Reaction of Phenyl Palladium(II) Azido Complexes with DMAD (Dimethyl Acetylendicarboxylate): Synthesis and Structures of *trans*-[PdL(C_6H_5){N_3C_2-3,4-(C(O)OMe)$_2$}] (L = PMe_3, PEt_3)

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Received April 4, 2001

Keywords : Azido, Cycloaddition, Triazolato, Structure, Palladium.

The cycloaddition of multiply-bonded organic compound to coordinated azido bond is well known as an useful method for generating various metal-bound heterocycles.[1-3] However, the cycloaddition on the metal azido complexes having alkyl or aryl ligand are relatively scarce. The organometallic complexes with the ligand might possess potential utility as a precursor of organometallic amide complex or organic amines since the azido group can be reduced easily with the use of suitable reducing agents. Recently, we have reported synthesis and some chemical reactions of alkyl and arylpalladium(II) azido complexes with CO, thiophenol including cycloaddition with isocyanide.[4] In this work we have examined reactions of arylpalladium(II) azido complexes with DMAD as one of multiply-bonded organic compound. We report here preparation and structures of palladium(II) complexes with heterocycle bound (triazolato) ring by the cycloaddition of DMAD into the Pd-azido bond.

Experimental Section

All the manipulations of air-sensitive compounds were performed under N_2 or argon atmosphere with the use of standard Schlenk technique. Solvents were distilled from Na-benzophenone. Elemental analyses were carried out by the analytical laboratory at Kangnung National University. IR spectra were recorded on a Hitachi 270-30 and Perkin Elmer BX spectrophotometer. NMR (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) spectra were obtained on JEOL Lamda 300 MHz spectrometers. Chemical shifts were referenced to an internal Me_4Si and to an external 85% H_3PO_4. *Trans*-PdPh(N_3)L_2 (L=PMe_3, PEt_3) were prepared from ligand exchange reactions of PdPh(N_3) (tmeda) (tmeda=N,N,N',N'-tetramethylethylenediamine)[4b] with corresponding tertiary phosphine ligand, respectively.

Reactions of *trans*-PdPh(N_3)L_2 (L = PMe_3, PEt_3) with DMAD (Dimethyl Acetylendicarboxylate). To a Schlenk flask containing *trans*-PdPh(N_3)(PMe_3)$_2$ (0.306 g, 0.81 mmol) was added THF (5 cm^3) and DMAD (0.127 g, 0.89 mmol) in that order. The initial yellow solution immediately turned to pale yellow with evolution of nitrogen. After stirring for 3h at room temperature, the reaction mixture was fully evaporated under vacuum and then the resulting solid was washed with hexane. Recrystallization from THF/Hexane gave pale yellow crystals of **1** (0.328 g, 78%). IR (KBr/cm^{-1}): 1738, 1713 (ν(CO), 1567 (ν(C=C), 1288, 1084, 954, 746. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 0.94 (t, 18H, J = 3.4 Hz, P(CH_3)$_3$), 3.95 (s, 6H, Me), 7.00-7.05 (m, 3H, Ph), 7.21-7.23 (m, 2H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 13.0 (t, J = 14.5 Hz, P(*C*H$_3$)$_3$), 52.0 (s, Me), 123.0, 127.8, 135.9 (t, J = 4.3 Hz, C=C), 139.9, 150.0 (t, J = 7.7 Hz, Ph), 162.6 (s, C=O). ^{31}P{^{1}H}NMR (120 MHz in $CDCl_3$, δ): -16.2(s). Anal. Calcd. for $C_{18}H_{29}N_3O_4P_2Pd$: C, 41.59; H, 5.62; N, 8.08. Found: C, 41.98; H, 5.68; N, 8.07.

