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Dinuclear palladium(I) complexes with isocyanide and N-donor bidentate ligands†

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Reactions of the dinuclear palladium(I) complex $[Pd_2Cl_2(RNC)_4]$ (R = 2,4,6-$Me_3C_6H_2$) **1** with the N-donor compounds 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), and 2,9-dimethyl-1,10-phenanthroline (dmphen) gave dipalladium(I) complexes with chelating N-donor ligands, $[Pd_2(RNC)_2L_2][PF_6]_2$ (L = bipy **2**, phen **3** or dmphen **4**). The structures of **2** and **4** were characterized by X-ray crystallography. The cation of **2** is composed of two Pd atoms joined by a σ bond [2.518(3) Å] each of which has a square-planar co-ordination involving a terminal isocyanide and a chelating bipy ligand. Complex **3** is expected to have a structure similar to **2** on the basis of spectroscopic data. Complex **4** exhibits a distorted dinuclear structure due to the steric bulk of the N-donor ligand. The Pd–Pd bond length is 2.599(2) Å. Each dmphen ligand chelates to a Pd atom and the isocyanide acts as a semibridging ligand. The similar reactions of complex **1** with 2,2′-biquinoline (bquin) and 1,8-naphthyridine (napy) afforded the isocyanide-bridged dipalladium(I) complexes, $[Pd_2(\mu\text{-}RNC)_2(bquin)_2][PF_6]_2$ **5** and $[Pd_2(\mu\text{-}RNC)_2(napy)_4][PF_6]_2$ **6**, in 24–36% yields. Complex **6** comprises a dinuclear palladium(I) core bridged by two isocyanide ligands [Pd–Pd 2.747(4) Å] with four terminal napy ligands co-ordinated in a monodentate fashion.

Di- and tri-nuclear complexes have been of general interest as models for the surface of heterogeneous catalysts. We have systematically studied di-, tri- and high-nuclearity complexes of palladium and platinum with isocyanide and diphosphine ligand by the use of chemical and electrochemical procedures.[2–7] Diphosphines (L–L), $Ph_2P(CH_2)_nPPh_2$ [n = 2 (dppe), 3 (dppp), or 4 (dppb)] and *cis*-$Ph_2PCH{=}CHPPh_2$ (dppen), introduced into the dipalladium(I) and diplatinum(I) cores ligated by isocyanides, have been shown to act as chelating ligands in $[M_2(L\text{–}L)_2(RNC)_2][PF_6]_2$ (M = Pd or Pt; R = 2,6-$Me_2C_6H_3$ or 2,4,6-$Me_3C_6H_2$),[5,6] in contrast to the bridging behaviour of $Ph_2PCH_2PPh_2$ (dppm).[4] The isocyanide-bridged dipalladium(I) cores, $Pd^I_2(\mu\text{-}RNC)_2$, have also been obtained by using pyridine and phenyl-substituted cyclopentadienyl groups, $C_5HPh_4^-$ and $C_5Ph_5^-$, as terminal ligands.[8–11] Here, we report the synthesis and characterization of dipalladium(I) complexes with N-based bidentate ligands which were used to elucidate their influence on the metal–metal bonded dipalladium structure in comparison with those of diphosphines.

Experimental

Dichloromethane was distilled over calcium hydride and diethyl ether over lithium aluminium hydride prior to use. Other reagents of the best commercial grade were used as received. The compound $[Pd_2Cl_2(2,4,6\text{-}Me_3C_6H_2NC)_4]$ was prepared by the known method.[12–14] All reactions were carried out under a nitrogen atmosphere with standard Schlenk and vacuum-line techniques. Abbreviations used; bipy = 2,2′-bipyridyl; phen = 1,10-phenanthroline; bquin = 2,2′-biquinoline; napy = 1,8-naphthyridine; dmphen = 2,9-dimethyl-1,10-phenanthroline.

Measurements

Proton NMR spectra were measured on a Bruker AC250 instrument at 250 MHz calibrated with tetramethylsilane as an external reference, infrared spectra on a JASCO FT/IR-5300 spectrometer as Nujol mulls.

Preparations

$[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2L_2][PF_6]_2$ (L = bipy 2, phen 3 or dmphen 4). Portions of bipy (43 mg, 0.272 mmol) and NH_4PF_6 (100 mg, 0.613 mmol) were added to a dichloromethane–acetone solution of $[Pd_2Cl_2(2,4,6\text{-}Me_3C_6H_2NC)_4]$ **1** (107 mg, 0.124 mmol). The mixture was stirred at room temperature for 3 h, and the solvent removed under reduced pressure. The residue was extracted with dichloromethane (20 cm^3), and the extract, after passing through a glass filter, was concentrated to *ca.* 5 cm^3. Diethyl ether and benzene were added, giving yellow crystals of $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(bipy)_2][PF_6]_2\cdot 1.5C_6H_6$ in 48% yield (73 mg, 0.0597 mmol), which were washed with Et_2O and dried *in vacuo* (Found: C, 47.9; H, 3.90; N, 6.60. Calc. for $C_{49}H_{47}F_{12}N_6P_2Pd_2$: C, 48.15; H, 3.85; N, 6.85%). IR (Nujol): ν(N≡C) 2170 (sh), 2166; ν(PF_6) 837 cm^{-1}. ^1H NMR (CD_3CN): δ 2.29 (s, *p*-Me), 2.41 (s, *o*-Me) and 7.8–9.6 (m, aryl).

