Platinumbis(azido)dppf Compound: Preparation, Structure, and Reactivity to Isocyanides of [Pt(dppf)(N_3)$_2$] (dppf = 1,1'-Bis(diphenylphosphino)ferrocene)

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The chemistry of the azido (N_3^-) ligand coordinated to late transition metals has received continual interests because of interesting magnetic, structural, and reactivity properties, including the 1,3-dipolar cycloaddition to give heterocycles and the thermal or photochemical N–N bond cleavage to give metal–imido (M=N–R) compounds.[1-5] In particular, group 10 metal–azido compounds containing phosphine or amine ligands have been intensely studied owing to their novel reactivity such as the formation of metal nitrides or clusters.[6-11]

Recently, we have reported the preparations, structures, and properties of several azido or bis(azido) compounds of Pd(II) and Pt(II) containing small tertiary phosphines.[12-15] In particular, we found that *cis*-[M(N_3)$_2$(PR_3)$_2$] (M = Pd or Pt; PR_3 = PMe_3 or PEt_3) reacted with 2 equiv of isocyanide (RNC: R = *t*-Bu, *n*-Bu, or cyclohexyl) to give *trans*-[M(CN_4(R))$_2$(PR_3)$_2$]. Moreover, the reaction of 2,6-dimethylphenyl isocyanide with *cis*-[Pd(N_3)$_2$(PR'_3)$_2$] (PR'_3 = PMe_3, PEt_3, or $PMePh_2$) led to *trans*-[Pd(CN_4(R))(N=C=NC_6H_3-2,6-Me_2)(PR'_3)$_2$] with the liberation of N_2, which contains a *C*-coordinated tetrazolato ligand and a carbodiimido ligand.[15] These results suggest that the reactivity of [M(N_3)$_2$(PR_3)$_2$] (M = Pd or Pt) depends at least on the type of the organic isocyanide. As an extension of our work, we have investigated the preparation and reactivity of the platinum–bis(azido) compound containing the dppf ligand (1,1'-bis(diphenylphosphino)ferrocene). We employed this sterically demanding, chelating phosphine ligand (dppf) due to its streic bulk that might lead to the formation of desirable bis(carbodiimido) compounds rather than either bis(tetrazolato) compounds or those containing one tetrazolato and one carbodiimido. The dppf ligand is one of the efficient stabilizing agents for transition metal-catalyzed cross-coupling reactions as well as a redox-active ligand for electrochemical studies.[16] Herein we report the preparation, structural characterization, and reactions with isocyanides of Pt(dppf)(N_3)$_2$.

Experimental Section

Unless otherwise stated, all reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were manipulated in a glove box filled with argon. [$PtCl_2$(SMe_2)$_2$], 1,1'-bis(diphenylphosphino)-ferrocene (dppf = Fe(η^5-$C_5H_4PPh_2$)$_2$), and [$PtCl_2$(dppf)] were prepared by literature methods.[17-19]

^{1}H-, ^{13}C{^{1}H}, and ^{31}P{^{1}H}-NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Institute.

Preparation of [Pt(N_3)$_2$(dppf)] (1). Compound **1** was prepared in one of the following two methods.

Method 1. A mixture of [$PtCl_2$(dppf)] (0.10 g, 0.122 mmol) and NaN_3 (0.016 g, 0.250 mmol) in 30 mL of CH_2Cl_2 was stirred at room temperature for 48 h. The orange-brown solution was filtered and then evaporated under vacuum. The residue was washed with diethyl ether (20 mL × 2) and hexane (20 mL × 2), and then dried under vacuum to give 0.055 g of **1** (0.067 mmol, 55%).

