

Hexapalladium cluster: Unique cluster construction reaction of cyclic $\text{Pd}_3(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_6$ and linear $[\text{Pd}_3(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_8]^{2+}$

Masato Ohashi, Jianjun Yi, Daisuke Shimizu, Tsuneaki Yamagata,
Takashi Ohshima, Kazushi Mashima *

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

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Abstract

Reaction of a triangle Pd(0) complex, $\text{Pd}_3(\text{CNXyl})_6$ (**1**; Xyl = 2,6- $\text{C}_6\text{H}_3\text{Me}_2$), with a dicationic linear trinuclear complex $[\text{Pd}_3(\text{CNXyl})_8][\text{PF}_6]_2$ (**3**) afforded a dicationic hexapalladium complex $[\text{Pd}_6(\text{CNXyl})_{12}][\text{PF}_6]_2$ (**4**), while the reaction of **1** with a dicationic dinuclear complex $[\text{Pd}_2(\text{CNXyl})_6][\text{PF}_6]_2$ (**2**) resulted in the formation of **3**. The molecular structure of the complex **4** was determined by X-ray crystallography and spectroscopic analysis.

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Keywords: Palladium; Isocyanide; Homoleptic complex; Hexanuclear cluster

1. Introduction

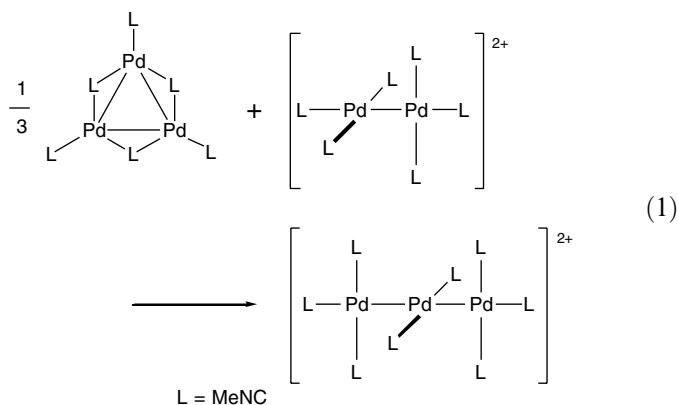
Polynuclear clusters with metal–metal bonds have attracted research interest due to not only their fundamental aspects as surface model of heterogeneous catalysts [1] but also their potential applications as electrochemical, photoelectric, and magnetic materials [2–4]. Among them, di- and trinuclear complexes with metal–metal bonds have been well documented as versatile starting materials to prepare new cluster complexes with higher nuclearity [5]. We have been intrigued by the insertion reaction of metal fragments into the metal–metal bonded clusters as an ideal synthetic method for constructing metal–metal bonded polynuclear complexes [6]. It is well known that one metal fragment of d^{10} transition metals can be inserted into the M(I)–M(I) bond of dinuclear complexes (M = Pt and Rh) to form heterotrinnuclear A-frame complexes: $[\text{Pt}_2\text{Pd}(\mu\text{-dppm})_2(\text{CNMe})_2]^{2+}$ [7], $[\text{Pt}_2(\mu\text{-HgCl}_2)\text{Cl}_2(\mu\text{-dppm})_2]$ [8], and $[(\text{CpRh})_2(\mu\text{-AuPPh}_3)(\mu\text{-CO})(\mu\text{-dppm})_2]^+$ [9] have been synthesized by the insertion reactions of $\text{Pd}(\text{CNMe})_2$, HgCl_2 ,

and $[\text{AuPPh}_3]^+$ into the corresponding Pt_2 and Rh_2 complexes, respectively. In the case of homoleptic palladium isocyanide complexes, although many di-, tri-, and multinuclear complexes with isocyanide ligands have been prepared by electrochemical reaction of metal ions in different formal oxidation states [10–16], such an insertion reaction of a ‘ $\text{Pd}^0(\text{CNMe})_2$ ’ fragment into a dicationic dipalladium complex $[\text{Pd}_2(\text{CNMe})_6]^{2+}$ with d^9 configuration has been successfully applied to yield the linear tripalladium complex $[\text{Pd}_3(\text{CNMe})_8]^{2+}$ (Eq. (1)) [12c]. The linear trinuclear derivative $[\text{Pd}_3(\text{XylNC})_8][\text{PF}_6]_2$ (**3**; Xyl = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) had already synthesized by the electrochemical reduction of $[\text{Pd}(\text{XylNC})_4]^{2+}$ [13g]. It was our surprise that there was no insertion reaction of a ‘ Pd^0L_2 ’ species into metal cluster compounds with higher nuclearity such as $[\text{Pd}_3\text{L}_8]^{2+}$, except for a linear tetrapalladium complex $[\text{Pd}_4(\mu\text{-}\eta^3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^3\text{-}1,8\text{-diphenylocta-}1,3,5,7\text{-tetraene})_2]^{2+}$, which was a product of the formal consecutive insertions of two Pd(0) to the Pd(I)–Pd(I) bond of the starting complex $\text{Pd}_2(\text{MeCN})_6^{2+}$ in the presence of tetraene ligands [17]. Distinct from the insertion reactions mentioned above, Harvey et al. had also reported the linear tetrapalladium complex $[\text{Pd}_4(\text{dmb})_4(\text{PPh}_3)_2]\text{Cl}_2$ (dmb = 1,8-diisocyanato-*p*-menthane) and its