Similar procedures using phen and dmphen instead of bipy gave yellow crystals of $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(phen)_2][PF_6]_2\cdot 0.5C_6H_6$ **3** and $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(dmphen)_2][PF_6]_2\cdot 0.5CH_2Cl_2$ **4** respectively. Complex **3** (Found: C, 47.6; H, 3.30; N, 7.45. Calc. for $C_{47}H_{41}F_{12}N_6P_2Pd_2$: C, 47.35; H, 3.45; N, 7.05%). IR (Nujol) ν(N≡C) 2153, ν(PF_6) 839 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.27 (s, *p*-Me), 2.36 (s, *o*-Me), 6.93 (s, *m*-H), 7.35 (s, C_6H_6) and 7.9–9.6 (m, aryl), yield 56%. Complex **4** (Found: C, 46.3; H, 3.70; N, 7.05. Calc. for $C_{48.5}H_{47}ClF_{12}N_6P_2Pd_2$: C, 46.5; H, 3.80; N, 6.70%): IR (Nujol) ν(N≡C) 2149 (sh), 2121, ν(PF_6) 839 cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 2.15 (s, *p*-Me), 2.56 (s, *o*-Me), 1.84, 3.02 (s, Me of dmphen), 5.31 (s, CH_2Cl_2), 6.61 (s, *m*-H) and 7.9–8.8 (m, aryl of dmphen); yield 41%.

$[Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2(bquin)_2][PF_6]_2\cdot 0.5CH_2Cl_2$ 5. To a solution (30 cm^3) of compound **1** (107 mg, 0.124 mmol) in dichloromethane–acetone were added bquin (70 mg, 0.272 mmol) and NH_4PF_6 (100 mg, 0.613 mmol). The mixture was stirred at room temperature for 3 h, then the solvent was removed under reduced pressure. The residue was extracted

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with dichloromethane (20 cm^3) and the extract concentrated to *ca.* 5 cm^3. Diethyl ether and benzene were added, giving orange crystals of $[Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2(bquin)_2][PF_6]_2\cdot0.5CH_2Cl_2$ in 24% yield (36 mg, 0.0298 mmol), which were washed with Et_2O and dried *in vacuo* (Found: C, 50.05; H, 3.70; N, 6.40. Calc. for $C_{56.5}H_{47}ClF_{12}N_6P_2$: C, 50.35; H, 3.50; N, 6.25%). IR (Nujol): ν(N≡C) 1966, 1937; $\nu(PF_6)$ 847 cm^{-1}. ^1H NMR (CD_3CN): δ 2.29 (s, *p*-Me), 2.41 (s, *o*-Me) and 7.8–9.6 (m, aryl).

$[Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2(napy)_4][PF_6]_2$ 6. Portions of napy (70 mg, 0.544 mmol) and NH_4PF_6 (100 mg, 0.613 mmol) were added to a solution (30 cm^3) of $[Pd_2Cl_2(2,4,6\text{-}Me_3C_6H_2NC)_4]$ **1** (107 mg, 0.124 mmol) in dichloromethane–acetone. The mixture was stirred at room temperature for 3 h, then the solvent was removed under reduced pressure. The residue was extracted with dichloromethane (20 cm^3) and the extract concentrated to *ca.* 5 cm^3. Diethyl ether and benzene were added, giving orange crystals of $[Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2(napy)_4][PF_6]_2$ **6** in 36% yield (59 mg, 0.0446 mmol), which were washed with Et_2O and dried *in vacuo* (Found: C, 47.1; H, 3.40; N, 10.9. Calc. for $C_{52}H_{46}F_{12}N_{10}P_2Pd_2$: C, 47.55; H, 3.55; N, 10.65%). IR (Nujol): ν(N≡C) 1993, 1933 (sh); $\nu(PF_6)$ 845 cm^{-1}. ^1H NMR (CD_3CN): δ 1.58 (s, *o*-Me), 2.04 (s, *p*-Me), 6.37 (s, *m*-H) and 7.5–9.4 (m, aryl of napy).

Crystallography

The crystals used in data collection were sealed into a glass tube capillary (0.7 mm outside diameter) with a droplet of the mother-liquor. Crystal data and experimental conditions are summarized in Table 1. All data were collected on a Rigaku AFC5S diffractometer equipped with graphite-monochromated Mo-Kα (λ = 0.710 69 Å) radiation. The cell constants were obtained from least-squares refinement of 22–25 reflections with $20 < 2\theta < 30°$. Three standard reflections were monitored every 150 and showed no systematic decrease in intensity. Reflection data were corrected for Lorentz-polarization and absorption effects (ψ-scan method).

