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Bis(phosphine) Pd(II)-azido complexes containing heterocyclic ligands: Reactivity toward organic isocyanides

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Abstract

Bis(phosphine) Pd–azido complexes containing heterocycles such as tetrazolyl, pyrazinyl, and thienyl groups reacted with aryl isocyanides to give the corresponding Pd–carbodiimido or –imidoyl carbodiimido complexes. These products were formed by the insertion of the isocyanides into the Pd–N (azido) or the Pd–C (heterocycles) bond. © 2007 Elsevier B.V. All rights reserved.

1. Introduction

Unsaturated molecules such as CO and isocyanides readily insert into palladium–carbon bonds to produce various organic compounds via palladium-catalyzed reactions [1–4]. In particular, the isocyanide insertion gives an imidoyl compound, an intermediate in catalytic reactions or a precursor of organic heterocycles in depalladation reactions [5–14].

Keywords: Azido; Carbodiimido; Imidoyl; Tetrazolyl; Thienyl; Palladium

We have published several papers on the reactivity of bis(azido) or mono(azido) complexes of group 10 metals $[M(N_3)_2L_n]$ or $[M(N_3)L'_n]$, in which supporting ligands are tertiary phosphines or *C*, *N*-chelated ligands, toward organic isocyanides to give the complexes containing a *C*-coordinated tetrazolato ring, a carbodiimido group, or a imidoyl group, depending on the nature of incoming isocyanides or coordinated ligands (Scheme 1) [15]. As an extension of our ongoing research, we set out to study the aforementioned reactivity for another family of Pd–azido complexes having heterocyclic ligands. In this paper, we report the preparation of bis(phosphine) Pd–azido com-

plexes containing the heterocyclic ligands and their reactivity toward organic isocyanides.

2. Results and discussion

2.1. Preparation of bis(phosphine) Pd(II)–azido complexes containing heterocyclic ligands

The starting complexes 1–5 $[Pd(R)(X)L_2]$ (L = tertiary phosphines; R = tetrazolyl, thienyl, pyrazinyl, and pyridyl; X = Cl, Br) were obtained by the oxidative addition of R– X to $[Pd(CH_2=CHPh)L_2]$ (L = PMe₃ or PMe₂Ph) [16,17], which was generated *in situ* from *trans*-[PdEt₂L₂] and styrene. The subsequent treatments of complexes 1–5 with excess NaN₃ produced the corresponding Pd–azido complexes 6–10 containing heterocyclic ligands in high yields (Scheme 2).

The IR spectra of complexes **6–10** display a strong N₃ stretch at 2032–2055 cm⁻¹. Crystal data of **6** are summarized in Table 1. Fig. 1 shows the molecular structure of **6**, which shows a slightly distorted square-planar structure, consisting of two *trans*-PMe₃ ligands, one tetrazolato ligand and one azido ligand. The tetrazolate ring is essentially planar and has a dihedral angle of $70.1(2)^{\circ}$ with

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respect to the equatorial plane. In addition, the dihedral angle between the tetrazolate and phenyl rings is $37.2(3)^{\circ}$.

Previously, we reported that the aryl palladium–azido bis(phosphine) complex $[ArPd(N_3)(PMe_3)_2]$ (Ar = phenyl, 2,6-diphenylpyridine) reacted with organic isocynaides to give the imidoyl Pd carbodiimido complex $[Pd(N=C=N-Ar'){C(=N-R)Ar}(PMe_3)_2]$ [15d]. On the basis of the above results, we decided to examine the same reactivity (isocyanide insertion) for palladium–azido complexes containing heterocyclic ligands. Treating the Pd–thienyl complexes **3** and **8** with isocyanide (2,6-dimethylphenyl



