Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 358 (2005) 650–658

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Reactivity of alkynyl Pd(II) azido complexes toward organic isocyanides, isothiocyanates, and nitriles

Yong-Joo Kim [a,*], Seung-Ha Lee [a], Sung-Hyun Lee [a], Sang Il Jeon [a], Mi S. Lim [b], Soon W. Lee [b]

[a] *Department of Chemistry, Kangnung National University, Kangnung 120, Kangnung 210-702, Korea*
[b] *Department of Chemistry, Sungkyunkwan University, Natural Science Campus, Suwon 440-746, Korea*

Received 4 August 2004; accepted 28 September 2004

Abstract

Alkynyl Pd(II) azido complexes of the type $[Pd(N_3)(C{\equiv}C{-}R)L_2]$ (**1**–**3**) were obtained by reactions of aqueous NaN_3 with $[Pd(Cl)(C{\equiv}C{-}R)L_2]$ (R = Ph or C(O)OMe). Treating compounds **1**–**3** with organic isocyanides (R–NC) afforded novel complexes, *trans*-$[Pd(C{\equiv}C{-}Ph)(N{=}C{=}N{-}R)(PMe_3)_2]$ (R = 2,6-$Me_2C_6H_3$ (**4**) or 2,6-$Et_2C_6H_3$ (**5**)) and *trans*-$[Pd(C{\equiv}C{-}R)(CN_4$-*t*-$Bu)L_2]$ (**6**: L = PMe_3, R = Ph; **7**: L = PEt_3, R = C(O)OMe; **8**: L = PMe_3, R = C(O)OMe), which contain either a carbodiimido or a *C*-coordinated tetrazolato group. Reactions of compounds **1** and **2** with R–N=C=S (R = 2,6-$Me_2C_6H_3$ or CH_2CH_3) and 1,4-phenylene diisothiocyanate ($C_6H_4(N{=}C{=}S)_2$) smoothly proceeded to give tetrazole–thiolato complexes, *trans*-$[Pd(C{\equiv}CPh)(SCN_4{-}R)L_2]$ (L = PMe_3, R = Et (**9**) or 2,6-$Me_2C_6H_3$ (**10**); L = PEt_3, R = 2,6-$Me_2C_6H_3$ (**11**)), and a phenylene-bridged dinuclear Pd(II) tetrazole–thiolato complex, $[(PEt_3)_2(C{\equiv}CPh)Pd(SCN_4{-}(\mu{-}C_6H_4){-}SCN_4)Pd(C{\equiv}CPh)(PEt_3)_2]$ (**12**), respectively. Complexes **9**–**12** contain the Pd–S bond that is formed by the dipolar cycloaddition of the organic isothiocyanate to the Pd–azido bond. In contrast, the vcorresponding reactions of compounds **1**and **2** with C_6F_5CN and Me_3SiCN (organic nitriles, R–CN) gave an *N*-coordinated Pd(II)-tetrazolato compound {*trans*-$[Pd(C{\equiv}C{-}Ph)(N_4C{-}C_6F_5)(PMe_3)_2]$ (**13**)} and a mixture of Pd(II)-cyano complexes {*trans*-$[Pd(C{\equiv}C{-}Ph)(CN)(PEt_3)_2]$ (**14**) and $[Pd(CN)_2(PEt_3)_2]$ (**15**)}, respectively. Bis(phosphine) bis(cyano) complexes of Pd and Ni, $[M(CN)_2L_2]$ (L = PEt_3, PMe_3; L_2 = DEPE), could be obtained independently by the reactions of $[M(N_3)_2L_2]$ with excess Me_3SiCN in organic solvents.

Keywords: Azido; Cycloaddition; Alkynyl; Carbodiimide; Palladium

1. Introduction

Dipolar cycloaddition of unsaturated organic compounds such as isocyanide, nitrile, and alkyne to an azido ligand, which gives metal complexes containing *C*- or *N*-coordinated heterocycles, has been an interesting subject for many decades [1–18]. We recently reported several late transition-metal complexes containing such heterocycles (*C*-coordinated), which were prepared by treating bis(phosphine) metal complexes of bis(azido) $[M(N_3)_2(PR_3)_2]$ and mono(azido) methyl or phenyl $[M(N_3)(R)(PR_3)_2]$ (R = Me or Ph) with organic isocyanides [19]. Although many derivatives of late transition-metal mono- or bis(azido) complexes have been employed to study on the formation of metal complexes containing the heterocycles mentioned above, azido metal–alkynyl complexes have been relatively unexplored. The alkynyl ligand exhibits interesting properties such as cluster formation involving the bridging alkynyl ligand in multinuclear complexes [20–22], its conversion

---

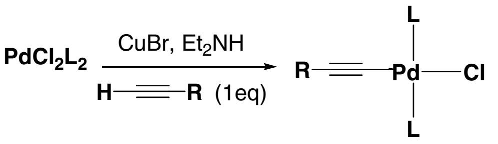
[*] Corresponding author. Tel.: +82 33 640 2308; fax: +82 33 647 1183.
E-mail address: yjkim@kangnung.ac.kr (Y.-J. Kim).

0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.09.056

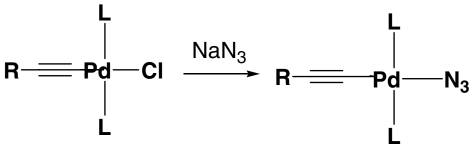
to the corresponding vinylidene species [23], and its potential optical or liquid crystalline properties as a molecular wire having linear —C≡C units [24]. We here wish to report the preparation of alkynyl palladium(II)-azido complexes and their reactivity toward organic isocyanides and organic pseudo-halides (isothiocyanates and nitriles).