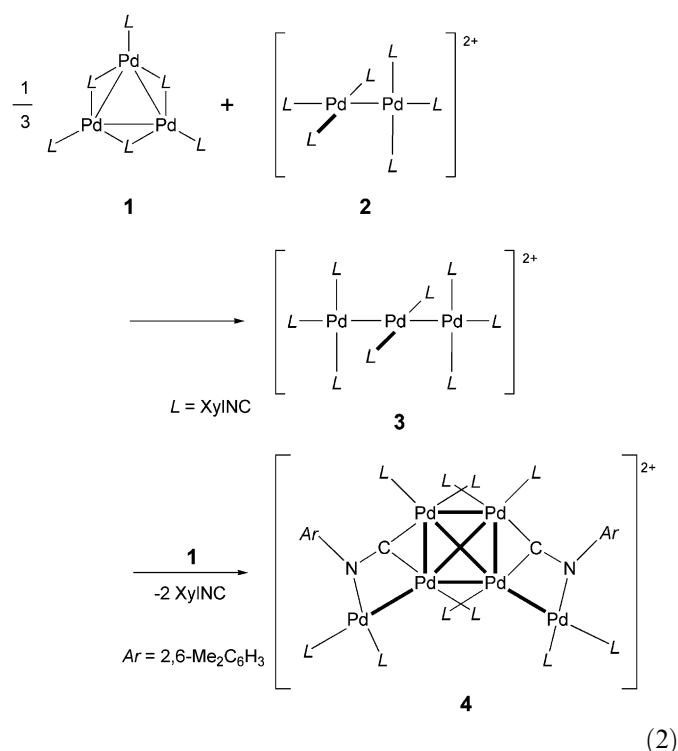
* Corresponding author. Tel./fax: +81 668 506 245.

E-mail address: mashima@chem.es.osaka-u.ac.jp (K. Mashima).

polymer derivative $\{[\text{Pd}_4(\text{dmb})_5](\text{CH}_3\text{COO})_2\}_n$ by using the bidentate dmb ligands [18].



Herein, we report that, by using 2,6-dimethylphenylisocyanide as a homoleptic ligand, a $\text{Pd}^0(\text{CNXyl})_2$ fragment that is derived from $[\text{Pd}(\text{CNXyl})_2]_3$ (**1**: Xyl = 2,6-Me₂C₆H₃) inserted into a Pd(I)–Pd(I) bond of a dicationic complex $[\text{Pd}_2(\text{CNXyl})_6][\text{PF}_6]_2$ (**2**) to yield not only an expectable linear trinuclear complex $[\text{Pd}_3(\text{CNXyl})_8][\text{PF}_6]_2$ (**3**) but also a dicationic hexanuclear palladium complex $[\text{Pd}_6(\text{CNXyl})_{12}][\text{PF}_6]_2$ (**4**) (Eq. (2)). The structural characterizations of **3** and **4** were conducted by X-ray analysis.



2. Experimental section

2.1. General procedures

All manipulations involving air- and moisture-sensitive compounds were carried out by using standard Schlenk

techniques under argon atmosphere. Dichloromethane and ether were dried and deoxygenated by distillation over P₂O₅ and sodium benzophenone ketyl, respectively, under argon atmosphere. Dehydrated acetone was degassed by trap-to-trap distillation before use. Complexes Pd₃(CNXyl)₆ (**1**) and $[\text{Pd}_2(\text{CNXyl})_6][\text{PF}_6]_2$ (**2**) were prepared according to the literature procedures [10,11].

2.2. Physical measurements

¹H and ¹³C NMR spectra were measured on a Varian-Mercury 300 spectrometer. All ¹H NMR chemical shifts were reported in ppm relative to proton impurity resonance in chloroform-*d* at δ 7.26. IR and Mass spectra were recorded on a Jasco FT/IR-230 spectrometer and on a PE-Sciex API-III plus spectrometer with ESI technique, respectively. Elemental analyses were performed on a Perkin–Elmer 2400 microanalyzer in the Faculty of Engineering Science, Osaka University. UV–Vis spectra were recorded on HP 8453 UV–Visible ChemStation using dichloromethane solutions in sealed cells. All melting points were measured in sealed tubes and were not corrected.