Table 1 X-ray data collection and structure refinements for 6, 11, 12 and 14

	6	11	12	14
Formula	$C_{13}H_{23}N_7P_2Pd$	C19H30NP2SBrPd	C ₂₈ H ₃₉ N ₃ P ₂ SPd	$C_{32}H_{36}N_6P_2Pd$
$F_{\rm w}$	445.72	552.75	618.02	673.01
Temperature (K)	296(2)	295(2)	295(2)	295(2)
Crystal size (mm)	$0.22 \times 0.20 \times 0.18$	$0.36 \times 0.34 \times 0.32$	$0.56 \times 0.54 \times 0.52$	$0.50 \times 0.44 \times 0.40$
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P\overline{1}$	$Pca2_1$
a (Å)	6.873(1)	10.517(2)	9.107 (1)	11.626(1)
b (Å)	23.602 (5)	11.745(2)	13.401(2)	11.701(1)
c (Å)	11.950 (2)	19.755(4)	13.823(2)	22.553(2)
β (°)	106.32 (1)	93.22(2)	75.88(1)	
$V(\text{\AA}^3)$	1860.4 (6)	2436.3(8)	1559.9(4)	3204.0(6)
Ζ	4	4	2	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.591	1.507	1.316	1.395
$\mu (\mathrm{mm}^{-1})$	1.178	2.622	0.784	0.710
<i>F</i> (000)	904	1112	640	1384
T_{\min}	0.5832	0.4700	0.4021	0.3739
T _{max}	0.6202	0.8280	0.7963	0.4409
Number of measured reflections	3514	6429	5657	5585
Number of unique reflections	3231	4239	5345	5585
Number of reflections with $I \ge 2\sigma(I)$	2450	3275	4980	5276
Number of refined parameters	209	226	317	371
Maximum in $\Delta \rho$ (e Å ⁻³)	0.607	1.081	0.444	0.285
Minimum in $\Delta \rho$ (e Å ⁻³)	-0.820	-0.675	-0.421	-0.494
Goodness-of-fit on F^2	1.035	1.030	1.037	1.031
R ^a	0.0453	0.0398	0.0347	0.0265
wR ₂ ^b	0.0990	0.0912	0.0983	0.0691

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

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



Fig. 1. ORTEP drawing [21] of **6** showing the atom-labelling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–C7 1.951(6), Pd1–N5 2.040(6), Pd1–P2 2.283(2), Pd1–P1 2.284(2), N1–C7 1.312(7), N1–N2 1.360(8), N2–N3 1.259(8), N3–N4 1.348(7), N4–C7 1.344(7), N4–C8 1.398(7), N5–N6 1.133(8), N6–N7 1.145(9); C7–Pd1–N5 176.1(2), C7–Pd1–P2 91.2(2), N5–Pd1–P2 92.6(2), P2–Pd1–P1 174.1(1), C7–N1–N2 107.3(5), N3–N2–N1 110.9(5), N2–N3–N4 106.2(5), C7–N4–N3 109.7(5), N6–N5–Pd1 132.1(6), N5–N6–N7 176.2(9), N1–C7–N4 105.9(5).



isocyanide) produced an imidoyl Pd complex (11) and an imidoyl Pd carbodiimide (12), respectively (Scheme 3). The reactivity depends on the amount of the added isocyanide. Whereas compound 11 was formed by the isocyanide insertion into the Pd–C bond (1:1 mole ratio), compound 12 was formed by the isocyanide insertion into both the Pd–C bond and the Pd–N bonds followed by N_2 extrusion (1:2 mole ratio). It should be mentioned that our group [17] and other groups [8b,18] reported the isocyanide insertion into palladium or platinum halides containing a thienyl group to produce the imidoyl halide complexes.

IR spectrum of complex 12 displays a sharp stretch at 2140 cm^{-1} due to the N=C=N group of the carbodiimido ligand as well as a strong stretch at 1556 cm⁻¹ assignable to



Fig. 2. ORTEP drawing of **11**. Selected bond lengths (Å) and angles (°): Pd1–C15 2.027(4), Pd1–P1 2.314(1), Pd1–P2 2.359(1), Pd1–Br1 2.5663(7), N1–C15 1.294(5), N1–C7 1.411(6), C15–C16 1.477(6); C15–Pd1–P1 91.5(1), C15–Pd1–P2 91.0(1), P1–Pd1–P2 173.11(5), C15–Pd1–Br1 175.5(1), P1–Pd1–Br1 90.38(4), P2–Pd1–Br1 87.54(4), C15–N1–C7 127.5(4), N1–C15–C16 114.7(4), N1–C15–Pd1 129.6(3), C16–C15–Pd1 115.8(3).

the imidoyl (-C=N(Ar)-) group. Molecular structures of **11** and **12** (Figs. 2 and 3) clearly show an imidoyl $\{-C=N(Ar)\}$ group, formed by the isocyanide insertion into the Pd-C bond. In addition, complex **12** has a carbodiimido (-N=C=N-Ar) group (in Fig. 3) *trans* to the imidoyl group.

