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Synthesis and properties of arylpalladium(II) azido complexes $PdAr(N_3)(PR_3)_2$. Nucleophilic reactions of the azido ligand with CO and with isocyanides to afford Pd(II) isocyanate, *C*-tetrazolate and carbodiimide complexes

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Abstract

The tmeda ligand in the complexes, $PdAr(N_3)(tmeda)$ is easily replaced by addition of tertiary phosphine or chelated phosphine to give the corresponding palladium(II) azido complexes with the phosphines ligand, $PdAr(N_3)L_2$ (**1**: Ar = Ph, L = PMe_3; **2**: Ar = Ph, L = PEt_3; **3**: Ar = tolyl, L = PMe_3; **4**: Ar = naphthyl, L = PMe_3; **5**: L_2 = dppe). Complex **3** was characterized by X-ray crystallography. Complexes **1**–**2** react with CO (1 atm) to afford Pd(II) isocyanates, $PdPh(NCO)L_2$ (**6**, L = PMe_3; **7**: L = PEt_3), in 98 and 76% yields, respectively. In contrast, the reaction of *trans*-$PdMe(N_3)(PMe_3)_2$ with CO gives acetylpalladium isocyanate, *trans*-$Pd(COMe)(NCO)(PMe_3)_2$ (**8**) in 96% yield, which is characterized by X-ray crystallography. Reactions of **1** with an equal amount of *tert*-butyl and cyclohexyl isocyanides cause 1,3-dipolar addition of the isocyanides to the azido ligand, to give the complexes, *trans*-$PdPh[CN_4(R)](PMe_3)_2$ (R = $C(CH_3)_3$, **9**; C_6H_{11}, **10**) with a five-membered heterocyclic ring (*C*-coordinated tetrazolato group). However, similar reactions of **1** and **3** with 2,6-dimethylphenyl isocyanide result in the unusual formation of Pd(II) complexes containing carbodiimido ligand, *trans*-(*p*-Y-C_6H_4)Pd(NCN-2,6-$Me_2C_6H_3$)$(PMe_3)_2$ (Y = H, **11**; Y = Me, **12**) in 51 and 94% yields, respectively. Reactions of **1** with protonating agents such as benzenthiol and phenylacetylene are also described.

Keywords: Palladium; Azido; Isocyanate; Carbodiimide; Tetrazolato

1. Introduction

The azido (N_3^-) group coordinated to transition metals has been intensively studied for many years, as one of the important pseudo-halogeno ligands including CN, SCN, and NCS [1]. The azido group can be easily introduced into transition metal complexes by metathesis reaction of NaN_3 with halogeno complexes of the transition metals. The azido ligand bonded to transition metals undergo thermally or photo induced cycloaddition or nitrene compounds formation, whereas halogeno or other pseudo-halogeno ligands compounds exhibit poorer chemical properties [2]. Several Group 10 metal azido complexes with chelating or tertiary phosphine and amine ligands were studied from the viewpoints of the structural and magnetic properties and reactions such as formation of metal nitrides species or cluster compounds [3–7]. Recently, we also reported synthesis and reactions of palladium(II) and platinum(II) azido complexes containing chelating diamines or bisphosphines and monodentate tertiary phosphines [8]. Among these studies of Group 10 metal azido complexes, those of chemical reactions on the metal azido complexes having alkyl or aryl ligand are scarce [5,8]. The organometallic complexes with the azido ligand possess potential utility as a precursor of organotransition metal amide complex or organic amines since the use of a suitable reducing agent would cause the hydrogenation of the coordinated azido

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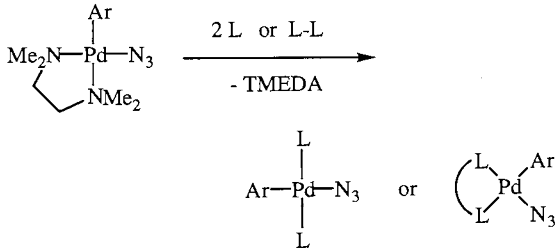
group, which can be extended to transformation of organic azides to amines catalyzed by Group 10 metal complexes.

As an extension of our recent work on the methylpalladium(II) and platinum(II) azido complexes, herein we report the preparation of arylpalladium(II) azido complexes and their chemical properties toward CO and isocyanides.

2. Results and discussion

2.1. Preparation of arylpalladium(II) azido complexes

It is well known that tmeda (*N*,*N*,*N′*,*N′*-tetramethylethylenediamine) or COD (1,5-cyclooctadiene) ligand coordinated to late transition metal is labile and easily replaced by other P-donor ligands [9–11]. Recently we reported the formation of methylpalladium(II) and -platinum(II) azido complexes containing tmeda or COD which is easily replaced with various tertiary or chelating phosphines to give the corresponding phosphine complexes with the azido ligand [8a,b]. In this work we applied similar ligand exchange reactions of PdAr(N_3)(tmeda) (Ar = phenyl, 4-methylphenyl, naphthyl) with PMe_3, PEt_3, and chelating phosphine as shown in Eq. (1). These reactions provide a convenient synthetic method for various new arylpalladium(II) azido complexes. The complexes **1**–**5** are isolated in 78–91% yields as colorless or pale-yellow crystalline solids, which are thermally stable in the solid state and in solution. The complexes were characterized by IR, NMR (^1H and $^{13}C\{^1H\}$) spectra and elemental analyses. Analytical and IR data, ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR data of the complexes are summarized in Tables 1–3, respectively. IR spectra show a strong absorption band due to asymmetric stretching vibrations $\nu(N_3)$ in the range 2028–2037 cm^{-1}.



