

One- or two-dimensional organometallic arrays containing PdIr₂(μ₃-S)₂ mixed-metal sulfido cluster units connected via the nicotinamide or isonicotinamide ligands on their Pd sites through hydrogen-bonding interactions

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Received 9 September 2003; accepted 25 November 2003

Abstract

Mixed-metal sulfido cluster [(PdCl₂)(Cp*Ir)₂(μ₃-S)₂] (Cp* = η⁵-C₅Me₅) dissolved in CH₂Cl₂ reacted with two equivalent of L (L = nicotinamide, isonicotinamide, or *N*-methylnicotinamide) in the presence of AgBF₄ to give the cationic clusters [(PdL₂)(Cp*Ir)₂(μ₃-S)₂][BF₄]₂. The single-crystal X-ray diffraction studies of these products have disclosed that in the solid state the PdIr₂S₂ cores are self-assembled to form one-dimensional chains through the intermolecular hydrogen-bonding between the amide groups for L = nicotinamide or two-dimensional sheets via the hydrogen-bonding between the amide groups and the BF₄ anions for L = isonicotinamide, whereas no organization of the cluster cores is observed for L = *N*-methylnicotinamide.

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Keywords: Mixed-metal sulfido clusters; Palladium; Iridium; Self-assembly; One-dimensional chain structure; Two-dimensional sheet structure

1. Introduction

Supramolecular frameworks containing transition metal species as building blocks are currently attracting significant attention due to their unique properties and their possible applications to high-performing materials. These extended arrays are constructed most conveniently through self-assembly of the building blocks by the aid of hydrogen-bonding interactions between the ligands bonded to the metals or bridging coordination of the multidentate ligands to two or more metals. However, despite the presence of a number of precedented examples of the well-defined metal-containing extended systems [1], those consisting of the metal clusters as the building blocks are quite rare (see, for example [2]). We wish to report here the self-assembly of

the PdIr₂S₂ cluster units yielding one-dimensional chain structure or two-dimensional sheet structure, where the aggregation of the clusters are driven by either the hydrogen-bonding interactions between the two amido groups of the nicotinamide ligands on the Pd atoms of the adjacent cluster cores or those between the amido hydrogens of the isonicotinamide ligands on the Pd atom and the BF₄ anions. During the initial submission of these results as a communication, Zheng and his coworkers reported the syntheses of *cis*- and *trans*-[Re₆(μ₃-Se)₈(PEt₃)₄(isonicotinamide)₂]²⁺, which form one-dimensional chains of the clusters through hydrogen-bonding between the ligated isonicotinamides in a solid state [3].

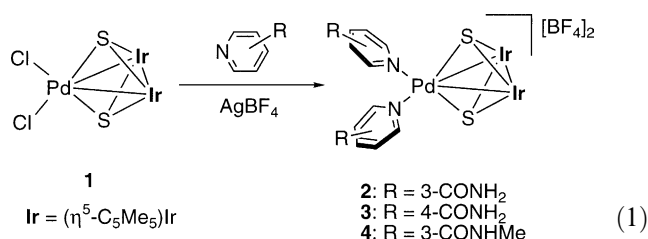
2. Results and discussion

When [(PdCl₂)(Cp*Ir)₂(μ₃-S)₂] (**1**, Cp* = η⁵-C₅Me₅) was treated with two equivalent of nicotinamide in the

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presence of two equivalent of AgBF_4 in CH_2Cl_2 at room temperature in the dark, a purple solid precipitated from the reaction mixture. Purification of this solid from MeCN–ether afforded $[\{\text{Pd}(3\text{-pyCONH}_2)_2\}(\text{Cp}^*\text{Ir})_2(\mu_3\text{-S})_2][\text{BF}_4]_2$ (**2**, py = pyridyl) as purple crystals with the composition **2** · MeCN in 54% yield (Eq. (1)). Cluster **2** was characterized by elemental analysis along with ^1H NMR spectroscopy, and the detailed structure in a solid state has been determined by an X-ray analysis.