Method 2. [$PtCl_2$(dppf)] (0.10 g, 0.122 mmol) and Mg (0.014 g, 0.35 mmol) in 30 mL of THF were cooled to 0 °C. After 10 min, neat $(CH_3)_3SiN_3$ (0.2 mL, 1.47 mmol) was added slowly to this solution. The mixture was stirred at 50 °C in a water bath for 60 h. The orange-brown solution was filtered and then evaporated under vacuum. The residue was washed with diethyl ether (20 mL × 2) and hexane (20 mL × 2) and then dried under vacuum to give 0.034 g of **1** (0.041 mmol, 34%). ^{1}H-NMR ($CDCl_3$): δ 7.41-7.79 (m, 20H), 4.21 (d, 4H), 4.39 (d, 4H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 135.1-129.1 (*Ph*), 76.4 (C_5H_4), 74.4 (C_5H_4), 66.6 (C_5H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 11.76 (J_{PtP} = 3589 Hz) IR: 2052 cm^{-1} (N_3). mp: 247-249 °C.

Preparation of [Pt($CN_4C_6H_{11}$)$_2$(dppf)] (2). To an orange-brown solution of compound **1** (0.03 g, 0.036 mmol) in 20 mL of CH_2Cl_2 was added neat cyclohexyl isocyanide (6.0 μL, 0.048 mmol) at room temperature. The solution was stirred for 24 h, and the solvent was removed under vacuum. The residue was washed with diethyl ether (20 mL × 2) and hexane (20 mL × 2), and then dried to give 0.015 g of compound **2** (0.016 mmol, 70%). ^{1}H-NMR ($CDCl_3$): δ 6.92-8.21 (m, 20H), 4.38 (d, 2H), 4.76 (d, 2H), 4.04 (d, 2H), 4.30 (d, 2H), 0.56-1.67 (br, 10H, cyclohexyl), 4.48 (m, 1H, cyclohexyl). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 139.2-128.7 (*Ph*), 75.8-71.5 (C_5H_4), 59.0 (cyclohexyl), 32.3 (cyclohexyl), 26.4

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(cyclohexyl), 26.0 (cyclohexyl). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 10.92 (J_{PtP} = 2259 Hz). mp: 170-172 °C. IR (KBr): 2230 (NCN) cm^{-1}. Anal. Calcd for $C_{48}H_{50}N_8P_2FePt$: C, 54.81; H, 4.75; N, 10.65. Found: C, 55.12; H, 5.18; N, 10.32.

Preparation of [Pt(CN_4-*t*-Bu)$_2$(dppf)] (3). This compound was prepared similar to compound **2**. Compound **1** (0.03 g, 0.036 mmol) was treated with excess *tert*-butyl isocyanide (0.1 mL, 0.884 mmol) to give 0.028 g of compound **3** (0.028 mmol, 78%). ^1H-NMR ($CDCl_3$): δ 6.70-8.27 (m, 20H), 4.40 (d, 2H), 4.87 (d, 2H), 3.84 (d, 2H), 4.24 (d, 2H), 1.18 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 153.9 (CN_4, J = 27.5 Hz), 152.8 (CN_4, J = 27.5 Hz), 138.3-128.6 (*Ph*), 77.9-72.7 (C_5H_4), 59.4 (CMe_3), 30.6 (CMe_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 10.80 (J_{PtP} = 2295 Hz). mp: 169-171 °C. IR (KBr): 2236 (NCN) cm^{-1}. Anal. Calcd for $C_{44}H_{46}N_8P_2FePt$: C, 52.87; H, 4.62; N, 11.21. Found: C, 52.78; H, 4.74; N, 11.36.

X-ray structure determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 28 (for **1**), 31 (for **2**·2$CHCl_3$), or 23 (for **3**·CH_2Cl_2) reflections in the range of 15.0° < 2θ < 25.0°. Three check-reflections were measured every 100 reflections throughout data collection and showed no noticeable variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with the use of SHELXTL programs.[20]