Structure solution and refinement. The structure of complex **2** was solved by direct methods with MITHRIL.[15] The two palladium atoms were located in the initial *E* map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. The coordinates of all hydrogen atoms were calculated at ideal positions with the C–H distance of 0.95 Å. The structure was refined on *F* with full-matrix least-squares techniques minimizing $\Sigma w(|F_o| - |F_c|)^2$. Final refinement with anisotropic thermal parameters for Pd, P, and F atoms and isotropic ones for C atoms converged to $R = 0.079$ and $R' = 0.062$. The structures of $\mathbf{4}\cdot2CH_2Cl_2$ and **6** were solved by direct methods with MITHRIL and the Patterson method, respectively. The hydrogen-atom coordinates were calculated as before and not refined. Final full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms converged to $R = 0.061$ and $R' = 0.048$ for $\mathbf{4}\cdot2CH_2Cl_2$ and $R = 0.072$ and $R' = 0.063$ for **6**.

Atomic scattering factors and values of f' and f'' for Pd, Cl, P, F, N and C were taken from the literature.[16] All calculations were carried out on a Digital VAX Station 3100 with the TEXSAN program system.[17] The perspective views were drawn by using the program PLUTO.[18]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/104.

Results and Discussion

Preparation and characterization of $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2L_2][PF_6]_2$ (L = bipy 2, phen 3, dmphen 4 or bquin 5)

The reaction of $[Pd_2Cl_2(2,4,6\text{-}Me_3C_6H_2NC)_4]$ **1** with 2 equivalents of N-donor (bipy, phen, dmphen) and an excess of NH_4PF_6 afforded yellow complexes formulated as $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2L_2][PF_6]_2$ (L = bipy **2**, phen **3** or dmphen **4**) in 41–56% yields. The IR spectra of **2**–**4** showed bands corresponding to the N≡C stretching of terminal isocyanides at 2121–2170 cm^{-1}. The ^1H NMR spectra indicated the presence of isocyanide and N-donor ligand in a 1 : 1 ratio. The structures of **2** and $\mathbf{4}\cdot2CH_2Cl_2$ were determined by X-ray crystallographic analyses.

Table 1 Crystallographic and experimental data for $[Pd_2(RNC)_2(bipy)_2][PF_6]_2$ **2** $[Pd_2(RNC)_2(dmphen)_2][PF_6]_2\cdot2CH_2Cl_2$ **4** and $[Pd_2(\mu\text{-}RNC)_2(napy)_4][PF_6]_2$ **6** ($R = 2,4,6\text{-}Me_3C_6H_2$)

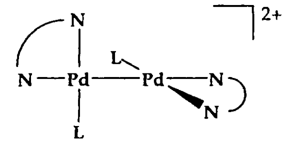
	2	4	6
Formula	$C_{40}H_{38}F_{12}N_6P_2Pd_2$	$C_{50}H_{50}Cl_2F_{12}N_6P_2Pd_2$	$C_{52}H_{46}F_{12}N_{10}P_2Pd_2$
M	1105.51	1379.53	1313.73
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	8.904(4)	13.275(11)	12.639(3)
b/Å	39.066(9)	32.589(13)	13.974(4)
c/Å	13.183(2)	14.152(9)	8.644(2)
α/°			100.72(2)
β/°	104.65(2)	114.83(6)	96.17(2)
γ/°			114.14(2)
U/Å³	4436	5556	1339.8
Z	4	4	1
T/°C	23	23	23
D_c/g cm⁻³	1.655	1.649	1.628
μ/cm⁻¹	9.56	9.68	8.06
Transmission factors	0.93–1.00	0.91–1.00	0.83–1.00
2θ Range/°	3–50	3–50	3–44
No. unique data	7959	10 017	2507
No. observed data	2116	4150	1479
	$[I \geqslant 2.5\sigma(I)]$	$[I \geqslant 3\sigma(I)]$	$[I \geqslant 3\sigma(I)]$
No. variables	329	685	352
*R**	0.079	0.061	0.072
*R′**	0.062	0.048	0.063

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 1/\sigma^2(F_o)$.

A perspective view of the cation of complex **2** is illustrated in Fig. 1, and selected bond lengths and angles are listed in Table 2. The complex cation consists of two palladium atoms joined by a Pd–Pd σ bond. The structure has a pseudo-C_2 symmetry and is similar to those of $[Pd_2(dppp)_2(2,4,6\text{-}Me_3C_6H_2NC)_2]^{2+}$ **7** and $[Pd_2(dppen)_2(2,6\text{-}Me_2C_6H_3NC)_2]^{2+}$ **8**.[6] The structural features of dinuclear palladium(I) isocyanide complexes are summarized in Table 3. Each Pd atom is ligated by two nitrogen atoms of a bidentate bipy ligand, a terminal carbon atom of $2,4,6\text{-}Me_3C_6H_2NC$, and another Pd atom in a planar array. The Pd–Pd bond is not supported by any bridging ligands. Its length [2.518(3) Å] is shorter than those found in $[Pd_2(MeNC)_6][PF_6]_2$ **9** [2.531(1) Å],[22–24] $[Pd_2Cl_2(Bu^tNC)_4]$ **10** [2.532(2) Å][14] and $[Pd_2I_2(MeNC)_4]$ **11** [2.533(1) Å][25] and much shorter than those in the dimers with chelating diphosphines, **7** [2.617(2) Å] and **8** [2.602(2) Å] (Table 3). Recently, the Pd–Pd bond distance of 2.500(1) Å found in $[Pd_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3(C_5H_4N\text{-}2)\}_2][BF_4]_2$ was reported as the shortest one so far observed in palladium(I) dinuclear systems,[26] and the value for **2** is the second shortest bond, due to the small *trans* influence of the pyridyl group. The dihedral angle between the two PdN_2C co-ordination planes is 81°, nearly perpendicular as observed in **7** (86), **8** (78), **9** (86.4),[22–24] **10** (82.7)[14] and **11** (85.3°).[25] This is probably due to the minimization of steric repulsion between the bulky isocyanide ligands.[6] The axial N atoms are almost collinear with the Pd–Pd bond. The average $Pd\text{–}Pd\text{–}N_{ax}$ angle is 174.8°. The PdN_2C_2 five-membered chelate rings are almost planar with an average bite angle of 78.4°. The averages of the Pd–C–N and C–N–C angles are 173 and 175°, respectively, which fall within the usual range for terminal isocyanides. The isocyanide ligands are bent toward the Pd–Pd bond, the average Pd–Pd–C angle being 79.9°. A similar inward bend has been observed in **7** (78.7) and **8** (81.8°).

