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Bis(azido) compounds of Pd and Pt with bulky phosphine ligands (dppn = 1,8-bis(diphenylphosphino)naphthalene, dppf = 1,1′-bis(diphenylphosphino)ferrocene, 1-dpn = 1-diphenylphosphino-naphthalene): Preparation, structures, and reactivity toward isocyanides

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Abstract

Pd-bis(azido) compounds [Pd(dppn)$(N_3)_2$] and [Pd(dppf)$(N_3)_2$], which contain bulky chelating bis(phosphine) ligands (dppn = 1,8-bis (diphenylphosphino)naphthalene, dppf = 1,1′-bis(diphenylphosphino)ferrocene), were prepared from the corresponding chlorides and NaN_3. We also prepared the Pt-bis(azido) compound [Pt(1-dpn)$(SMe_2)(N_3)_2$] containing a bulky monodentate phosphine (1-dpn = 1-diphenylphosphino-naphthalene). All these compounds underwent [2 + 3] cycloaddition with isocyanides (R–NC, R = cyclohexyl, *tert*-butyl, 2,6-dimethylphenyl) to convert azido ligands to five-membered, *C*-coordinated tetrazolate rings. In addition, we observed the [Pd(dppn)Cl_2]-mediated C–C coupling of PhC≡CH to generate the η^2-PhC≡C–C≡CPh ligand. All compounds have been structurally characterized by X-ray diffraction.

Keywords: dppn; dppf; 1-dpn; Pd- and Pt-bis(azido) compounds; Isocyanide

1. Introduction

[2 + 3] Cycloaddition of unsaturated organic compounds, such as isocyanide, nitrile, carbon disulfide, and alkyne, to the metal–azido bond has long been attracted [1–11]. These reactions usually give *C*- or *N*-coordinated tetrazolato or triazolato metal compounds, depending on the nature of the unsaturated compounds and spectator ligands.

We previously reported the preparation, structure, and reactivity of the Pt-bis(azido) compound, [Pt(dppf)$(N_3)_2$], which contains a bulky chelating ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) [12]. Reactions of [Pt(dppf)$(N_3)_2$] with isocyanide (R–NC, R = *tert*-butyl or cyclohexyl) gave *C*-coordinated tetrazolato Pt compounds. We also reported the structure of a cyclic dimer [$Pd_2(C_8H_4N_6)_2(PMe_3)_4$], which was prepared from $Pd(PMe_3)_2(N_3)_2$ and 1,4-phenylene diisocyanide ($C_6H_4(NC)_2$) [13]. This cyclic compound contains both carbodiimido and *C*-tetrazolato ligands, formed by concomitant N–C coupling with N_2 elimination (for the carbodiimido ligand) and [2 + 3] cycloaddition (for the *C*-tetrazolato ligand). In addition, we have studied cycloaddition of alkynes mediated by Pd and Rh complexes for several years [14–17]. In particular, we found that [Pd(dppf)Cl_2] mediated the trimerization of phenylethynes (PhC≡CH) in the presence of triethylamine in ethanol to give [Pd(dppf)(2,3,5-triphenylfulvene)], which contains a fulvene group [15].

As a continuous research, we decided to investigate the reactivity of bis(azido) compounds of Pd and Pt that contain bulky phosphine ligands, including dppf, 1,8-bis(diphenylphosphino)naphthalene (dppn), and 1-(diphenylphosphino)-naphthalene (1-dpn). Our study was focused on the reactivity of these compounds toward isocyanides (R–NC, R = cyclohexyl, *tert*-butyl, 2,6-dimethylphenyl). Herein, we report the preparation, structures, and reactivity of [Pd(dppn)$(N_3)_2$] (**1**), [Pd(dppf)$(N_3)_2$] (**4**), and [Pt(1-dpn)$(SMe_2)(N_3)_2$] (**6**).

2. Experimental

All reactions have been performed at room temperature under argon. Sodium azide, cyclohexyl isocyanide, *tert*-butyl

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isocyanide, 2,6-dimethylphenyl isocyanide, and phenylethyne (phenylacetylene, PhC≡CH) were purchased. [Pd(dppn)Cl_2] [18], [Pd(dppf)Cl_2] [19], and [Pt(1-dpn)(SMe_2)Cl_2] [18] were prepared by the literature methods. All products were recrystallized from CH_2Cl_2-pentane.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer. IR spectra were recorded with a Nicolet 320 FT IR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Center.

2.1. Preparation of [Pd(dppn)(N_3)$_2$] (**1**)

NaN_3 (0.064 g, 0.891 mmol) was added to 30 ml of THF containing [Pd(dppn)Cl_2] (0.20 g, 0.297 mmol), and then the resulting slurry was stirred for 48 h. The solvent was removed under vacuum to give yellow solids, which were extracted with 30 ml of CH_2Cl_2. The solvent was evaporated under vacuum and washed with hexane (2×10 ml) to give yellow solids of **1** (0.17 g, 0.248 mmol, 84%). ^1H NMR ($CDCl_3$): δ 8.21 (2H, d, $J = 3.5$ Hz, Np), 7.54 (2H, t, $J = 7.5$ Hz, Np), 7.44 (2H, m, Np), 7.41–7.23 (20H, m, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.1–120.1 (Np+PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.2. Anal. Calcd for $C_{34}H_{26}N_6P_2Pd$: C, 59.45; H, 3.81; N, 12.23. Found: C, 60.01; H, 3.98; N, 11.99. Mp (dec.): 143–145 °C. IR (KBr): 2063 (N_3) cm^{-1}.

2.2. Preparation of [Pd(dppn)(CN_4–Cy)$_2$] (2)

To a yellow solution of compound **1** (0.10 g, 0.148 mmol) in 25 ml of CH_2Cl_2 was added excess cyclohexyl isocyanide (0.097 g, 0.885 mmol). The resulting solution was stirred for 6 h, and the solvent was removed under vacuum and washed with hexane (2×10 ml) to give bright yellow solids of **2** (0.056 g, 0.062 mmol, 42%). δ 8.16 (2H, d, $J = 7.0$ Hz, Np), 7.52–7.46 (4H, m, Np), 7.35–7.12 (20H, broad, m, PPh_2), 4.67 (2H, m, cyclohexyl), 1.67–1.07 (20H, broad, m, cyclohexyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.8 (dd, $J_{C-P} = 166$ (trans), 25 (cis), CN_4), 138.9–123.4 (Np+PPh_2), 58.9 (cyclohexyl), 54.1 (cyclohexyl), 33.8 (cyclohexyl), 25.9 (cyclohexyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.4. Anal. Calcd for $C_{48}H_{48}N_8P_2Pd$: C, 63.68; H, 5.34; N, 12.38. Found: C, 63.54; H, 5.47; N, 12.55. Mp (dec.): 178–180 °C. IR (KBr): 2127 (s) cm^{-1}.

2.3. Preparation of [Pd(dppn)(η^2-PhC≡C–C≡CPh)] (3)

To a yellow solution of [Pd(dppn)Cl_2] (0.15 g, 0.214 mmol) in 25 ml of CH_2Cl_2 and 15 ml of ethanol was added 0.12 ml of NEt_3 (0.087 g, 0.860 mmol) and 0.23 ml of PhC≡CH (0.22 g, 2.15 mmol). The solution was stirred for 10 h, and the resulting solution was concentrated under vacuum to give a bright brown powder. The resulting precipitates were filtered and washed with diethyl ether (2×10 ml) and hexane (2×10 ml) to give yellow solids of **3** (0.083 g, 0.105 mmol, 49%). δ 8.21–8.14 (2H, m, Np), 7.53–7.39 (4H, m, Np), 7.37–7.17 (30H, m, PPh_2+phenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.6–122.0 (Np+PPh_2+phenyl), 81.8 (C≡C), 74.1 (C≡C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.4 (1P, d, $J = 73.3$ Hz), 9.5 (1P, d, $J = 73.3$ Hz). Anal. Calcd for $C_{50}H_{36}P_2Pd$: C, 74.59; H, 4.51. Found: C, 74.85; H, 4.38. Mp (dec.): 144–146 °C. IR (KBr): 2156 (C≡C) cm^{-1}.