2.3. Synthesis of $[\text{Pd}_3(\text{CNXyl})_8][\text{PF}_6]_2$ (**3**)

To a deep red solution of **1** (0.31 g, 0.28 mmol) in dichloromethane (10 mL) was added a yellow solution of **2** (1.10 g, 0.85 mmol) in acetone (15 mL) via a syringe. After the reaction mixture was stirred for several hours at room temperature, some precipitated materials were filtered off to give a bright red solution. The solution was then concentrated to ca. 5 mL under reduced pressure. The resulting solution was layered with ether (10 mL) to give yellow crystalline products, which were filtered, washed with ether (10 mL), and then dried in vacuo for 2 h. Complex **3** was obtained as yellow solids (1.32 g, 94%), m.p. 196–203 °C. ¹H NMR (300 MHz, CDCl₃, 35 °C): δ 2.36–2.59 (br, 48H, CH₃), 7.10–7.35 (m, 24H, C₆H₃). ¹³C NMR (75 MHz, CDCl₃, 35 °C): δ 18.8 (CH₃), 19.2 (CH₃), 125.3, 128.5, 128.6, 130.8, 131.1, 131.3, 135.7, 135.8, 135.9. IR (nujol/NaCl): ν(NC)/cm⁻¹ 2148 (s, N≡C), 2121 (s, N≡C), 845 (s, PF₆). UV (CH₂Cl₂): λ_{max} 265 (ε = 6.8 × 10⁴), 443 (ε = 1.8 × 10⁴). ESI-MS: *m/z* = 1619 (3), 1380 (20, [3–L–PF₆]⁺), 1143 (28, [Pd₂L₆(PF₆)⁺), 1012 (8, [Pd₂L₅(PF₆)⁺), 904 (17), 773 (30), 618 (100 (base peak), [3–L–2(PF₆)²⁺), 499 (10). Anal. Calc. for C₇₂H₇₂F₁₂N₈P₂D₃: C, 52.14; H, 4.38; N, 6.76. Found: C, 52.21; H, 4.37; N, 6.82%.

2.4. Synthesis of $[\text{Pd}_6(\text{CNXyl})_{12}][\text{PF}_6]_2$ (**4**)

2.4.1. Method 1: Reaction of **3** with **1**

A solution of **1** (0.22 g, 0.20 mmol) in dichloromethane (5 mL) was added into a yellow solution of **3** (0.30 g, 0.18 mmol) in dichloromethane (10 mL) via syringe. After the reaction mixture was stirred overnight at room temperature, all volatiles were removed under reduced pressure.

Extraction with acetone (10 mL) gave a deep red solution. The resulting solution was concentrated under reduced pressure to give red crystalline products, which were washed with ether (10 mL) and then dried in vacuo for 2 h. **4** was obtained as deep red crystals (0.40 g, 88%), m.p. 98–105 °C.

¹H NMR (300 MHz, CDCl₃, 35 °C): δ 2.10–2.52 (t, br, 72H, CH₃), 7.09–7.33 (m, br, 36H, C₆H₃). ¹³C NMR (75 MHz, CDCl₃, 35 °C): δ 18.8 (CH₃), 19.2 (CH₃), 128.5, 128.6, 130.8, 131.1, 135.7, 135.8. IR (nujol): ν(NC)/cm⁻¹ 2128 (s, N≡C), 1679 (m, N=C), 843 (s, PF₆). ESI-MS: *m/z* = 2222 (5, [4-L-PF₆]⁺), 2091 (2, [4-2L-PF₆]⁺), 1946 (7), 1882 (2, [Pd₅L₁₀(CH₃CN)]⁺), 1619 (12), 973 (100 (base peak), [4-2L-2(PF₆)²⁺], 618 (76, [Pd₃L₇]²⁺ or [Pd₆L₉+CH₃CN]³⁺), 467 (48, [Pd₆L₁₂+3CH₃CN]⁵⁺). Anal. Calc. for C₁₀₈H₁₀₈F₁₂N₁₂P₂Pd₆: C, 51.83; H, 4.35; N, 6.72. Found: C, 51.98; H, 4.36; N, 6.65%.

2.4.2. Method 2: One-pot reaction of **1** with **2**

A 100 mL schlenk tube was charged with the triangular complex **1** (44 mg, 0.04 mmol) and the dicationic dinuclear complex **2** (39 mg, 0.03 mmol), and then 10 mL of dichloromethane was added to the mixture with vigorous stirring. After the reaction mixture was stirred overnight at room temperature, removal of all volatiles under reduced pressure followed by washing with ether (10 mL × 3) gave 72 mg of multicomponent mixture containing **4**, confirmed based on the observation of the corresponding ion peaks attributable to **4** in the ESI-MS spectrum of the reaction mixture.

2.5. Crystallographic data collections and structure determination

The molecular structure of the cationic part of **3** was determined on the basis of the X-ray diffraction study for the BF₄⁻ salt. Yellow prism crystals of **3** and red crystals of **4** suitable for X-ray crystallography were mounted on the end of glass fibers with white vaseline wrapped. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate equipped with a sealed tube X-ray generator (50 kV, 40 mA) with graphite monochromated Mo Kα (0.71075 Å) radiation in a nitrogen stream at 213(1) K (**3**) and 120(1) K (**4**).

