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Synthesis and structural analysis of palladium(II) pyridinylpyrazole complexes by ^{1}H-, ^{13}C-, ^{15}N-NMR and X-ray diffraction. Comparison of binuclear methylpalladium, chloromethylpalladium, and dichloropalladium complexes by ^{15}N-NMR

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Abstract

MePdCl[3-methyl-5-(2-pyridinyl)pyrazole] (**1** and **2**), $PdCl_2$[3-methyl-5-(2-pyridinyl)pyrazole] (**3**), and bis{MePd[3-methyl-5-(2-pyridinyl)pyrazole]} (**4**) were synthesized, and structural assignment was performed by ^{1}H-, ^{13}C-, ^{15}N-NMR spectroscopy. By comparison of their ^{15}N-NMR spectra, the relationship between bond strength of the palladium–nitrogen bond and chemical shift was analyzed. X-ray diffraction analysis of **4** was also achieved.

Keywords: Palladium; Pyridinylpyrazole; ^{15}N-NMR

1. Introduction

An alkyl palladium complex having a bisnitrogen ligand has recently been recognized as an effective catalyst for organic synthesis. In particular, as Brookhart and co-workers developed bulky tetraaryl borate as a counter anion of a cationic complex, the chemistry of the cationic monoalkyl palladium(II) complex having the bisnitrogen ligand has spread to useful carbon–carbon bond formations [1]. In palladium-catalyzed reactions, ligands coordinating palladium have an important role in determining the reactivity and selectivity. Therefore, analysis of the state of the coordinated atom is necessary to understand the reactivity of the complex. Phosphine ligands have been well studied by ^{31}P-NMR spectroscopy because ^{31}P has a 1/2 spin and exists abundantly in nature. On the other hand, direct observation by ^{15}N-NMR spectroscopy tends to be neglected because of its low natural abundance and the severe sensitivity of the ^{15}N nucleus [2]. We [3] and others [4] recently reported that ^{15}N-NMR spectra were easily obtained by a PFG–HMBC method at natural abundance rates. Actually, the ^{15}N-NMR spectra of some η^3-allylpalladium complexes having pyridinylpyrazole, pyridinylimidazole, and oxazolidinylpyrazole were measured by the PFG–HMBC method [5]. In this paper, we report the synthesis and ^{1}H-, ^{13}C-, and ^{15}N-NMR analysis of the methylpalladium(II) pyridinylpyrazole complexes **1**, **2** and **4**. In particular, comparison of binuclear methylpalladium **4**, chloromethylpalladium **1** and **2**, and dichloropalladium **3** by ^{15}N-NMR is discussed. Single-crystal X-ray structure determination of **4** was also achieved.

2. Results

We selected a pyridinylpyrazole as a bisnitrogen ligand for a monoalkyl palladium complex. A pyridinylpyrazole is an unsymmetrical bisnitrogen ligand, and when it is coordinated with a metal three nitrogen atoms on pyridine and pyrazole rings enter entirely different states. Their ^{15}N-NMR data give us various information including the state of the metal–nitrogen bond. We synthesized three pyridinylpyrazole

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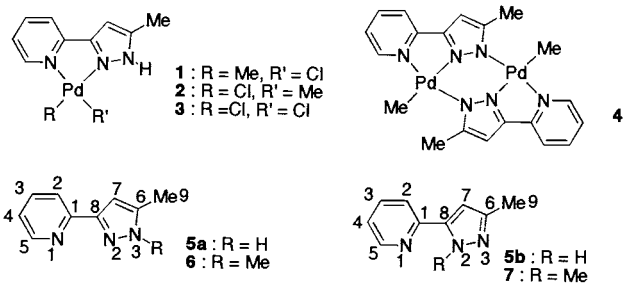
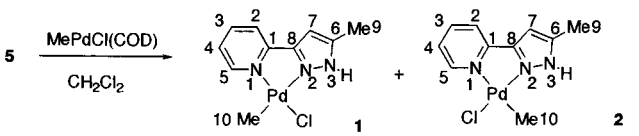


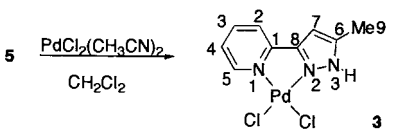
Scheme 1.

