(6)C(14)C(15)	121.2(8)
C(22)–C(24)	1.519(13)	C(26)–C(27)	1.496(13)	C(13)C(14)C(15)	132.7(8)	N(7)C(16)C(18)	109.7(7)
C(27)–C(29)	1.380(16)	C(27)–C(28)	1.446(16)	N(7)C(16)C(17)	120.2(9)	C(18)C(16)C(17)	130.0(8)
C(27)–C(30)	1.517(18)			C(19)C(18)C(16)	107.8(8)	C(18)C(19)N(8)	105.2(8)
Angle	ω, deg	Angle	ω, deg	C(18)C(19)C(20)	133.7(9)	N(8)C(19)C(20)	121.0(8)
N(1)Pd(1)N(3)	89.2(2)	N(1)Pd(1)N(5)	177.2(2)	O(2)C(21)O(1)	125.8(8)	O(2)C(21)C(22)	118.5(8)
N(3)Pd(1)N(5)	89.9(2)	N(1)Pd(1)O(1)	92.0(2)	O(1)C(21)C(22)	115.7(8)	C(25)C(22)C(23)	108.2(9)
N(3)Pd(1)O(1)	176.5(2)	N(5)Pd(1)O(1)	89.1(2)	C(25)C(22)C(24)	112.0(9)	C(23)C(22)C(24)	108.3(9)
N(1)Pd(1)Pd(2)	62.13(17)	N(3)Pd(1)Pd(2)	61.17(17)	C(25)C(22)C(21)	110.2(8)	C(23)C(22)C(21)	110.8(8)
N(5)Pd(1)Pd(2)	115.12(17)	O(1)Pd(1)Pd(2)	122.21(14)	C(24)C(22)C(21)	107.2(7)	O(4)C(26)-O(3)	124.5(8)
N(4)Pd(2)N(2)	88.3(2)	N(4)Pd(2)N(7)	175.8(2)	O(4)C(26)C(27)	118.7(9)	O(3)C(26)C(27)	116.9(8)
N(2)Pd(2)N(7)	91.9(2)	N(4)Pd(2)O(3)	92.0(2)	C(29)C(27)C(28)	114.9(13)	C(29)C(27)C(26)	115.8(11)
N(2)Pd(2)O(3)	175.8(2)	N(7)Pd(2)O(3)	88.2(2)	C(28)C(27)C(26)	114.9(10)	C(29)C(27)C(30)	102.9(12)
N(4)Pd(2)Pd(1)	61.69(17)	N(2)Pd(2)Pd(1)	61.50(17)	C(28)C(27)C(30)	101.4(13)	C(26)C(27)C(30)	104.2(11)

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic factors ($Å^2, \times 10^3$) for complex **4**