Complex **2** was analogously prepared (71%). IR (KBr/cm^{-1}): 1740, 1710 (ν (CO), 1568 (ν (C=C), 1284, 1084, 1036, 739. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.01 (m, 18H, P(CH$_2$CH_3)$_3$), 1.19 (br, 12H, P(CH_2CH$_3$)$_3$), 3.94 (s, 6H, Me), 6.90 (m, 1H, Ph), 7.00 (m, 2H, Ph), 7.31 (br, 2H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 7.67 (s, P(CH$_2$*C*H$_3$)$_3$), 13.7 (br s, P(*C*H$_2$CH$_3$)$_3$), 51.9 (s, Me), 122.7 (s, Ph), 127.6 (s, Ph), 136.1 (s, Ph), 139. 6 (s, C=C), 150.1 (s, Ph), 163.2 (s, C=O). ^{31}P{^{1}H}NMR (120 MHz in $CDCl_3$, δ): 11.90(s).

Anal. Calcd. for $C_{24}H_{41}N_3O_4P_2Pd$: C, 47.73; H, 6.84; N, 6.96. Found: C, 48.08; H, 6.92; N, 6.98.

X-ray Structure Determination. All X-ray data were collected with use of 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 27 reflections in the range $10.0^o < 2\theta < 25.0^o$. Intensity data were corrected for Lorenz and polarisation effects. Decay corrections were also made. The intensity data were empirically corrected with y-scan data. All calculations were carried out with use of the SHELX-97 programs.[5] The structures were solved by the direct method 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 maps and refined isotropically. The crystal data and details in structure refinement of **1** and **2** are summarized in Table 1. Final atomic positional parameters are shown in Table 3 and Table 4.

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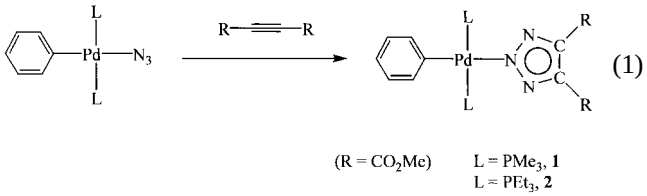
Table 1. X-ray data collection and structure refinement for **1** and **2**

Complex	**1**	**2**
formula	$C_{18}H_{29}N_3O_4P_2Pd$	$C_{24}H_{41}N_3O_4P_2Pd$
fw	519.78	603.94
temperature, K	296(2)	296(2)
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	Cc
a, Å	14.336(1)	14.0307(11)
b, Å	11.566(1)	12.6868(9)
c, Å	14.800(3)	17.2906(10)
β, deg	104.74(1)	104.783(6)
V, Å^3	2373.2(5)	2975.9(4)
Z	4	4
d_{cal}, g cm^3	1.455	1.348
μ, mm^{-1}	0.943	0.762
F(000)	1064	1256
T_{min}	0.1242	0.7184
T_{max}	0.5937	0.9206
2q range (º)	3.5-50	3.5-50
scan type	ω	ω
scan speed	variable	variable
No. of reflns measured	3563	2707
No. of reflns unique	3415	2707
No. of reflns with I > 2σ(I)	2390	2616
No. of params refined	254	307
Max., in $\Delta\rho$ (e Å^{-3})	0.946	0.566
Min., in $\Delta\rho$ (e Å^{-3})	-0.933	-0.258
GOF on F^2	1.069	1.069
R	0.0715	0.0267
wR_2[a]	0.1913	0.0716

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

Results and Discussion

Phenylpalladium azido complexes $PdPh(N_3)L_2$ (L=PMe_3, PEt_3) react with DMAD in CH_2Cl_2 at room temperature to give new triazolato complexes [$PdL(C_6H_5)\{N_3C_2$-3,4-$(C(O)OMe)_2\}$] (L=PMe_3,1; PEt_3, 2) by cycloaddition of DMAD into the Pd-azido bond as shown in eq. 1.



(1)

These reactions are easily confirmed by the IR spectra of the reaction mixture, which shows a disappearance of the asymmetric stretching band of ν (N_3) group at *ca.* 2030 cm^{-1}, and appearance of new bands at 1710-1740 cm^{-1} and 1567-1568 cm^{-1} due to ν (CO) and ν (C=C) of the product. The reaction cleanly occurred without other isomer such as N(1)-triazolato ring -bound complex.

