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Cyclization of Dinuclear Aryl- and Aroylpalladium Complexes with the Metal Centers Tethered by an Oligo(ethylene oxide) Chain. Intramolecular Transmetalation of the Cationic Dinuclear Arylpalladium Complexes

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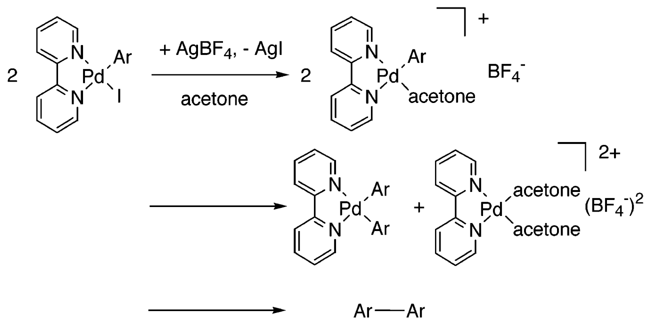
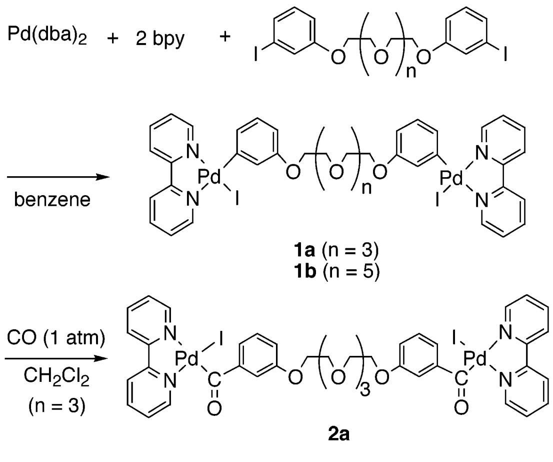
Summary: The reaction of the dinuclear palladium(II) complexes $[(bpy)(I)Pd\{C_6H_4(OCH_2CH_2)_{0.5n+0.5}\}]_2O$ *(n = 3, 5) and* $[(bpy)(I)Pd\{COC_6H_4(OCH_2CH_2)_2\}]_2O$ *with* $AgBF_4$ *produces crown ethers including a biphenylene or diaryl ketone part via intramolecular transfer of the aryl ligand and subsequent reductive elimination of the macrocyclic products.*

Transition-metal-complex-promoted coupling of organic halides leads to C−C bond formation under mild conditions.[1] Preparation of macrocycles using the coupling reaction of organic dihalides with transition-metal complexes has been reported in a limited number of papers,[2] which may compete with intermolecular coupling of the substrates to give the linear oligomers. These intermolecular and intramolecular reactions mostly involve the organotransition-metal complexes as the crucial intermediates. Recently, we reported that [Pd(Ar)I(bpy)] (Ar = Ph, $C_6H_4Me_2$-3,5) reacts readily with $AgBF_4$ to form the cationic arylpalladium complexes $[Pd(Ar)(solv)(bpy)]^+(BF_4)^-$ (solv = THF, acetone), which cause transmetalation of the aryl ligand and reductive elimination of biaryl from the diarylpalladium complex, as shown in Scheme 1.[3,4] The analogous reaction of dinuclear palladium complexes with a long tether that binds the two aryl ligands coordinated to the respective Pd centers would form a macrocyclic product via the intramolecular coupling of the aryl ligands. In this paper, we report the efficient cyclization of the dinuclear organopalladium complexes involving a cationic intermediate.

Scheme 1



Scheme 2



Dinuclear palladium(II) complexes having a bridging ligand, $[(bpy)(I)Pd\{C_6H_4(OCH_2CH_2)_{0.5n+0.5}\}]_2O$ (**1a**,**b**, *n* = 3, 5) and $[(bpy)(I)Pd\{COC_6H_4(OCH_2CH_2)_2\}]_2O$ (**2a**), are prepared from $\{m\text{-}IC_6H_4(OCH_2CH_2)_{0.5n+0.5}\}_2O$, Pd$(dba)_2$ (dba = dibenzylideneacetone), bpy, and CO, as summarized in Scheme 2.[5−7] The $^{13}C\{^1H\}$ NMR spectrum of **2a** contains the carbonyl carbon of the aroyl ligands at 224.5 ppm. The ^1H and $^{13}C\{^1H\}$ NMR spectra indicate the symmetrical molecular structure formed

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(1) (a) Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613. (b) Semmelhack, M. F. *Org. React.* **1972**, *19*, 115. (c) Baker, R. *Chem. Rev.* **1973**, *73*, 487.

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(3) Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087.

(4) Reports of related reactions of cationic monoorganopalladium complexes. See: (a) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441. (b) Kawataka, F.; Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Organometallics* **1994**, *13*, 3517. (c) Kawataka, F.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 654. (d) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1995**, 1101.

(5) $\{m\text{-}IC_6H_4(OCH_2CH_2)_{0.5n+0.5}\}_2O$ species were prepared by a method similar to that already reported: Virtue, G. A.; Coyne, N. E.; Hamilton, D. G. *J. Org. Chem.* **2002**, *67*, 6856.