Atom	*x*	*y*	*z*	U_{eq}
Pd(1)	–205(1)	7028(1)	6880(1)	25(1)
Pd(2)	–148(1)	8822(1)	8039(1)	25(1)
O(1)	1457(3)	6616(2)	6007(1)	32(1)
O(2)	2914(3)	7692(2)	6264(2)	38(1)
O(3)	700(3)	8345(2)	9211(1)	33(1)
O(4)	1801(4)	6629(2)	8982(2)	61(1)
N(1)	–885(3)	8585(2)	6388(2)	23(1)
N(2)	–914(3)	9337(2)	6884(2)	24(1)
N(3)	–1939(3)	7392(2)	7700(2)	26(1)
N(4)	–1900(3)	8109(2)	8208(2)	26(1)
N(5)	477(3)	5470(2)	7431(2)	34(1)
N(6)	807(4)	5228(2)	8235(2)	38(1)
N(7)	1652(3)	9505(2)	7814(2)	27(1)
N(8)	2642(3)	9272(2)	7184(2)	28(1)
C(1)	–1361(4)	10330(3)	6429(2)	27(1)
C(2)	–1499(5)	11321(3)	6805(2)	37(1)
C(3)	–1625(4)	10215(3)	5634(2)	28(1)
C(4)	–1311(4)	9102(3)	5631(2)	26(1)
C(5)	–1451(4)	8513(3)	4943(2)	35(1)
C(6)	–3265(4)	7060(3)	7872(2)	32(1)
C(7)	–3668(5)	6279(3)	7401(3)	41(1)
C(8)	–4083(4)	7565(3)	8500(2)	38(1)
C(9)	–3199(4)	8227(3)	8696(2)	31(1)
C(10)	–3521(5)	8995(3)	9299(2)	41(1)
C(11)	408(4)	4556(3)	7174(2)	38(1)
C(12)	19(5)	4546(3)	6305(3)	50(1)
C(13)	735(5)	3729(3)	7844(3)	50(1)
C(14)	984(5)	4170(3)	8507(3)	48(1)
C(15)	1369(7)	3708(4)	9385(3)	67(1)
C(16)	2027(4)	10297(3)	8119(2)	33(1)
C(17)	1119(6)	10788(3)	8806(2)	48(1)
C(18)	3292(4)	10542(3)	7669(2)	36(1)
C(19)	3666(4)	9873(3)	7085(2)	32(1)
C(20)	4944(4)	9718(3)	6454(2)	42(1)
C(21)	2598(4)	7053(3)	5866(2)	28(1)
C(22)	3609(4)	6748(3)	5129(2)	29(1)
C(23)	4894(4)	7164(3)	4931(2)	36(1)
C(24)	5833(5)	6893(3)	4260(2)	43(1)
C(25)	5494(5)	6196(3)	3787(2)	41(1)
C(26)	4201(5)	5794(3)	3979(2)	40(1)
C(27)	3263(4)	6066(3)	4645(2)	32(1)
C(28)	1652(5)	7369(3)	9387(2)	38(1)
C(29)	2652(5)	7154(4)	10153(2)	52(1)
C(30)	3525(6)	6099(5)	10469(3)	76(1)
C(31)	4552(7)	5882(6)	11167(4)	94(2)
C(32)	4628(7)	6745(6)	11515(4)	96(2)
C(33)	3826(6)	7818(6)	11198(3)	83(1)
C(34)	2828(5)	8002(5)	10515(3)	61(1)

2.016(2) Å; Pd(2)–N(7), 2.007(2) Å), and the terminal acetate anion (Pd(1)–O(1), 2.015(2) Å; Pd(2)–O(3), 2.026 Å).

The hydrogen atoms of the NH fragments of the coordinated Hdmpz molecules form short hydrogen bonds with the oxygen atoms of acetate anions coordinated to the other palladium(II) atom (N···O 2.688(3), 2.709(3) Å, H–O 1.84, 1.85 Å) similar to the H-bonds formed in the copper(II) square planar complex $(Hdmpz)_2Cu(\mu\text{-}dmpz)_2(OOCBu^t)_2$ [6, 17]. It is noteworthy that the acetonitrile molecule of solvation present in the crystal cell does not form intermolecular hydrogen bonds, unlike that in the nickel complex $Ni_2(\mu\text{-}OOCMe)_4(Hdmpz)_2 \cdot 2NCMe$ [6, 18].

The replacement of acetate anions by more basic pivalate anions in complex **3** (Fig. 2) has almost no effect on its geometry. Thus, according to X-ray diffraction data, the Pd···Pd distance (3.2546(1) Å) is also nonbonding; the Pd–N bond lengths of pyrazolate anions (Pd(1)–N(2), 1.997(5) Å; Pd(1)–N(4), 2.006(5) Å; Pd(2)–N(1), 2.001(5) Å; Pd(2)–N(3), 1.995(6) Å) are close to those found in **3**; finally, the lengths Pd–O and Pd–N bonds with the terminal pyrazole molecule and pivalate anion almost do not change (Pd(1)–O(1), 2.013(4) Å; Pd(1)–N(5), 2.016(5) Å; Pd(2)–O(3), 2.004(5) Å; Pd(2)–N(7), 2.026(5) Å). The crystal cell of complex **3** was also found to contain an acetonitrile molecule of solvation, the intramolecular hydrogen bonds being similar to those in **2** (O···N, 2.708(6), 2.727(6) Å; H–O, 1.84, 1.85 Å).