Complexes **1-2** are isolated as yellow crystalline solids, which are thermally stable in the solid state as well as in solution. The complexes are characterized by IR, NMR (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}), and elemental analyses. ^{1}H NMR spectrum of **1** shows a singlet at δ 3.95 due to two OMe groups, which means the symmetrical N(2)-bound to Pd center of the triazolato ring because for the N(1) isomer magnetically unequivalent two methoxy signals are expect-

Table 2. Selected bond distances (Å) and bond angles (º) in **1** and **2**

Complex **1**					
Pd1-C1	1.954(8)	Pd1-N1	2.045(7)	Pd1-P2	2.307(3)
Pd1-P1	2.308(3)	O1-C15	1.12(1)	O2-C17	1.48(1)
O3-C16	1.25(2)	O4-C16	1.28(2)	O4-C18	1.44(1)
N1-N2	1.37(1)	N1-N3	1.37(1)	N2-C13	1.35(1)
N3-C14	1.37(1)	C13-C14	1.34(2)		
C1-Pd1-N1	176.9(3)	C1-Pd1-P2	88.6(2)	N1-Pd1-P2	90.6(2)
C1-Pd1-P1	88.2(2)	N1-Pd1-P1	92.5(2)	P2-Pd1-P1	176.40(9)
N2-N1-N3	108.5(7)	N2-N1-Pd1	121.2(5)	N3-N1-Pd1	130.2(5)
C13-N2-N1	107.6(8)	C14-N3-N1	105.9(8)	C14-C13-N2	108.4(8)
C14-C13-C15	126.4(10)	N2-C13-C15	125.1(11)	C13-C14-N3	109.6(8)
C13-C14-C16	129.6(9)	N3-C14-C16	120.8(10)		
Complex **2**					
Pd1-C1	2.006(5)	Pd1-N1	2.101(4)	Pd1-P1	2.315(2)
O1-C21	1.171(7)	O2-C21	1.328(7)	O2-C22	1.443(9)
O3-C23	1.309(8)	O3-C24	1.454(9)	O4-C23	1.187(7)
N1-N2	1.318(5)	N1-N3	1.346(6)	N2-C20	1.343(7)
N3-C19	1.337(6)	C19-C20	1.388(7)		
C1-Pd1-N1	179.20(19)	C1-Pd1-P1	87.26(15)	N1-Pd1-P1	92.51(13)
C1-Pd1-P2	87.10(15)	N1-Pd1-P2	93.20(13)	P1-Pd1-P2	172.42(5)
N2-N1-N3	112.8(4)	N2-N1-Pd1	123.0(3)	N3-N1-Pd1	124.1(3)
N1-N2-C20	105.7(4)	C19-N3-N1	105.4(4)	N3-C19-C20	107.8(4)
N3-C19-C21	119.4(4)	C20-C19-C21	132.8(4)	N2-C20-C19	108.2(4)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Pd(1)	5643(1)	2255(1)	794(1)	44(1)
P(1)	5304(2)	2232(3)	-816(2)	55(1)
P(2)	6067(2)	2344(2)	2404(2)	48(1)
O(1)	1391(9)	3572(13)	1145(14)	202(9)
O(2)	2445(8)	4856(9)	1254(8)	106(3)
O(3)	1106(7)	1216(11)	160(9)	132(4)
O(4)	2027(6)	250(11)	1327(7)	109(4)
N(1)	4213(5)	2262(6)	781(5)	40(2)
N(2)	3745(5)	3270(7)	875(6)	55(2)
N(3)	3577(6)	1363(7)	718(7)	62(2)
C(1)	7011(5)	2338(6)	822(5)	27(2)
C(2)	7463(8)	3483(9)	844(8)	64(3)
C(3)	8450(8)	3581(10)	890(8)	68(3)
C(4)	9011(8)	2624(12)	921(8)	81(4)
C(5)	8619(8)	1536(11)	916(8)	64(3)
C(6)	7645(7)	1441(9)	869(7)	55(3)
C(7)	4374(11)	1267(13)	-1341(9)	97(4)
C(8)	6243(10)	1854(17)	-1365(9)	115(6)
C(9)	4840(13)	3602(12)	-1319(11)	105(5)
C(10)	5151(9)	1850(12)	2951(10)	86(4)
C(11)	6363(12)	3812(11)	2833(9)	92(4)
C(12)	7117(9)	1537(12)	3036(8)	80(4)
C(13)	2833(8)	2995(10)	886(8)	63(3)
C(14)	2728(6)	1847(11)	789(6)	55(3)
C(15)	2109(9)	3814(12)	1033(13)	94(5)
C(16)	1877(8)	1116(13)	774(10)	81(4)
C(17)	1714(14)	5655(14)	1452(15)	161(10)
C(18)	1230(10)	-463(15)	1405(12)	119(6)