(1)

1: Ar = C_6H_5, L = PMe_3;
2: Ar = C_6H_5, L = PEt_3;
3: Ar = $C_6H_4CH_3$-*p*, L = PMe_3;
4: Ar = 1-$C_{10}H_7$, L = PMe_3;
5: Ar = C_6H_5, L - L = $Ph_2P(CH_2)_2PPh_2$

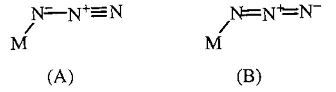
Colorless crystals of **3** were obtained from an ether solution at −30°C and analyzed by X-ray crystallography. The molecule of **3** depicted in Fig. 1 contains a 4-methylphenyl, two PMe_3 at mutually *trans* positions, and one azido ligand around the square-planar Pd center. The plane of the tolyl group lies almost perpendicular to the coordination plane. The Pd–N1 bond length (2.114(3) Å) is close to that of *trans*-PdMe(N_3)(PMe_3)$_2$ (2.132(9) Å) [8b], and is slightly longer than that of (tmeda)Pd(N_3)(C_6H_4-*p*-Me) (2.017(9) Å) [8a], [($C_6H_5CH_2$)$_3$P]$_2$Pd(N_3)$_2$ (2.045(6) Å) [12], and $Pd_2(N_3)^{2-}$ (2.004(5) Å) [13], implying a larger *trans* influence of phenyl ligand than azido group. The bond angle N1–N2–N3 (176.3 (4)°) belongs to the range of previously reported coordinated azide (173–180°) [2c]. A longer N1–N2 (1.176 (4) Å) distance than the N2–N3 (1.152 (4) Å) distance indicates contribution

Table 1
Color, yield, analytical and IR results for complexes **1**–**13**

Complex	Color	Yield (%)	Analyses [a]			IR (cm^{-1}) [b]
			C (%)	H (%)	N (%)	
1	Pale yellow	91	37.97 (38.16)	6.29 (6.14)	10.80 (11.13)	2032 $\nu(N_3)$
2	Colorless	78	46.63 (46.81)	7.50 (7.64)	8.91 (9.10)	2028 $\nu(N_3)$
3	Colorless	86	39.67 (39.86)	6.43 (6.43)	10.75 (10.73)	2035 $\nu(N_3)$
4	Pale yellow	78	44.96 (44.93)	5.88 (5.89)	9.72 (9.82)	2037 $\nu(N_3)$
5	Pale yellow	80	61.06 (61.60)	4.75 (4.68)	6.57 (6.73)	2028 $\nu(N_3)$
6	Colorless	98	41.25 (41.34)	5.78 (6.14)	3.67 (3.71)	2180 ν(NCO)
7	Pale yellow	77	49.34 (49.41)	7.62 (7.64)	3.03 (3.03)	2180 ν(NCO)
8	Colorless	96	31.04 (31.46)	6.05 (6.16)	3.94 (4.08)	2176 ν(NCO) 1642 ν(CO)
9	Colorless	78	44.01 (44.31)	6.91 (7.00)	11.91 (12.16)	
10	White	51	45.55 (46.87)	7.18 (7.04)	9.94 (11.51)	
11	Colorless	51	52.48 (52.46)	6.64 (6.71)	5.72 (5.83)	2127 ν(NCN)
12	White	94	53.34 (53.40)	6.79 (6.92)	5.62 (5.66)	2149 ν(NCN)
13	White	71	49.18 (48.60)	6.56 (6.34)	6.90 (7.21)	

[a] Calculated values are given in parentheses.

[b] KBr disks.

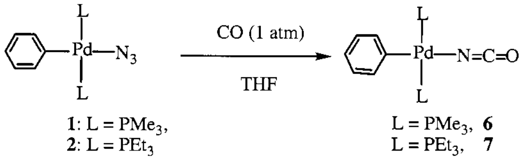


Scheme 1.

of structure (A) rather than the alternative resonance structure shown in Scheme 1.

2.2. Reactions of phenyl(or methyl)palladium(II) azido complexes with CO

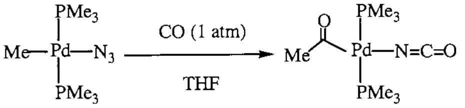
Reactions of **1** and **2** with CO (1 atm) at room temperature (r.t.) in THF, smoothly proceed to give isocyanato complexes *trans*-$PdPh(NCO)L_2$ (L = PMe_3, **6**; PEt_3, **7**) in 98 and 76% yields, respectively, as shown in Eq. (2).