ligands (**5**, **6** and **7**) and palladium complexes (**1**, **2**, **3** and **4**) (Scheme 1). The synthesis of the pyridinylpyrazole ligands (**5**, **6** and **7**) was described in our previous paper [5a]. Chloromethylpalladium and dichloropalladium complexes (**1**, **2** and **3**) were easily obtained by treatment of pyridinylpyrazole **5** with appropriate palladium species[2] (Schemes 2 and 3). We also tried to synthesize dimethylpalladium pyridinylpyrazole complex **8** according to Canty's method [6]; however, only the binuclear methylpalladium complex **4** was obtained in a 10% yield. The binuclear complex **4** is considered to be produced from two dimethylpalladium pyridinylpyrazole **8** molecules by elimination of methane (Scheme 4). The binuclear complex **4** was also obtained by treatment of MeLi with a mixture of **1** and **2** in a 14% yield.

All pyridinylpyrazoles and palladium complexes were characterized by ^{1}H-, ^{13}C-, and ^{15}N-NMR, and their data are listed in Table 1. Complex **4** was determined to be a binuclear structure by FAB mass spectra data, and ^{1}H- and ^{13}C-NMR data showed only one set of pyridinylpyrazole ligand and methylpalladium group. These results mean that complex **4** has a symmetrical structure. Further, as a NOE from the methyl group (10-Me) was observed at 9′-Me and H5, the structure of the binuclear complex was judged to be **4**. As described below, the structure was also established by X-ray diffraction analysis. Assignment of ^{1}H-NMR signals was performed by coupling patterns and *J* values, and ^{13}C-NMR signals of carbons that were connected to



Scheme 2.



Scheme 3.

[2] MePdCl(cod) [2a] and $PdCl_2(CH_3CN)_2$ were used.

protons were assigned by PFG–HMQC spectral data. Quaternary carbons were also assigned by PFG–HMBC. Thus, the long-range correlations between C1 and H3, C1 and H5, C6 and H7, C6 and 9-Me, and C8 and H7 were observed. Complexes **1** and **2** are inseparable tautomeric isomers to each other, and they are in equilibrium via ligand rotation. ^{1}H- and ^{13}C-NMR signals of **1** and **2** showed only one kind of compound in DMSO, whereas different signals of **1** and **2** could be measured in a mixture of CD_2Cl_2 and CD_3OD. When a 1:1 CD_2Cl_2–CD_3OD mixture was used, the ratio of **1** and **2** was 1:6. In the case of a 4:1 CD_2Cl_2–CD_3OD mixture, the ratio of **1** and **2** was 1:4. All ^{1}H- and ^{13}C-NMR signals were assigned by PFG–HMQC and PFG–HMBC, and the distinction between **1** and **2** was achieved by NOE differential experiments by irradiation on 10-Me resonances. Thus, a NOE from 10-methyl (0.91 ppm) to H5 (8.42 ppm) was observed in the case of **1**, but no NOE from 10-methyl (0.97 ppm) was observed in the case of the major isomer **2**. In the ^{1}H–^{15}N PFG–HMBC spectra of a **1** and **2** mixture, long-range correlations between N1 and H2, N1 and H4, N1 and H5, N2 and H7, N3 and H7, and N3 and 9-Me were observed for both compounds. Long-range correlations via the palladium atom from 10-Me of major **2** were observed at both N1 (*trans* position) and N2 (*cis* position), whereas a long-range correlation from 10-Me of minor **1** was observed at only N2 (*trans* position). Similarly, all NMR signals of dichloropalladium complex **3** were assigned.

Single-crystal X-ray structure determination of **4** was achieved (Fig. 1); significant interatomic parameters are collected in Tables 2–5. Complex **4** was a symmetrical, almost flat molecule, but two methyl groups (C10 and C20) on each palladium were a little apart from the plane. Thus, the distortion angle of the least-squares plane of the Pd1–N2–N3–Pd2–N5–N6 ring and the two methyl carbons (C10 and C20) attached to palladium was 14.8, and the two methyl groups were oriented in opposite directions. The distances between Pd1–N1, Pd1–N2, and Pd1–N6 were 2.055(2), 2.153(2), and 2.019(2) Å, respectively, and the Pd1–N2 bond was extremely extended.