2.4. Preparation of [Pd(dppf)(N_3)$_2$] (**4**)

NaN_3 (0.075 g, 1.038 mmol) was added to 30 ml of CH_2Cl_2 containing [Pd(dppf)Cl_2] (0.20 g, 0.346 mmol), and then the resulting slurry was stirred for 48 h. The solvent was removed under vacuum to give dark orange solids, which were extracted with 30 ml of CH_2Cl_2. The solvent was evaporated under vacuum and washed with hexane (2×10 ml) to give orange solids of **4** (0.185 g, 0.249 mmol, 72%). ^1H NMR ($CDCl_3$): δ 7.80–7.26 (20H, m, PPh_2), 4.42 (4H, d, $J = 1.5$ Hz, C_5H_4), 4.23 (4H, d, $J = 1.5$ Hz, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.1–129.4 (PPh_2), 76.86–74.54 (C_5H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.8. Anal. Calcd for $C_{34}H_{28}N_6P_2FePd$: C, 54.83; H, 3.79; N, 11.28. Found: C, 54.85; H, 3.95; N, 11.04. Mp (dec.): 225–226 °C. IR (KBr): 2043 (N_3) cm^{-1}.

2.5. Preparation of [Pd(dppf)(CN_4-t-Bu)$_2$] (**5**)

This compound was prepared similarly to compound **2**. Compound **4** (0.10 g, 0.134 mmol) was treated with excess *tert*-butyl isocyanide (0.067 g, 0.806 mmol) to give yellow solids of **5** (0.058 g, 0.064 mmol, 48%). ^1H NMR ($CDCl_3$): δ 8.21–6.63 (20H, broad, m, PPh_2), 4.82 (2H, s, C_5H_4), 4.36 (2H, s, C_5H_4), 4.25 (2H, s, C_5H_4), 3.83 (2H, s, C_5H_4), 1.22 (18H, s, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.3–128.7 (PPh_2), 77.9–72.7 (C_5H_4), 58.88 (CMe_3), 30.20 (CMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.4. Anal. Calcd for $C_{44}H_{46}N_8P_2FePd$: C, 58.01; H, 5.09; N, 12.30. Found: C, 58.85; H, 5.30; N, 11.99. Mp (dec.): 148–150 °C. IR (KBr): 2236 (s) cm^{-1}.

2.6. Preparation of [Pt(1-dpn)(SMe_2)(N_3)$_2$] (**6**)

This compound was prepared similarly to compound **4**. [Pt(1-dpn)(SMe_2)Cl_2] (0.30 g, 0.468 mmol) was treated with excess NaN_3 (0.09 g, 1.415 mmol) to give yellow solids of **6** (0.27 g, 0.398 mmol, 87%). ^1H NMR ($CDCl_3$): δ 8.37 (1H, d, $J = 8.5$ Hz, Np), 8.00 (2H, d, $J = 8.0$ Hz, Np), 7.93 (2H, d, $J = 8.0$ Hz, Np), 7.77–7.40 (10H, broad, m, PPh_2), 7.22 (2H, quartet, $J = 7.0$ Hz, Np), 2.06 (6H, s, SMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.9–128.7 (Np+PPh_2), 29.7–22.3 (SMe_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 5.43 ($J_{pt-p} = 3554$ Hz).Anal. Calcd for $C_{24}H_{23}SPN_6Pt$: C, 44.10; H, 3.55; N, 12.86. Found: C, 44.25; H, 3.38; N, 12.65. Mp (dec.): 163–166 °C. IR (KBr): 2053 (N_3) cm^{-1}.

2.7. Preparation of [Pt(t-Bu–NC)$_2$(CN_4–t-Bu)$_2$] (7)

This compound was prepared similarly to compound **2**. Compound **6** (0.10 g, 0.153 mmol) was treated with excess *tert*-butyl isocyanide (0.08 g, 0.99 mmol) to give pale-yellow solids of **7** (0.057 g, 0.093 mmol, 61%). ^1H NMR ($CDCl_3$): δ 1.78 (18H, s, CN_4-*t*-C_4H_9), 1.43 (18H, s, *t*-C_4H_9–NC).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.2, 30.9, 29.9 (*t*-C_4H_9). Anal. Calcd for $C_{20}H_{36}N_{10}Pt$: C, 39.27; H, 5.93; N, 19.63. Found: C, 39.45; H, 6.18; N, 20.02. Mp (dec.): 108–111 °C. IR (KBr): 2197 (s) cm^{-1}.

2.8. Preparation of [Pt(2,6-Me_2–C_6H_3–NC)$_2$(CN_4–2,6-Me_2–C_6H_3)$_2$] (**8**)

This compound was prepared similarly to compound **7**. Compound **6** (0.10 g, 0.153 mmol) was treated with excess 2,6-dimethylphenyl isocyanide (0.120 g, 0.92 mmol) to give pale-yellow solids of **8** (0.074 g, 0.092 mmol, 60%). ^1H NMR ($CDCl_3$): δ 7.28–7.19 (6H, m, CN_4–2,6-Me_2–C_6*H_3*), 7.10–7.04 (6H, m, 2,6-Me_2–C_6H_3–NC), 2.20 (12H, m, CN_4–2,6-*Me_2*–C_6H_3), 1.74 (12H, s, 2,6-*Me_2*–C_6H_3–NC). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.4–125.3 (phenyl), 18.9 (CN_4–2,6-*Me_2*–C_6H_3). 18.6 (2,6-*Me_2*–C_6H_3–NC). Anal. Calcd for $C_{36}H_{36}N_{10}Pt$: C, 53.79; H, 4.51; N, 17.42. Found: C, 54.17; H, 4.40; N, 17.61. Mp (dec.): 154–156 °C. IR (KBr): 2216 (s) cm^{-1}.

2.9. X-ray structure determination

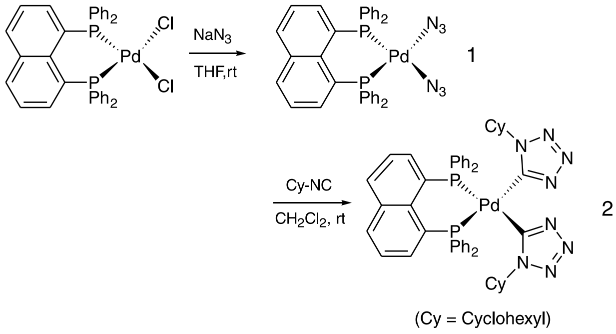
All X-ray data were collected on a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with the use of the SHELXTL programs [20]. All crystal structures were solved by direct methods. All non-hydrogen atoms were anisotropically, unless otherwise specified. All hydrogen atoms were generated in ideal positions and refined in a riding model. In the crystal of **2**·pentane, the co-crystallized pentane showed extreme structural disorder and its carbon atoms were refined isotropically. Details on crystal data and intensity data are given in Table 1.