(2)

The reaction was monitored by the IR spectra of the reaction mixture, which shows a decrease in the intensity of the asymmetric stretching band of the N_3 group at ca. 2030 cm^{-1}, and growth of a new band at 2180 cm^{-1} of the product. The reactions occurred cleanly and gave no other by products such as benzoyl isocyanato complex, $PhC(=O)Pd(NCO)L_2$ or benzoyl azido complex, $PhC(=O)Pd(N_3)L_2$. Complexes **6** and **7** are obtained as colorless crystals and characterized by IR, NMR (^{1}H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-), and elemental analyses (Tables 1–3). A weak ^{13}C-NMR signal at 128 ppm of **6** is assigned to the quaternary carbon of N=C=O, indicating a conversion of the azido to the isocyanate ligand.

The reaction of *trans*-$PdMe(N_3)(PMe_3)_2$ [8b] with CO (1 atm) gives the acetylpalladium isocyanato complex *trans*-$Pd(COMe)(NCO)(PMe_3)_2$ (**8**) in 96% yield as shown in Eq. (3).



(3)

The reaction results in both CO insertions into the Pd–methyl bond to give an acyl group and conversion of the azido ligand to an isocyanato group coordinated to Pd center. The IR spectrum of **8** shows a strong absorption bands at 1642 cm^{-1} due to carbonyl in the acyl group and at 2176 cm^{-1} due to the isocyanato group. The former band falls within the value (1610–1675 cm^{-1}) of acyl group coordinated Pd center [14]. The ^{1}H-NMR signal at 2.30 ppm of **8** is attributed to the CH_3 hydrogen of the acetyl ligand. The $^{13}C\{^1H\}$-NMR spectrum contains a signal at 228.9 and 128.5 ppm, which are assigned to the carbonyl carbon of the acetyl ligand and the quaternary carbon of the N=C=O ligand, respectively. All these spectroscopic data of **8** are well consistent with the proposed structure.

Table 2
^{1}H-NMR data for complexes **1**–**13** [a]

Complex	PR_3 [b]	Others [c]
1	1.14 (t, 18H, 4 Hz, PMe_3)	6.82 (t, 1H), 6.93 (t, 2H), 7.12 (d, 2H)
2	1.09 (q, 18H, 8 Hz, $P(CH_2CH_3)_3$) 1.51 (m, 12H, $P(CH_2CH_3)_3$)	6.85 (t, 1H), 6.97 (t, 2H), 7.19 (d, 2H)
3	1.18 (t, 18H, 3 Hz, PMe_3)	2.21 (s, 3H, $-CH_3$), 6.83 (d, 2H), 7.03 (d, 2H)
4	1.08 (t, 18H, 3 Hz, PMe_3)	7.14–7.19 (m, 1H), 7.36–7.45 (m, 4H) 7.66–7.71 (m, 1H), 8.39–8.42 (m, 1H)
5	2.18 (m, 2H, P–CH_2) 2.46 (m, 2H, P–CH_2)	6.76–6.87 (m, 3H), 7.09–7.15 (2H) 7.28–7.47 (m, 17H), 7.83–7.90 (m, 3H)
6	1.16 (t, 18H, 4 Hz, PMe_3)	6.87 (t, 1H), 6.99 (t, 2H), 7.20 (d, 2H)
7	1.01 (q, 18H, 8 Hz, $P(CH_2CH_3)_3$) 1.48 (m, 12H, PCH_2)	6.83 (t, 1H), 6.95 (t, 2H), 7.20 (d, 2H)
8	1.38 (t, 18H, 4 Hz, PMe_3)	2.30 (s, 3H, $-COCH_3$)
9	0.96 (t, 18H, 3 Hz, PMe_3)	1.84 (s, $C(CH_3)_3$), 6.90 (t, 1H), 7.02 (br, 2H), 7.34 (br, 2H)
10	0.97 (t, 18H, 4 Hz, PMe_3)	1.25–1.48 (m, 4H, $-C_6H_{11}$), 1.79–2.16 (m, 7H, $-C_6H_{11}$) 4.55 (m, 1H, $-C_6H_{11}$), 6.92 (t, 1H), 7.05 (t, 2H), 7.34 (br, 2H)
11	1.16 (t, 18H, 4 Hz, PMe_3)	2.39 (s, 6H, $(CH_3)_2$–C_6H_3), 6.66 (t, 1H), 6.88–7.01 (m, 5H), 7.22 (d, 2H)
12	1.16 (t, 18H, 4 Hz, PMe_3)	2.21 (s, 3H, C_6H_4-*p*-CH_3), 2.38 (s, 6H, $(CH_3)_2$–C_6H_3) 6.65 (t, 1H), 6.83 (d, 2H), 6.91 (d, 2H), 7.06 (d, 2H)
13	1.12 (t, 18H, 3 Hz, PMe_3)	6.89 (t, 1H), 6.92 (t, 1H), 7.04 (m, 4H), 7.37 (d, 2H), 7.62 (d, 2H)

[a] At 25°C in $CDCl_3$. 500 MHz for **1**, **2**, **5**, **6**, **8**–**10**, and **13**. 300 MHz for **3**, **4**, **7**, **11**, and **12**.

[b] Apparent triplet or quintet due to virtual coupling unless otherwise stated. Splitting, due to the virtual coupling, is in parentheses.

[c] Aryl hydrogens unless otherwise stated.