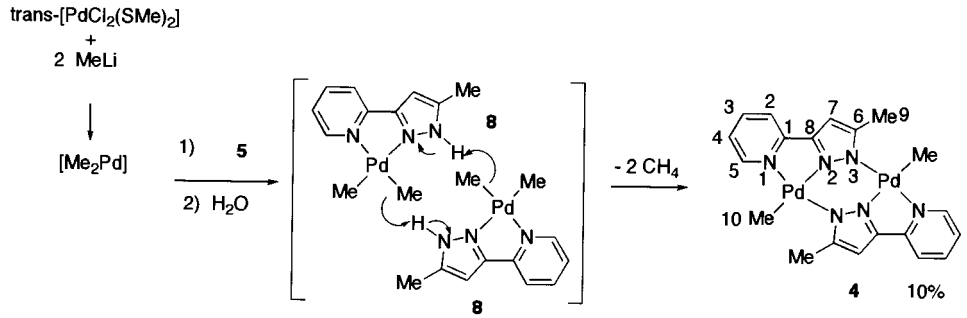
3. Discussion

^{15}N-NMR data of binuclear complex **4** were characteristic. Thus, the N1 (202.7 ppm) and N3 (212.8 ppm) of **4** appeared in a higher field than those of several palladium pyridinylpyrazole complexes in our previous and present ^{15}N-NMR studies. In general, the chemical shift of ^{15}N-NMR is strongly affected by a substituent group at the *trans* position (*trans* influence) [7]. As in the case of **4**, N1 and N3 are located in the *trans* position to each other, and the upper-field shift can be ex-

Table 1
NMR data of **1**–**7**

	1 {$CD_2Cl_2+CD_3OD$ (4:1)}	**2** {$CD_2Cl_2+CD_3OD$ (4:1)}	**3** (DMSO-d_6)	**4** (CD_2Cl_2)	**5** {$CD_2Cl_2+CD_3OD$ (1:1)}	**6** (DMSO-d_6)	**7** (DMSO-d_6)
N1	201.8	238.2	193.8	202.7	273.2	284.4	286.1
N2	235.8	200.0	187.1	260.7	ND [c]	281.4	172.7
N3	178.3	177.0	184.6	212.8	ND [c]	179.6	291.5
H2	7.76 (ddd, 7.7, 1.5, 0.7)	7.69 (ddd, 7.7, 1.5, 0.7)	8.13 (ddd, 7.3, 1.5, 0.7)	7.55 (dd, 7.3, 1.0)	7.82	7.85 (br.d, 7.3)	7.69 (br.d, 7.8)
H3	7.92 (ddd, 7.7, 7.7, 1.5)	7.91 (ddd, 7.7, 7.7, 1.5)	8.23 (ddd, 7.3, 7.3, 1.5)	7.81 (ddd, 7.3, 7.3, 1.5)	7.69	7.76 (ddd, 7.3, 7.3, 1.5)	7.84 (ddd, 7.8, 7.8, 2.0)
H4	7.39 (ddd, 7.7, 5.5, 1.5)	7.41 (ddd, 7.7, 5.5, 1.5)	7.62 (ddd, 7.3, 5.9, 1.5)	7.17 (ddd, 7.3, 5.4, 1.0)	7.17	7.23 (ddd, 7.3, 4.9, 1.0)	7.33 (ddd, 7.8, 4.9, 1.5)
H5	8.42 (ddd, 5.5, 1.5, 0.7) [a]	8.73 (ddd, 5.5, 1.5, 0.7)	8.86 (ddd, 5.9, 1.5, 0.7)	8.34 (br.d, 5.4) [b]	8.49	8.52 (ddd, 4.9, 1.5, 1.0)	8.63 (br.dd, 4.9, 2.0)
H7	6.56 (s)	6.58 (s)	7.03 (s)	6.48 (s)	6.61	6.59 (s)	6.51 (s)
9-Me	2.37 (s)	2.39 (s)	2.36 (s)	2.30 (s) [b]	2.34	2.27 (s)	2.16 (s)
NMe, NH			13.83 (s)			3.77 (s)	4.03 (s)
10-Me	0.91 (s) [a]	0.97 (s)		0.81 (s) [b]			
C1	153.37	150.13	150.91	156.18		152.15	149.34
C2	122.19	120.75	122.20	120.70		118.92	122.61
C3	139.28	139.00	141.16	138.58		136.70	137.26
C4	124.68	124.91	125.07	121.95		122.26	122.54
C5	148.48	148.64	149.44	147.67		149.16	149.04
C6	142.69	143.42	144.16	153.23		140.07	145.89
C7	102.74	103.25	104.01	104.11		103.63	106.03
C8	149.95	153.14	151.17	150.60		149.16	141.25
C9	10.85	10.92	10.89	15.72		10.81	13.11
C(NMe)						36.24	38.81
C10	−0.31	−10.70		−1.81			