Note that **3** is soluble in nonpolar organic solvents. Its recrystallizastion gave single crystals containing a hexane molecule of solvation. The replacement of the solvation molecule does not result in considerable changes in the complex geometry (Pd···Pd 3.2488(8), Pd–μ-N, 1.987(6)–2.001(6) Å; Pd–N, 2.006(6)–2.0013(6) Å; Pd–O, 2.011(5)–2.014(5) Å) or the character of intramolecular hydrogen bonds (O···N 2.711(6), 2.723(6) Å; H–O, 1.82, 1.83 Å).

Finally, the appearance of more sterically crowded and the least basic benzoate anion (complex **4**, Fig. 3) only slightly increases the metal–metal distance (to 2.2637(4) Å), while the geometry of the rest of the complex (Pd–μ-N, 1.988(2)–1.995(3) Å; Pd–N, 2.012(3)–2.016(3) Å; Pd–O, 2.023(2)–2.029(2) Å) and the intramolecular hydrogen bonds (O···N 2.701(3)–2.706(3) Å; H–O, 1.83, 1.86 Å) are retained.

Previously, analogous complexes were obtained in reactions of $Pd_2(\mu\text{-}dmpz)_2(dmpz)_2(Hdmpz)_2$ with benzoic acid derivatives $H_2CC_6H_4$–R (R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH); their geometry is almost the same as that found for complex **4** [19] (Pd···Pd 3.269, 3.272; Pd–μ-N, 1.989(2)–2.001(2) Å, 1.986(2)–1.998(2) Å; Pd–N, 2.011(2)–2.016(2), 2.014(2)–2.017(2) Å; Pd–O, 2.001(5)–2.015(2), 2.001(2)–2.004(2) Å for the structurally characterized *p*-OCH_3 and *p*-OH).