Crystals of **8** were analyzed by X-ray crystallography. The molecular structures of **8** with the atomic numbering scheme are shown in Fig. 2. The molecule of **8** has a square planar coordination around a Pd center containing two PMe_3 ligands, an acetyl, and an isocyanato ligand. The isocyanato (N=C=O) and acetyl ligands are at mutually *trans* positions. The acetyl plane is essentially perpendicular to the equatorial plane with a dihedral angle of 86.0(2)°. The Pd–N bond distance of 2.119(5) Å is close to that found in **3** (2.114(3) Å) and that of *trans*-$PdPh(NHPh)(PMe_3)_2$ (2.116(13) Å) [15]. The CO (1.187 Å) bond distance in the NCO ligand is longer than the CN (1.127 Å) distance similarly to those found in other

Table 3
$^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR data for complexes **1**–**13**

	$^{13}C\{^1H\}$ [a]		$^{31}P\{^1H\}$ [b]
	PR_3 [c]	Others [d]	
1	13.17 (t, 14 Hz, PMe_3)	122.9 (s), 127.8 (s), 135.9 (s), 159.5 (t)	−15.7
2	7.8 (s, $P(CH_2CH_3)_3$) 13.9 (t, 13 Hz, PCH_2)	122.3 (s), 127.5 (s), 136.0 (t, $J = 4$ Hz), 150.7 (s)	14.6
3	13.2 (t, 14 Hz, PMe_3)	20.7 (s, CH_3), 128.6 (s), 131.9 (s), 135.5 (t, 5 Hz), 145.2 (t, $J = 8$ Hz)	−15.9
4	13.4 (t, 14 Hz, PMe_3)	122.8, 124.4, 125.0, 125.4, 128.2, 132.3, 132.6 (t, $J = 3$ Hz), 134.0, 139.0, 153.1 (t, $J = 9$ Hz) (naphthyl)	−14.5
5	22.5 (dd, $-CH_2$) $J = 11$, 21 Hz 29.9 (dd, $-CH_2$) $J = 22$, 31 Hz	127.8, 127.9, 128.7, 128.8, 129.0, 129.1, 129.3, 129.7, 130.8, 131.0, 131.6, 131.2, 131.2, 132.9, 133.0, 133.2, 133.3, 135.1, 135.2, 135.1, 135.2	32.7, 50.4, $J = 28$ Hz
6	13.4 (t, 15 Hz, PMe_3)	122.8 (s), 127.6 (s), 128.3 (s, NCO), 136.1 (t, $J = 5$ Hz), 150.4 (s)	−16.4
7 [e]	7.82 (s, $P(CH_2CH_3)_3$) 14.1 (t, 13 Hz, PCH_2)	122.2, 127.4 (Ph), 136.4 (t, $J = 4$ Hz), 150.3 (Ph)	14.6
8	14.1 (t, 14 Hz, PMe_3)	42.0 (t, $J = 18$ Hz, $-COCH_3$), 128.5 (s, NCO), 228.8 (s, $-COCH_3$)	−18.7
9	14.5 (t, 15 Hz, PMe_3)	31.3 (s, $C(CH_3)_3$), 57.2 (s, $C(CH_3)_3$), 122.7 (s), 126.9 (s), 127.3 (s), 137.9 (s), 138.4 (s), 160.4 (t, $J = 10$ Hz), 168.4 (t, 16 Hz, CN_4 (t-Bu))	−18.1
10	14.5 (t, 15 Hz, PMe_3)	22.6 (s, C_6H_{11}), 25.8 (s, C_6H_{11}), 34.0 (s, C_6H_{11}), 58.8 (s, C_6H_{11}), 122.8 (s), 126.9 (s), 127.4 (s), 137.1 (s), 138.3 (s), 161.3 (t, $J = 10$ Hz), 171.3 (t, $J = 17$ Hz, $CN_4(C_6H_{11})$)	−17.0
11 [e]	13.5 (t, 14 Hz, PMe_3)	19.4 (s, $(CH_3)_2$–C_6H_3), 119.1 (s), 122.7 (s), 127.6 (s), 127.7 (s), 130.9 (s), 136.2 (t, $J = 5$ Hz), 145.2 (s), 150.9 (bs)	−16.3
12 [e]	13.6 (t, 14 Hz, PMe_3)	19.5 (s, C_6H_4-p-Me), 20.7 (s, $(CH_3)_2$–C_6H_3), 119.1, 127.7, 128.6, 130.9, 131.8), 131.9 (s), 135.9 (t, $J = 5$ Hz), 145.3 (s)	−16.4
13	13.9 (t, 15 Hz, PMe_3)	120.9, 122.6), 127.4, 127.5, 132.5 (s), 136.6 (t, $J = 5$ Hz), 149.9 (s), 159.0 (t, $J = 8$ Hz)	−16.4

[a] At 25°C in $CDCl_3$. 125 MHz for **1**, **2**, **5**, **6**, **8**–**10**, and **13**. 75 MHz for **3**, **4**, **7**, **11**, and **12**.

[b] At 25°C in $CDCl_3$. 200 MHz for **1**, **2**, **5**, **6**, **8**–**10**, and **13**. 120 MHz for **3**, **4**, **7**, **11**, and **12**.

[c] Apparent triplet or quintet due to virtual coupling except **5**. Splitting due to the virtual coupling are in parentheses except **5**.

[d] Aromatic carbons unless otherwise stated.