Each indexing was performed from 2 oscillations exposed for 300 s for **3** and from 3 oscillations exposed for 90 s for **4**, respectively. The unit cell parameters and the orientation matrix for data collection were determined by the least-squares refinement with the setting angles listed in Tables 1 and 2. A symmetry-related absorption was corrected by use of the program ABCOR [19a] with transmission factors ranging from 0.7416 to 0.8615 (**3**) and from 0.5585 to 0.7922 (**4**). Details of the data collection were summarized in Tables 1 and 2.

2.6. Structure determination and refinement

The structure of **3** was solved by direct methods (SIR-92) [19b] and refined on *F*² by full-matrix least-squares methods,

Table 1
Crystallographic data of **3** · 2CH₂Cl₂^{a,b}

Complex	3
Empirical formula	C ₇₄ H ₇₆ B ₂ Cl ₄ F ₈ N ₈ Pd ₃
Formula weight	1712.13
Temperature (K)	213(1)
Radiation (Å)	Mo Kα, 0.71069
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$ (#2)
<i>a</i> (Å)	12.7528(2)
<i>b</i> (Å)	13.22951(17)
<i>c</i> (Å)	12.00303(13)
α (°)	106.9176(18)
β (°)	103.460(3)
γ (°)	88.8418(16)
Volume (Å ³)	1881.76(4)
<i>Z</i>	1
Calculated density (Mg m ⁻³)	1.511
2θ _{max} (°)	55.0
Limiting indices	-16 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 17, -15 ≤ <i>l</i> ≤ 15
Absorption coefficient (mm ⁻¹)	0.918
<i>F</i> (000)	864
Crystal size (mm)	0.49 × 0.31 × 0.22
Goodness-of-fit on <i>F</i> ²	1.041
Reflections collected/unique [<i>R</i> _{int}]	18765/8474 [0.028]
Completeness to θ = 27.48	98.0%
No. of variables	448
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0349, 0.0880
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0415, 0.0920

^a $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$. The function minimized: $w(F_o^2 - F_c^2)^2$.

Table 2
Crystallographic data of **4** · 2CH₂Cl₂ · H₂O^{a,b}

Complex	4
Empirical formula	C ₁₁₀ H ₁₁₄ Cl ₄ F ₁₂ N ₁₂ OP ₂ Pd ₆
Formula weight	2690.27
Temperature (K)	120(1)
Radiation (Å)	Mo Kα, 0.71075
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	29.6755(17)
<i>b</i> (Å)	17.5501(11)
<i>c</i> (Å)	23.0315(14)
β (°)	92.830(2)
Volume (Å ³)	11980.4(13)
<i>Z</i>	4
Calculated density (Mg m ⁻³)	1.508
2θ _{max} (°)	62.9
Limiting indices	-43 ≤ <i>h</i> ≤ 43, -25 ≤ <i>k</i> ≤ 25, -33 ≤ <i>l</i> ≤ 33
Absorption coefficient (mm ⁻¹)	1.081
<i>F</i> (000)	5451
Crystal size (mm)	0.51 × 0.47 × 0.34
Goodness-of-fit on <i>F</i> ²	0.969
Reflections collected/unique [<i>R</i> _{int}]	97317/19787 [0.1175]
Completeness to θ = 31.51	99.0%
No. of variables	689
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0870, 0.2456
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1827, 0.2786

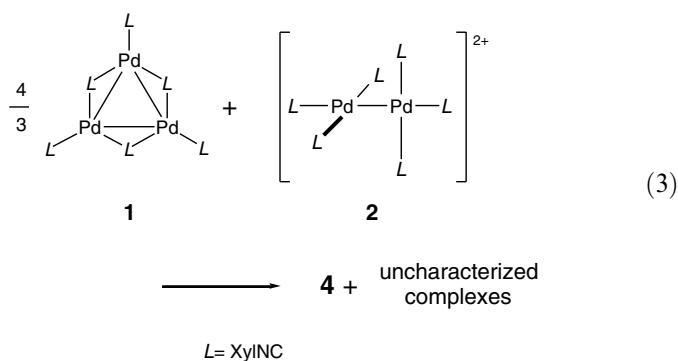
^a $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$. The function minimized: $w(F_o^2 - F_c^2)^2$.

using SHELXL-97 [19c]. The structure of **4** was solved by direct methods (SIR-97)[19b] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97. Measured non-equivalent reflections with $I > 2.0\sigma(I)$ were used for the structure determination. The non-hydrogen atoms were refined anisotropically. In the final refinement cycle for **3** and **4**, hydrogen atoms coordinates were induced at idealized positions and were given the same temperature factor as that of carbon atom to which they were bonded. All calculations of least-squares refinements were performed with SHELXL-97 programs on Origin 3400 computer of Silicon Graphics Inc. at the Research Center for Structural Biology Institute for Protein Research, Osaka University.

