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Communications

Generation of Oligoene Species Capped by Palladium(II) Moieties from a Dinuclear Palladium(I) Complex and Alkyne

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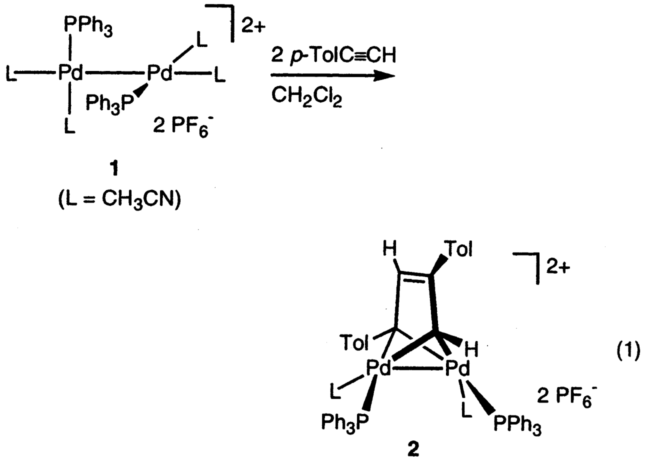
Summary: The Pd−Pd-bonded complex [$Pd_2(CH_3CN)_6$][BF_4]$_2$ reacts with dimethyl acetylenedicarboxylate (DMAD) in the presence of nitrogen chelate ligands, affording oligoene species capped by Pd(II) moieties. The mono-, di-, and triene complexes have been successively isolated and structurally characterized by X-ray crystallographic analyses.

The reactivity of palladium clusters has long been investigated because of its relevance to the catalytic activity of palladium nanoparticles, colloids, or other heterogeneous systems.[1] Typically, easily accessible and rigidly supported dipalladium complexes such as $Pd_2(\mu\text{-dppm})_2X_2$ have been well-investigated.[2] However, even when reactive substrates such as alkyne were employed, only coordination of the substrate at the dipalladium center has been observed,[2,3] and further transformation has never been characterized in a well-defined manner, probably because of the low substitutional lability and high configurational rigidity of the coordination products. To study a stoichiometric class of transformations involving palladium clusters, we recently synthesized the substitutionally labile dipalladium(I) complexes $[Pd_2(CH_3CN)_n(PPh_3)_{6-n}]^{2+}$ ($n = 4-6$) containing a reactive Pd−Pd bond.[4] During the course of the reactivity study of these complexes, it has been found that when the bisphosphine complex $[Pd_2(CH_3CN)_4(PPh_3)_2][PF_6]_2$ (**1**) is employed,[4b] a terminal arylalkyne is dimerized on the Pd−Pd bond, affording the novel μ-butenediylidene dipalladium species **2** (eq 1).[5] However, it remained unclear whether the alkyne dimerization proceeded in a stepwise way or via one-step, concerted [2 + 2] cyclization involving the metal center. Moreover, observation of the further reaction of **2** with alkynes was unsuccessful. Herein, we have found that alkyne inserts into a Pd−Pd bond successively to afford the Pd(II)-capped oligoene species. Use of the phosphine-free Pd−Pd complex $[Pd_2(CH_3CN)_6][BF_4]_2$ (**3**),[4a] dimethyl acetylenedicarboxylate (DMAD), and N,N-chelate ligands provides the products enough stability to be isolated. This observation suggests that a metal−metal bond possibly plays an important role in the mechanism of a



1
($L = CH_3CN$)

2

(1)

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(1) (a) Moiseev, I. I.; Vargaftik, M. N. *New J. Chem.* **1998**, 1217 and references therein. For an example of recent advances, see: (b) Niu, Y. H.; Yeung, L. K.; Crooks, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 6840 and references therein.