[a] NOE from 0.91 (PdMe) was observed at 8.42 (H5).
[b] NOE from 0.81 (PdMe) was observed at 2.30 (PyMe) and 8.34 (H5).
[c] ND, not detected. Although ^{15}N-NMR of pyridinylpyrazole ligand **5** was also measured, N2 and N3 could not be observed because of tautomerism of the pyrazole part.



Scheme 4.

plained by their *trans* influence of nitrogen. On the other hand, the N2 signal was observed at 260.7 ppm, and the value was the lowest one among pyridinylpyrazoles coordinated with palladium in our studies. The low chemical shift value could not be explained only by the *trans* influence of the methyl group, and the value was similar to that of free pyrazoles, such as N2 in **6** or N3 in **7**, rather than pyrazoles coordinated with palladium. This suggested that the bond between palladium and N2 was extended or weakened in the case of **4** and X-ray diffraction analysis supported the prediction: the N2–Pd bond was extremely extended and the angles of N2–Pd1–N1 (79.66(8)°) and N2–Pd1–N6 (98.87(8)°) were separated by 90. These data mean that the Pd–N2 bond is weaker than Pd–N1 and Pd–N6 in the solid state. The relationship between the weakness of the Pd–N2 bond and the ^{15}N-NMR data is interesting. Thus, the ^{15}N-NMR spectrum has the potential not only to determine structure but also obtain much chemical information between metal and nitrogen ligands in solution.

4. Conclusions

Structural assignments of palladium(II) complexes having pyridinylpyrazole ligands were performed by ^{1}H-, ^{13}C-, and ^{15}N-NMR spectroscopy. Chemical shifts of ^{15}N-NMR spectra were compared among them and it was observed that the values include information on bond strength between palladium and nitrogen ligands. In the case of binuclear complex **4**, the Pd–N2 bond was extended in both the solid state and in solution. Such information concerning metal and nitrogen ligands in solution is useful to design organometallic catalysts having nitrogen ligands.

5. Experimental

5.1. General procedure

Dehydrated ether and MeLi (1.1 M ether solution) were purchased from Kanto Chemical Co., Inc. NMR solvent (CD_2Cl_2, methanol-d_4, and DMSO-d_6) was used without purification or drying. NMR spectra were recorded using Jeol α-600 and Jeol AL-300 spectrometers. ^{1}H-NMR chemical shifts are reported in ppm from residual $CDHCl_2$ (5.320), CD_2HOD (3.330 in a mixture of CD_2Cl_2 and CD_3OD), and DMSO (2.490). ^{13}C-NMR chemical shifts are reported in ppm from residual CD_2Cl_2 (53.80), CD_3OD (49.00 in a mixture of CD_2Cl_2 and CD_3OD), and DMSO (39.50). ^{15}N-NMR spectra were obtained by the ^{1}H–^{15}N PFG–HMBC method, and chemical shifts are reported in ppm from NH_4NO_3 (0 ppm) in DMSO-d_6 as an external reference. Melting points were determined on a Yanaco MP-500 melting point apparatus and were not corrected. FAB mass spectral analyses were performed on a Jeol JMS-HX100 spectrometer with nitrobenzyl alcohol as a matrix. X-ray analysis was performed on a Enraf–Nonius CAD4 apparatus.