Table 9. Bond lengths (*d*) and bond angles (ω) for complex **4**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Pd(1)–N(1)	1.989(2)	Pd(1)–N(3)	1.989(3)	C(6)–C(8)	1.379(5)	C(6)–C(7)	1.498(5)
Pd(1)–N(5)	2.016(3)	Pd(1)–O(1)	2.023(2)	C(8)–C(9)	1.392(5)	C(9)–C(10)	1.484(5)
Pd(2)–N(2)	1.988(2)	Pd(2)–N(4)	1.995(3)	C(11)–C(13)	1.395(5)	C(11)–C(12)	1.490(6)
Pd(2)–N(7)	2.012(3)	Pd(2)–O(3)	2.029(2)	C(13)–C(14)	1.365(6)	C(14)–C(15)	1.491(6)
O(1)–C(21)	1.279(4)	O(2)–C(21)	1.235(4)	C(16)–C(18)	1.392(5)	C(16)–C(17)	1.479(5)
O(3)–C(28)	1.286(4)	O(4)–C(28)	1.233(5)	C(18)–C(19)	1.369(5)	C(19)–C(20)	1.487(5)
N(1)–C(4)	1.334(4)	N(1)–N(2)	1.370(4)	C(21)–C(22)	1.512(5)	C(22)–C(23)	1.385(5)
N(2)–C(1)	1.348(4)	N(3)–C(6)	1.349(4)	C(22)–C(27)	1.386(5)	C(23)–C(24)	1.384(5)
N(3)–N(4)	1.359(4)	N(4)–C(9)	1.347(4)	C(24)–C(25)	1.386(5)	C(25)–C(26)	1.379(5)
N(5)–N(6)	1.340(4)	N(5)–C(11)	1.346(5)	C(26)–C(27)	1.376(5)	C(28)–C(29)	1.495(5)
N(6)–C(14)	1.352(4)	N(7)–N(8)	1.341(4)	C(29)–C(30)	1.384(6)	C(29)–C(34)	1.386(7)
N(7)–C(16)	1.344(4)	N(8)–C(19)	1.341(4)	C(30)–C(31)	1.415(7)	C(31)–C(32)	1.363(9)
C(1)–C(3)	1.380(5)	C(1)–C(2)	1.494(5)	C(32)–C(33)	1.390(9)	C(33)–C(34)	1.386(6)
C(3)–C(4)	1.399(5)	C(4)–C(5)	1.496(5)				
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	Angle
N(1)Pd(1)N(3)	88.46(10)	N(1)Pd(1)N(5)	177.38(12)	N(3)C(6)C(7)	121.2(3)	C(8)C(6)C(7)	130.0(3)
N(3)Pd(1)N(5)	89.65(12)	N(1)Pd(1)O(1)	92.40(10)	C(6)C(8)C(9)	106.0(3)	N(4)C(9)C(8)	108.4(3)
N(3)Pd(1)O(1)	176.05(10)	N(5)Pd(1)O(1)	89.61(11)	N(4)C(9)C(10)	121.0(3)	C(8)C(9)C(10)	130.6(3)
N(2)Pd(2)N(4)	88.75(11)	N(2)Pd(2)N(7)	89.15(11)	N(5)C(11)C(13)	108.2(4)	N(5)C(11)C(12)	121.1(3)
N(4)Pd(2)N(7)	176.88(11)	N(2)Pd(2)O(3)	177.30(10)	C(13)C(11)C(12)	130.6(4)	C(14)C(13)C(11)	107.2(3)
N(4)Pd(2)O(3)	93.90(10)	N(7)Pd(2)O(3)	88.23(10)	N(6)C(14)C(13)	106.3(4)	N(6)C(14)C(15)	120.9(4)
C(21)O(1)Pd(1)	122.0(2)	C(28)O(3)Pd(2)	116.6(2)	C(13)C(14)C(15)	132.8(4)	N(7)C(16)C(18)	108.5(3)
C(4)N(1)N(2)	108.5(2)	C(4)N(1)Pd(1)	133.4(2)	N(7)C(16)C(17)	121.3(3)	C(18)C(16)C(17)	130.1(3)
N(2)N(1)Pd(1)	118.02(19)	C(1)N(2)N(1)	108.5(2)	C(19)C(18)C(16)	106.8(3)	N(8)C(19)C(18)	106.4(3)
C(1)N(2)Pd(2)	132.5(2)	N(1)N(2)Pd(2)	118.77(18)	N(8)C(19)C(20)	121.5(3)	C(18)C(19)C(20)	132.0(3)
C(6)N(3)N(4)	108.3(3)	C(6)N(3)Pd(1)	132.0(2)	O(2)C(21)O(1)	126.2(3)	O(2)C(21)C(22)	118.9(3)
N(4)N(3)Pd(1)	119.7(2)	C(9)N(4)N(3)	108.6(3)	O(1)C(21)C(22)	114.9(3)	C(23)C(22)C(27)	119.5(3)
C(9)N(4)Pd(2)	133.9(2)	N(3)N(4)Pd(2)	117.3(2)	C(23)C(22)C(21)	119.5(3)	C(27)C(22)C(21)	121.1(3)
N(6)N(5)C(11)	107.0(3)	N(6)N(5)Pd(1)	120.4(2)	C(24)C(23)C(22)	120.2(3)	C(23)C(24)C(25)	119.9(4)
C(11)N(5)Pd(1)	131.5(3)	N(5)N(6)C(14)	111.1(3)	C(26)C(25)C(24)	119.8(4)	C(27)C(26)C(25)	120.5(4)
N(8)N(7)C(16)	106.6(3)	N(8)N(7)Pd(2)	120.0(2)	C(26)C(27)C(22)	120.2(3)	O(4)C(28)O(3)	125.8(3)
C(16)N(7)Pd(2)	132.9(2)	N(7)N(8)C(19)	111.5(3)	O(4)C(28)C(29)	119.3(4)	O(3)C(28)C(29)	114.9(4)
N(2)C(1)C(3)	108.4(3)	N(2)C(1)C(2)	120.9(3)	C(30)C(29)C(34)	119.3(4)	C(30)C(29)C(28)	119.6(5)
C(3)C(1)C(2)	130.7(3)	C(1)C(3)C(4)	106.1(3)	C(34)C(29)C(28)	120.9(4)	C(29)C(30)C(31)	120.6(6)
N(1)C(4)C(3)	108.5(3)	N(1)C(4)C(5)	122.0(3)	C(32)C(31)C(30)	117.5(6)	C(31)C(32)C(33)	123.7(6)
C(3)C(4)C(5)	129.5(3)	N(3)C(6)C(8)	108.8(3)	C(34)C(33)C(32)	117.2(6)	C(29)C(34)C(33)	121.6(5)