In contrast, the corresponding reactions of the tetrazolato or pyrazinyl analogs $[R(N_3)PdL_2]$ (R = tetrazolyl; L = PMe₃ (6), PMe₂Ph (7); R = pyrazinyl, L = PMe₃ (9)) with 2 equiv or more organic isocyanides led to the formation of carbodiimido complexes (13–15) (Scheme 4). No products resulting from the isocyanide insertion into the Pd–C (heterocycles) bond were observed.

IR spectra of complexes **13–15** also display a sharp band at 2106–2138 cm⁻¹ due to the NCN groups of the carbodiimido groups. The ORTEP drawing of compound **14** is shown in Fig. 4, which illustrates a square-planar coordination sphere of Pd containing two PMe₂Ph ligands, one 2,6dimethylphenyl carbodiimido ligand and one tetrazolyl ligand.

It has been observed that azido complexes **6** and **7** first produced a mixture of a bis(tetrazolyl) complex [RPdL₂{CN₄(2,6-*Me*₂C₆H₃)}] and a mono(carbodiimido) complex [RPdL₂(N=C=N-2,6-*Me*₂C₆H₃)] (**13** and **14**) in the mole ratio of 3:7 at room temperature, and this mixture subsequently converted to the mono(carbodiimido) complexes when heated at 60 °C. These results are consistent with our previous observation that bis(azido) bis(phosphine) complexes $M(N_3)_2L_2$ (M = Ni, Pd, Pt; L = PR₃) reacted with organic isocyanides to give the corresponding bis(carbodiimido)complexes via a bis(tetrazolato) intermediate [L₂M{CN₄(Ar)}₂] [15a]. Unexpectedly, heating the mono carbodiimido complex **13** at 80 °C does not convert



Fig. 3. ORTEP drawing of **12**. Selected bond lengths (Å) and angles (°): Pd1–C16 2.003(3), Pd1–N1 2.093(3), Pd1–P1 2.3055(9), Pd1–P2 2.3551(9), N1–C7 1.126(5), N2–C7 1.248(5), N2–C8 1.393(5), N3–C16 1.283(4), N3–C17 1.407(4); C16–Pd1–N1 177.23(12), C16–Pd1–P1 91.52(8), N1–Pd1–P1 91.05(11), C16–Pd1–P2 90.94(8), N1–Pd1–P2 86.64(11), P1–Pd1–P2 172.31(4), C7–N1–Pd1 167.8(4), C7–N2–C8 131.2(4), C16–N3–C17 126.3(3), N1–C7–N2 169.5(5).



Scheme 4.



Fig. 4. ORTEP drawing of **14**. Selected bond lengths (Å) and angles (°): Pd1–C17 1.994(3), Pd1–N1 2.038(3), Pd1–P1 2.3171(8), Pd1–P2 2.3241(8), N1–C24 1.174(5), N2–C24 1.241(5), N3–C17 1.324(4), N3–N4 1.356(5), N4–N5 1.285(5), N5–N6 1.368(4), N6–C17 1.349(5); C17–Pd1–N1 177.23(14), C17–Pd1–P1 90.28(9), N1–Pd1–P1 89.88(9), C17–Pd1–P2 91.64(8), N1–Pd1–P2 87.90(9), P1–Pd1–P2 173.38(4), C24–N1–Pd1 150.9(3), C24–N2–C25 124.2(4), C17–N3–N4 107.1(3), N5–N4–N3 111.1(3), N4–N5–N6 106.0(3), C17–N6–N5 108.7(3).



the 1-phenyl-5-tetrazolato ring (Scheme 5A) into the corresponding carbodiimido group. As shown in Schemes 4 and 5, the subsequent formation of the Pd–bis(carbodiimido) complexes (Scheme 5A) via the nitrogen extrusion from the tetrazolato rings in **13** and **14** was not observed. In contrast, we previously reported that reactions of the bis(azido)–Pd(II) or –Pt(II) complexes with aryl isocyanides ultimately gave bis(carbodiimido) complexes [M(N=C=N-Ar)₂L₂] via the intermediate tetrazolyl M(II) carbodiimide [M{CN₄(Ar)}(N=C=N-Ar')L₂] (Scheme 5B). Therefore, these results indicate that the formation of the carbodiimido group is dominated by the steric bulk rather than the electronic factor of the substituents on the heterocyclic ligand.