5.2. Reaction of trans-[$PdCl_2(SMe_2)_2$] with MeLi and ligand **5**

5.2.1. Synthesis of dimer **4**

MeLi (1.3 ml, 1.43 mmol, 1.1 M ether solution) was added to a suspension of *trans*-$PdCl_2(SMe)_2$ (200 mg, 0.682 mmol) in diethyl ether (40 ml) at − 60°C under argon. The mixture was stirred for 1 h. Pyrazole ligand **5** (109 mg, 0.682 mmol) was added to the mixture and the resulting mixture was stirred with slow warming to − 15°C. Water (0.4 ml) was added to the mixture giving a clear yellow solution and brown solid. The solution was passed through a column packed with Celite® and $MgSO_4$. The filtrate was concentrated under reduced pressure, the residual light yellow solid was dissolved in CH_2Cl_2 (15 ml), and the solution was filtered with a membrane filter. The filtrate was concentrated and the crude product was recrystallized from CH_2Cl_2–ether to give dimer **4** (40 mg, 10%) as yellow cubes. M.p. 190°C (dec.). Anal. Calc. for $C_{20}H_{22}N_6Pd_2$: C, 42.96; H, 3.97; N, 15.03. Found: C, 42.89; H, 3.79; N, 14.85%. FAB MS, *m*/*z* (intensity) 523 (4.8), 524 (7.6), 525 (19.0), 526 (32.4), 527 (41.0), 528 (45.7), 529 (43.8), 530 [M^+ − 2(methyl), 49.5], 531 (35.2), 532 (32.4), 533 (18.1), 534 (15.2), 535

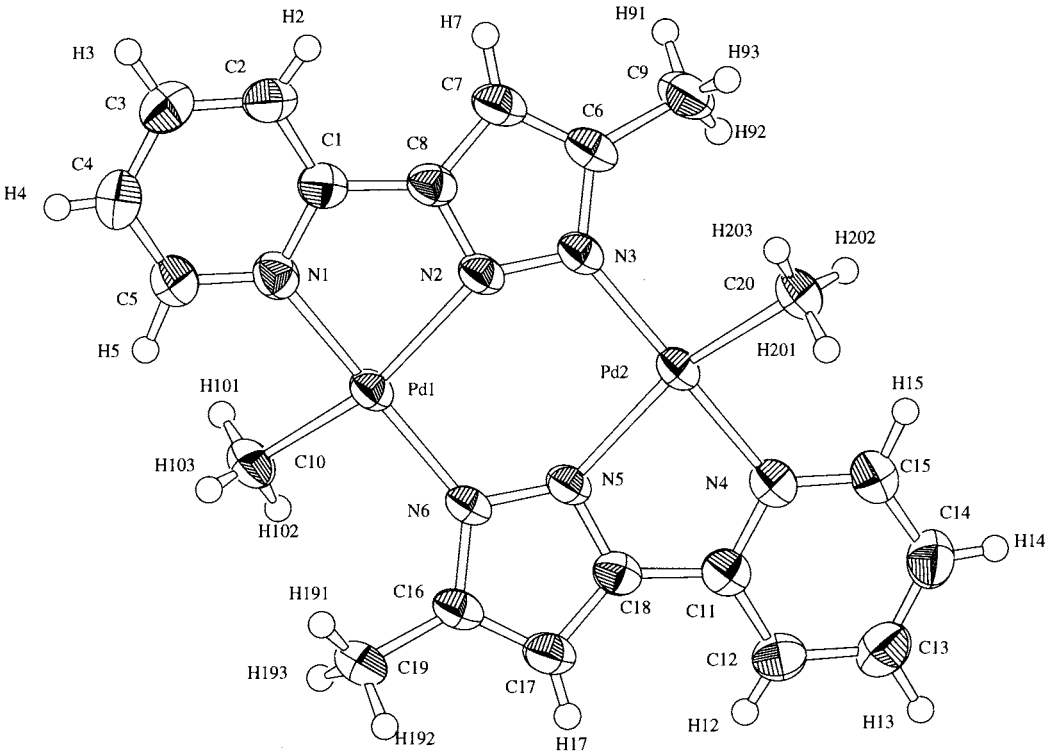


Fig. 1. Molecular structure for **4**.