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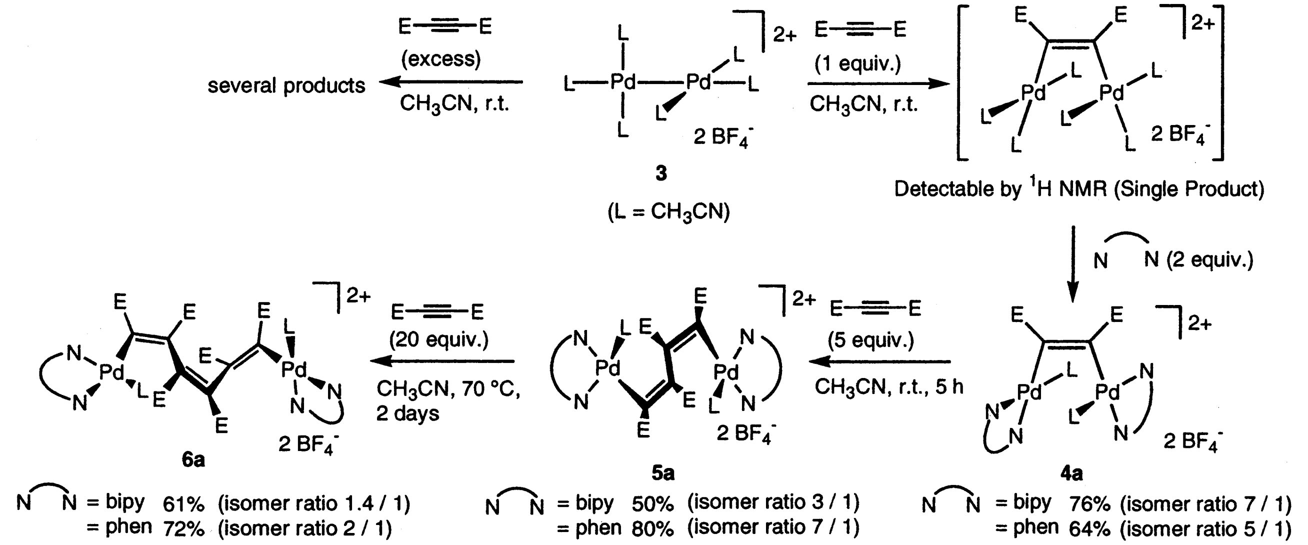
Scheme 1[a]



[a] E = COOMe.

polymerization reaction initiated by metal clusters or colloids:[6] e.g., metal−metal bond cleavage is possibly involved in the initiation step, affording active species having polymerization sites at both chain ends.

The reaction of homoleptic acetonitrile complex $[Pd_2(CH_3CN)_6][BF_4]_2$ (**3**) with DMAD (1 equiv) afforded a new complex, showing a ^1H NMR resonance at δ 3.70 (in CD_3CN), which has been ascribed to the Me protons of the product. Further addition of DMAD resulted in the consumption of the initial product and generation of several products. However, these products could not be characterized at this stage. Addition of bidentate nitrogen ligands (2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen)) to the mono(alkyne) adduct, which was generated in situ, afforded isolable complexes as a mixture of two isomers[7] (**4a-bipy**/**4b-bipy** 7/1, **4a-phen**/**4b-phen** 5/1, each ratio at equilibrium) (Scheme 1). The structure of the isomer **4a-bipy**, having pseudo-C_2 symmetry, was determined by X-ray structure analysis (Figure 1), showing that one DMAD molecule formally inserted into the Pd−Pd bond to yield the μ-η^1:η^1-ethenediyl complex $[Pd_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C(E)C(E)\}(CH_3CN)_4][BF_4]_2$. This product is quite similar to those previously obtained from the reaction of $[Pd_2(dppm)_2X_2]$ with alkynes.[2]