From the similarity of the spectral data of complexes **3** and **2** and that of the co-ordination behaviour of phen and bipy, **3** was assumed to have the dipalladium(I) structure observed in **2**.

The asymmetric unit of complex $\mathbf{4}\cdot 2CH_2Cl_2$ contains the complex cation, two hexafluorophosphate anions, and two dichloromethane molecules. There is no unusual contact between them. A perspective drawing of the complex cation with the atomic numbering scheme is given in Fig. 2. Selected bond distances and angles are listed in Table 4. The structure is essentially similar to that of **2**, but the geometry around the Pd atoms is fairly distorted. Each Pd atom is co-ordinated by two nitrogen atoms of dmphen, one carbon atom of isocyanide, and the neighbouring Pd atom in a planar fashion. The $Pd\text{–}Pd\text{–}N_{eq}$ angles [N_{eq} = N(3), N(5)] are expanded (average 105.8°) and the Pd–Pd–C [C=C(1), C(2)] reduced (average 68.2°) from ideal square planar so as to avoid the steric repulsions between the bulky ligands. The dihedral angle between the two co-ordination planes, PdN_2C, is also reduced from an ideal value of 90 to 69°. The Pd–Pd bond length is 2.599(2) Å which is 0.081 Å longer than that of **2**. The most conspicuous feature is the co-



L = $2,4,6\text{-}Me_3C_6H_2NC$, $\overset{\frown}{N\,N}$ = bipy **2** or phen **3**

Table 2 Selected bond distances (Å) and angles (°) for complex **2** with estimated standard deviations (e.s.d.s) in parentheses

Pd(1)–Pd(2)	2.518(3)	Pd(1)–N(3)	2.06(2)
Pd(1)–N(4)	2.10(2)	Pd(1)–C(1)	1.92(2)
Pd(2)–N(5)	2.09(2)	Pd(2)–N(6)	2.08(2)
Pd(2)–C(2)	1.89(3)	N(1)–C(1)	1.13(2)
N(1)–C(11)	1.40(2)	N(2)–(2)	1.17(3)
N(2)–C(21)	1.38(3)		
Pd(2)–Pd(1)–N(3)	96.6(6)	Pd(2)–Pd(1)–N(4)	174.3(6)
Pd(2)–Pd(1)–C(1)	78.9(7)	N(3)–Pd(1)–N(4)	78.8(8)
N(3)–Pd(1)–C(1)	171.8(9)	N(4)–Pd(1)–C(1)	105.1(9)
Pd(1)–Pd(2)–N(5)	97.5(5)	Pd(1)–Pd(2)–N(6)	173.3(6)
Pd(1)–Pd(2)–C(2)	80.8(7)	N(5)–Pd(2)–N(6)	78.0(8)
N(5)–Pd(2)–C(2)	172.9(9)	N(6)–Pd(2)–C(2)	103(1)
C(1)–N(1)–C(11)	175(2)	C(2)–N(2)–C(21)	175(3)
Pd(1)–N(3)–C(31)	127(2)	Pd(1)–N(3)–C(35)	115(2)
Pd(1)–N(4)–C(41)	129(2)	Pd(1)–N(4)–C(45)	113(2)
Pd(2)–N(5)–C(51)	124(2)	Pd(2)–N(5)–C(55)	113(2)
Pd(2)–N(6)–C(61)	129(2)	Pd(2)–N(6)–C(65)	117(2)
Pd(1)–C(1)–N(1)	174(2)	Pd(2)–C(2)–N(2)	172(2)