[e] NCN and NCO carbon signals are weak and not observed.

transition metal isocyanates [1]. The CN bond length is nearer to that of reported the C≡N (1.16 Å) [16] rather than the C–N single bond distance (1.47 Å) (see Table 4 for a full list of bond lengths and angles).

It is assumed that the CO coordinates in the central metal atom as the initial step and is followed by the interaction between azido group and the coordinated CO and then finally N–N_2 bond cleaves to give the isocyanato group. Another possibility of the prior dissociation of azido anion or phosphine ligand has been considered. Earlier work by Beck and co-workers demonstrated that several transition metal azido complexes react with CO to give corresponding isocyanato complexes [2a,17]. They also suggested the mechanism by the basis of kinetic experiments. Several additional examples of the complexes by other researcher also have been reported [18,19].

Different products in the preceding two reactions (Eqs. (2) and (3)) show that CO is inserted into the Pd–methyl bond more easily than the Pd–phenyl bond under mild conditions and vice versa, indicate that the M–C (sp^2) bond is more kinetically stable than the M–C(sp^3) bond toward CO.

2.3. Reactions of **1** with isocyanides

We have further developed small-molecule insertion reactions using isocyanides, which are isoelectronic with

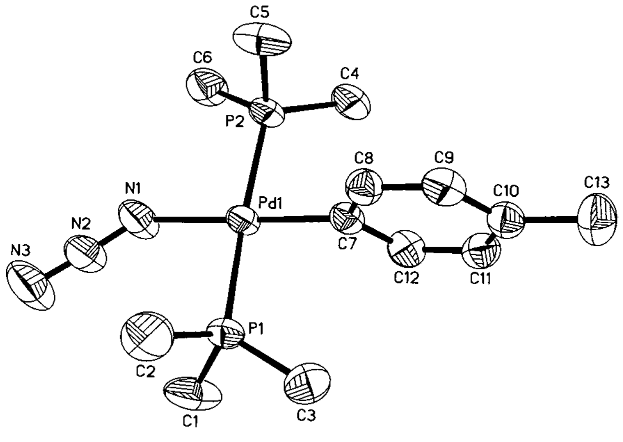


Fig. 1. An ORTEP drawing of **3** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

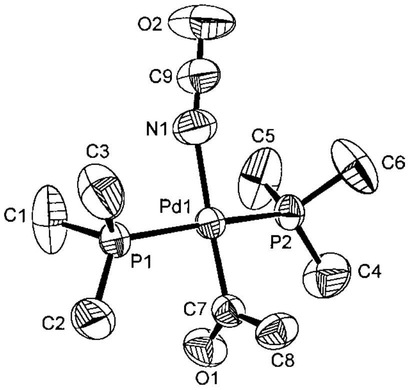


Fig. 2. An ORTEP drawing of **8** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

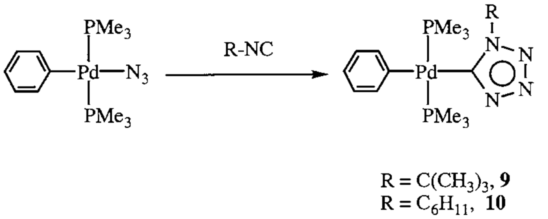
Table 4
Selected bond distances (Å) and bond angles (°) for **3**, **8**, and **11**

	3	**8**	**11**
Bond distances			
Pd1–C7	2.010(3)	1.963(5)	2.014(3)
Pd1–N1	2.114(3)	2.119(5)	2.087(3)
Pd1–P1	2.3106(8)	2.324(1)	2.3111(9)
Pd1–P2	2.3252(8)	2.318(1)	2.3231(8)
N1–N2	1.176(4)		
N2–N3	1.152(4)		
O1–C7		1.200(6)	
O2–C9		1.187(6)	
N1–C9		1.127(7)	
C7–C8		1.499(7)	
N1–C13			1.172(4)
N2–C13			1.270(4)
N2–C14			1.408(4)
Bond angles			
C7–Pd1–N1	178.44(12)	175.8(2)	175.36(11)
P1–Pd1–P2	174.77(3)	170.27(5)	169.62(3)
C7–Pd1–P1	87.58(8)	89.0(1)	85.28(9)
N1–Pd1–P1	93.37(8)	91.3(1)	92.99(8)
C7–Pd1–P2	87.75(8)	89.9(1)	88.88(9)
N1–Pd1–P2	91.24(8)	90.5(2)	93.45(8)
N2–N1–Pd1	132.4(2)		
N3–N2–N1	176.3(4)		
C9–N1–Pd1		166.9(5)	
O1–C7–C8		119.7(5)	
O1–C7–Pd1		125.4(4)	
C8–C7–Pd1		115.0(4)	
N1–C9–O2		178.8(7)	
N1–C13–N2			172.8(3)