As shown in Fig. 1(a), **2** has a triangular PdIr_2 core capped with two $\mu_3\text{-S}$ ligands. The bonding parameters associated with the PdIr_2S_2 core listed in Table 1 are essentially the same as those in the $[\{\text{Pd}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\}(\text{Cp}^*\text{Ir})_2(\mu_3\text{-S})_2][\text{BPh}_4]_2 \cdot \text{CH}_3\text{COCH}_3$ previously reported [4]. If the PdIr bonds are ignored, the geometry around Pd is square planar with two sulfide and two nicotinamide ligands, where the nicotinamides are bonded to the Pd site in a manner that the pyridine ring and the basal N_2S_2 plane are mutually oriented perpendicularly. Interestingly, the X-ray analysis has disclosed further that the cluster cations are connected through intermolecular hydrogen-bonding ($-\text{NH}\cdots\text{O}=\text{C}<$) between the amide groups with the $\text{H}\cdots\text{O}$ distances at 2.00(8) or 2.2(1) Å (Chart 1), affording a linear assembly of these cluster units along the *a*-axis. The bundle of these chains is shown in Fig. 1(b). The remaining NH hydrogens that are not involved in the hydrogen-bonding between the two amide groups are interacting with the BF_4 anions ($-\text{NH}\cdots\text{FBF}_3$) with the $\text{H}\cdots\text{F}$ distances at 2.2(2) or 2.1(2) Å.

For comparison, the reactions of **1** with related amides such as isonicotinamide and *N*-methylnicotinamide were also undertaken and the products have been fully characterized. Thus, analogous treatment of **1** with isonicotinamide in CH_2Cl_2 gave $[\{\text{Pd}(4\text{-pyCONH}_2)_2\}(\text{Cp}^*\text{Ir})_2(\mu_3\text{-S})_2][\text{BF}_4]_2$ (**3**) as a purple solid, which was crystallized from MeCN–ether in 52% isolated yield. From the reaction of **1** with *N*-methylnicotinamide under the similar conditions, $[\{\text{Pd}(3\text{-pyCONHMe})_2\}(\text{Cp}^*\text{Ir})_2(\mu_3\text{-S})_2][\text{BF}_4]_2$ (**4**) was obtained as purple crystals in 65% yield (Eq. (1)). Both clusters have also been characterized by the X-ray analyses, whose core structures are essentially the same as that of **2**. Selected bond lengths associated with the cluster cores in **3** and **4** are summarized in Table 1.

Fig. 2 depicts the packing of **3**, where the cluster cations are mutually linked through the hydrogen-bonding between the amide hydrogens and the BF_4 anions ($-\text{NH}\cdots\text{FBF}_2\text{F}\cdots\text{HN}$) with the $\text{H}\cdots\text{F}$ distances at 2.12(2) and 2.08(2) Å. Both hydrogens in the amido group undergo hydrogen-bonding with the different BF_4 anions to be linked to the different neighboring clusters, affording the sheet expanding parallel to the *ab*-plane. The amide oxygen atoms are not involved in the hydrogen-bonding network. These sheets pile up towards the direction of the *c*-axis to give the layered structure.

For **4**, although the X-ray analysis has disclosed that the amide hydrogens of the two *N*-methylnicotinamide ligands in the cluster core are each bonded to the BF_4 anions through hydrogen-bonding ($-\text{NH}\cdots\text{FBF}_3$) with the $\text{H}\cdots\text{F}$ distances at 2.02.2 Å (Fig. 3), no interactions are observable between these units consisting of the hydrogen-bonded cluster cation and the anions. It is noteworthy that the packings of the cluster cores in the crystals depends strikingly upon the nature of the nicotinamides, viz. directions to which the N–H bonds are pointing.

Related work on the self-assembly of the mononuclear $\text{Pd}(\text{L}_2)$ fragment (L_2 = diphosphines, bipyridine; L = monophosphine) using nicotinamides has appeared recently [5], while the formation of the self-assembled polymers containing, e.g., the hexanuclear Mo [6], dinuclear Zn [7], or mononuclear Pd or Fe [8] fragments combined via the hydrogen-bondings using the amido groups has been reported.

In conclusion, one-dimensional chain and two-dimensional sheet formed by the self-assembly of the $\text{PdIr}_2(\mu_3\text{-S})_2$ clusters have been exploited. The cluster cores are arranged via the hydrogen-bonding between the amide groups in the nicotinamides bound to the Pd site or that between the amide hydrogens of the isonicotinamides and the BF_4 anions. It has also been exploited that the similar networks form by employment of PF_6 and CF_3SO_3 anions in place of BF_4 anion, which will be described elsewhere. The study on the properties of these polymeric products is now in progress.