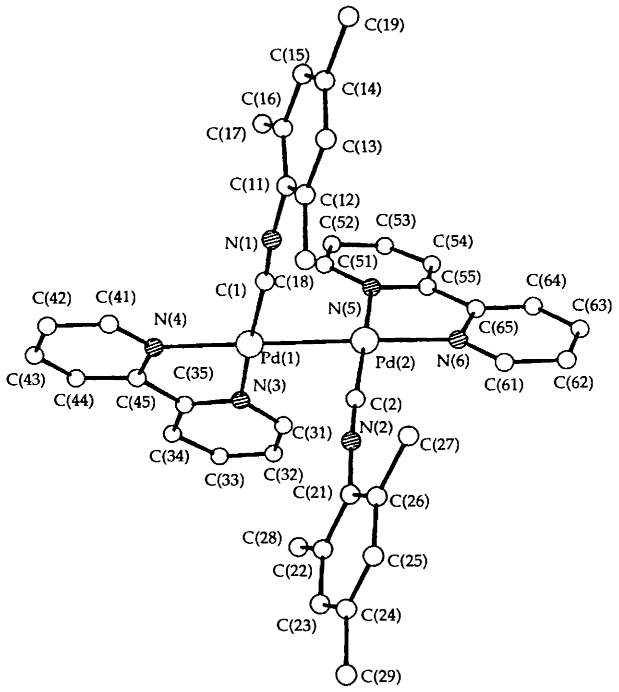


Fig. 1 Perspective drawing of the cation of complex **2** $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(bipy)_2]^{2+}$. All non-hydrogen atoms are shown as circles and hydrogen atoms are omitted for clarity

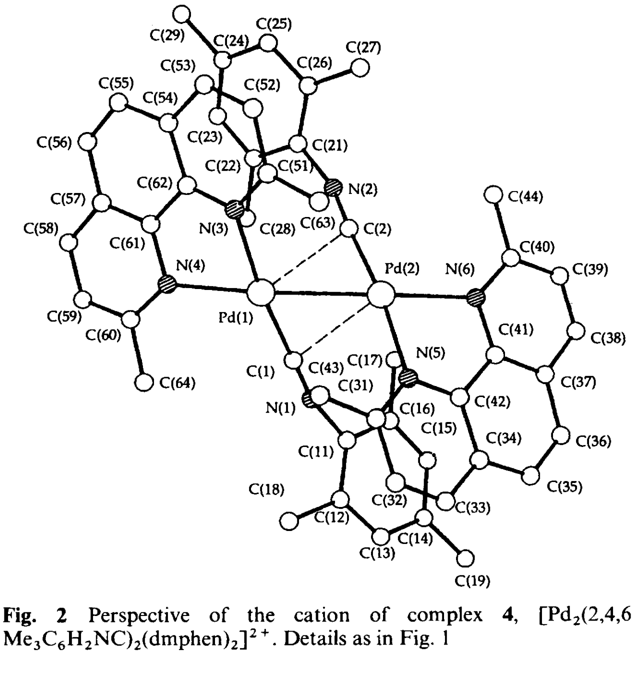
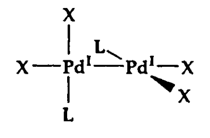


Fig. 2 Perspective of the cation of complex **4**, $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(dmphen)_2]^{2+}$. Details as in Fig. 1

Table 3 Structural parameters of dipalladium(I) complexes containing isocyanides

Complex		Structure	Pd–Pd/Å	θ^a/°
9	$[Pd_2(MeNC)_6]^{2+}$	I	2.531(1)	86.4
10	$[Pd_2Cl_2(Bu^tNC)_4]$	I	2.532(2)	82.7
11	$[Pd_2I_2(MeNC)_4]$	I	2.533(1)	85.3
7	$[Pd_2(dppp)_2(2,4,6\text{-}Me_3C_6H_2NC)_2]^{2+}$	I	2.617(2)	86
8	$[Pd_2(dppen)_2(2,4\text{-}Me_2C_6H_3NC)_2]^{2+}$	I	2.602(2)	78
2	$[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(bipy)_2]^{2+}$	I	2.518(3)	81
4	$[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(dmphen)_2]^{2+}$	II	2.599(2)	69
	$[Pd_2(\mu\text{-}SPPh_2)_2(MeNC)_2]^b$	III	2.608(1)	0
	$[Pd_2(\mu\text{-}\eta^3\text{-}C_9H_7)_2(Bu^tNC)_2]^c$	III	2.648(2)	126^d
	$[Pd_2(\mu\text{-}\eta^3\text{-}C_9H_7)_2(2,6\text{-}Me_2C_6H_3NC)_2]^c$	III	2.656(2)	147^d
14	$[Pd_2(\eta\text{-}C_5Ph_5)_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2]$	IV	2.632(5)	119.7^e
12	$[Pd_2Cl_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2(py)_2]$	IV	2.662(1)	129.8^e
15	$[Pd_2(\eta\text{-}C_5HPh_4)_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2]$	IV	2.673(1)	135.0^e
	$[\{Pd_2(\mu\text{-}Bu^tNC)_2(\mu\text{-}O_2CMe)_2\}_2]^c$	IV	2.655(3)	138^e
13	$[Pd_2\{HB(pz)_3\}_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2]$	IV	2.757(4)	180.0^e
6	$[Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2(napy)_4]^{2+}$	IV	2.747(4)	180.0^e
	$[Pd_2(\mu\text{-}MeNC)(2,4,6\text{-}Me_3C_6H_2NC)_2(dppm)_2]^{2+f}$	V	3.215(2)	106^g
	$[Pd_2Cl_2(\mu\text{-}PhNC)(dppm)_2]^{2+h}$	V	3.188(4)	107.5

[a] The dihedral angle between the two co-ordination planes. [b] Ref. 19. [c] Ref. 10, C_9H_7 = indenyl. [d] Approximate value derived from the Pd–Pd–C angle. [e] Dihedral angle between the two PdC_2 planes. [f] Ref. 20. [g] Pd–C–Pd angle. [h] Ref. 21.