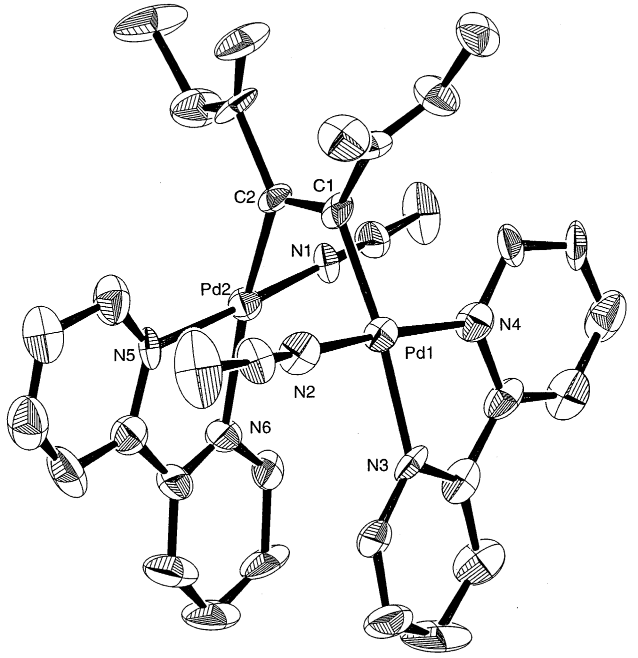


Figure 1. ORTEP drawing of **4a-bipy** (30% probability, counteranions are omitted for clarity). Selected distances (Å) and angles (deg): Pd1···Pd2 = 2.975(3), Pd1−C1 = 1.98(3), Pd2−C2 = 1.95(3), C1−C2 = 1.38(3); Pd1−C1−C2 = 112(2), C1−C2−Pd2 = 115(2).

The observation of only a cis-addition product suggested that the insertion of the DMAD molecule into a Pd−Pd bond occurs via a migratory insertion mechanism, similar to that usually accepted for insertion of alkyne into Pd−C bonds in mononuclear species.

The reaction of **4-bipy** or **4-phen** with excess DMAD (5 equiv) in CH_3CN at ambient temperature afforded the DMAD-dimerized product $[Pd_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C(E)C(E)C(E)C(E)\}(\text{phen or bipy})_2(CH_3CN)_2][BF_4]_2$ (**5-bipy** or **5-phen**). The structure of the major isomer **5a-bipy**, having pseudo-C_2 symmetry, was determined by X-ray

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[2] (a) Lee, C.-H.; Hunt, C.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2498. (b) Werner, H.; Thometzek, P.; Zenkert, K.; Goddard, R.; Kraus, H.-J. *Chem. Ber.* **1987**, *120*, 365. (c) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1988**, 457.

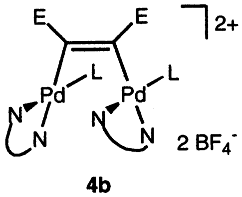
[3] Durà-Vilà, V.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2000**, *600*, 198.

[4] (a) Murahashi, T.; Nagai, T.; Okuno, T.; Matsutani, T.; Kurosawa, H. *Chem. Commun.* **2000**, 1689. (b) Murahashi, T.; Otani, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H.; Sakaki, S. *J. Am. Chem. Soc.* **1998**, *120*, 4536.

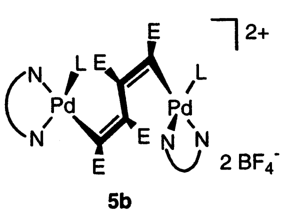
[5] Murahashi, T.; Otani, T.; Okuno, T.; Kurosawa, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 537.

[6] *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998.

[7] (a) Two isomers in **4**−**6** are assumed to arise from the combination of atropisomerism with respect to the Pd−C bond at two Pd units. It remains unclear whether the isomer characterized by X-ray studies for **4** is the major or the minor isomer, due to the fast attainment of the equilibrium state. (b) For clarity in Scheme 1, only one of the isomers is shown for **4**−**6**. The other isomers for **4** and **5** are



4b



5b

and that for **6** is shown in Chart 1.