3. Experimental

3.1. General considerations

All manipulations were carried out under an atmosphere of N_2 . IR and NMR spectra were recorded on JASCO FT/IR 420 and JEOL alpha-400 spectrometers, respectively. Elemental analyses were performed on a Perkin–Elmer 2400 series II CHN analyzer. Complex **1** was prepared as reported previously [4], while other

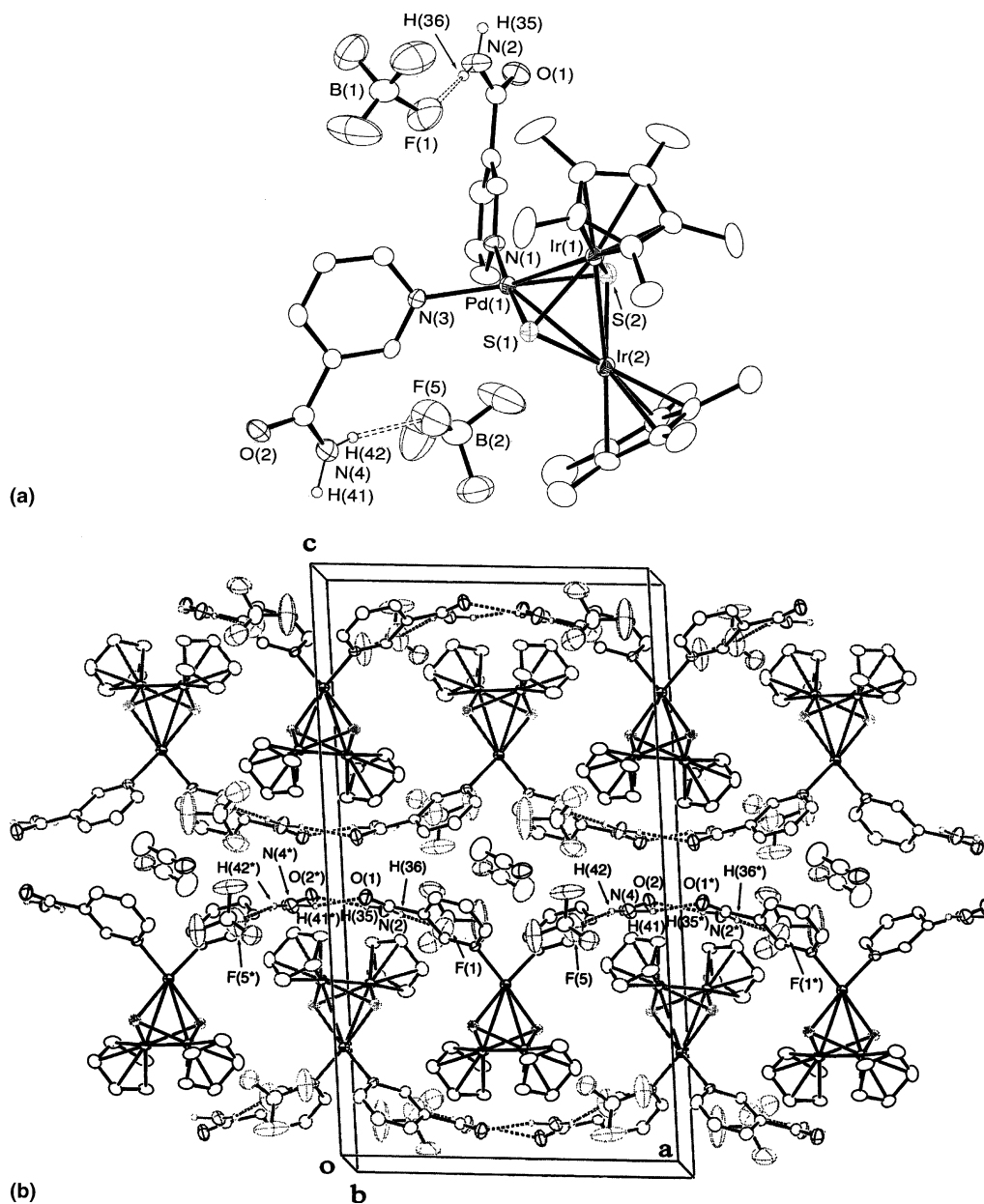


Fig. 1. An ORTEP drawing for **2** (a) and a polymeric chain structure in the crystal (b). Hydrogen-bonding distances: O(1)··H(41), 2.00(8); F(1)··H(36), 2.2(2); O(2)··H(35), 2.2(1); F(5)··H(42), 2.1(2) Å. For clarity, methyl groups of the Cp* ligands and CH hydrogen atoms are omitted in (b).

chemicals were commercially obtained and used as received.