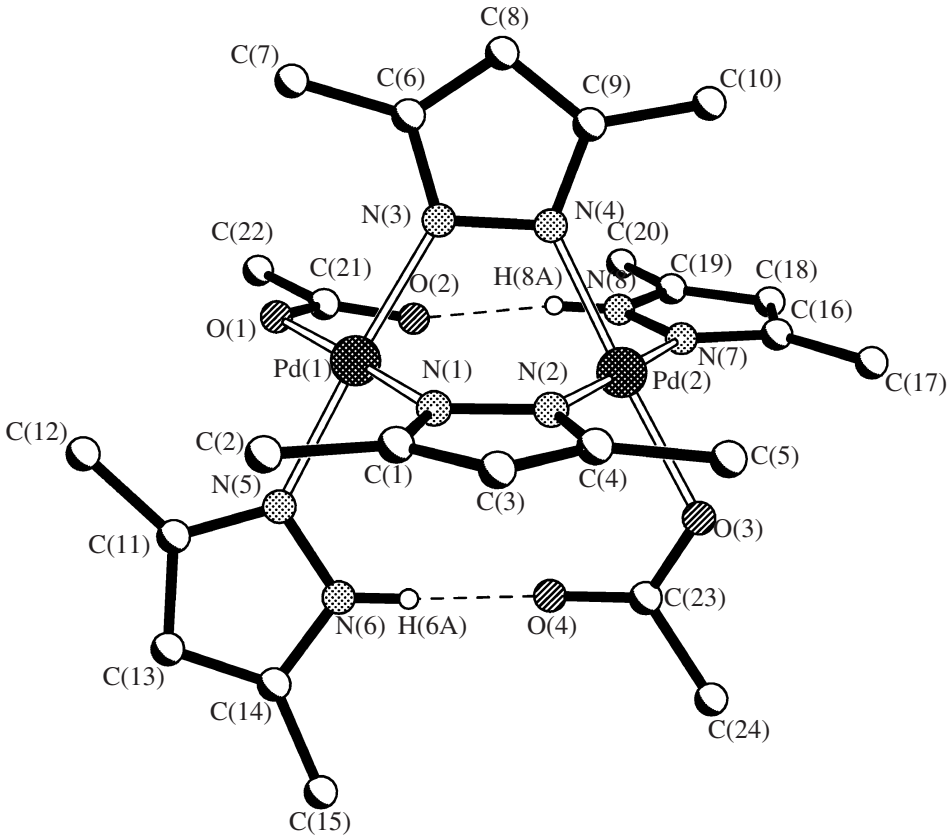


Fig. 1. Structure of complex **2**.