Table 1
X-ray data collection and structure refinement details

	1	2·Pentane	3	4·CH_2Cl_2	5·CH_2Cl_2	6	7	8
Formula	$C_{34}H_{26}N_6P_2Pd$	$C_{53}H_{60}N_8P_2Pd$	$C_{50}H_{36}P_2Pd$	$C_{35}H_{30}Cl_2FeN_6P_2Pd$	$C_{45}H_{48}Cl_2FeN_8P_2Pd$	$C_{24}H_{23}N_6PPtS$	$C_{20}H_{36}N_{10}Pt$	$C_{36}H_{36}N_{10}Pt$
F_w	686.95	977.43	805.13	829.74	996.00	653.60	611.68	803.84
Temp (K)	296(2)	296(2)	296(2)	296(2)	295(2)	296(2)	295(2)	296(2)
Crystal color	Yellow	Yellow	Orange	Red	Brown	Yellow	White	White
Crystal shape	Rod	Rod	Block	Rod	Block	Block	Block	Block
Crystal size (mm^3)	0.80×0.42 ×0.38	0.70×0.42 ×0.38	0.26×0.16 ×0.12	0.82×0.20 ×0.16	0.48×0.40 ×0.34	0.20×0.18 ×0.08	0.42×0.12 ×0.06	0.36×0.26 ×0.16
Cryst syst	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*−1	*P*2$_1$/*c*	*P*-1	*P*2$_1$/*n*	*P*−1	*P*2$_1$	*P*2$_1$/*c*	*P*2$_1$/*c*
a (Å)	10.052(6)	20.260(2)	10.371(2)	11.126(3)	10.535(3)	9.397(3)	9.958(3)	15.518(2)
b (Å)	12.308(7)	12.947(2)	13.864(3)	18.170(4)	11.615(2)	12.833(2)	23.841(4)	10.994(2)
c (Å)	14.111(7)	18.670(2)	14.521(3)	17.686(4)	20.755(4)	10.905(2)	12.384(2)	21.767(4)
α (°)	101.721(4)		98.00(3)		76.671(8)			
β (°)	108.953(6)	97.416(9)	91.43(1)	107.10(2)	80.90(1)	108.03(2)	107.80(1)	110.34(1)
γ (°)	111.223(7)		111.80(1)		66.94(1)			
V (Å^3)	1434(1)	4857(1)	1913.0(7)	3417(1)	2267.3(8)	1250.5(5)	2799.4(9)	3482(1)
Z	2	4	2	4	2	2	4	4
D_{calcd} (g cm^{-3})	1.591	1.337	1.398	1.613	1.459	1.736	1.451	1.533
μ (mm^{-1})	0.796	0.493	0.604	1.237	0.947	5.782	5.037	4.070
F(000)	696	2040	824	1672	1020	636	1216	1600
T_{max}	0.8765	0.3148	0.8441	0.4140	0.6287	0.8046	0.8090	0.7314
T_{min}	0.5902	0.2807	0.5077	0.3472	0.5767	0.4191	0.4283	0.2861
2θ Range (°)	3.5–50	3.5–50	3.5–50	3.5–50	3.5–50	3.5–50	3.5–50	3.5–50
No. of reflns measured	5175	8644	7019	6273	8381	2433	5210	7885
No. of unique reflns	4872	8360	6623	5948	7910	2286	4914	6081
No. of reflns with $I > 2\sigma(I)$	4438	6777	3247	4644	7182	1688	2729	4630
No. of params refined	389	527	478	425	533	299	281	425
Max in Δρ (e Å^{-3})	0.618	1.000	0.423	0.631	0.705	1.048	0.718	0.544
Min in Δρ (e Å^{-3})	−0.605	−0.952	−0.521	−0.584	−0.55	−0.715	−0.627	−0.613
GOF on F^2	1.088	1.030	0.998	1.011	1.04	1.044	1.001	1.019
*R*1[a]	0.0315	0.0476	0.0740	0.0359	0.0306	0.0475	0.0574	0.0339
*wR*2[b]	0.0837	0.1251	0.1155	0.0763	0.0763	0.0799	0.0950	0.0690

[a] $R1 = \sum||F_o| - |F||/\sum|F_o|$.

[b] $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.



Scheme 1.

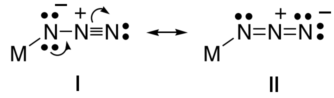
3. Results and discussions

All compounds (**1**–**8**) in this study are air-stable both in the solid state and in solution and have been fully characterized by spectroscopy (NMR and IR), elemental analysis, and X-ray diffraction.

3.1. Preparation, structure, and reactivity of **1**

[Pd(dppn)Cl_2] reacted with excess sodium azide (NaN_3) to give [Pd(dppn)$(N_3)_2$] (**1**) in 84% yield (Scheme 1). The IR spectrum of **1** shows a strong absorption band at 2063 cm^{-1} corresponding to the azide group.

The molecular structure of **1** with the atom-numbering scheme is shown in Fig. 1, which displays one chelating dppn and two azido (N_3^-) ligands. The coordination sphere of the Pd metal can be described as a distorted square plane. The equatorial plane, defined by N1, N4, P1, P2, and Pd1, is roughly planar with an average atomic displacement of 0.121 Å. The naphthalene plane is twisted by 39.5(1)° with respect to the equatorial plane. The N–N–N bond angles of the azido ligands are 176.4(4) and 176.1(4)°. In the azido ligands, all N–N bond lengths (1.140(5)–1.155(4) Å) are equal within experimental error, which indicates the azido ligands prefer the resonance form **II** [2]. On the other hand, several Pd–azido complexes containing different N–N bond lengths, in which N(bound)–N(central) lengths are distinctly longer than N(central)–N(distant) lengths, were recently reported [21–23].



As mentioned in Introduction, reactions of metal–azido compounds with isocyanides frequently convert the azido