Table 1. X-ray data collection and structure refinement

	1	2·2CHCl$_3$	3·CH$_2$Cl$_2$
formula	$C_{34}H_{28}N_6$-P_2FePt	$C_{50}H_{52}N_8$-P_2Cl_6FePt	$C_{45}H_{48}N_8$-P_2Cl_2FePt
fw	833.50	1290.58	1084.69
temperature, K	296(2)	296(2)	295(2)
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	10.957(1)	15.537(2)	10.503(1)
b, Å	12.377(1)	16.806(2)	11.628(1)
c, Å	15.236(1)	20.591(3)	20.823(1)
α, deg	107.776(7)		76.472(7)
β, deg	94.098(7)	100.23(1)	80.854(6)
γ, de	114.408(6)		67.114(8)
V, Å^3	1744.5(3)	5291(1)	2271.4(4)
Z	2	4	2
d_{cal}, g cm^{-3}	1.587	1.620	1.586
μ, mm^{-1}	4.544	3.322	3.625
T_{min}	0.2296	0.0848	0.0593
T_{max}	0.6922	0.5396	0.1143
F(000)	816	2576	1084
No. of reflections measured	6293	8538	8387
No. of reflections unique	5972	8280	7946
No. of reflections with $I > 2\sigma(I)$	5557	5717	7412
No. of parameters refined	398	624	533
2θ range (°)	3.5-50.0	3.5-50.0	3.5-50.0
scan type	ω	ω	ω
scan speed	variable	variable	variable
GOF (goodness-of-fit on F^2)	1.077	0.990	1.049
Max., min. in Δρ (e Å^{-3})	2.200, -2.222	0.665, -0.662	1.225, -0.746
R	0.0425	0.0533	0.0297
wR_2[a]	0.1079	0.0977	0.0746

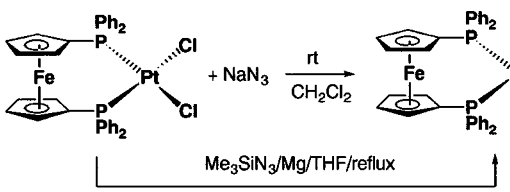
[a] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

All crystal structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the two co-crystallized chloroform molecules in **2**·2$CHCl_3$ were not located. All remaining hydrogen atoms were generated in ideal positions and refined in a riding model.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 182496 for **1**, 182495 for **2**·2$CHCl_3$, and 182494 for **3**·CH_2Cl_2. Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or *http://www.ccdc.cam.ac.uk*).

Results and Discussion

Preparation of [Pt(N_3)$_2$(dppf)] (1). The platinum–bis(azido)–dppf compound (**1**) can be prepared in two ways. In dichloromethane at room temperature, [PtCl_2(dppf)] reacts with an inorganic azide (NaN_3) to give compound **1** (eq 1). In a refluxing THF, the reaction of [PtCl_2(dppf)] with an organic azide (Me_3SiN_3) in the presence of Mg also leads to the formation of **1**. However, the latter reaction requires more vigorous conditions (the reducing agent Mg, the refluxing THF, and a longer reaction time) and gave a lower yield.



(1)

Interestingly, the platinum–bis(azido) compound **1** is thermally stable in the solid state and in solution. For example, **1** melts at 247-249 °C without the liberation of N_2. The IR spectrum of **1** shows a strong absorption band at 2052 cm^{-1} corresponding to the azido group. On treatment with excessive HCl in diethyl ether, compound **1** is converted back to the starting material (eq 2).

$$\mathbf{1} + \text{HCl (in Et}_2\text{O)} \rightarrow [\text{PtCl}_2\text{(dppf)}] \quad (2)$$

Structure of compound 1 The molecular structure of **1** is shown in Figure 1, which displays two azido (N_3^-) and one

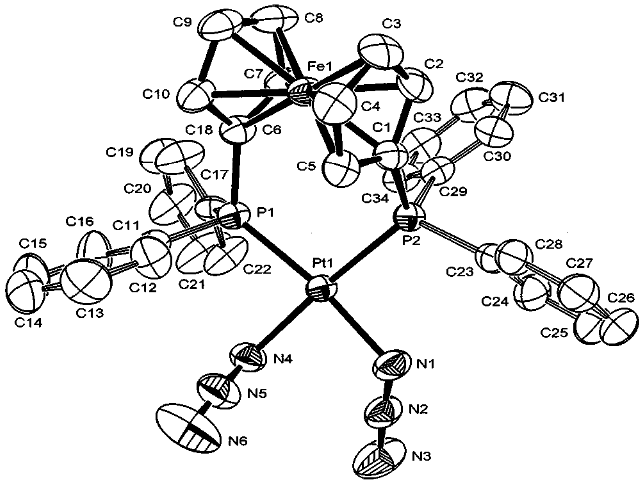
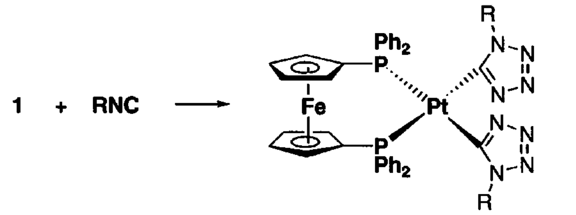