3. Results and discussion

A homoleptic linear tripalladium complex $[\text{Pd}_3(\text{XylNC})_8][\text{PF}_6]_2$ (**3**; Xyl = 2,6-Me₂C₆H₃) was prepared by the reaction of a triangle Pd(0) complex $\text{Pd}_3(\text{XylNC})_6$ (**1**), which is a source compound of highly reactive and coordinatively unsaturated 'Pd⁰(XylNC)₂' species, with three equivalents of a dicationic dinuclear complex $[\text{Pd}_2(\text{XylNC})_6][\text{PF}_6]_2$ (**2**), being accordance with the previously reported the synthesis method for $[\text{Pd}_3(\text{MeNC})_8]^{2+}$ [12c]. In this reaction, one 'Pd⁰(XylNC)₂' fragment formally inserted into the Pd(I)–Pd(I) bond. We carried out the further insertion reaction into the dipalladium complex **2**: treatment of **2** with four-thirds equivalent of **1** resulted in the formation of a complicated mixture (Eq. (3)), in which a novel hexapalladium cluster $[\text{Pd}_6(\text{XylNC})_{12}][\text{PF}_6]_2$ (**4**) was contained on the basis of FAB-MS spectroscopy. At the first stage of this reaction, we observed that the color of the reaction mixture turned to yellow and then immediately to deep red, implying that the first reaction involved the formation of the linear trinuclear complex **3**. We could find that treatment of the isolated linear dicationic complex **3** with an equimolar amount of **1** gave the dicationic hexapalladium complex **4** in an excellent yield (Eq. (2)). It is of interest that the reaction of the dicationic dinuclear complex **2** with **1** resulted in the selective insertion of one 'Pd⁰(XylNC)₂' fragment, while the reaction of **1** with the isolated dicationic linear trinuclear complex **3** afforded the dicationic hexapalladium complex **4** predominantly. We could not, however, detect and isolate any other tetranuclear and pentanuclear palladium species in these reactions.



As mentioned above, the alternative method for the synthesis of the linear trinuclear complex **3** and its spectral data had already reported [13g], and thus, it was identified by comparison between the δ_{H} values as well as the stretching frequency attributable to the terminal isocyanides (vide infra) and those reported values. In the ¹H NMR spectrum of **3** measured at 50 °C, the methyl groups of the isocyanide ligands were observed to be equivalent. With drop of the temperature down to –40 °C, the signal gradually broadened and then split into multiple singlets. This implies the site-exchange of the isocyanide ligands among three kinds of coordination sites, *outer-axial*, *outer-equatorial*, and *inner* ones. We were able to determine the accurate structure of the linear tripalladium complex **3** by means of X-ray diffraction study. The molecular structure of the cationic part of **3** is illustrated in Fig. 1. The selected bonds and angles are listed in Table 3.

Complex **3** is a 44e species consisting of the three 16e Pd centers and the formal Pd–Pd bond order should be 1 according to the EAN rule. The inner palladium atom is located at a crystallographic inversion center and thus the Pd–Pd–Pd angle (180°) is perfectly linear. The Pd–Pd bond distance (2.60342(19) Å) is quite similar to that of the linear tripalladium derivative $[\text{Pd}_3(\text{MeNC})_6(\text{PPh}_3)_2][\text{PF}_6]_2$ (2.5921(5) Å) [12c]. Each palladium atom possesses the square-planar coordination geometry: the outer palladium atoms are surrounded by three isocyanide ligands and the inner palladium atom, while the inner palladium forming two Pd–Pd bonds is in a square-planar configuration comprised of two palladium atoms and two isocyanide ligands in *trans* arrangement. Noteworthy is that the coordination planes of the two outer Pd centres are parallel with each other and are oriented perpendicular to that of the central Pd atom. The mean bond distance of the six equatorial Pd–C bonds (1.969 Å) is significantly shorter than that of the two axial Pd–C bonds (2.075(3) Å). Similar elongation of the axial Pd–C bonds was observed in the dinuclear isocyanide complex $[\text{Pd}_2(\text{MeNC})_6]^{2+}$ [12e]. The equatorial XylNC ligands in **3** coordinated in a specifically linear manner with an average bond angle of Pd–C–N (174.8°), while the axial ones coordinated in a bent fashion with the averaged value of 164.5(3)°. All of the XylNC ligands were almost linear with an average C–N–Xyl bond angle of 175.5° and the C≡N bond distances were within the range from 1.151(4) to 1.157(4) Å, suggesting that the back-bonding interaction from the palladium atom to the CNXyl moiety is very weak. These are consistent with the observation that two $\nu(\text{NC})$ absorptions were observed at 2148 and 2121 cm^{–1}, assignable to terminal isocyanides.