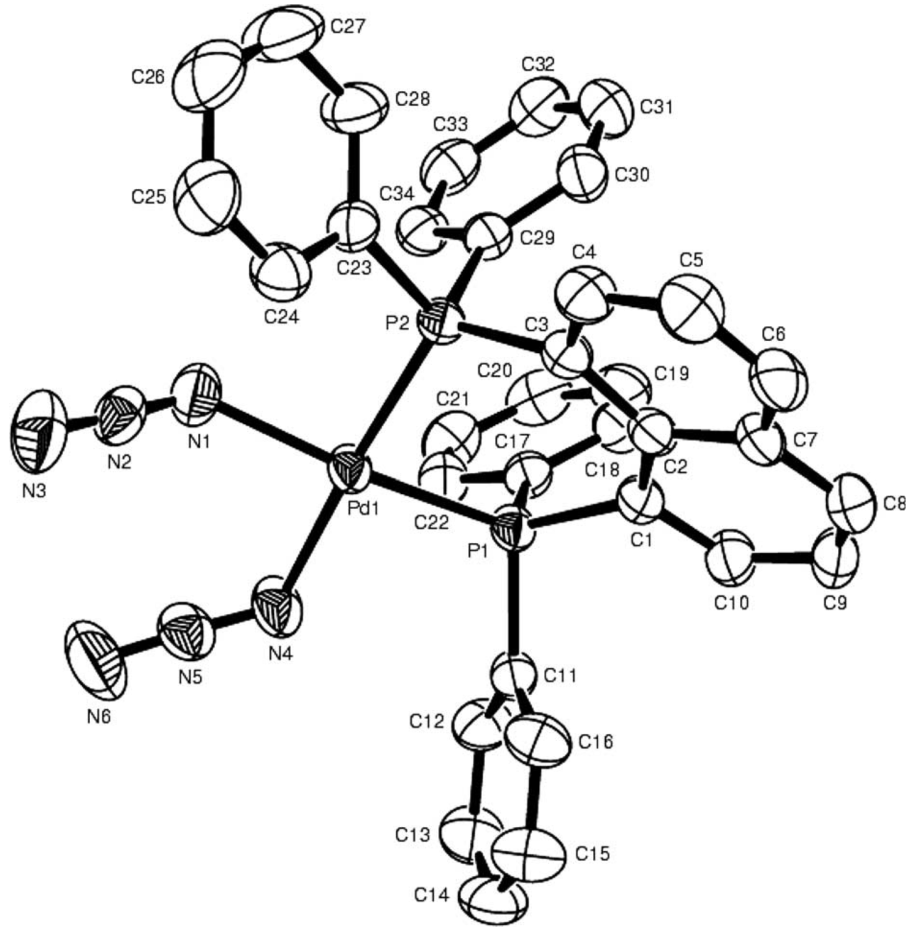


Fig. 1. ORTEP drawing of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond distances (Å) and bond angles (°): Pd1–N1 2.035(3), Pd1–N4 2.056(3), Pd1–P2 2.1999(11), Pd1–P1 2.2188(11), N1–N2 1.155(4), N2–N3 1.152(4), N4–N5 1.151(4), N5–N6 1.140(5); N1–Pd1–N4 90.72(13), N1–Pd1–P2 92.96(10), N4–Pd1–P2 176.32(8), N1–Pd1–P1 166.93(9), N4–Pd1–P1 89.54(9), P2–Pd1–P1 86.86(2), N2–N1–Pd1 129.6(3), N3–N2–N1 176.4(4), N5–N4–Pd1 121.6(2), N6–N5–N4 176.1(4).

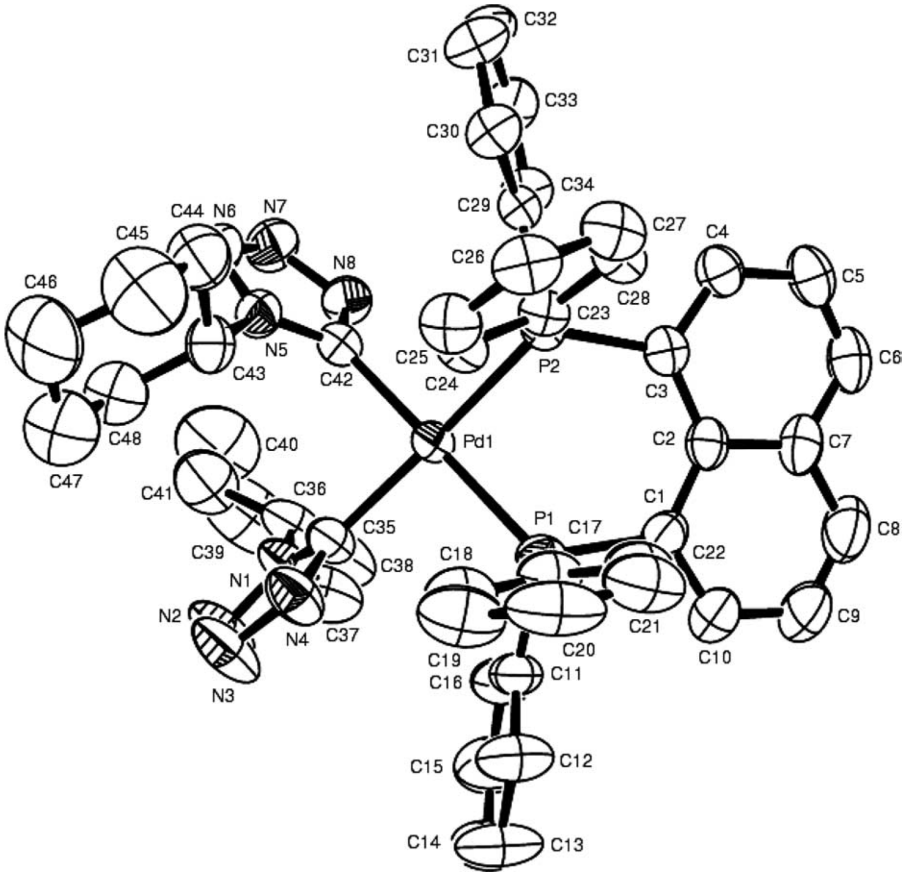


Fig. 2. ORTEP drawing of **2**. Pd1–C35 2.039(4), Pd1–C42 2.046(4), Pd1–P2 2.2936(10), Pd1–P1 2.3017(11), N1–C35 1.347(5), N1–N2 1.356(5), N1–C36 1.452(5), N2–N3 1.273(6), N3–N4 1.364(5), N4–C35 1.322(5), N5–C42 1.344(5), N5–N6 1.357(5), N5–C43 1.461(5), N6–N7 1.285(6), N7–N8 1.362(5), N8–C42 1.336(5); C35–Pd1–C42 87.35(16), N2–Pd1–P1 87.07(4), N4–C35–N1 106.6(3), N8–C42–N5 106.3(3).

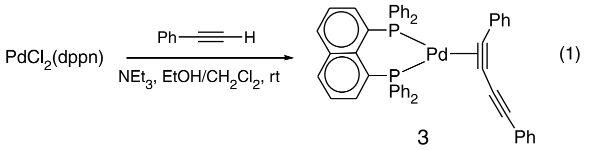
ligand to the *C*-coordinated tetrazolate ring, a five-membered heterocycle, resulting from the [2+3] cycloaddition of the azido and the isocyanide groups [2–11]. In a similar way, treating metal–azido compounds with nitriles, alkynes, and CS_2 gives *N*-coordinated tetrazolato [4,5,9], triazolato [3,4,9], and thiatriazolato [2,4,10] compounds, respectively. On the basis of these facts, we have carried out similar cycloaddition reactions with several isocyanides.

The Pd-bis(azido) compound **1** reacted with excess cyclohexyl isocyanide in CH_2Cl_2 to give [Pd(dppn)(CN_4–Cy)$_2$] (**2**), which contains two *C*-coordinated tetrazolate rings (Scheme 1). These results indicate that compound **1** prefers to undergo [2+3] cycloaddition, rather than N–C coupling to give a carbodimido (N=C=N) group, in spite of steric congestion due to the bulky, chelating dppn ligand that might suppress the cycloaddition reactivity. The same reactivity was also observed for the platinum analog [Pt(dppf)(N_3)$_2$] [12]. In the IR spectrum of compound **2**, the N_3 absorption band at 2063 cm^{-1} in the starting compound **1** disappeared, and a new absorption appeared at 2127 cm^{-1}, presumably due to the formation of the tetrazolato ligand.

The molecular structure of **2** is presented in Fig. 2, which shows two *C*-coordinated tetrazolate rings and one chelating dppn ligand. The coordination sphere of Pd can be described as square planar. The equatorial plane, defined by C35, C42, P1, P2, and Pd1, is relatively planar with an average atomic displacement of 0.094 Å. Two tetrazolate rings are essentially planar with average atomic displacements of 0.001 and 0.005 Å. These two rings are mutually perpendicular with a dihedral angle of 75.1(1)°, and also virtually perpendicular to the equatorial plane with dihedral angles of 74.0(1) and 60.6(1)°. The naphthalene plane is twisted out of the equatorial plane by 40.7(1)°.

*3.2. Preparation and structure of **3***

As mentioned in Section 1, we previously reported the [Pd(dppf)Cl_2]-mediated trimerization of phenylethynes (PhC≡CH) in the presence of triethylamine in ethanol to give [Pd(dppf)(2,3,5-triphenylfulvene)] [15]. Under the same reaction conditions except the spectator ligand (dppf → dppn), we treated [Pd(dppn)Cl_2] with PhC≡CH. This reaction did not produce the expected compound [Pd(dppn)(2,3,5-triphenylfulvene)], but it proceeded to give the unexpected compound [Pd(dppn)(η^2-PhC≡C–C≡CPh)] (**3**) (Eq. (1)). Unfortunately, we cannot give a reasonable explanation for the different reactivity between [Pd(dppf)Cl_2] and compound **3**. The structural formula of compound **3** tells us that phenylethyne underwent C–C coupling to give 1,4-diphenyl-1,3-butadiyne, which is bound to the Pd metal in the π manner. We speculate that the base NEt_3 deprotonates the Ph–C≡C–H proton to give Ph–C≡C$^-$, which binds to the metal to give the intermediate [Pd(dppn)(Ph–C≡C)$_2$]. The phenylethynyl ligands in the intermediate then undergo C–C coupling to give η^2-PhC≡C–C≡CPh in compound **3**.