Figure 1. *ORTEP* drawing of **1**, showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond distances (Å) and bond angles (°): Pt1–N1 2.071(6), Pt1–N4 2.079(5), Pt1–P2 2.259(2), Pt1–P1 2.263(2), N1–N2 1.174(9), N2–N3 1.151(10), N4–N5 1.187(9), N5–N6 1.129(11); N1–Pt1–N4 87.4(2), P2–Pt1–P1 99.49(5), N2–N1–Pt1 121.0(5), N3–N2–N1 174.9(8), N5–N4–Pt1 118.7(5), N6–N5–N4 174.0(9).

dppf ligands. The coordination sphere of the Pt metal can be described as a distorted square plane. The equatorial plane, defined by N1, N4, P1, P2, and Pt1, is roughly planar with the average atomic displacement of 0.1551 Å. The bond angles (174.9(8)° and 174.0(9)°) of N–N–N in the azio ligand are consistent with the range found for coordinated azido ligands (173-180°).[21]

The two Cp rings are not perfectly parallel but twisted from each other with the dihedral angle of 4.6(3)°. The torsion angle of P1–C1–C6–P2 is 34.1(3)°, indicating that the two Cp rings adopt a gauche (or staggered) conformation. For comparison, the ideal torsion angles for the gauche and eclipsed conformations are 36° and 72°, respectively. Both distances of Fe–Ct (Ct: a centroid of the Cp ring) are 1.641 Å, and the angle of the Ct1–Fe–Ct2 (Ct1: C1–C5; Ct2: C6–C10) is 178.86°. The bite angle of P1···Pt···P2 is 61.87(4)°, and the distance of P1···P2 is 3.451(2) Å. The above bonding parameters within a ferrocene moiety are consistent with those found in octahedral platinum compounds in which the dppf group acts as a ligand.[16] The distance of Pt···Fe is 4.222(1) Å, which clearly rules out direct interactions between the two metals.

Reactions of 1 with isocyanides. When [$PtCl_2$(dppf)] is directly treated with isocyanide, no reaction occurs. On the other hand, the platinum–bis(azido) compound **1** reacts with *tert*-butyl and cyclohexyl isocyanides to give sterically congested compounds (**2** and **3**), which contain two *C*-bonded tetrazolate rings and one dppf ligand (eq 3). This reaction is somewhat unusual because the reaction might have given either a mono(carbodiimido) or even a bis(carbodiimido) compound to relieve the steric hindrance in the product. Analogous cycloaddition reactions of platinum–bis(azido) compounds with isocyanides were previously studied by Beck and co-workers.[22-26] According to their works, the reactions of compounds of Pd(II), Cu(I), Ag(I), and Au(I) having terminal or bridging azido ligands with CS_2 or CF_3CN gave the compounds containing the *N*-coordinated tetrazolate ring. On the other hand, as stated above, *cis*-[$M(N_3)_2(PR_3)_2$] reacted with isocyanide to give either *trans*-[$M(CN_4(R))_2(PR_3)_2$] or *trans*-[$Pd(CN_4(R))(N{=}C{=}N{-}R)(PR_3)_2$] with the change in the configuration from *cis* to *trans*. In addition, *cis*-[$M(N_3)_2$(dppe)] (dppe = $Ph_2PCH_2CH_2PPh_2$), which contains the chelating bidentate ligand (dppe) similar to compound **1**, reacted with 2,6-dimethylphenyl isocyanide to a bis(carbodiimido) compound, *cis*-[$M(N{=}C{=}N{-}C_6H_3\text{-}2,6\text{-}Me_2)_2$(dppe)].[15] Considering the steric bulk of the dppe and dppf lignads, it might be deduced that the steric factor does not play a dominant role in deriving the reaction to form bis(carbodiimido) compounds in our system.