The hexapalladium complex **4** is relatively air-stable in solid condition, however, when it was dissolved in CH₂Cl₂ and then exposed to the atmosphere, a gradual decomposition, changing of the color of the solution from red to green, was observed. The ¹H NMR spectrum of **4** was almost meaningless for characterization since it showed only two broad signals assignable to the methyl groups and the aromatic regions of the 2,6-C₆H₃Me₂ moieties

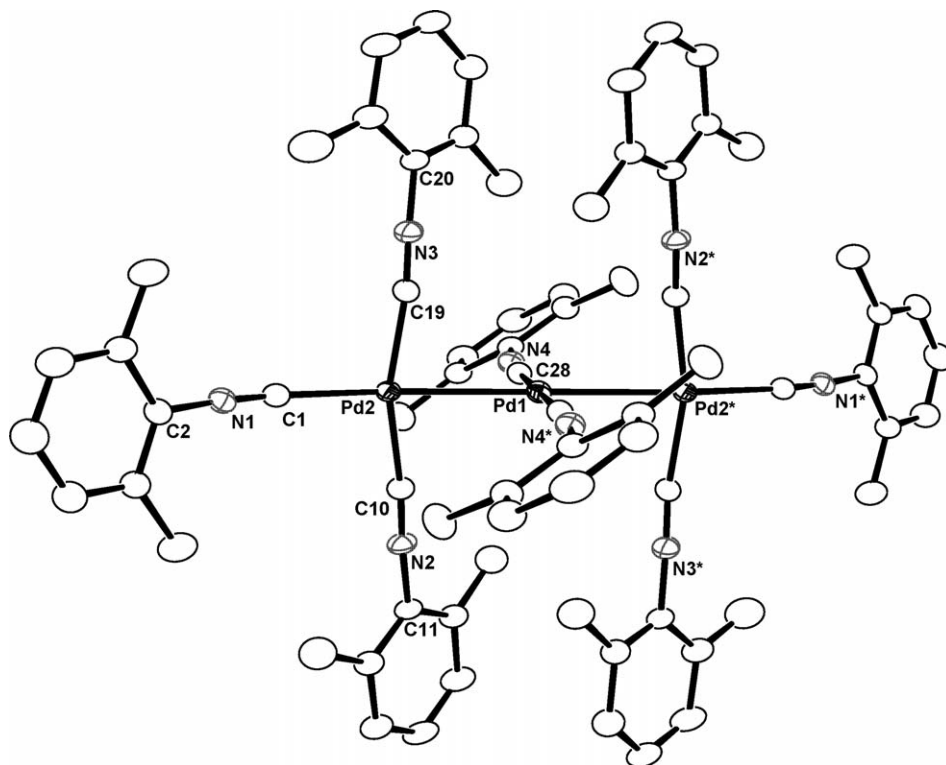


Fig. 1. ORTEP drawing of the cationic part of **3** showing the 50% probability thermal ellipsoids (hydrogen atoms and solvent molecules are omitted for clarity).

Table 3
Selected bond lengths (Å) and angles (°) for **3**

Pd1–Pd2	2.60342(19)	N1–C1	1.152(4)
Pd1–C28	1.954(3)	N2–C10	1.157(4)
Pd2–C1	2.075(3)	N3–C19	1.156(4)
Pd2–C10	1.978(3)	N4–C28	1.151(4)
Pd2–C19	1.976(3)		
Pd2–Pd1–Pd2*	180.000(8)	Pd2–C1–N1	164.5(3)
C28–Pd1–C28*	180.0(2)	Pd2–C10–N2	174.5(3)
C1–Pd2–Pd1	160.03(12)	Pd2–C19–N3	172.5(3)
C10–Pd2–C1	100.38(11)	Pd1–C28–N4	177.5(2)
C19–Pd2–C1	98.97(11)	C1–N1–C2	175.0(3)
C10–Pd2–Pd1	80.56(8)	C10–N2–C11	176.4(3)
C19–Pd2–Pd1	82.16(8)	C19–N3–C20	177.8(3)
		C28–N4–C29	172.9(3)

Symmetry transformations used to generate equivalent atoms (*): $-x, -y, -z$.

most probably due to the fluxional processes of the isocyanide ligands. The accurate description of **4** was confirmed by an X-ray diffraction study.

Figs. 2 and 3 show ORTEP drawings of the cationic part of **4** and its Pd₆ skeleton, respectively. The selected bonds and angles are summarized in Table 4. The dicationic complex **4** has a Pd₄ tetrahedron core, to which other two palladium atoms attached. One of the edge (2.9487(11) Å) of the tetrahedron, Pd1–Pd1*, is obviously longer than the rest of the edges (ave. 2.802 Å), and furthermore, all of these Pd–Pd distances in **4** are significantly longer than mean distances of the triangular frame found in neutral species

Pd₃(μ-CNCy)₃(CNCy)₃ (ave. 2.651(2) Å) [16] and Pd₃(μ-SO₂)₂(CN^tBu)₃ (ave. 2.743 Å) [20] probably due to being positively charged. The Pd–Pd–Pd angles within the Pd₄ core lie in the range from 57.474(19)° to 63.43(3)°, being slightly deviated from the ideal tetrahedron angle (60°).