(1)

The molecular structure of **3** is shown in Fig. 3. The square-planar compound **3** has one chelating dppn and one η^2-butadiyne ligand. The dihedral angle between Plane 1 (Pd1, P1, and P2) and Plane 2 (Pd1, C41, and C42) is 3.5(7)°. The phenyl groups in dppn are extremely twisted out of the naphthalene plane with dihedral angles in the range of 66.6(2)–77.4(2)°. Six carbon atoms (C35 and C41–C45) in the butadiyne framework are essentially coplanar with an average atomic displacement of 0.007 Å.

3.3. Preparation, structure, and reaction of 4

Like compound **1**, [Pd(dppf)(N$_3$)$_2$] (**4**) was prepared from [Pd(dppf)Cl$_2$] and NaN$_3$ by the simple and straightforward metathesis (Scheme 2). The Pt analog [Pt(dppf)(N$_3$)$_2$] was previously reported by our group [12]. The IR spectrum of **4** displays a strong absorption band at 2043 cm^{-1} assigned to the azide group.

The molecular structure of **4** is shown in Fig. 4, which shows a square-planar complex with one chelating dppf and two azido ligands. The equatorial plane, defined by N1, N4, P1, P2, and Pd1, is roughly planar with an average displacement of 0.013 Å. The N–N–N bond angles of the azido ligands are 175.1(4) and 175.5(4)°. As is the case of compound **1**, the azido ligands in compound **4** appear to adopt the resonance form **II**, in which the N–N bond lengths are essentially same.

Two Cp rings are not perfectly parallel but twisted from each other with a dihedral angle of 3.7(3)°. The torsion angle of P1–C1–C6–P2 is 38.0(2)°, indicating a gauche conformation of the two Cp rings. For comparison, the ideal torsion angles for the gauche and eclipsed conformation are 36 and 72°, respectively. The distances of Fe–Ct (Ct is the centroid of the Cp ring) are 1.636 and 1.641 Å, and the angle of the Ct1–Fe–Ct2 (Ct1: C1–C5; Ct2: C6–C10) is 179.71°. In addition, the P1···P2 distance is 3.489(1) Å. The above bonding parameters within a ferrocene moiety are relatively consistent with those found for square-planar palladium complexes in which the dppf group acts as a ligand [24]. The distance of Pd···Fe is 4.236(1) Å, which clearly rules out direct bonding interaction between the two metals.

Like compound **1**, compound **4** underwent [2+3] cycloaddition with isocyanide to convert the azido ligand to the *C*-coordinated tetrazolate ring. Compound **4** reacted with excess *tert*-butyl isocyanide in CH$_2$Cl$_2$ to give [Pd(dppf)(CN$_4$–

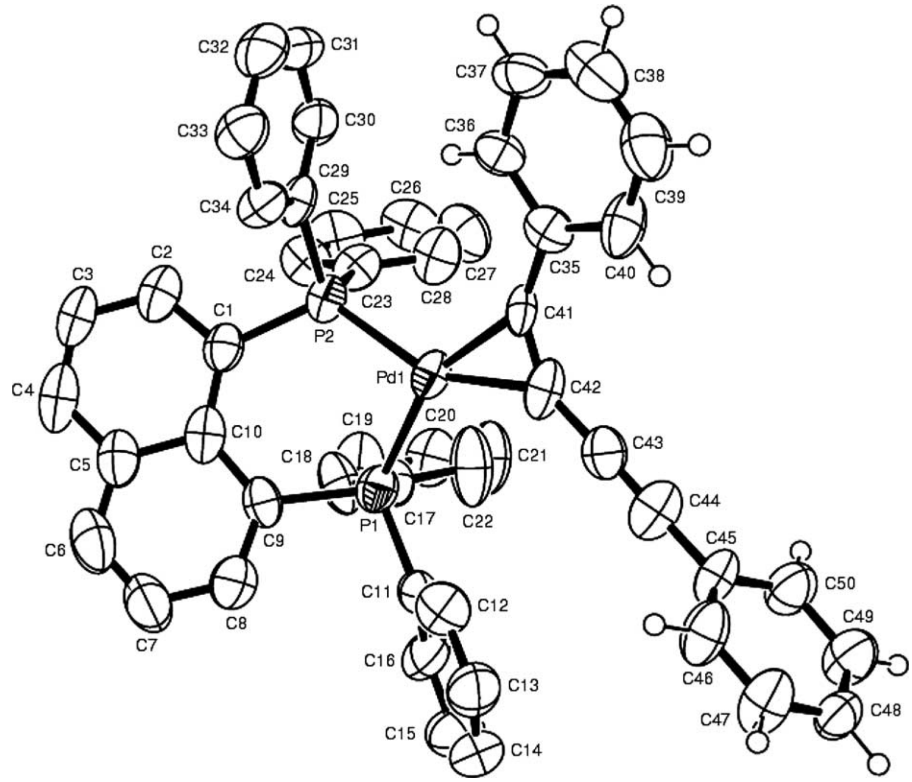
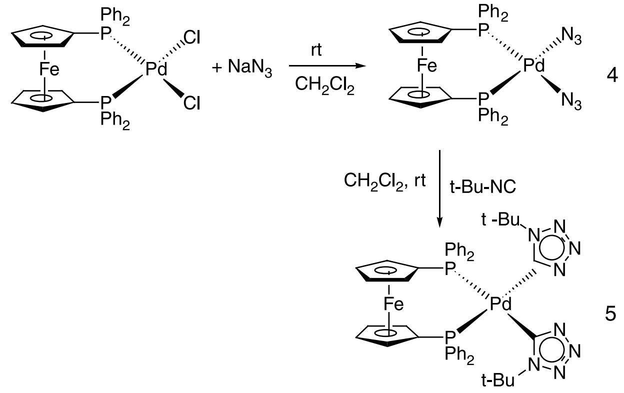


Fig. 3. ORTEP drawing of **3**. Pd1–C41 2.051(8), Pd1–C42 2.054(8), Pd1–P1 2.271(2), Pd1–P2 2.283(2), C35–C41 1.459(10), C41–C42 1.267(11), C42–C43 1.404(11), C43–C44 1.214(11), C44–C45 1.400(11); C41–Pd1–C42 35.9(3), P1–Pd1–P2 88.18(8), C42–C41–C35 139.0(8), C41–C42–C43 145.8(9), C44–C43–C42 178.1(10), C43–C44–C45 178.4(9).



Scheme 2.

t-Bu)$_2$] (**5**) (Scheme 2). As is the case for the conversion of compound **1** to compound **2**, the IR spectrum of compound **5** shows a new strong absorption band at 2236 cm^{-1}, which is absent in that of the starting compound **4** that exhibits the azide band at 2043 cm^{-1}.

The molecular structure of the square-planar compound **5** is presented in Fig. 5. Compound **5** has two *C*-coordinated tetrazolate rings (CN$_4$–*t*-Bu) and one bidentate dppf ligand. The equatorial plane, defined by C35, C40, P1, P2, and Pd1, is relatively planar with an average atomic displacement of 0.005 Å. Two tetrazolate rings (C35, N1–N4; C40, N5–N8) are essentially planar with average atomic displacements of 0.002 and 0.004 Å, respectively. These two rings are mutually perpendicular with a dihedral angle of 77.3(1)° and are virtually perpendicular to the equatorial plane with dihedral angles of 80.0(1) and 80.5(1)°. The *tert*-butyl groups on two tetrazolate rings seem to orient as far as possible, which probably arises from the steric congestion.