3.2. Preparation of **2**

A mixture containing **1** (47 mg, 0.053 mmol), AgBF₄ (21 mg, 0.11 mmol), and nicotinamide (13 mg, 0.11 mmol) in CH₂Cl₂ (5 cm³) was stirred at room temperature for 24 h in the dark. A purple solid precipitated, which was filtered off and extracted with MeCN (5 cm³). Addition of ether (18 cm³) afforded **2**·MeCN as purple crystals (35 mg, 54% yield). ¹H NMR (CD₃CN, ppm):

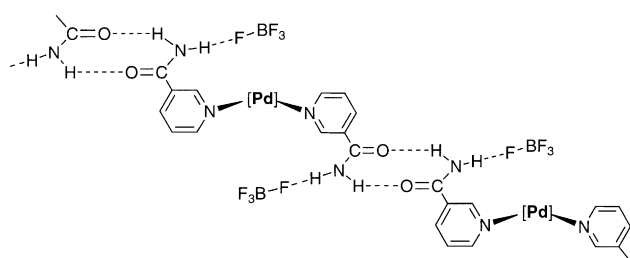
8.67 (br, 2H, H²-py), 8.34 (br, 2H, H⁶-py), 8.24 (d, *J* = 8 Hz, 2H, H⁴-py), 7.53 (dd, *J* = 8 and 5 Hz, 2H, H⁵-py), 6.92 (br, 2H, NH), 6.30 (br, 2H, NH), 2.17 (s, 30H, Cp*). IR (KBr, cm⁻¹): 3418, 3202 (N–H), 1689 (C=O), 1083 (B–F). Anal. Calc. for C₃₄H₄₅O₂N₅S₂B₂F₈Ir₂Pd: C, 31.80; H, 3.53; N, 5.45. Found: C, 31.42; H, 3.46; N, 5.33%.

3.3. Preparation of **3**

This compound was obtained similarly from **1** (53 mg, 0.059 mmol), AgBF₄ (23 mg, 0.12 mmol), and

Table 1
Selected bond distances in clusters **2**, **3**, and **4**

	2	4		3
Ir(1)–Ir(2)	2.9177(6)	2.9444(9)	Ir(1)–Ir(1)*	2.912(1)
Ir(1)–Pd(1)	2.9771(7)	2.9145(9)	Ir(1)–Pd(1)	2.966(1)
Ir(2)–Pd(1)	2.9960(7)	3.019(1)		
Ir(1)–S(1)	2.294(2)	2.301(3)	Ir(1)–S(1)	2.294(3)
Ir(1)–S(2)	2.292(2)	2.291(3)	Ir(1)–S(1)*	2.282(4)
Ir(2)–S(1)	2.290(2)	2.303(2)		
Ir(2)–S(2)	2.298(2)	2.286(3)		
Pd(1)–S(1)	2.286(2)	2.289(3)	Pd(1)–S(1)	2.289(4)
Pd(1)–S(2)	2.283(2)	2.287(2)		
Pd(1)–N(1)	2.093(6)	2.087(8)	Pd(1)–N(1)	2.09(1)
Pd(1)–N(2)	2.099(6)	2.096(7)		



[Pd]: Pd site in the PdIr₂S₂ core

Chart 1.

isonicotinamide (14 mg, 0.12 mmol) as purple crystals in 52% yield (32 mg). ¹H NMR (CD₃CN, ppm): 8.26 (m,

4H, H^{2,6}-py), 7.71 (m, 4H, H^{3,5}-py), 6.99 (s, 2H, NH), 6.16 (s, 2H, NH), 2.13 (s, 30H, Cp*). IR (KBr, cm⁻¹): 3449, 3398, 3346 (N–H), 1680 (C=O), 1059 (B–F). Anal. Calc. for C₃₂H₄₂O₂N₄S₂B₂F₈Ir₂Pd: C, 30.91; H, 3.40; N, 4.51. Found: C, 30.67; H, 3.32; N, 4.70%.