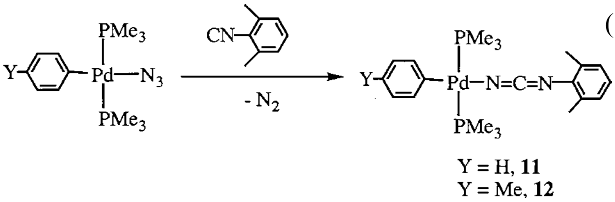
CO. Previously we observed 1,3-dipolar addition of isocyanides to the azido moiety of methylpalladium(II) and platinum(II) azido complexes giving five-membered heterocycles [8b]. In this work we have carried out similar additional reactions using various isocyanides. Reactions of an equimolar amount of *tert*-butyl isocyanide and cyclohexyl isocyanide with **1** in THF at r.t. give the complexes with a five-membered heterocyclic ring (*C*-coordinated tetrazolato ring), *trans*-PdPh[CN$_4$(R)](PMe$_3$)$_2$ (R = *t*-Bu, (**9**); R = cyclohexyl, (**10**) in 51 and 78% yield as shown in Eq. (4). The complexes were obtained as colorless crystals, which are stable in solid state and in solution, and characterized by IR, NMR, and elemental analyses. The product formation was easily confirmed by disappearance of ν(N$_3$) absorption band. Other insertion products such as imino acyl complex, *trans*-PhC(=NR)PdN$_3$(PMe$_3$)$_2$ by isocyanide insertion into the Pd–phenyl bond were not observed.

The cycloaddition reactions of late transition metal complexes using isocyanides to give the complexes with *C*-coordinated tetrazolato ring, have been originally studied by Beck and co-workers [20], whereas similar reactions of azido complexes of Pd(II) [19], Co(II) [21], Cu(I), Ag(I), and Au(I) [22] having terminal or bridging azido ligands with CS$_2$ or CF$_3$CN to give the complexes with *N*-coordinated tetrazolato ring have also been studied by several research groups.

Similar reactions of **1** and **3** with 2,6-dimethylphenyl isocyanide under similar conditions unusually afford the palladium(II) complexes containing carbodiimido ligand, *trans*-(*p*-Y-C$_6$H$_4$)Pd(NCN-2,6-Me$_2$C$_6$H$_3$)(PMe$_3$)$_2$ (Y = H, (**11**); Y = Me, (**12**)) in 51 and 94% yields, respectively, as shown in Eq. (5).



(4)



(5)

The carbodiimido complexes **11** and **12** exhibit new strong ν(NCN) IR bands at 2126 and 2149 cm^{-1}. Their completion can be monitored easily by the disappearance of the asymmetric stretching band of the N$_3$ group, at ca. 2030 cm^{-1} in the IR spectrum of the reaction mixture. The reactions occurred cleanly and gave no other by products such as the tetrazolato complex, *trans*-(*p*-Y-C$_6$H$_4$)Pd[CN$_4$(2,6-Me$_2$C$_6$H$_3$)](PMe$_3$)$_2$ and the iminoacyl complex, *trans*-(*p*-Y-C$_6$H$_4$)C(=NR)PdN$_3$(PMe$_3$)$_2$. To our knowledge, complexes **11** and **12** are the first isolated examples of Group 8–10 transition metal carbodiimido complexes.

Fig. 3 shows the molecular structure of **11**, which has a slightly distorted square-planar coordination, containing two PMe$_3$, phenyl, and NCN-2,6-Me$_2$C$_6$H$_3$ group. The carbodiimido (N=C=N) group with an approximate linear angle (N1–C13–N2, 172.8°) is out of the equatorial plane. The Pd–N (2.087 Å) distance falls in the range of Pd–N distances as the case previously discussed metal azides and other comparable bond lengths are not available, because there have been no related reports. However, interestingly, the N1–C13 (1.172 Å) bond distance is very close to the general C≡N (1.16 Å) and is shorter than that of N2–C13 (1.270 Å). This feature is similar to the NC (1.139 Å) and CN (1.314 Å) bond lengths of $(CO)_5CrNCN(C_2H_5)_2$ [23], prepared from the reaction of $[(CO)_5CrCN(C_2H_5)_2][BF_4]$ with $[N(C_4H_9)]N_3$. Beck and co-workers [20d] reported the preparation of an Au carbodiimide complex from the thermolysis of $AsPh_4[Au(CN_4CH_2C_6H_5)_4]$. Polymerization of carbodiimide has been reported recently by the use of transition metal complexes as the catalyst [24]. The carbodiimide complexes are considered as an important intermediate in the polymerization.

The phenyl- and methylpalladium azido complexes with a *trans* structure, react with CO and CNR to afford various kinds of products as described previously. The reactions probably involves initial nucleophilic attack of the azido ligand to CO or CNR molecules coordinated to the Pd center to form a new C–N bond. Ensuing elimination of N_2 molecule or cyclization occurs to give isocyanate complex or *C*-tetrazolato complex. Direct formation of the carbodiimide complex is a new reaction and seems to involve initial formation of the *C*-coordinated tetrazolato complex, which undergoes elimination of an N_2 molecule to give the product. The carbodiimide formation may be explained by the electronic or steric factor of the coordinated ligands around the Pd center as well as attacking isocyanide.