2. Results and discussion

Alkynyl palladium(II) azido complexes **1**–**3** have been prepared by usual coupling reactions and then subsequent metathetical substitution with NaN_3 as shown in Eqs. (1) and (2). These complexes have been obtained as white crystalline solids in high yields and characterized by IR, NMR, and elemental analyses. Formation of those complexes can be readily conformed by monitoring the strong absorption bands in the range of 2050–2100 cm $^{-1}$ due to the N_3 and C≡C stretching bands.



(1)

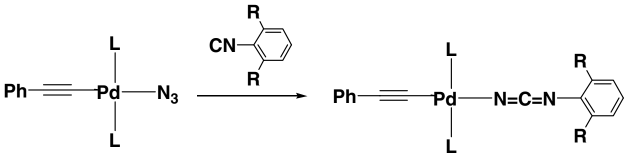


(2)

R = Ph, L = PMe_3 (**1**), PEt_3, (**2**)
R = MeO(CO), L = PMe_3 (**3**)

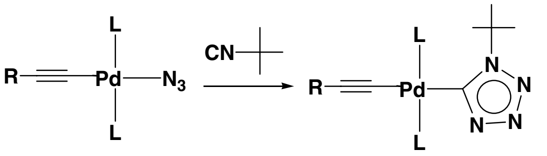
2.1. Reactions with isocyanides

As mentioned in Section 1, we recently reported that bis(phosphine) group 10 metal complexes, $[M(N_3)_2(PR_3)_2]$ and $[M(N_3)(R)(PR_3)_2]$ (R = Me or Ph), reacted with various isocyanides to give complexes containing carbodiimido or tetrazolato groups through cyclodaddition of isocyanides to the metal–azido bond [19]. On the basis of these results, we have examined the reactivity of alkynyl palladium(II) azido complexes toward isocyanides as shown in Eq. (3). Treatment of the isocyanide with the azido complex caused immediate evolution of nitrogen gas, and their reaction was monitored by the IR spectra, which showed the disappearance of an asymmetric stretching N_3 band at ca. 2050 cm^{-1} and the appearance of new strong bands at ca. 2170 cm^{-1} and 2117–2128 cm^{-1} due to the carbodiimido (N=C=N) and C≡C groups, respectively, in the products, *trans*-$[Pd(C{\equiv}CPh)(N{=}C{=}N{-}R)(PMe_3)_2]$ (R = $2,6\text{-}Me_2C_6H_3$ (**4**) or $2,6\text{-}Et_2C_6H_3$ (**5**)). On the other hand, analogous reactions of **1**–**3** with *tert*-butyl isocyanide gave Pd(II) complexes having a *C*-coordinated tetrazolato ring, *trans*-$Pd[(C{\equiv}C{-}R)(CN_4\text{–}t\text{-}Bu)L_2]$ (R = Ph, L = PMe_3 (**6**) or PEt_3 (**7**); R = C(O)OMe, L = PMe_3, (**8**)), as shown in Eq. (4). Carbodiimido complexes **4**–**8** were isolated in high yields and characterized by IR, NMR, and elemental analyses. Molecular structures of **5** and **6** were determined by X-ray crystallography.



L = PMe_3, R = Me, **4**
L = PMe_3, R = Et, **5**

(3)



R = Ph L = PMe_3, **6**; PEt_3, **7**
R = C(O)OMe L = PMe_3, **8**

(4)

No other products (for example, an imino-bonded complex formed by the isocyanide insertion into the Pd–C bond) were observed. The formation of carbodiimido Pd(II) complexes appears to involve an initial formation of a *C*-coordinated tetrazolato ring by the cycloaddition of isocyanide into the palladium–azido bond and then the subsequent ring conversion to an end-on NCN group with the elimination of N_2 to give a final product. In a recent work, we reported that the formation of the carbodiimido or *C*-coordinated tetrazolato group was dependent not only on the type of an attacking isocyanide and but also on the steric bulk of alkyl substituents on the aryl ring that might facilitate N_2 elimination from the tetrazolato ring to give the corresponding carbodiimido group [19a,19b].

Figs. 1 and 2 show the molecular structures of *trans*-$[Pd(C{\equiv}CPh)(N{=}C{=}N{-}C_6H_3\text{-}2,6\text{-}Et_2)(PMe_3)_2]$ (**5**) and *trans*-$[Pd(C{\equiv}CPh)(CN_4\text{-}t\text{-}Bu)(PMe_3)_2]$ (**6**), respectively. Crystal data are summarized in Table 1. Fig. 1 clearly shows the square-planar geometry of complex **5**, which contains two PMe_3, one alkynyl, and one end-on carbodiimido ($NCN\text{–}C_6H_3\text{-}2,6\text{-}Et_2$) ligands. The linear phenylethynyl group is located *trans* to the carbodiimido group. A triplet in $^{13}C\{^1H\}$ NMR, which is coupled with two phosphine ligands and corresponds to the alkynyl carbon ($C_\alpha{\equiv}C$ or $C{\equiv}C_\beta$) directly bonded to the Pd metal, supports the *trans*-geometry of the complexes. Furthermore, a singlet at −12.3 ppm in $^{31}P\{^1H\}$ NMR also supports the *trans*-structure. The phenyl ring in the carbodiimido ligand is nearly perpendicular to the