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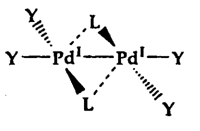

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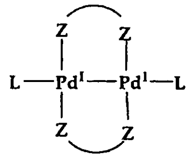

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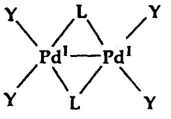

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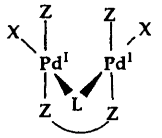


V

Table 4 Selected bond distances (Å) and angles (°) for complex **4** with e.s.d.s in parentheses

Pd(1)–Pd(2)	2.599(2)	Pd(1)–N(3)	2.11(1)
Pd(1)–N(4)	2.14(1)	Pd(1)–C(1)	1.95(1)
Pd(2)–N(5)	2.123(9)	Pd(2)–N(6)	2.14(1)
Pd(2)–C(2)	1.89(1)	N(1)–C(1)	1.14(1)
N(1)–C(11)	1.39(1)	N(2)–C(2)	1.17(1)
N(2)–C(21)	1.42(1)		
Pd(2)–Pd(1)–N(3)	105.1(3)	Pd(2)–Pd(1)–N(4)	166.0(2)
Pd(2)–Pd(1)–C(1)	68.9(4)	N(3)–Pd(1)–N(4)	78.0(4)
N(3)–Pd(1)–C(1)	173.1(5)	N(4)–Pd(1)–C(1)	106.9(5)
Pd(1)–Pd(2)–N(5)	106.4(3)	Pd(1)–Pd(2)–N(6)	166.5(3)
Pd(1)–Pd(2)–C(2)	67.4(4)	N(5)–Pd(2)–N(6)	78.9(4)
N(5)–Pd(2)–C(2)	171.4(4)	N(6)–Pd(2)–C(2)	105.9(5)
C(1)–N(1)–C(11)	165(1)	C(2)–N(2)–C(21)	163(1)
Pd(1)–N(3)–C(51)	129(1)	Pd(1)–N(3)–C(62)	110.0(9)
Pd(1)–N(4)–C(60)	132.6(8)	Pd(1)–N(4)–C(61)	108.8(8)
Pd(2)–N(5)–C(31)	130.4(9)	Pd(2)–N(5)–C(42)	108.8(8)
Pd(2)–N(6)–C(40)	131.1(9)	Pd(2)–N(6)–C(41)	109.3(8)
Pd(1)–C(1)–N(1)	180(1)	Pd(2)–C(2)–N(2)	176(1)

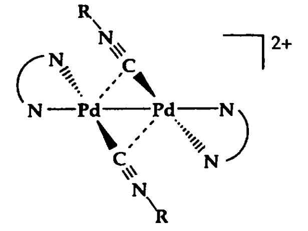
ordination of the terminal isocyanides. Owing to the steric factors as mentioned above, the inward bend of the terminal isocyanide ligands is considerable, resulting in short contacts between the terminal carbon atom of RNC and the adjacent Pd atom [Pd(1)···C(2) 2.56(1), Pd(2)···C(1) 2.63(1) Å]. The values of the interatomic distances are approximately intermediate between the sums of the covalent radii and of the van der Waals radii, and may comprise an interaction between the filled d orbitals of the palladium with the empty π* orbitals of the isocyanide ligand on the adjacent metal. The average C–N–C angle of the isocyanides is 164° and in contrast to the bent C–N–C structure (137°) of the four-electron (σ,π) donating, doubly bridging isocyanide in $[Mn_2(dppm)_2(CO)_4(\mu\text{-}p\text{-}MeC_6H_4NC)]$, where the terminal carbon donates a pair of electrons to one Mn (Mn–C 1.81 Å) and the C=N unit donates a second pair of electrons to the other Mn (Mn–C 2.14, Mn–N 2.12 Å).[27] A structural study of linear semibridging isocyanide is extremely rare as compared with that of CO, and its successful isolation in **4** might be ascribable to the steric bulk of the dmphen ligands.

When bquin was used an orange complex formulated as $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(bquin)_2][PF_6]_2\cdot0.5CH_2Cl_2$ **5** was obtained in 24% yield. The IR spectrum showed a strong band centred at 1966 cm^{-1}, which is characteristic of an isocyanide-bridged dipalladium(I) structure as observed in $[Pd_2Cl_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2(py)_2]$ **12** (py = pyridine) (1976 cm^{-1}),[8] $[Pd_2\{HB(pz)_3\}_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2]$ **13** (1997 cm^{-1}),[11] $[Pd_2(\eta\text{-}C_5Ph_5)_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2]$ **14** (1956 cm^{-1}) and $[Pd_2(\eta\text{-}C_5HPh_4)(\mu\text{-}2,4,6\text{-}Me_3NC)_2]$ **15** (1953 cm^{-1}),[11] whereas the possibility of a terminal RNC structure cannot be ruled out. On the basis of the IR spectral data and the crystal structures of **12** and $[Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2(napy)_4][PF_6]_2$ **6** (see below), complex **5** is, at present, assumed to have the $Pd_2(\mu\text{-}RNC)_2$ core as depicted, where the bridging isocyanides adopt a C–N–C linear form.