(8.6), 536 (6.7), 537 (5.7), 538 (6.7), 539 (15.2), 540 (33.3), 541 (67.6), 542 (80.0), 543 (88.6), 544 (82.9), 545 [M^+ − methyl, 100.0], 546 (55.2), 547 (71.4), 548 (24.8), 549 (33.3), 550 (12.4), 551 (11.4), 552 (5.7), 553 (4.8), 554 (6.7), 555 (10.5), 556 (18.1), 557 (27.6), 558 (30.5), 559 (32.4), 560 [M^+, 31.4], 561 (30.5), 562 (23.8), 563 (21.0), 564 (12.4), 565 (10.5), 566 (5.7), 567 (4.8).

5.3. PdClMe{pyridinyl(Me)pyrazole} *1* and *2*

A mixture of (cod)PdClMe (530 mg, 2.00 mmol) and ligand **5** (410 mg, 2.04 mmol) in ether (20 ml) was stirred for 6 h. After evaporation of solvent the residue was washed with a 1:1 mixture of acetone and ether. The resulting powder was dried under reduced pressure to give a mixture of **1** and **2** (554 mg, 88%) as light yellow powder. The solids tenaciously retain fractional amounts of solvent.

Compounds **1** and **2**: m.p. 140°C (dec.). Anal. Calc. for $C_{10}H_{12}N_3ClPd$: C, 38.00; H, 3.83; N, 13.29. Found: C, 41.32; H, 4.76; N, 11.27%. ^{1}H-NMR (600 MHz, DMSO-d_6, 25°C): δ 13.50 (br.s), 8.65 (br), 8.09 (br.dd, $J = 7.7$, 7.7 Hz), 8.03 (br.d, $J = 7.7$ Hz), 7.57 (br.dd, $J = 7.7$, 5.2 Hz), 6.98 (s), 2.35 (s, 3H), 0.83 (br.s, 3H). ^{13}C-NMR (75 MHz, DMSO-d_6, 25°C): δ 152.00, 149.00, 147.73, 143.17, 139.40, 124.88, 120.98, 103.46, 10.75.

5.4. Reaction of PdClMe{pyridinyl(Me)pyrazole} *1* and *2* with MeLi

5.4.1. Synthesis of dimer *4*

MeLi (1.27 ml, 1.4 mmol, 1.1 M ether solution) was added to a suspension of a **1** and **2** mixture (200 mg, 0.633 mmol) in diethyl ether (40 ml) at − 55°C

Table 2
Crystallographic data for **4**

Formula	$C_{20}H_{22}N_6Pd_2$
Formula weight	559.23
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.3998(3)
b (Å)	10.927(1)
c (Å)	21.2730(8)
α (°)	90
β (°)	92.287(4)
γ (°)	90
V (Å^3)	1951.1(2)
Z	4
Crystal size (mm^3)	$0.25 \times 0.25 \times 0.25$
$D_{calc.}$ (g cm^{-3})	1.904
$F(000)$	1104.00
No. of data collected	4824
$2\theta_{max}$ (°)	54.9
No. of unique data	4716
No. of reflections with $I \geq 3.0\sigma(I)$	3691
R	0.023
R_w	0.035
Residual ρ_{max} (e Å^{-3})	0.52

Table 3
Bond lengths (Å) for **4**

Pd(1)–N(1)	2.055(2)
Pd(1)–N(2)	2.153(2)
Pd(1)–N(6)	2.019(2)
Pd(1)–C(10)	2.040(3)
Pd(2)–N(3)	2.023(2)
Pd(2)–N(4)	2.058(2)
Pd(2)–N(5)	2.151(2)
Pd(2)–C(20)	2.044(3)
N(1)–C(1)	1.352(3)
N(1)–C(5)	1.356(4)
N(2)–N(3)	1.360(3)
N(2)–C(8)	1.347(3)
N(3)–C(6)	1.368(3)
N(4)–C(11)	1.348(3)
N(4)–C(15)	1.347(4)
N(5)–N(6)	1.368(3)
N(5)–C(18)	1.339(3)
N(6)–C(16)	1.375(3)
C(1)–C(2)	1.385(4)
C(1)–C(8)	1.447(4)
C(2)–C(3)	1.370(4)
C(3)–C(4)	1.382(5)
C(4)–C(5)	1.369(4)
C(6)–C(7)	1.370(4)
C(6)–C(9)	1.491(4)
C(7)–C(8)	1.386(4)
C(11)–C(12)	1.383(4)
C(11)–C(18)	1.445(4)
C(12)–C(13)	1.390(4)
C(13)–C(14)	1.354(5)
C(14)–C(15)	1.387(5)
C(16)–C(17)	1.358(4)
C(16)–C(19)	1.506(4)
C(17)–C(18)	1.392(4)