Bonding parameters in the dppf moiety in compound **5** are essentially the same as those in compound **4**. Two Cp rings have a dihedral angle of 3.2(2)°. The P1–C1–C6–P2 torsion angle of 39.9(1)° indicates a slight distortion from a gauche conformation of the two Cp rings. The distances of Fe–Ct (Ct is the centroid of the Cp ring) are 1.647 and 1.646 Å, and the angle of the Ct1–Fe–Ct2 (Ct1: C1–C5; Ct2: C6–C10) is 179.71°. The distances of P1···P2 and Pd···Fe are 3.679(1) and 4.335(1) Å, respectively.

3.4. Preparation, structure, and reaction of **6**

We have so far used bulky chelating bis(phosphine) ligands, dppf and dppn, in preparing compounds **1**–**5**. For a comparison study, we decided to examine the reactions of isocyanides with [Pt(1-dpn)(SMe$_2$)(N$_3$)$_2$] (**6**), which contains a bulky monodentate phosphine ligand, 1-(diphenylphosphino)naphthalene (1-dpn). Compounds **6** was prepared from [Pt(1-dpn)(SMe$_2$)-Cl$_2$] and NaN$_3$ (Scheme 3). The IR spectrum of **6** shows a strong absorption band at 2053 cm^{-1} corresponding to the azide group.

The molecular structure of **6** is shown in Fig. 6, which displays one dppn and SMe$_2$ and two azido ligands. The coordination sphere of the Pt metal can be described as square planar. The equatorial plane, defined by N1, N4, P1, S1, and Pd1, is roughly planar with an average atomic displacement of

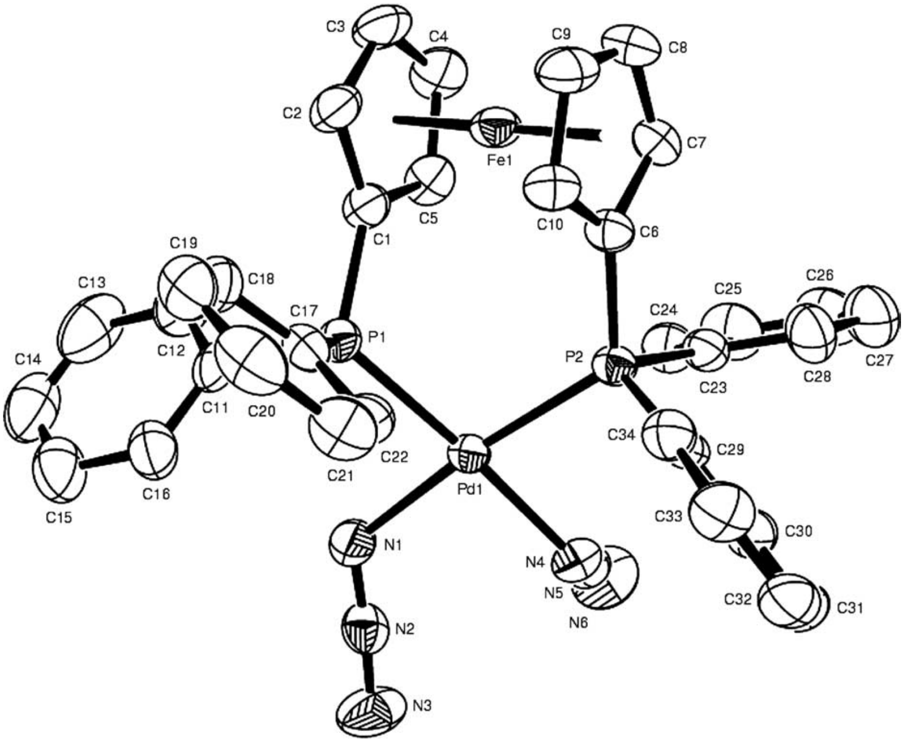


Fig. 4. ORTEP drawing of **4**. Pd1–N4 2.069(3), Pd1–N1 2.072(3), Pd1–P1 2.2832(11), Pd1–P2 2.2882(10), N1–N2 1.170(4), N2–N3 1.147(5), N4–N5 1.194(4), N5–N6 1.156(5); N4–Pd1–N1 90.52(13); N4–Pd1–P1 176.45(9), N1–Pd1–P1 86.45(10), N4–Pd1–P2 83.50(9), N1–Pd1–P2 173.97(1), P1–Pd1–P2 99.50(4), N2–N1–Pd1 121.2(3), N3–N2–N1 175.1(4), N5–N4–Pd1 118.8(3), N6–N5–N4 175.5(4).

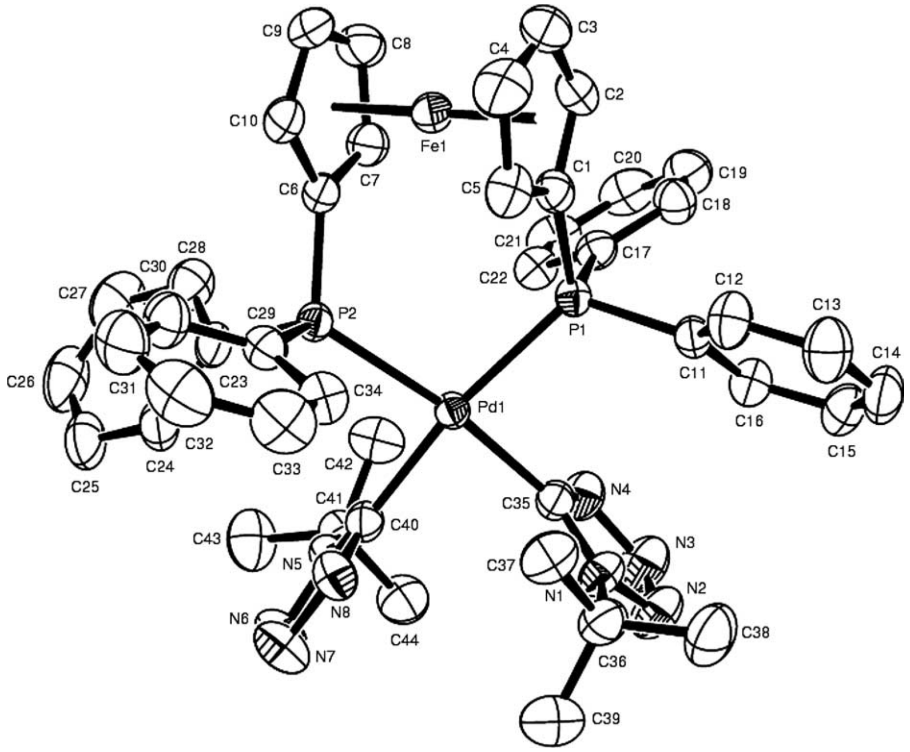


Fig. 5. ORTEP drawing of **5**. Pd1–C40 2.056(3), Pd1–C35 2.062(3), Pd1–P1 2.3643(8), Pd1–P2 2.3762(7), N1–N2 1.365(3), N1–C35 1.373(3), N1–C36 1.497(4), N2–N3 1.296(4), N3–N4 1.376(4), N4–C35 1.301(4), N5–N6 1.367(3), N5–C40 1.370(3), N5–C41 1.497(4), N6–N7 1.288(4), N7–N8 1.383(3), N8–C40 1.285(4); C40–Pd1–C35 84.55(10), P1–Pd1–P2 101.79(3), N4–C35–N1 107.6(2), N8–C40–N5 107.2(2).