In summary, we examined the reactivity of the bis(phosphine) Pd-azido complexes having heterocyclic ligands toward organic isocyanides. The isocyanides inserted into the Pd-C (heterocyclic) or Pd-N (azido) bond to give Pd-imidoyl or Pd-imidoyl-carbodiimide complexes, depending on the nature of the heterocyclic ligands. Whereas the isocyanide insertion into Pd-C bond (heterocycles) does not occur for the bis(phosphine) Pd-azido complexes containing tetrazolyl or pyrazinyl heterocyclic ligand, it does occur for the thienvl Pd complex to give an imidoyl Pd carbodiimide. This reactivity maybe due to higher electron-withdrawing property or electron delocalization of the tetrazolyl or pyrazinyl group compared with the thienyl group toward organic isocyanide. Earlier works by Mantovani and co-workers [8] described that isocyanide insertion into 2-pyridyl Pd bromide is slower than that into the thienyl Pd complex, due to the higher electronegativity of nitrogen compared with sulfur. This work provides a synthetic route to various Pd-carbodiimido complexes having heterocyclic ligands as well as mechanistic aspects for their formation.

3. Experimental

All manipulations of air-sensitive compounds were performed under N_2 or Ar by Schlenk-line techniques. Solvents were distilled from Na-benzophenone. The analytical laboratories at Basic Science Institute of Korea and at Kangnung National University carried out elemental analyses. IR spectra were recorded on a Perkin–Elmer BX spectrophotometer. NMR (¹H, ¹³C{¹H}, and ³¹P{¹H}) spectra were obtained in CDCl₃ on a JEOL Lamda 300 MHz spectrometer. Chemical shifts were referenced to internal Me₄Si and to external 85% H₃PO₄. Complexes *trans*-[PdEt₂L₂] (L = PMe₃ and PMe₂Ph) were prepared by the literature method [15]. 2,6-Diethylphenyl isocyanide was prepared as described in the literature [19].

The starting complexes, *trans*-[PdCl(1-phenyl-1-tetrazolyl)(PMe₃)₂] (**1**, 83%), [PdCl(1-phenyl-5-tetrazolyl)(PMe₂-Ph)₂] (**2**, 92%), [PdCl(2-thienyl)(PMe₃)₂] (**3**, 54%), [PdCl(2pyrazinyl)(PMe₃)₂] (**4**, 72%) and [PdCl(2-pyridyl)(PMe₃)₂] (**5**, 74%), were prepared analogously by literature methods [16b,17].

Further treatments of 1-5 with NaN₃ have been made (see Sections 3.1–3.3).

3.1. Reactions of $[Pd(R)XL_2]$ (R = 1-phenyl-5-tetrazolyl, 2-thienyl and 2-pyrazinyl) with NaN₃

To a Schlenk flask containing **1** (0.433 g, 0.99 mmol) were added CH₂Cl₂ (3 cm³) and a NaN₃ solution (0.128 g, 1.97 mmol) dissolved in H₂O (2 cm³) in that order. After stirring for 11 h at room temperature, the solvent was completely evaporated to give pale yellow solids, which were extracted with CH₂Cl₂. Recrystallization from CH₂Cl₂/hexane gave pale yellow solids of [PdN₃(1-phenyl-5-tetrazolyl)(PMe₃)₂] (**6**) (0.258 g, 77%). *Anal.* Calc. for C₁₃H₂₃N₇P₂Pd: C, 35.03; H, 5.20; N, 22.00. Found: C, 35.00; H, 5.09; N, 22.48%.

Complexes $[PdN_3(1-phenyl-5-tetrazolyl)(PMe_2Ph)_2]$ (7, 89%), $[PdN_3(2-thienyl)(PMe_3)_2]$ (8, 76%), $[PdN_3(2-pyrazi-nyl)(PMe_3)_2]$ (9, 58%), and $[PdN_3(2-pyridyl)(PMe_3)_2]$ (10, 77%) were prepared analogously.