under argon. The mixture was slowly warmed to −12°C. Water (0.8 ml) was added to the mixture giving a clear yellow solution and white solid. The solution was passed quickly through a column packed with Celite® and $MgSO_4$. The yellow solution turned into a white suspension. The resulting mixture was concentrated under reduced pressure and the crude product was recrystallized from CH_2Cl_2–ether to give dimer **4** (48 mg, 14%) as yellow cubes.

5.5. $PdCl_2${pyridinyl(Me)pyrazole} (3)

A mixture of $PdCl_2(CH_3CN)_2$ (259 mg, 1.00 mmol) and ligand **5** (159 mg, 1.00 mmol) in CH_2Cl_2 (10 ml) was stirred for 2 h. The resulting insoluble solid was washed with CH_2Cl_2 and dried under reduced pressure to give **3** (330 mg, 98%) as an orange powder. The solids tenaciously retain fractional amounts of impurity. M.p. 283°C (dec.). Anal. Calc. for $C_9H_9N_3Cl_2Pd \cdot 1/2CH_2Cl_2$: C, 30.11; H, 2.66; N, 11.09. Found: C, 30.12; H, 2.80; N, 11.06%.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Table 4
Bond angles (°) for **4**

N(1)–Pd(1)–N(2)	79.66(8)
N(1)–Pd(1)–N(6)	173.66(8)
N(1)–Pd(1)–C(10)	90.0(1)
N(2)–Pd(1)–N(6)	98.87(8)
N(2)–Pd(1)–C(10)	161.8(1)
N(6)–Pd(1)–C(10)	92.9(1)
N(3)–Pd(2)–N(4)	173.23(9)
N(3)–Pd(2)–N(5)	98.91(8)
N(3)–Pd(2)–C(20)	93.0(1)
N(4)–Pd(2)–N(5)	79.41(8)
N(4)–Pd(2)–C(20)	90.3(1)
N(5)–Pd(2)–C(20)	162.1(1)
Pd(1)–N(1)–C(1)	114.6(2)
Pd(1)–N(1)–C(5)	128.0(2)
C(1)–N(1)–C(5)	117.4(2)
Pd(1)–N(2)–N(3)	136.8(2)
Pd(1)–N(2)–C(8)	108.4(2)
N(3)–N(2)–C(8)	107.9(2)
Pd(2)–N(3)–N(2)	119.7(2)
Pd(2)–N(3)–C(6)	132.2(2)
N(2)–N(3)–C(6)	107.9(2)
Pd(2)–N(4)–C(11)	114.4(2)
Pd(2)–N(4)–C(15)	127.3(2)
C(11)–N(4)–C(15)	118.2(2)
Pd(2)–N(5)–N(6)	136.9(2)
Pd(2)–N(5)–C(18)	109.0(2)
N(6)–N(5)–C(18)	108.3(2)
Pd(1)–N(6)–N(5)	119.9(1)
Pd(1)–N(6)–C(16)	133.2(2)
N(5)–N(6)–C(16)	106.8(2)
N(1)–C(1)–C(2)	122.0(3)
N(1)–C(1)–C(8)	115.2(2)
C(2)–C(1)–C(8)	122.8(2)
C(1)–C(2)–C(3)	119.6(3)
C(2)–C(3)–C(4)	119.0(3)
C(3)–C(4)–C(5)	119.1(3)
N(1)–C(5)–C(4)	122.9(3)
N(3)–C(6)–C(7)	109.1(2)
N(3)–C(6)–C(9)	124.9(3)
C(7)–C(6)–C(9)	125.8(3)
C(6)–C(7)–C(8)	105.5(2)
N(2)–C(8)–C(1)	119.1(2)
N(2)–C(8)–C(7)	109.6(2)
C(1)–C(8)–C(7)	131.0(3)
N(4)–C(11)–C(12)	121.7(3)
N(4)–C(11)–C(18)	115.6(2)
C(12)–C(11)–C(18)	122.8(2)
C(11)–C(12)–C(13)	119.3(3)
C(12)–C(13)–C(14)	119.0(3)
C(13)–C(14)–C(15)	119.6(3)
N(4)–C(15)–C(14)	122.2(3)
N(6)–C(16)–C(17)	109.9(2)
N(6)–C(16)–C(19)	123.7(2)
C(17)–C(16)–C(19)	126.3(3)
C(16)–C(17)–C(18)	105.3(2)
N(5)–C(18)–C(11)	119.0(2)
N(5)–C(18)–C(17)	109.6(2)
C(11)–C(18)–C(17)	131.2(2)