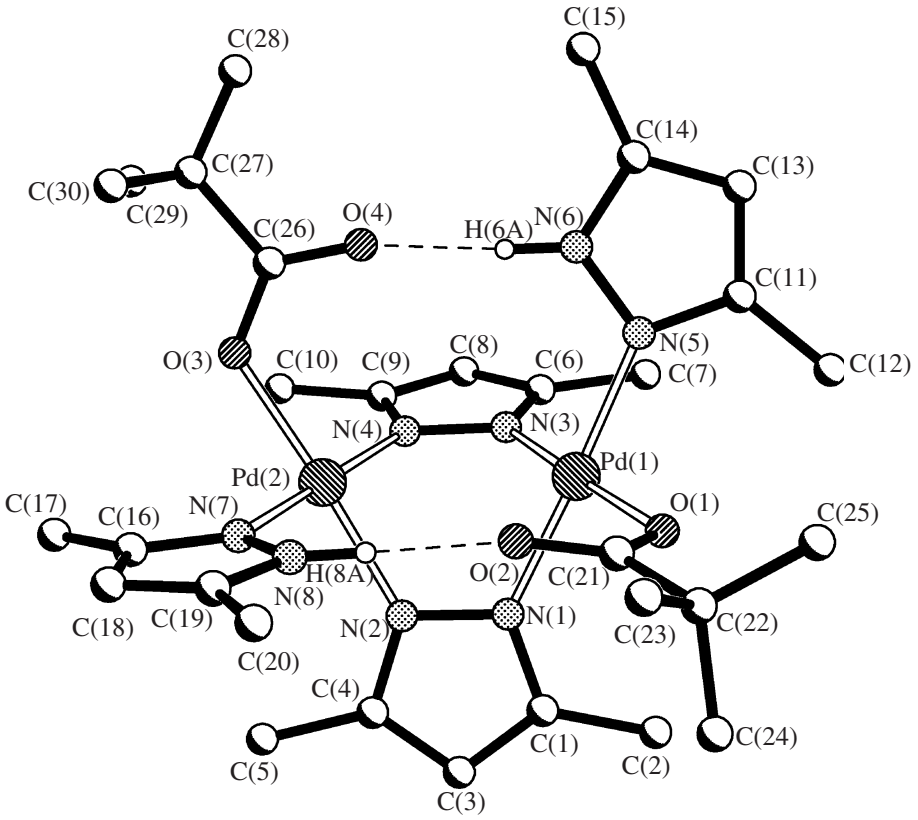


Fig. 2. Structure of complex **3**.

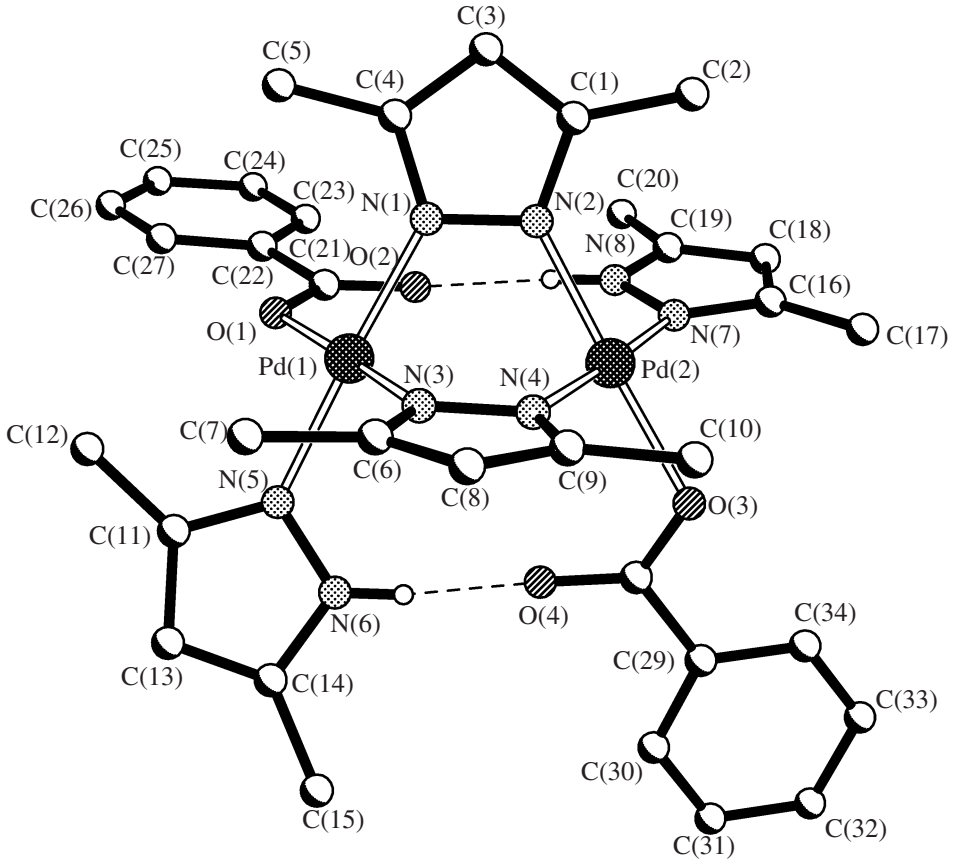


Fig. 3. Structure of complex **4**.