2.4. Other reactions of **1**

In order to get further insight on chemical properties of the azido complexes we have examined reactions of benzenethiol and phenylacetylene with **1**. The reaction of **1** with an equimolar amount of benzenethiol at r.t., produced a thiolato complex *trans*-$PdPh(SPh)(PMe_3)_2$ (**13**) in 71% yield, as a white solid, as shown in Eq. (6).

$$\begin{array}{l} trans\text{-}PdPh(N_3)(PMe_3)_2 + \underset{(1\ eq)}{HSPh} \longrightarrow \underset{\mathbf{13},\ 71\%}{trnas\text{-}PdPh(SPh)(PMe_3)_2} \\ \\ trans\text{-}PdPh(N_3)(PMe_3)_2 + \underset{(4\ eq)}{HSPh} \longrightarrow \underset{(62\ \%)}{\mathbf{13}} + \underset{(12\ \%)}{trans\text{-}Pd(SPh)_2(PMe_3)_2} \end{array} \quad (6)$$

The isolated complex is soluble in ether and hexane. However, the same reaction of an excess amount of benzenethiol gave **13** (62%) as a major product and a bisthiolato complex, *trans*-$Pd(SPh)_2(PMe_3)_2$ (12%) as a minor product, which was identified by comparison of the NMR data with that of the authentic complex. A similar reaction of **1** with an excess amount of phenylacetylene, did not occur and resulted in stoichiometric recovery of the starting complex. Previously we have reported that reaction of *trans*-$PdMe(N_3)(PMe_3)_2$ with an equimolar or excess amount of phenylacetylene at r.t. in THF afforded a bisacetylide complex, $Pd(C{\equiv}CPh)_2(PMe_3)_2$ [8b]. These results indicate that the Pd–phenyl bond is more stable than the Pd–methyl bond toward protonating agents.

In summary, we have prepared new arylpalladium(II) azido complexes with a *trans* structure and the reaction with CO, CNR and HSPh to convert the azido ligand to N=C=O, CN_4R, and SPh ligands, respectively. The products of the two former reactions suggest nucleophilic attack of the azido ligand bonded to the metal center toward electrophilic carbons of CO and CNR or protic hydrogen of HSPh. The functionality of the azido ligand bonded to the metal center having aryl or alkyl ligand seems to be of interest as the reaction intermediate of the corresponding synthetic organic reactions catalyzed by the Group 10 metals.

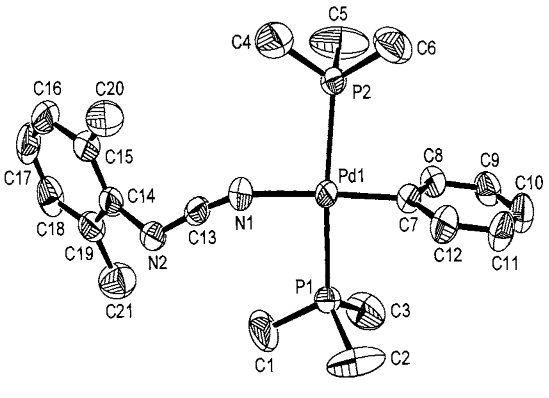


Fig. 3. An ORTEP drawing of **11** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

3. Experimental

All the manipulations of air-sensitive compounds were performed under N_2 or argon atmosphere with use of standard Schlenk technique. Solvents were distilled from Na-benzophenone. $PdAr(N_3)(tmeda)$ (Ar = C_6H_5, C_6H_4-*p*-Me, and 1-naphthyl) [8a] and *trans*-$PdMe(N_3)(PMe_3)_2$ [8b] were prepared by the literature method. Elemental analyses were carried out by the analytical laboratory at Basic Science Institute of Korea. IR spectra were recorded on a Hitachi 270–30 and Perkin–Elmer BX spectrophotometer. NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectra were obtained on Bruker-300 and 500 MHz and on JEOL Lamda 300 MHz spectrometers. Chemical shifts were referenced to an internal Me_4Si and to an external 85% H_3PO_4.

3.1. Preparation of arylpalladium(II) azido complexes (**1**–**5**)

To a stirred THF (30 ml) solution containing $PdPh(N_3)(tmeda)$ (0.424 g, 1.24 mmol) was slowly added PMe_3 (0.282 ml, 2.73 mmol) at r.t. by a syringe. After stirring for 1 h, the pale yellow solution was evaporated and the resulting solid was washed with hexane. Recrystallization from THF–hexane gave pale yellow crystals of **1** (0.424 g, 91%). Complexes **2**–**5** were prepared analogously.

3.2. Reactions of **1** and **2** with CO

Complex **1** (0.300 g, 0.80 mmol) was dissolved in THF (3 ml) at r.t. After evacuation of the system, CO (1 atm) was introduced and the initial solution slowly turned colorless. After stirring for 24 h the solvent was evaporated under reduced pressure to give a white solid. Recrystallization from THF–hexane gave colorless crystals of **6** (0.295 g, 98%).

Reaction of **2** with CO proceeded analogously, to give **7** as pale yellow crystals (77%).

3.3. Reaction of *trans*-$PdMe(N_3)(PMe_3)_2$ with CO

trans-$PdMe(N_3)(PMe_3)_2$ (0.327 g, 1.035 mmol) was dissolved in THF (4 ml) at r.t. After evacuation of the system, CO (1 atm) was introduced and the initial solution slowly turned colorless. After stirring for 48 h the solvent was evaporated under reduced pressure to give a white solid. Recrystallization from THF–hexane gave colorless crystals of **8** (0.343 g, 96%).