3.4. Preparation of **4**

A mixture containing **1** (60 mg, 0.067 mmol), *N*-methylnicotinamide (18 mg, 0.13 mmol), and AgBF₄ (26 mg, 0.13 mmol) in CH₂Cl₂ (5 cm³) was stirred at room temperature for 12 h and the resultant purple solution was filtered. Addition of ether (18 cm³) gave **4** as purple crystals in 86% yield (55 mg). ¹H NMR (CD₃CN, ppm):

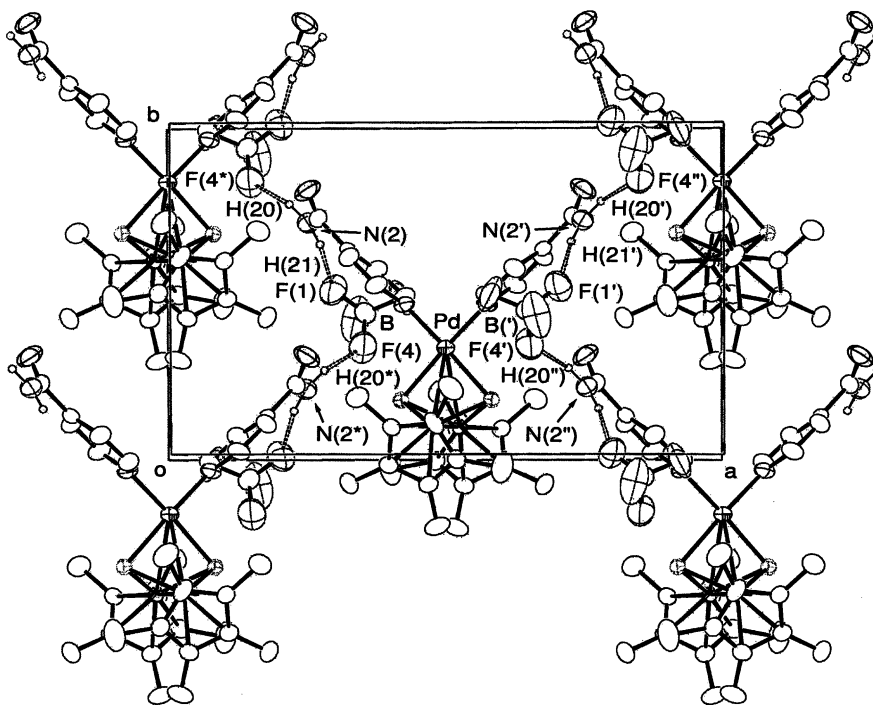


Fig. 2. Two-dimensional network observed in the crystal of **3**. Clusters are assembled in a sheet through hydrogen-bonding between the amide hydrogen and the BF₄ anion. Hydrogen-bonding distance: F(4)··H(20), 2.08(2); F(1)··H(21), 2.12(2) Å.

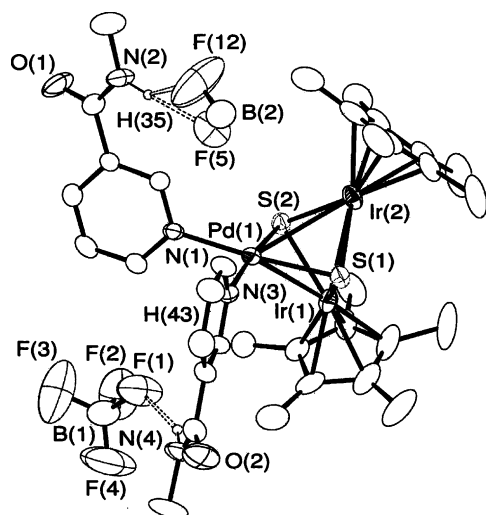


Fig. 3. An ORTEP drawing for **4**. For the BF_4 anion containing B(2), the F atoms are disordered at 10 positions, among which only two having the hydrogen-bonding interactions with N(2)–H(35) are shown. Hydrogen-bonding distance: F(1)···H(43), 2.00(1); F(5)···H(35), 2.15(2); F(12)···H(35), 2.18(8) Å.