ed. The $^{13}C\{^1H\}$ NMR spectrum also show a corresponding signal at δ 52.0 due the OMe group. Complex **2** also shows a similar signal in the ^1H and $^{13}C\{^1H\}$-NMR spectrum. Earlier studies demonstrated that reactions of Pd[2a], Ni[2c], and Co[6] azido complexes with DMAD proceed to give N(2)-bound heterocycle complexes, respectively. Also, Nag *et al.*[2c] reported conversion of the N(1)-bound triazole to the N(2)-bound isomer from the cycloaddition reaction of NiL(N3) (L =chelated amine) with DMAD. However, Beck and his co-workers[7] showed that $Pd(PPh_3)_2(N_3)_2$ reacted with DMAD to give a N(1)-bound heterocycle palladium complex and a N(1, 2)-bound heterocycle palladium dimer. These results indicate that the cycloaddition of DMAD into the metal azido bond gives various heterocycle isomers depending on the nitrogen coordination.

Yellow single crystals of **1** and **2** suitable for X-ray crystallography were obtained from THF/*n*-hexane solution at -30 °C. Molecular structures of **1** and **2** with the atomic numbering scheme are shown in Figure 1 and 2. Selected bond distances and angles are given in Table 2. The coordination sphere of the Pd metal in **1** and **2** can be described as a square plane, with two each tertiary phosphines. The five-membered ring, triazolato ring (C_2H_3-3,4-(C(O)OMe)$_2$, and

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Pd(1)	-33(1)	7028(1)	3011(1)	41(1)
P(1)	-1737(2)	6963(1)	2628(1)	48(1)
P(2)	1673(2)	6854(2)	3371(1)	56(1)
O(1)	-194(5)	11667(4)	2568(3)	104(2)
O(2)	-968(4)	11479(4)	1299(3)	83(1)
O(3)	494(7)	8946(4)	213(3)	135(3)
O(4)	538(4)	10629(3)	496(3)	81(1)
N(1)	8(3)	8409(3)	2349(2)	48(1)
N(2)	251(4)	8413(4)	1661(3)	54(1)
N(3)	-248(3)	9369(3)	2558(2)	49(1)
C(1)	-78(4)	5723(4)	3655(3)	48(1)
C(2)	-9(4)	4708(4)	3369(4)	55(1)
C(3)	41(5)	3824(5)	3860(5)	74(2)
C(4)	-1(5)	3940(5)	4644(5)	76(2)
C(5)	-95(5)	4939(5)	4931(4)	72(2)
C(6)	-121(4)	5820(5)	4456(3)	56(1)
C(7)	-2223(5)	5732(5)	2125(4)	76(2)
C(8)	-1877(9)	5524(8)	1384(5)	125(4)
C(9)	-2327(5)	7065(6)	3452(4)	77(2)
C(10)	-2064(9)	8079(7)	3911(6)	119(4)
C(11)	-2299(5)	7997(4)	1913(4)	66(2)
C(12)	-3414(6)	7970(5)	1611(6)	86(2)
C(13)	2077(6)	5881(6)	2732(6)	92(2)
C(14)	1651(7)	6032(8)	1879(5)	106(3)
C(15)	2359(6)	8015(5)	3262(5)	80(2)
C(16)	2222(8)	8871(7)	3802(6)	108(3)
C(17)	2242(7)	6366(11)	4375(7)	136(5)
C(18)	3312(10)	6188(17)	4570(10)	215(9)
C(19)	-183(4)	10009(4)	1959(3)	46(1)
C(20)	137(4)	9413(4)	1401(3)	48(1)
C(21)	-428(4)	11133(4)	1998(3)	55(1)
C(22)	-1223(7)	12583(6)	1245(5)	100(3)
C(23)	395(5)	9746(5)	664(3)	69(2)
C(24)	766(14)	9198(9)	-523(7)	193(9)