Two extrusive palladium atoms, Pd3 and Pd3*, are bonded to Pd2 and Pd2* of the tetrahedron core, respectively, with the shortest Pd–Pd bond distance of 2.6527(7) Å in **4**, which is, however, longer than Pd(I)–Pd(I) bond distances found not only in dinuclear isocyanide derivatives, Pd₂I₂(MeNC)₄ (2.533(1) Å) [12a], [Pd₂(MeNC)₆]²⁺ (2.5310(9) Å) [12e], and Pd₂Cl₂(^tBuNC)₄ (2.532(2) Å) [13k], but also in linear trinuclear Pd₃²⁺ complexes, [Pd₃(CNMe)₆(PPh₃)₂]²⁺ (2.5921(5) Å) [12c] and **3** (2.60342(19) Å). The geometry at the overhanging palladium atom is distorted square-planer with Pd3 bonded to the Pd2 atom of the tetrahedron core, the C37 and C46 atoms of two terminal isocyanide ligands, and the N1 atom of the triply bridged one (vide infra) through a lone pair on the N atom with the Pd–N bond distance of 2.079(6) Å.

It is noteworthy that two isocyanide ligands coordinate to the hexapalladium core in a μ₃-fashion and that they act as a four-electron donor, and consequently, complex **4** is a coordinatively saturated 86e species consisting of the six 16e Pd centers and the formal Pd–Pd bond order should be 5/8. Such a μ₃-coordinating manner of isocyanide has been observed in some metal clusters such as Ru₃(CO)₆(μ₃-PPhCH₂PPh₂)(μ₃-CNCy)(CNCy)₂ [21a], Pt₇(CNXyl)₁₂ [13l], Ni₄(CN^tBu)₇ [15], and Os₆(CO)₁₈(μ₃-CNC₆H₄Me-

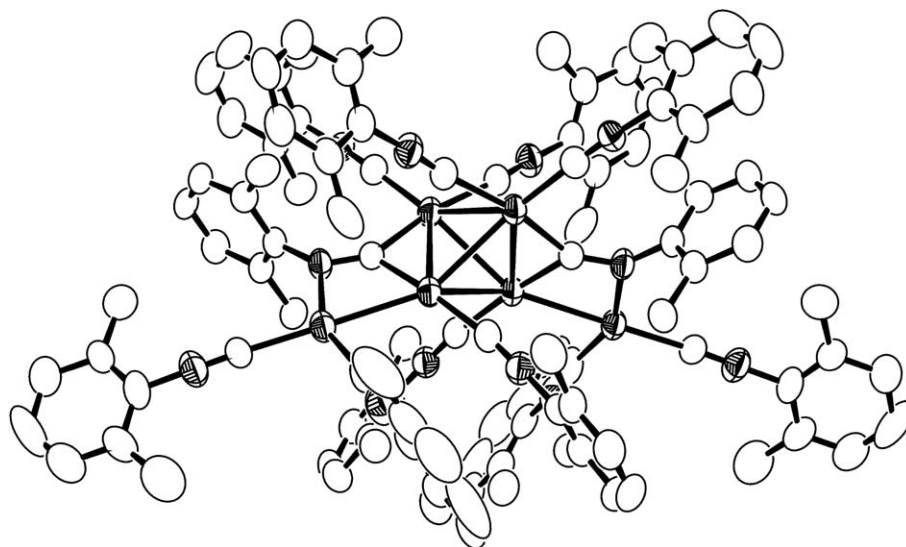


Fig. 2. ORTEP drawing of the cationic part of **4** showing the 50% probability thermal ellipsoids (hydrogen atoms and solvent molecules are omitted for clarity).

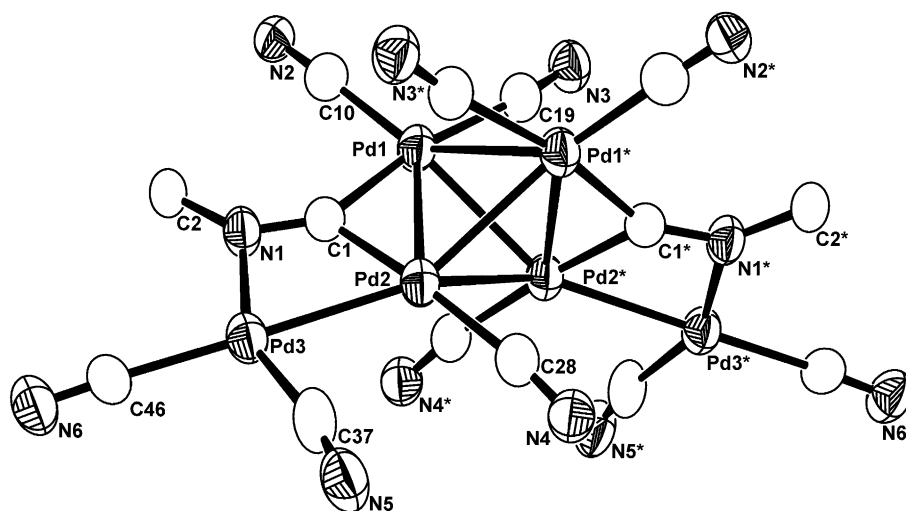


Fig. 3. Skeleton of the Pd₆ core in the cationic part of **4**.

p)(CNC₆H₄Me-*p*) [**21b**], however, this is the first example of the palladium cluster. Each carbon atom of these μ₃-isocyanide ligands, C1 and C1*, bridge a suite of opposite sides of the tetrahedron core, Pd1–Pd2 and Pd1*–Pd2*, respectively, with the average Pd–C_{br} bond distance of 1.987 Å. This value is comparable with those observed in [Pd₂Cl₂(μ-CNXyl)₂(py)₂](ave. 2.01 Å) [13], and however, shorter than the known Pd–C_{br} bond distances found in Pd₅(μ-SO₂)₃(μ-CNXyl)₂(CNXyl)₅ (2.266(6) and 2.303(7) Å) [14c] and Pd₃(μ-CNCy)₃(CNCy)₃ (ave. 2.072(13) Å) [16].