Preparation and characterization of $[Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2(napy)_4][PF_6]_2$ 6

Since 1,8-naphthyridine (napy) has the potential to bridge between two metal atoms like dppm its reaction with complex **1** was examined. The reaction with 2 equivalents of napy afforded orange crystals of $[Pd_2(2,4,6\text{-}Me_3C_6H_2NC)_2(napy)_4][PF_6]_2$ **6** in 15% yield. When 4 equivalents of napy were used the yield increased to 36%. The ^1H NMR spectrum indicated the presence of $2,4,6\text{-}Me_3C_6H_2NC$ and napy ligands in 1:2 ratio. In the IR spectrum a characteristic band for the N≡C stretching vibration of bridging isocyanides with linear C–N–C form was observed at 1993 cm^{-1}. The structure was confirmed by X-ray crystallography.

A perspective drawing of the cation of complex **6** with the atomic numbering scheme is shown in Fig. 3, and selected bond lengths and angles are in Table 5. The complex cation consists of two palladium atoms bridged by two isocyanides. The structure has a crystallographically imposed inversion centre at the middle of the Pd–Pd bond, resulting in a planar Pd_2C_2 core.



R = 2,4,6-$Me_3C_6H_2$, N⌒N = dmphen **4**

Table 5 Selected bond distances (Å) and angles (°) for complex **6** with e.s.d.s in parentheses

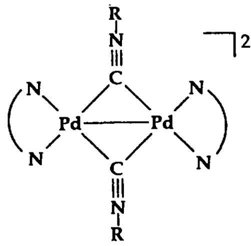
Pd(1)–Pd(1*)	2.747(4)	Pd(1)–N(2)	2.18(2)
Pd(1)–N(4)	2.17(2)	Pd(1)–C(1)	1.94(2)
Pd(1)–C(1*)	1.93(3)	N(1)–C(1)	1.24(2)
N(1)–C(111)	1.43(2)		
Pd(1*)–Pd(1)–N(2)	137.1(4)	Pd(1*)–Pd(1)–N(4)	132.6(5)
Pd(1*)–Pd(1)–C(1)	44.7(8)	Pd(1*)–Pd(1)–C(1*)	45.0(7)
N(2)–Pd(1)–N(4)	90.3(6)	N(2)–Pd(1)–C(1)	178(1)
N(2)–Pd(1)–C(1*)	92.1(8)	N(4)–Pd(1)–C(1)	87.8(9)
N(4)–Pd(1)–C(1*)	177.6(9)	C(1)–Pd(1)–C(1*)	90(1)
C(1)–N(1)–C(111)	170(2)	Pd(1)–N(2)–C(21)	125(2)
Pd(1)–N(2)–C(28)	119(2)	Pd(1)–N(4)–C(11)	127(2)
Pd(1)–N(4)–C(18)	116(2)	Pd(1)–C(1)–Pd(1*)	90(1)
Pd(1)–C(1)–N(1)	136(2)	Pd(1*)–C(1)–N(1)	134(2)

The Pd–Pd bond length of 2.747(4) Å is significantly longer than normal for single Pd–Pd bonds, and is, however, close to that of **13** [2.757(4) Å] which also possesses the planar $Pd_2(\mu\text{-}RNC)_2$ core (Table 3). The Pd_2C_2 ring is almost square with Pd(1)–C(1)–Pd(1*) 90(1), C(1)–Pd(1)–C(1*) 90(1)°, Pd(1)–C(1) 1.94(2) and Pd(1)–C(1*) 1.93(3) Å. The two isocyanides symmetrically bridge the two Pd atoms with a linear C–N–C form. The C(1)–N(1) bond length and C(1)–N(1)–C(111) angles are 1.24(2) Å and 170(2)°, respectively, indicating a weak back bonding interaction from the occupied d orbital of the Pd_2 unit to the π^* orbitals of the isocyanides. A similar feature has been observed in the palladium(I) dimer $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$ [$\tilde{\nu}$(CO) = 1906 cm^{-1}].[28] The terminal sites of each palladium atom are capped by two napy molecules which act as monodentate ligands.