Complex 7: Anal. Calc. for $C_{23}H_{27}N_7P_2Pd$: C, 48.47; H, 4.78; N, 17.21. Found: C, 48.76; H, 4.83; N, 17.00%. Complex 8: Anal. Calc. for $C_{10}H_{21}N_3P_2SPd$: C, 31.30; H, 5.52; N, 10.95. Found: C, 31.59; H, 5.50; N, 10.83%. Complex 9: Anal. Calc. for $C_{10}H_{21}N_5P_2Pd$: C, 31.63; H, 5.57; N, 18.45. Found: C, 31.38; H, 5.59; N, 17.93%. Complex 10: Anal. Calc. for $C_{11}H_{22}N_4P_2Pd$: C, 34.89; H, 5.86; N, 14.80. Found: C, 34.53; H, 5.79; N, 14.21%.

3.2. Reactions of $[PdN_3 (2-thienyl)(PMe_3)_2]$ and $[PdBr(2-thienyl)(PMe_3)_2]$ with $CN-2,6-Me_2C_6H_3$

To a Schlenk flask containing $[PdN_3(2-thienyl)(PMe_3)_2]$ (0.284 g, 0.74 mmol) were added $CH_2Cl_2(5 \text{ ml})$ and CN-Ar($Ar = 2,6-Me_2C_6H_3$) (0.194 g, 1.48 mmol) in that order. The initial colorless solution immediately turned to a pale yellow solution with evolution of nitrogen. After stirring for 16 h at room temperature, the solvent was completely evaporated under vacuum, and then the resulting residue was solidified with diethyl ether. The solids were filtered off and washed with diethyl ether to give crude solids. Recrystallization from $CH_2Cl_2/hexane$ gave pale yellow crystals of **12**, $[Pd(N=C=N-Ar){C(=N-Ar)-2-thienyl}-(PMe_3)_2$ (0.180 g, 39%). *Anal.* Calc. for $C_{28}H_{39}N_3P_2SPd$: C, 54.41; H, 6.36; N, 6.80. Found: C, 54.22; H, 6.43; N, 6.64%.

Complex [PdBr{C(=N-Ar')-2-thienyl}(PMe_3)₂] (11, 50%) was prepared analogously. *Anal.* Calc. for $C_{19}H_{30}BrNP_2SPd$: C, 41.28; H, 5.47; N, 2.53. Found: C, 41.26; H, 5.45; N, 2.42%.

3.3. Reactions of $[Pd(R)N_3L_2]$ (R = 1-phenyl-5-tetrazolyl and 2-pyrazinyl) with $CN-2,6-Me_2C_6H_3$

To a Schlenk flask containing $[Pd(R)N_3(PMe_3)_2]$ (R = 1-phenyl-5-tetrazoyl) (0.157 g, 0.35 mmol) were added CH₂Cl₂ (2 ml) and CN–Ar (Ar = 2,6-*Me*₂C₆H₃) (0.047 g, 0.36 mmol) in that order. The initial colorless solution immediately turned to a pale yellow solution with N₂ evolution. After stirring for 16 h at room temperature, the solvent was completely evaporated under vacuum, and then the resulting residue was solidified with diethyl ether. The solids were filtered off and washed with diethyl ether to give crude solids. Recrystallization from CH₂Cl₂/hexane gave pale yellow crystals of [Pd(R)(N=C=N-Ar)(PMe_3)_2] (13, 0.148 g, 77%) (s). *Anal.* Calc. for C₂₂H₃₂N₆P₂Pd: C, 48.14; H, 5.88; N, 15.31. Found: C, 48.64; H, 6.25; N, 14.74%.

Complexes $[Pd(R)(N=C=N-Ar)(PMe_2Ph)_2]$ (R = 1-phenyl-5-tetrazolyl) (14, 58%) and $[Pd(R)(N=C=N-Ar)(PMe_3)_2]$ (R' = 2-pyrazinyl) (15, 69%) were prepared analogously.

Complex 14: Anal. Calc. for $C_{32}H_{36}N_6P_2Pd$: C, 57.11; H, 5.39; N, 12.49. Found: C, 57.24; H, 5.45; N, 12.63%. Complex 15: Anal. Calc. for $C_{19}H_{30}N_4P_2Pd$: C, 47.26; H, 6.26; N, 11.60. Found: C, 46.37; H, 6.56; N, 11.10%.

3.4. X-ray structure determination

All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with χ -scan data. All calculations were carried out with the use of SHELXTL programs [20]. All structures were solved by direct methods. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode.

Details on crystal data, intensity collection, and refinement details are given in Table 1.

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Appendix A. Supplementary material

CCDC 653959, 653960, 653961 and 653962 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre 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.ica.2007.10.026.

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