8.65 (d, $J = 2$ Hz, 2H, H^2 -py), 8.43 (dd, $J = 6$ and 2 Hz, 2H, H^6 -py), 8.35 (dt, $J = 8$ and 2 Hz, 2H, H^4 -py), 7.57 (dd, $J = 8$ and 6 Hz, 2H, H^5 -py), 7.40 (br q, 2H, NH), 2.92 (d, $J = 5$ Hz, 6H, NMe), 2.22 (s, 30H, Cp*). IR (KBr, cm^{-1}): 3405 (N–H), 1677 (C=O), 1083 (B–F).

Anal. Calc. for $\text{C}_{34}\text{H}_{46}\text{O}_2\text{N}_4\text{S}_2\text{B}_2\text{F}_8\text{Ir}_2\text{Pd}$: C, 32.12; H, 3.65; N, 4.41. Found: C, 32.13; H, 3.64; N, 4.42%.

3.5. X-ray crystallography

Single crystals of **2**·MeCN, **3**, and **4** were sealed in glass capillaries under argon and mounted on a Rigaku Mercury CCD area detector with a graphite-monochromatized Mo $\text{K}\alpha$ source. Details are shown in Table 2.

Structure solution and refinements were carried out by using CrystalStructure program package [9]. The positions of non-hydrogen atoms were determined by Patterson methods (SHELX-97) [10] and subsequent Fourier synthesis (DIRDIF-99) [11], which were refined anisotropically. The NH hydrogens in **2** were also found in the Fourier map, which were refined isotropically, whereas those in **3** and **4** were placed at the calculated positions, assuming the planar amido moieties. All other hydrogens were also placed at the ideal positions and these as well as the NH hydrogens in **3** and **4** were included in the final stages of the refinements with fixed parameters. For one BF_4 anion in **4**, the F atoms were located at ten positions, which were modeled as three orientationally disordered anions B(2)F(5)F(6)F(7)F(8), B(2)F(5)F(9)F(10)F(11), and B(2)F(6)F(12)F(13)F(14), with the occupancies of 0.4, 0.3, and 0.3, respectively.

Table 2
Crystallographic data for **2**, **3**, and **4**

	2 ·MeCN	3	4
Formula	$\text{C}_{34}\text{H}_{45}\text{N}_5\text{O}_2\text{B}_2\text{F}_8\text{S}_2\text{PdIr}_2$	$\text{C}_{32}\text{H}_{42}\text{N}_4\text{O}_2\text{B}_2\text{F}_8\text{S}_2\text{PdIr}_2$	$\text{C}_{34}\text{H}_{46}\text{N}_4\text{O}_2\text{B}_2\text{F}_8\text{S}_2\text{PdIr}_2$
Formula weight	1284.33	1243.28	1271.33
Space group	$P2_1/n$ (no. 14)	$Pbcn$ (no. 60)	$P\bar{1}$ (no. 2)
Unit cell dimensions			
a (Å)	13.079(3)	17.775(3)	10.994(2)
b (Å)	14.088(3)	10.885(2)	13.186(3)
c (Å)	23.891(3)	20.788(4)	16.608(2)
α (°)	90.00	90.00	88.48(1)
β (°)	93.66(2)	90.00	75.16(1)
γ (°)	90.00	90.00	70.81(1)
V (Å ³)	4393(1)	4022(1)	2193.5(7)
Z	4	4	2
ρ_{calc} (g cm^{-3})	1.942	2.053	1.925
μ_{calc} (cm^{-1})	66.30	72.38	66.38
Crystal size (mm ³)	0.20 × 0.20 × 0.30	0.50 × 0.50 × 0.05	0.60 × 0.60 × 0.40
Number of data used	7302	2505	5645
Number of variables	563	262	597
Transmission factor	0.30–1.00	0.20–1.00	0.58–1.00
R^a	0.038	0.052	0.040
wR_2^b	0.098	0.120	0.093
Goodness-of-fit (GOF) ^c	1.03	1.02	0.98
Residual peaks (e Å^{-3})	1.77, −1.72	1.60, −1.30	1.13, −1.28

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

$$^c \text{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\{(\text{no. observed}) - (\text{no. variables})\}} \right]^{1/2}.$$

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 205340–205342 for compounds **2**, **3**, and **4**, respectively. Copies of this information is available 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>).

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 14078206, Reaction Control of Dynamic Complexes) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and by CREST of JST (Japan Science and Technology Corporation).

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