Thus, we found that instead of the expected replacement of labile acetonitrile by two-electron carboxylate anion, the considered reaction occurs as deprotonation of the palladium-coordinated pyrazole with destruction of the heterometallic complex **1** and generation of acetic acid molecules and some unknown products containing cobalt. Probably, similar transformations occur during degradation of the heterometallic complexes $Pd(\mu\text{-}OOCMe)_4L$ (M = Zn, Ni, Co, Mn, L = OH_2, NCMe) in the reactions with *trans*-azobenzene at room temperature where, instead of coordination of the N_2Ph_2 molecule to the metal, its *ortho*-metallation takes place to give the binuclear complex $(PhN{=}NC_6H_4)_2Pd_2(\mu\text{-}OOCMe)_2$ [20].

ACKNOWLEGDMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 08-03-01063 and 08-03-90455), the Council of the President of the Russian Federation for Support of Leading Scientific Schools of Russia, grant NSh-1733.2008.3), Presidium and the Division of Chemistry and Material Science of the RAS (the programs "Theoretical and Experimental Study of the Nature of Chemical Bond and Mechanisms of Important Chemical Reactions and Processes" and "Targeted Synthesis of Inorganic Compounds and Design of Functional Materials").

REFERENCES

1. G. La Monica and G. A. Ardizzoia, Prog. Inorg. Chem. **46**, 151 (1997).
2. M. A. Halcrow, J. Chem. Soc., Dalton Trans., 2059 (2009).
3. A. Cingolani, S. Galli, N. Masciocchi, et al., J. Am. Chem. Soc. **127**, 6144 (2005).
4. N. Masciocchi, G. A. Ardizzoia, S. Brenna, et al., Inorg. Chem. **41**, 6080 (2002).
5. A. Cingolani, S. Galli, N. Masciocchi, et al., J. Chem. Soc., Dalton Trans., 2486 (2006).
6. S. E. Nefedov, Russ. J. Inorg. Chem. **51** (Suppl. 1), 49 (2006).
7. N. Yu. Kozitsyna, S. E. Nefedov, F. M. Dolgushin, et al., Inorg. Chim. Acta **359**, 2072 (2006).
8. N. Yu. Kozitsyna, S. E. Nefedov, Zh. V. Dobrokhotova, et al., Ross. Nanotekhnol. **3** (3–4), 100 (2008).
9. S. E. Nefedov, N. Yu. Kozitsyna, M. N. Vargaftik, and I. I. Moiseev, Polyhedron **28**, 172 (2009).
10. A. A. Markov, A. P. Klyagina, S. P. Dolin, et al., Zh. Neorg. Khim. **54** (6), 950 (2009) [Russ. J. Inorg. Chem. **54** (6), 885 (2009)].

11. O. P. Tkachenko, A. Yu. Stakheev, L. M. Kustov, et al., Catal. Lett. **112**, 155 (2006).
12. E. V. Perova, F. M. Miloserdov, M. A. Yakovleva, and S. E. Nefedov, Zh. Neorg. Khim. **54** (9) (2009) [Russ. J. Inorg. Chem. **54** (9) (2009)].
13. SMART (control) and SAINT (integration) Software, Version 5.0, Bruker AXS, Inc., Madison, WI, 1997.
14. G. M. Sheldrick, SADABS, Program for Scaling and Correction of Area Detector Data, Univ. of Göttingen (1997).
15. S. E. Nefedov, M. N. Vargaftik, and I. I. Moiseev, Inorg. Chem. Commun. **9**, 755 (2006).
16. S. E. Nefedov, N. Yu. Kozitsyna, Zh. V. Dobrokhotova, et al., Inorg. Chem. Commun. **10**, 948 (2007).
17. T. O. Denisova, E. V. Amel'chenkova, I. V. Pruss, et al., Zh. Neorg. Khim. **51** (7), 1098 (2006) [Russ. J. Inorg. Chem. **51** (7), 1020 (2006)].
18. T. O. Denisova, G. G. Aleksandrov, O. P. Fialkovskii, and S. E. Nefedov, Zh. Neorg. Khim. **48** (9), 1340 (2003) [Russ. J. Inorg. Chem. **48** (9), 1476 (2003)].
19. I. Ara, J. Fornies, R. Lasheras, et al., Eur. J. Inorg. Chem. **5**, 948 (2006).
20. S. E. Nefedov, E. B. Perova, I. A. Yakushev, et al., Inorg. Chem. Commun. **12**, 454 (2009).