3.4. Reaction of **1** and **4** with *tert*-butyl and cyclohexyl isocyanides

To a THF (5 ml) solution containing **1** (0.267 g, 0.71 mmol) was added *tert*-butyl isocyanide (0.071 g, 0.85 mmol) at r.t. The initial yellow solution turned colorless. After stirring for 4 h, the reaction mixture was stored at −20°C for ca. 12 h and the resulting white precipitate was washed with hexane (2 × 3 ml). Recrystallization from THF–hexane gave colorless crystals of *trans*-$PdPh[CN_4(R)](PMe_3)_2$ ($R = C(CH_3)_3$) (**9**, 0.253 g, 78%). Reaction of **1** with cyclohexyl isocyanide gave *trans*-$PdPh[CN_4(R)](PMe_3)_2$ ($R = C_6H_{11}$) (**10**) analogously (51%).

3.5. Reactions of **1** and **3** with 2,6-dimethylphenyl isocyanide

To a CH_2Cl_2 (1 ml) solution containing **1** (0.211 g, 0.56 mmol) was added 2,6-dimethylphenyl isocyanide (0.073 g, 0.56 mmol) at r.t. The initial pale yellow solution instantly turned yellow with evolution of nitrogen. After stirring for 3 h the reaction mixture was fully evaporated and then the resulting solid was washed with hexane (3 × 2 ml). Recrystallization from CH_2Cl_2–hexane gave colorless crystals of *trans*-$PdPh(N{=}C{=}N{-}R)(PMe_3)_2$ ($R = 2,6\text{-}Me_2C_6H_3$) (**11**, 0.136 g, 51%). Reaction of **3** with 2,6-dimethylphenyl isocyanide proceeded analogously to give *trans*-$Pd(C_6H_4$-*p*-$Me)(N{=}C{=}N{-}R)(PMe_3)_2$ ($R = 2,6\text{-}Me_2C_6H_3$) (**12**, 0.449 g, 94%).

3.6. Reactions of **1** with HSPh and diphenylacetylene

To a THF (4 ml) solution of **1** (0.222 g, 0.59 mmol) was added benzenethiol (0.065 g, 0.59 mmol) at r.t. The initial colorless solution instantly turned yellow. After stirring for 2 h the yellow solution was fully evaporated to give a yellowish residue. Addition of hexane dissolved the residue. Cooling of the filtered solution for several hours at −30°C produced a white precipitate, which was collected by filtration to give *trans*-$PdPh(SPh)(PMe_3)_2$ (**13**, 0.188 g, 71%) as a white solid. *trans*-$Pd(SPh)_2(PMe_3)_2$ was obtained from a similar reaction in low yield (12%), or reaction of *trans*-$PdMe_2(PMe_3)_2$ with excess benzenethiol and identified by comparison of the spectroscopic data with the authentic complexes.

Similar reaction with excess amount of phenylacetylene resulted in recovery of the starting material.

3.7. X-ray structure determination

All X-ray data were collected using a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 51 reflections in the range $10.0° < 2\theta < 25.0°$. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out using the SHELX-97 programs [25]. The structure was solved by direct methods and refined by full-matrix least-squares calculations of F^2 values, initially with isotropic, and finally anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were located in the difference Fourier map and refined isotropically.

The crystal data, and details in structure refinement of **3**, **8**, and **11** are summarized in Table 5.

4. Supplementary material

Crystallographic data (excluding structural factors) for the structure in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 137699–137701.

Table 5
Crystallographic data and refinement details for **3**, **8**, and **11**

	3	**8**	**11**
Chemical formula	$C_{13}H_{25}N_3P_2Pd$	$C_9H_{21}NO_2P_2Pd$	$C_{21}H_{32}N_2P_2Pd$
Formula weight	391.70	343.61	480.83
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_{1/c}$	*Pbca*	$P2_{1/c}$
a (Å)	13.021(1)	10.152(1)	14.624(3)
b (Å)	6.8472(7)	13.547(2)	8.769(2)
c (Å)	20.260(1)	22.144(2)	18.890(4)
β (°)	98.315(9)		108.75(1)
V (Å^3)	1787.3(3)	3045.6(7)	2293.6(7)
Z	4	8	4
μ (mm^{-1})	1.209	1.413	0.956
F(000)	800	1392	992
D_{calc} (g cm^{-3})	1.456	1.499	1.392
Crystal size (mm)	0.72 × 0.14 × 0.12	0.80 × 0.60 × 0.12	0.52 × 0.36 × 0.10
Scan range	$3.5° < 2\theta < 50°$	$3.5° < 2\theta < 50°$	$3.5° < 2\theta < 50°$
Measured reflections	3279	2619	4474
Unique reflections	3132	2617	4037
Used reflections [$I \geq 2\sigma(I)$]	2709	2206	3471
No. of parameters	172	137	236
Goodness-of-fit on F^2	1.027	1.025	1.039
Max/min in $\Delta\rho$ (e Å^{-3})	0.377, −0.490	0.698, −1.258	0.361, −0.344
T_{min}, T_{max}	0.3283, 0.3679	0.2209, 0.2820	0.4720, 0.5227
R (wR_2 ^{a})	0.0282 (0.0698)	0.0430 (0.1147)	0.0305 (0.0753)

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

Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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