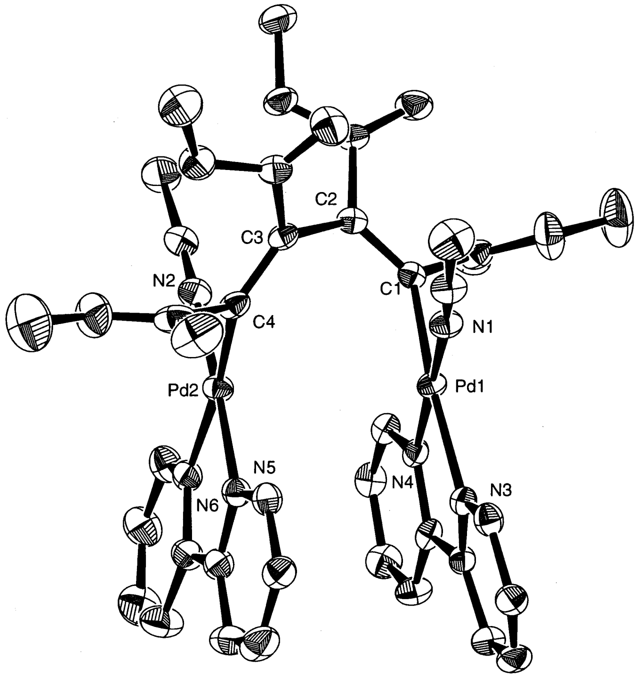


Figure 2. ORTEP drawing of **5a-bipy** (30% probability, counteranions are omitted for clarity). Selected distances (Å) and angles (deg): Pd1−C1 = 1.99(1), Pd2−C4 = 1.99(1), C1−C2 = 1.34(2), C2−C3 = 1.52(2), C3−C4 = 1.36(2); Pd1−C1−C2 = 127.6(8), C1−C2−C3 = 124.3(10), C2−C3−C4 = 124.3(10), C3−C4−Pd2 = 128.6(9).

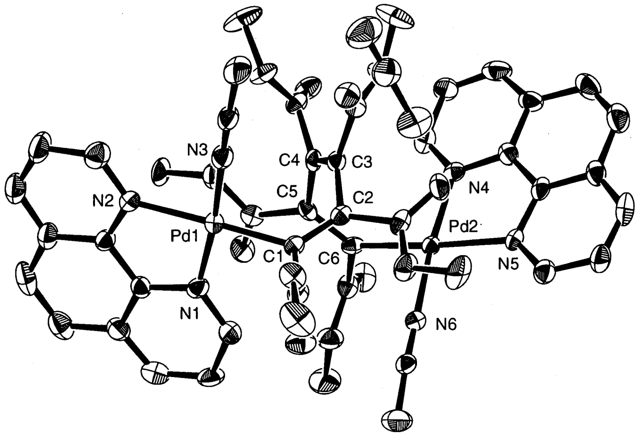
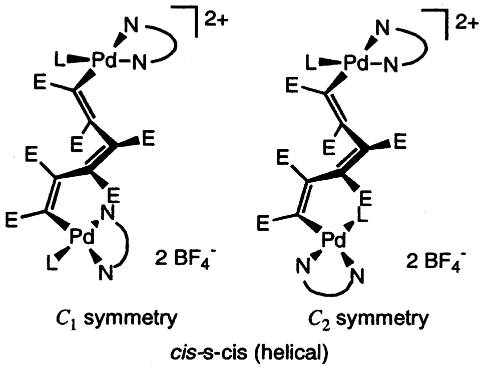


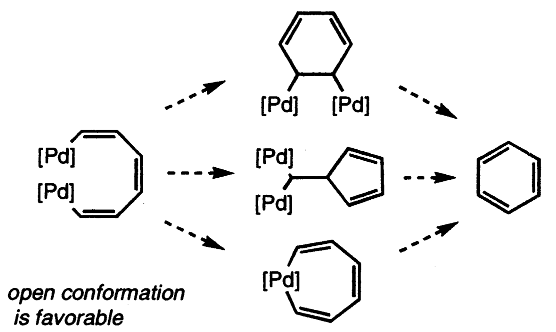
Figure 3. ORTEP drawing of **6a-phen** (30% probability, counteranions are omitted for clarity). Selected distances (Å) and angles (deg): Pd1−C1 = 1.99(1), Pd2−C6 = 1.97(2), C1−C2 = 1.34(2), C2−C3 = 1.54(2), C3−C4 = 1.34(2), C4−C5 = 1.50(2), C5−C6 = 1.37(2); Pd1−C1−C2 = 123(1), C1−C2−C3 = 121(1), C2−C3−C4 = 125(1), C3−C4−C5 = 126(1), C4−C5−C6 = 122(1).

structure analysis (Figure 2).[6] This reveals that the second DMAD molecule was inserted into one of the Pd−C bonds of **4-bipy**, again in a cis manner. Then, the reaction of **5-bipy** or **5-phen** with a large excess of DMAD under the more severe conditions (70 °C, 2 days) afforded the DMAD-trimerized product $[Pd_2\{\mu\text{-}\eta^1:\eta^1\text{-}C(E)C(E)C(E)C(E)C(E)C(E)\}(\text{phen or bipy})_2(CH_3CN)_2][BF_4]_2$ (**6-bipy** or **6-phen**, two isomers)[7] (Scheme 1). The X-ray structure analysis of the major isomer of **6a-phen** (Figure 3) showed a helical configuration of the $-\{C(E){=}C(E)\}_3-$ linkage with two Pd configurations opposite to each other (C_1 symmetry). The ^{1}H NMR spectrum of this isomer (**6a-phen**) showed six methyl signals consistent with the C_1 symmetry, while only three methyl signals appeared for the other, possibly due to C_2 symmetry of the latter (Chart 1). In contrast, ^{1}H NMR spectra of **5** showed no apparent signal pattern indicative of C_1 symmetry (four methyl signals); two methyl signals were observed for the major isomer, but the signal pattern for the minor isomer was not fully assigned, due to the overlap with those of the major isomer.[8]