The ^1H NMR spectra of complexes **2**–**4** exhibited symmetrical spectral patterns for the bidentate N-donor ligands, indicating the palladium centre to be fluxional through axial–equatorial ligand exchange. The spectral patterns in CD_2Cl_2 remain invariant over the temperature range from 25 to −80 °C, however, suggesting that the energy barrier for such exchange is very low. This feature is similar to that found in the well studied system $[Pd_2(MeNC)_6]^{2+}$,[13,29] and is in contrast to non-fluxional dipalladium phosphine complexes $[Pd_2(L\text{-}L)_2(RNC)_2]^{2+}$ and $[Pd_2(PMe_3)_6]^{2+}$.[30]

References

1 Part 42, T. Igoshi, T. Tanase and Y. Yamamoto, *J. Organomet. Chem.*, 1995, **494**, 37.
2 Y. Yamamoto, K. Takahashi and H. Yamazaki, *J. Am. Chem. Soc.*, 1986, **108**, 2458.
3 T. Tanase, Y. Kudo, M. Ohno, K. Kobayashi and Y. Yamamoto, *Nature (London)*, 1990, **344**, 526.
4 T. Tanase, T. Horiuchi, Y. Yamamoto and K. Kobayashi, *J. Organomet. Chem.*, 1992, **440**, 1.
5 Y. Yamamoto and H. Yamazaki, *Organometallics*, 1993, **12**, 933.
6 T. Tanase, K. Kawahara, H. Ukaji, K. Kobayashi, H. Yamazaki and Y. Yamamoto, *Inorg. Chem.*, 1993, **32**, 3682.
7 T. Tanase, H. Ukaji, Y. Kudo, M. Ohno, K. Kobayashi and Y. Yamamoto, *Organometallics*, 1994, **13**, 1374.
8 Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 1986, **25**, 3327.



R = 2,4,6-$Me_3C_6H_2$, N⌒N = bquin **5**

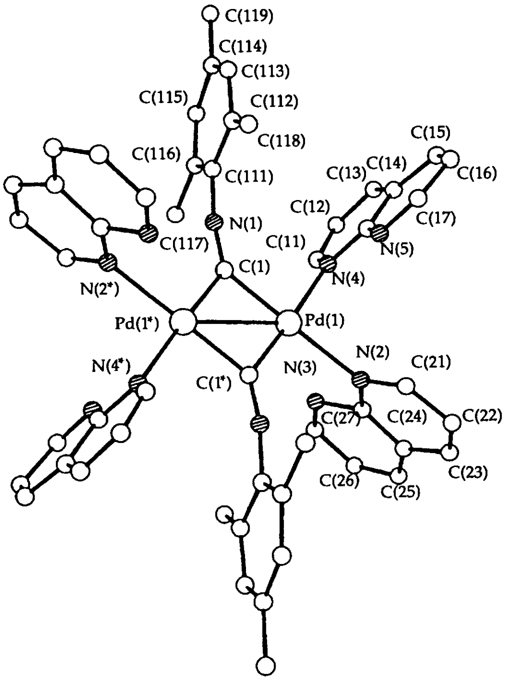


Fig. 3 Perspective of the cation of complex **6**, $[Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2(napy)_4]^{2+}$. Details as in Fig. 1

9 T. Tanase, T. Nomura, Y. Yamamoto and K. Kobayashi, *J. Organomet. Chem.*, 1991, **410**, C25.
10 T. Tanase, T. Nomura, T. Fukushima and Y. Yamamoto, *Inorg. Chem.*, 1993, **32**, 4578.
11 T. Tanase, T. Fukushima, T. Nomura and Y. Yamamoto, *Inorg. Chem.*, 1994, **33**, 32.
12 S. Otsuka, Y. Tatsuno and K. Ataka, *J. Am. Chem. Soc.*, 1971, **93**, 6705.
13 J. R. Boehm and A. L. Balch, *Inorg. Chem.*, 1977, **16**, 778.
14 Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1843.
15 C. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **17**, 42.
16 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*; Kynoch Press, Birmingham, 1974, vol. 4; D. T. Cromer, *Acta Crystallogr.*, 1965, **18**, 17.
17 TEXSAN, Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985.
18 S. Motherwell and W. Clegg, PLUTO, Program for Plotting Molecular and Crystal Structures, University of Cambridge, 1978.
19 B. Messbauer, H. Meyer, B. Walther, M. J. Heeg, A. F. M. M. Rahman and J. P. Oliver, *Inorg. Chem.*, 1983, **22**, 272.
20 M. M. Olmstead, H. Hope, L. S. Benner and A. L. Balch, *J. Am. Chem. Soc.*, 1977, **56**, 5502.
21 M. A. Khan and A. J. McAlees, *Inorg. Chim. Acta*, 1985, **104**, 109.
22 D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg and J. S. Miller, *J. Am. Chem. Soc.*, 1975, **97**, 1961.
23 S. Z. Goldberg and R. Eisenberg, *Inorg. Chem.*, 1976, **15**, 535.
24 T. D. Miller, M. A. S. Clair, M. K. Reinking and C. P. Kubiak, *Organometallics*, 1983, **2**, 767.
25 N. M. Rutherford, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1984, **23**, 2833.
26 K. Tani, S. Nakamura, T. Yamagata and Y. Kataoka, *Inorg. Chem.*, 1993, **32**, 5398.

27 L. S. Benner, M. M. Olmstead and A. L. Balch, *J. Organomet. Chem.*, 1978, **159**, 289.
28 A. G. M. Barrett and P. Quayle, *J. Chem. Soc., Chem. Commun.*, 1981, 1076.
29 C. H. Lindsay, L. S. Benner and A. L. Balch, *Inorg. Chem.*, 1980, **19**, 3503.
30 W. Lin, S. R. Wilson and G. S. Girolami, *Inorg. Chem.*, 1994, **33**, 2265.

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