Table 5
Atomic coordinates for **4**

Atom	*x*	*y*	*z*
Pd(1)	0.17081(2)	0.10680(2)	0.330434(9)
Pd(2)	0.34023(2)	0.12156(2)	0.155927(9)
N(1)	0.0538(3)	0.0489(2)	0.3513(1)
N(2)	0.0731(3)	0.0693(2)	0.23731(10)
N(3)	0.1306(3)	0.0468(2)	0.17956(9)
N(4)	0.5658(3)	0.1785(2)	0.1353(1)
N(5)	0.4377(3)	0.1604(2)	0.24879(9)
N(6)	0.3802(2)	0.1814(2)	0.30707(9)
C(1)	0.1410(3)	0.0043(2)	0.3016(1)
C(2)	0.2948(3)	0.0387(3)	0.3075(1)
C(3)	0.3632(4)	0.0339(3)	0.3649(2)
C(4)	0.2772(4)	0.0153(3)	0.4155(2)
C(5)	0.1249(4)	0.0549(3)	0.4073(1)
C(6)	0.0307(3)	0.0352(2)	0.1496(1)
C(7)	0.0914(4)	0.0630(3)	0.1879(1)
C(8)	0.0614(3)	0.0036(2)	0.2425(1)
C(9)	0.0593(4)	0.0927(3)	0.0874(2)
C(10)	0.2436(4)	0.0858(3)	0.4225(1)
C(11)	0.6524(3)	0.2228(2)	0.1850(1)
C(12)	0.8062(3)	0.2651(3)	0.1790(1)
C(13)	0.8755(4)	0.2586(3)	0.1208(2)
C(14)	0.7903(4)	0.2107(3)	0.0714(2)
C(15)	0.6350(4)	0.1720(3)	0.0793(1)
C(16)	0.4848(3)	0.2605(2)	0.3374(1)
C(17)	0.6059(3)	0.2881(3)	0.2995(1)
C(18)	0.5732(3)	0.2238(2)	0.2440(1)
C(19)	0.4588(4)	0.3134(3)	0.4016(1)
C(20)	0.2683(4)	0.1397(3)	0.0635(1)
H(2)	0.336(3)	0.067(3)	0.273(1)
H(3)	0.465(4)	0.063(3)	0.371(1)
H(4)	0.312(4)	0.019(3)	0.451(2)
H(5)	0.050(3)	0.087(2)	0.442(1)
H(7)	0.178(4)	0.114(3)	0.179(2)
H(12)	0.855(4)	0.292(3)	0.212(2)
H(13)	0.982(4)	0.290(3)	0.117(1)
H(14)	0.826(4)	0.203(3)	0.034(2)
H(15)	0.565(4)	0.143(3)	0.044(2)
H(17)	0.688(3)	0.335(2)	0.305(1)
H(91)	0.005(3)	0.168(3)	0.087(1)
H(92)	0.165(4)	0.105(3)	0.083(2)
H(93)	0.014(4)	0.050(3)	0.055(2)
H(101)	0.213(4)	0.007(4)	0.432(2)
H(102)	0.355(4)	0.079(3)	0.424(1)
H(103)	0.206(3)	0.138(3)	0.448(1)
H(191)	0.350(4)	0.320(3)	0.409(1)
H(192)	0.512(4)	0.391(3)	0.400(2)
H(193)	0.508(3)	0.265(2)	0.434(1)
H(201)	0.297(5)	0.230(4)	0.056(2)
H(202)	0.308(4)	0.093(3)	0.037(1)
H(203)	0.169(4)	0.140(3)	0.061(2)

Data Centre, CCDC no. 133318 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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