(3)

R = cyclohexyl (**2**); *t*-Bu (**3**)

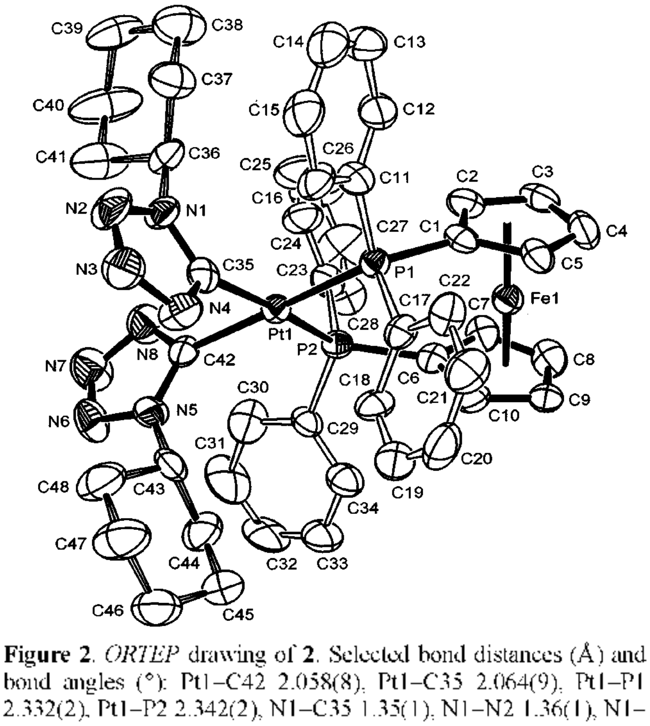


Figure 2. *ORTEP* drawing of **2**. Selected bond distances (Å) and bond angles (°): Pt1–C42 2.058(8), Pt1–C35 2.064(9), Pt1–P1 2.332(2), Pt1–P2 2.342(2), N1–C35 1.35(1), N1–N2 1.36(1), N1–C36 1.46(1), N2–N3 1.28(1), N3–N4 1.36(1), N4–C35 1.33(1), N5–C42 1.36(1), N5–N6 1.36(1), N5–C43 1.46(1), N6–N7 1.27(1), N7–N8 1.36(1), N8–C42 1.32(1); C42–Pt1–C35 84.7(3), P1–Pt1–P2 101.43(8), C35–N1–N2 108.9(7), C35–N1–C36 129.0(7), N2–N1–C36 122.1(7), N3–N2–N1 106.1(7), N2–N3–N4 111.4(8), C35–N4–N3 106.3(8), C42–N5–N6 107.7(7), C42–N5–C43 130.3(7), N6–N5–C43 121.9(7), N7–N6–N5 106.5(8), N6–N7–N8 112.3(8), C42–N8–N7 105.1(8).

Structures of 2 and 3. The molecular structures of **2** and **3** are shown in Figures 2 and 3, respectively. Each compound has two *C*-bonded tetrazolate rings and one bidentate dppf ligand. The coordination sphere of each Pt can be described as distorted square-planar. The equatorial plane, defined by two tetrazolate-ring carbon atoms, two phosphorus atoms, and the Pt metal, is relatively planar with the average atomic displacement of 0.073 Å for **2** or 0.004 Å for **3**.

Two heterocyclic five-membered tetrazolate rings in each compound are essentially planar with the average atomic displacement of 0.001-0.008 Å. These two rings are mutually perpendicular with the dihedral angle of 79.1(3)° (**2**) or 76.2(2)° (**3**), and are also virtually perpendicular to the equatorial plane with the dihedral angles of 76.5(3)°-85.5(2)°. The substituents [cyclohexyl (**2**) or *tert*-butyl (**3**)] on the two tetrazolate rings seem to orient as far as possible. The relative orientation of the substituents probably result from the steric congestion due to the streically demanding tetrazolato ligands formed in the reaction.