Chart 1



Scheme 2



(COOMe groups were omitted for clarity.)

It should be mentioned that the alkyne-trimer complex $L_nPd-(C(E){=}C(E))_3-R$ generated by the reaction of mononuclear Pd−R (R = alkyl, aryl, halogen) complex was reported to be susceptible to isomerization to the intramolecularly cyclized five-membered ring products.[9] However, in the present case, formation of the five-membered-ring product from the alkyne trimer **6-phen** has not been observed, probably because of the bulkiness of the Pd units at both chain ends, which would prevent intramolecular cyclization (Scheme 2). The formation of substituted benzene C_6E_6 from **6-phen** proceeded only very slowly at least in CD_3CN (C_6E_6 was not observed on heating in CD_3CN at 70 °C for 2 h),[10] probably because the isomerization to the five- or six-membered-ring intermediate or the intramolecular trienyl transfer from one Pd atom to the other to form the mononuclear palladacycloheptatriene moiety is extremely sluggish (Scheme 2).[11]

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[8] The ^{1}H NMR study of **5** at −40 °C in CD_3CN showed no exchange process about the methyl signals for either isomer.

[9] (a) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161 and references therein. (b) LaPointe, A. M.; Brookhart, M. *Organometallics* **1998**, *17*, 1530. (c) Yagyu, T.; Osakada, K.; Brookhart, M. *Organometallics* **2000**, *19*, 2125. (d) Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087. (e) Successive insertions of alkyne into mononuclear $Pd^{II}-R$ complexes have been also reported: Reddy, K. R.; Surekha, K.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2001**, *20*, 5557.

[10] Formation of a small amount of C_6E_6 (19%) was observed after heating at 70 °C for 1 day. The slow formation of C_6E_6 was also observed when bipy was added to the CD_3CN solution of **6-bipy** at ambient temperature (7 days was required for complete consumption of **6-bipy**).

In summary, it is revealed that the oligoene species capped by Pd(II) moieties is easily generated by the reaction of substitutionally labile dipalladium species without bridging ligands. Such metal-bicapped species M−(hydrocarbon-bridge)−M thus formed are of interest as potential intermediates in block polymerization,[12,13] such as one involving 1,3-diene and isocyanide studied by Novak et al.[13] Although the preparation of metal-bicapped species usually requires several elaborate steps,[12−14] the present case suggests more convenient generation of such species from a metal−metal-bonded complex. A survey of Pd−Pd complex induced alkyne and alkene polymerization with high performance is now under investigation.

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Supporting Information Available: Details of the X-ray single-crystal structural analyses for **4a-bipy**, **5a-bipy**, and **6a-phen**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] It has been known that when R in the complex $L_nPd-(C(E)=C(E))_3-R$ is halogen, the initially formed five-membered-ring product is converted to substituted benzene.[9a] Such a process cannot be ruled out in the present case.

[12] (a) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Chem. Eur. J.* **2000**, *6*, 983. (b) Onitsuka, K.; Yanai, K.; Takei, F.; Joh, T.; Takahashi, S. *Organometallics* **1994**, *13*, 3862. (c) Onitsuka, K.; Joh, T.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 851.

[13] Deming, T. J.; Novak, B. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2366.

[14] For preparation of group 10 metal-bicapped oligoene species: (a) Uson, R.; Vicente, J.; Chicote, M. T.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1131. (b) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Wehman, E.; van Koten, G. *J. Am. Chem. Soc.* **1984**, *106*, 8002. (c) Lawrie, C. J.; Gable, K. P.; Carpenter, B. K. *Organometallics* **1989**, *8*, 2274. (d) Bonrath, W.; Michaelis, S.; Pörschke, K. R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 298.