Both the elongation of the C1–N1 bond length (1.244(8) Å) and the bending of the C1–N2–C2 angle (133.9(7)°) of the bridging isocyanide ligands are consistent with a reduction of the C–N bond order, as observed in Ru₃(CO)₆(μ₃-PPhCH₂PPh₂)(μ₃-CNCy)(CNCy)₂ [**21a**] and Pd₃(μ-CNCy)₃(CNCy)₃ [16]. This is probably due to the back-bonding interaction from Pd1 and Pd2 atoms to the carbon one. These reflect the ν(NC) absorptions of **4**, which

are observed at 2128 and 1679 cm⁻¹, assignable to terminal and bridging isocyanides, respectively.

All of the terminal isocyanide ligands were almost linear with an average C_{ter}–N–Xyl bond angle of 175.2°, and Pd–C_{ter} bond distances are ranging from 1.916(9) to 2.050(7) Å, comparable to those found for Pd₅(μ-SO₂)₃(μ-CNXyl)₂(CNXyl)₅ (1.973(7)–2.024(6) Å) [14c], Pd₃(μ-SO₂)₂(CNXyl)₂(PPh₃)₃ (ave. 2.049(4) Å) [14d], Pd₃(μ-CNCy)₃(CNCy)₃ (ave. 2.004(14) Å) [16], and Pd₃(μ-SO₂)₂(CN^tBu)₃ (1.99(3)–2.13(3) Å) [20].

In conclusion, we found that the dinuclear linear complex **2** underwent not only a normal, equimolar insertion of ‘Pd(CNXyl)₂’ fragment, source of which is the triangular complex **1**, but also a multiple insertion to afford the prospective linear trinuclear complex **3** and the unexpected hexapalladium complex **4**, respectively. Complex **4**, the skeleton of which contains a Pd tetrahedron core and two Pd atoms stretched out of it symmetrically, was selec-

Table 4
Selected bond lengths (Å) and angles (°) for **4**

Pd1–Pd2*	2.7800(7)	Pd1–C10	1.992(8)
Pd1–Pd2	2.8300(8)	Pd1–C19	2.031(8)
Pd1–Pd1*	2.9481(12)	Pd2–C28	1.994(8)
Pd2–Pd2*	2.7941(11)	Pd3–C37	1.937(9)
Pd2–Pd3	2.6535(7)	Pd3–C46	2.034(7)
Pd1–C1	2.003(7)	N2–C10	1.154(9)
Pd2–C1	1.977(7)	N3–C19	1.143(9)
Pd3–C1	2.513(7)	N4–C28	1.159(9)
Pd3–N1	2.074(6)	N5–C37	1.158(10)
N1–C1	1.247(8)	N6–C46	1.135(9)
<hr/>			
Pd2–Pd1–Pd1*	57.475(19)	N1–C1–Pd2	126.6(6)
Pd2*–Pd1–Pd2	59.74(2)	N1–C1–Pd1	142.8(6)
Pd2*–Pd1–Pd1*	59.127(18)	Pd2–C1–Pd1	90.6(3)
Pd1*–Pd2–Pd1	63.40(3)	C1–N1–C2	133.4(7)
Pd2*–Pd2–Pd1	59.244(19)	C1–N1–Pd3	95.1(5)
Pd1*–Pd2–Pd2*	61.020(18)	C2–N1–Pd3	131.5(4)
Pd3–Pd2–Pd1	108.80(2)		
Pd3–Pd2–Pd1*	151.79(3)	Pd1–C10–N2	178.3(7)
Pd3–Pd2–Pd2*	141.059(3)	Pd1–C19–N3	170.1(7)
C37–Pd3–C46	106.5(3)	Pd2–C28–N4	171.1(7)
C46–Pd3–N1	101.5(3)	Pd3–C37–N5	169.7(7)
C37–Pd3–Pd2	77.5(2)	Pd3–C46–N6	176.3(8)
N1–Pd3–Pd2	74.50(15)		

Symmetry transformations used to generate equivalent atoms (*): $-x, y, -z + 1/2$.

tively produced by the reaction of **3** with an equimolar amount of **1**.

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Appendix A. Supplementary data

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-292412 (**3**) and CCDC-292413 (**4**). These data can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.01.030](https://doi.org/10.1016/j.jorganchem.2006.01.030).

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