The two Cp rings in compounds **2** and **3**, as in compound **1**, are twisted from each other with the dihedral angle of 5.2(4)° (**2**) or 4.4(4)° (**3**). As expected, the conformation of the two Cp rings in the dppf ligand severely deviates from the gauche conformation with the P1–C1–C6–P2 torsion angle of 51.4(6)° or 52.7(3)°. The Fe–Ct distances are 1.657 Å and 1.661 Å (**2**) or 1.648 Å and 1.649 Å (**3**). The Ct1–Fe–Ct2 (Ct1: C1–C5; Ct2: C6–C10) angle is 169.13° (**2**) or 179.51° (**3**). The P···Fe···P bite angle is 64.53(6)° (**2**) or 65.10 (3)° (**3**), and the P1···P2 distance is 3.617(3) Å (**2**) or 3.637(1) Å (**3**). The long Pt···Fe (4.344(1) or Å (**2**) 4.331(1) Å (**3**)) distance indicates no direct interactions between the two metals.

In summary, we have prepared a platinum–bis(azido)dppf compound, $[Pt(N_3)_2(dppf)]$, which was treated with isocyanide (RNC; R = *t*-Bu or C_6H_{11}) to give a bis(terazolato) compound, $[Pt(CN_4{-}R)_2(dppf)]$. All compounds have been structurally characterized by X-ray diffraction.

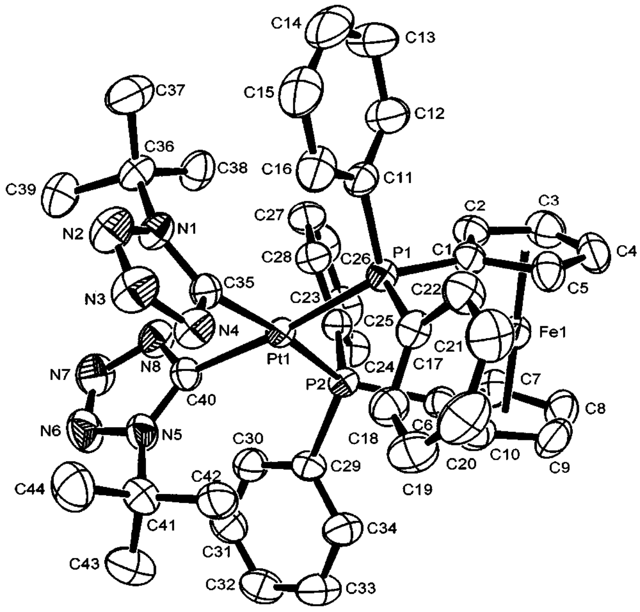


Figure 3. *ORTEP* drawing of **3**. Selected bond distances (Å) and bond angles (°): Pt1–C40 2.066(4), Pt1–C35 2.067(4), Pt1–P2 2.342(1), Pt1–P1 2.351(1), N1–C35 1.361(5), N1–N2 1.365(5), N1–C36 1.506(5), N2–N3 1.289(6), N3–N4 1.361(5), N4–C35 1.330(5), N5–C40 1.356(5), N5–N6 1.374(5), N5–C41 1.495(6), N6–N7 1.295(6), N7–N8 1.366(5), N8–C40 1.345(5); C40–Pt1–C35 85.2(2), P2–Pt1–P1 101.59(3), C35–N1–N2 108.5(3), C35–N1–C36 135.5(3), N2–N1–C36 115.9(3), N3–N2–N1 106.9(3), N2–N3–N4 110.3(3), C35–N4–N3 107.7(3), C40–N5–N6 108.8(4), C40–N5–C41 135.6(3), N6–N5–C41 115.5(3), N7–N6–N5 106.4(4), N6–N7–N8 110.8(4), C40–N8–N7 106.9(4).

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