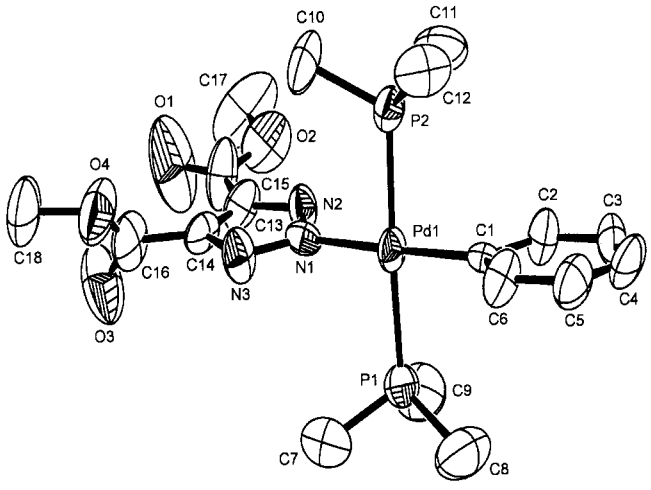


Figure 1. *ORTEP* drawing of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

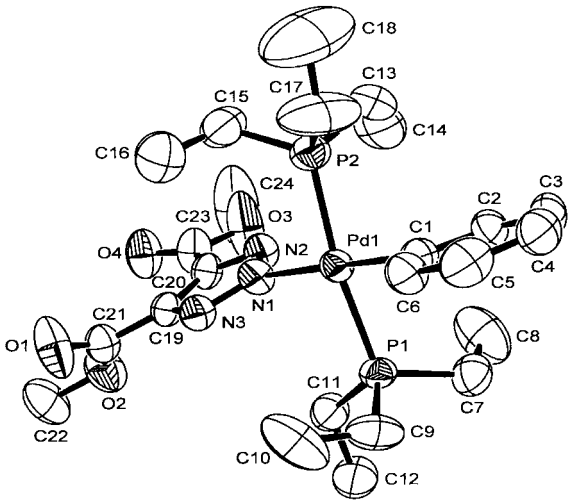


Figure 2. *ORTEP* drawing of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

the phenyl ligand are mutually trans. The phenyl ring of **1** and **2** is slightly twisted out of the triazolato ring with a dihedral angle of 8.1(3) °C, 13.9(5) °C and is almost perpendicular to the square plane. The ORTEP drawing clearly shows the symmetrical N(2)-bound to Pd center of the triazolato ring. The Pd-N bond length (2.101 Å) of **2** is slightly longer than that (2.045 Å) of **1**, indicating more steric bulkiness of PEt_3 than of PMe_3. The bond lengths fall in the range of Pd-N distances as the case previously reported metal azide or amide complex such as $[(C_6H_5CH_2)_3P]_2Pd(N_3)_2$ (2.045 Å)[8] and *trans*-$PdPh(NHPh)(PMe_3)_2$ (2.116 Å)[9] and *trans*-$Pd(C_4H\text{-}p\text{-}CH_3)(N_3)(PMe_3)_2$ (2.119 Å)[4a] and other comparable bond lengths are not available, because there have been no reports about structural data of late transition metal triazolato complexes. Each bond lengths in the triazolato ring of **1** and **2** appear to be almost identical in the range of 1.32-1.39 Å. These results are indicative of partial double bonding and of being aromatic in the triazolato ring.

In summary we have demonstrated cycloaddition reaction using phenylpalladium(II) azido complexes with DMAD to give new heterocycle -bound complex by the 1,3-cycloaddition of DMAD into the Pd-azido bond. Isolated complexes have been determined by X-ray diffraction.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2000-041-D00157).

Supplementary Material Available. Tables of full bond distances and angles, anisotropic thermal parameters, positional parameters for hydrogen atoms, torsion angles: listings of observed and calculated structure factors are available from the author (Y.-J. Kim).

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