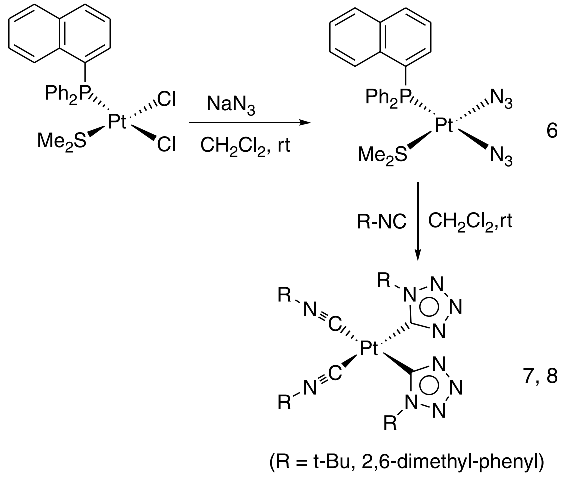
0.027 Å. With respect to the equatorial plane, the naphthalenyl ring (C1–C10) has a dihedral angle of 65.8(3)°. The P1–Pt1–S1 bond angle is 95.6(1)°.

The Pt-bis(azido) compound **6** reacted with excess *tert*-butyl isocyanide and 2,6-dimethylphenyl isocyanide in CH_2Cl_2 to give [Pt(*t*-Bu–NC)$_2$(CN$_4$–*t*-Bu)$_2$] (**7**) and [Pt(2,6-Me$_2$–C$_6$H$_3$–NC)$_2$(CN$_4$–2,6-Me$_2$–C$_6$H$_3$)$_2$] (**8**), respectively (Scheme 3). In these reactions, the incoming isocyanides replaced both the 1-dpn and SMe_2 ligands during the reactions.

The molecular structures of compounds **7** and **8** are shown in Figs. 7 and 8, respectively. Each square-planar compound has two *C*-coordinated tetrazolate rings and two isocyanide ligands. The equatorial plane, defined by two carbon atoms of the tetrazolate ring, two carbon atoms of the isocyanide, and the Pt metal, is somewhat planar with an average atomic displacement of 0.216 (for **7**) or 0.001 Å (for **8**). Consistent with our expectation, compounds **7** and **8** have new absorption bands at 2197 and 2216 cm^{-1}, respectively, arising from the newly formed tetrazolate rings.

Bond lengths (1.97(1)–1.99(1) Å) between Pt and the isocyanide carbon (Pt–C(RNC)) are a little shorter than those (2.01(1)–2.04(1)) between Pt and the *C*-tetrazolate carbon (Pt–C(CN$_4$)). Two tetrazolate rings in each compound are essentially planar with an average atomic displacement of 0.003–0.008 Å. These two rings are mutually perpendicular with a dihedral angle of 85.1(4) (**7**) or 70.4(2)° (**8**), and are also essentially perpendicular to the equatorial plane with a dihedral angle of 78.5(4) (**7**) or 66.4(2)° (**8**). The substituents (*tert*-butyl (**7**) or 2,6-dimethylphenyl (**8**)) on the two tetrazolate rings seem to orient as far as possible.

Kim and co-workers recently reported a couple of papers on the reactions between 2,6-dimethylphenyl isocyanide (2,6-Me$_2$C$_6$H$_3$–NC) and Pd-bis(azido) complexes [Pd(PR$_3$)$_2$(N$_3$)$_2$] (PR$_3$ = PMe$_3$, PMe$_2$Ph, PEt$_3$, PMePh$_2$, PEt$_3$, depe, dppp, dppe) [25,26]. According to their results, those compounds containing small phosphines gave either (carboimido)(tetrazolato) complexes [Pd(PR$_3$)$_2$(N=C=N–R)(CN$_4$–R)] or bis(carboimido) complexes [Pd(PR$_3$)$_2$(N=C=N–R)$_2$]. By contrast, those compounds containing bulky chelating bis(phosphine) ligands (depe, dppp, dppe) exclusively produced



Scheme 3.

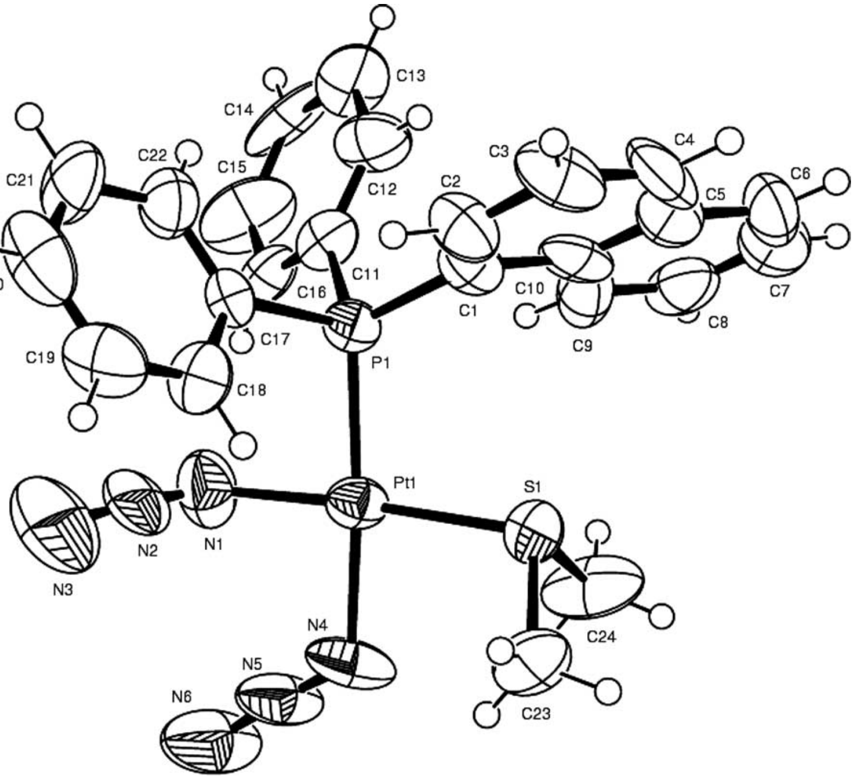


Fig. 6. ORTEP drawing of **6**. Pt1–N1 2.00(2), Pt1–N4 2.070(17), Pt1–P1 2.252(5), Pt1–S1 2.277(5), N1–N2 1.10(3), N2–N3 1.19(3), N4–N5 1.14(2), N5–N6 1.17(3), N1–Pt1–N4 88.4(9); P1–Pt1–S1 95.64(19), N2–N1–Pt1 120.2(18), N1–N2–N3 174(3), N5–N4–Pt1 123.5(18), N4–N5–N6 176(2).

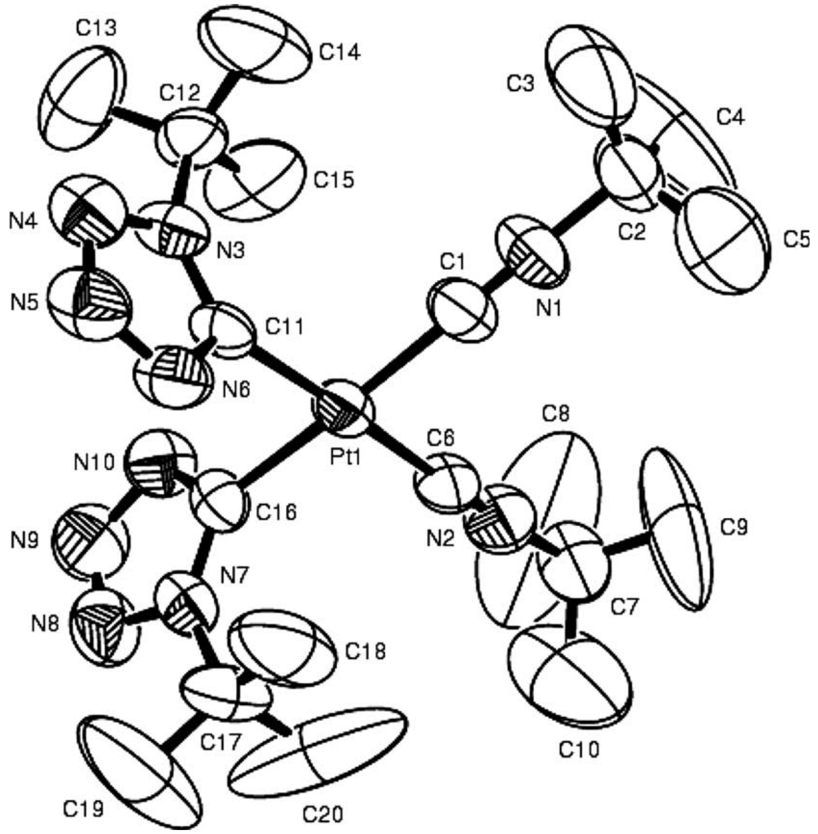


Fig. 7. ORTEP drawing of **7**. Pt1–C1 1.970(13), Pt1–C6 1.996(12), Pt1–C11 2.012(11), Pt1–C16 2.032(10), N3–C11 1.343(12), N3–N4 1.359(12), N3–C12 1.495(13), N4–N5 1.312(12), N5–N6 1.348(12), N6–C11 1.351(12), N7–C16 1.337(12), N7–N8 1.362(12), N7–C17 1.493(14), N8–N9 1.289(13), N9–N10 1.364(13), N10–C16 1.344(12); C1–Pt1–C6 92.0(5), C11–Pt1–C16 86.3(4), C1–N1–C2 172.5(13), C6–N2–C7 176.6(13), N1–C1–Pt1 178.3(12), N2–C6–Pt1 175.1(12).

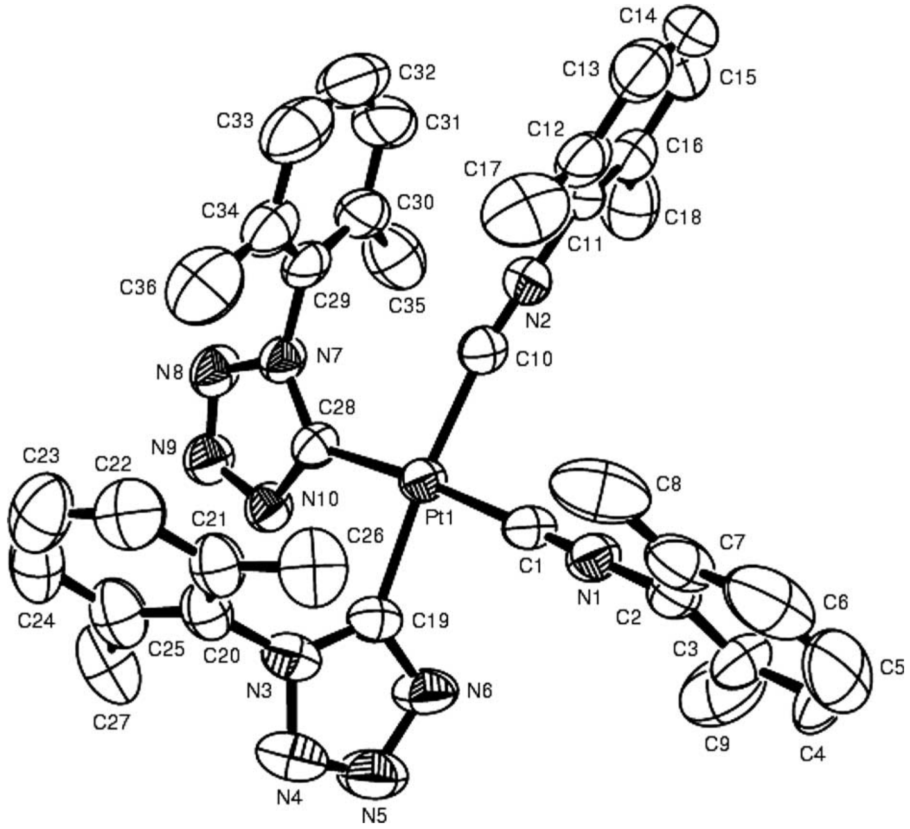


Fig. 8. ORTEP drawing of **8**. Pt1–C1 1.968(6), Pt1–C10 1.978(5), Pt1–C19 2.029(5), Pt1–C28 2.042(5), N3–C19 1.357(7), N3–N4 1.338(7), N3–C20 1.433(7), N4–N5 1.282(8), N5–N6 1.368(7), N6–C19 1.319(7), N7–C28 1.355(6), N7–N8 1.371(6), N7–C29 1.429(7), N8–N9 1.290(6), N9–N10 1.356(6), N10–C28 1.323(6); C1–Pt1–C10 87.9(2), C1–Pt1–C28 175.0(2), C1–N1–C2 179.5(7), C10–N2–C11 174.5(5).

bis(carboimido) complexes. However, our results in this study revealed that Pd- and Pt-bis(azido) complexes containing bulky phosphine ligands (dppf, dppn, 1-dpn), chelating or monodentate, underwent only [2+3] cycloaddition with isocyanides (R–NC, R=cyclohexyl, *tert*-butyl, 2,6-dimethylphenyl) to convert azido ligands to *C*-coordinated tetrazolate rings. Considering the steric bulk of the phosphine ligands, such results are somewhat unusual. In addition, among the four azido complexes (**2, 5, 7,** and **8**) only complex **2** exhibited phosphorus–carbon (in the terazolato ring) couplings in the form of a double of a doublet [$J_{C\text{–}P}=166$ (*trans*), 25 (*cis*)] in its $^{13}C\{^{1}H\}$ NMR spectrum. The fact that the other three compounds do not exhibit the peaks corresponding to the coordinated carbon in the tetrazolato ring can probably be due to the quaternary nature of this carbon.

4. Conclusions

We have prepared two Pd-bis(azido) compounds containing bulky chelating bis(phosphine) ligands, [Pd(dppn)$(N_3)_2$] and [Pd(dppf)$(N_3)_2$], as well as one Pt-bis(azido) containing a bulky monodentate phosphine ligand [Pt(1-dpn)$(SMe_2)(N_3)_2$]. In spite of the steric bulk of the phosphine ligands, all those bis(azido) compounds underwent only [2+3] cycloaddition with isocyanides to convert the azido ligands to the corresponding five-membered, *C*-coordinated tetrazolate rings. In particular, in the reactions of [Pt(1-dpn)$(SMe_2)(N_3)_2$], the incoming isocyanides replaced both the 1-dpn and SMe_2 ligands, together with the conversion of the azido ligands to the tetrazolate rings. Consequently, these reactions gave bis(tetrazolato) compounds, which do not contain carbodimido ligands resulting from the N–C coupling with N_2 elimination. In addition, we observed the [Pd(dppn)Cl_2]-mediated C–C coupling of PhC≡CH to generate the η^2-PhC≡C–C≡CPh ligand.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: CCDC No. 282328 for **1**, 282329 for **2**·pentane, 282330 for **3**, 282331 for **4**·CH_2Cl_2, 282332 for **5**·CH_2Cl_2, 282333 for **6**, 282334 for **7**, and 282335 for **8**. 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 www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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