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(7) Insertion of CO into the palladium−aryl bond of the palladium(II) complex with diimine ligands: (a) van Asselt, R.; Gielens, E. E. C. G.; Rulke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977. (b) Vicente, J.; Abad, J. A.; Frankland, A. D.; de Arellano, M. C. R. *Chem. Eur. J.* **1999**, *5*, 3066. (c) Vicente, J.; Abad, J. A.; Förtsch, W. *Organometallics* **2001**, *20*, 2704.

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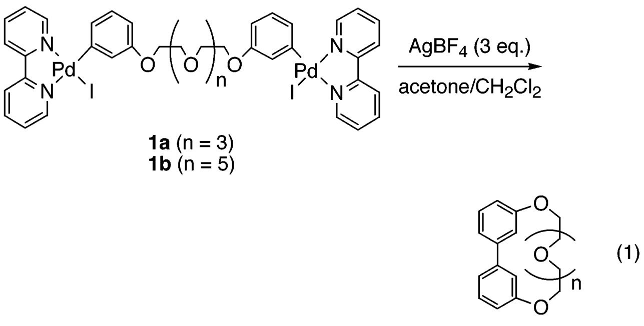
through insertion of CO into both of the palladium−carbon bonds.

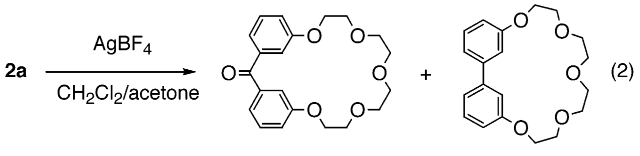
Complexes **1a**,**b** in acetone/CH_2Cl_2 (100 mM) react with $AgBF_4$ to produce the crown ethers **3a**,**b**, which contain a 3,3′-biphenylene part. The reaction of **1a** with $AgBF_4$ in a 1:3 molar ratio forms the cyclization product **3a** in over 99% yield based on the initially used **1a** (eq 1). The reaction with $AgBF_4$/Pd in a 1:2 ratio forms the product in 80% yield. Since the C−C bond formation giving the macrocyclic product takes place efficiently in a 100 mM solution of the complex, special techniques for the cyclization such as high dilution of the complexes are not required. The reaction of **1a** with $AgBF_4$ in MeCN produces a cationic dipalladium complex with acetonitrile ligands, $[\{(bpy)(NCMe)Pd\{C_6H_4(OCH_2CH_2)_2\}_2O\}]^{2+}(BF_4^-)_2$, rather than the cyclic product. The results resemble those of the reactions of Pd(Ph)I(bpy) with $AgBF_4$ in acetone and in MeCN to produce biphenyl and Pd(Ph)(NCMe)(bpy), respectively.[3] The cyclization in eq 1 involves the arylcationic intermediate, formed upon contact with $AgBF_4$, analogously to the reaction of Pd(Ph)I(bpy).



1a (n = 3)
1b (n = 5)

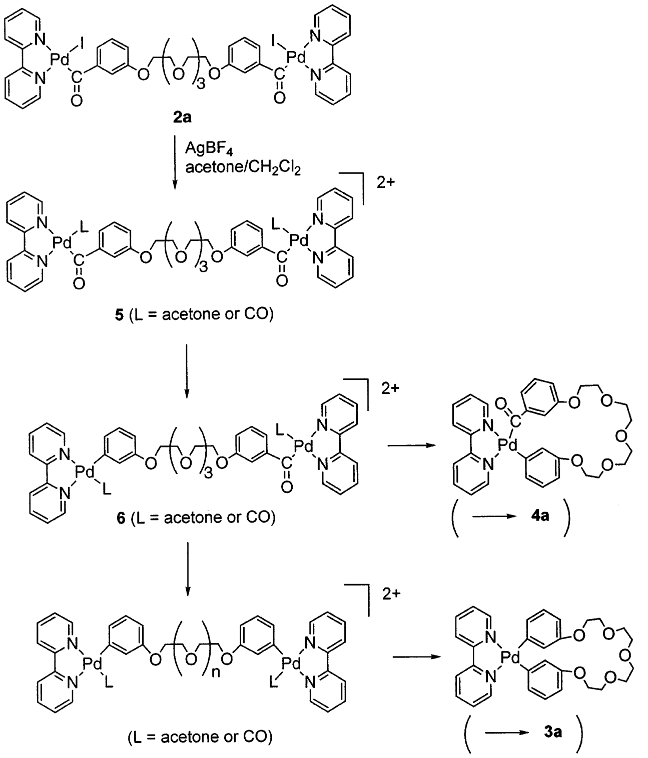
3a, >99% (n = 3)
3b, >99% (n = 5)

The bis(aroylpalladium) complex **2a** also reacts with an excess of $AgBF_4$ under Ar to produce the crown ether **4a** (94%), which has a carbonyl group between the two phenylene groups (eq 2).[8] Accompanying formation of **3a** in a small amount (6%) is also observed. The reaction under CO gives **3a** (<1%) and **4a** (2%) in much lower yields than that under Ar. Scheme 3 depicts the proposed pathways of the reaction. The dicationic complex $[\{(bpy)(L)Pd\{COC_6H_4(OCH_2CH_2)_2\}_2O\}]^{2+}(BF_4^-)_2$ (**5**; L = acetone, CO), formed by the reaction of $AgBF_4$ with **2a**, undergoes decarbonylation of one of the aroyl ligands to produce a complex containing arylpalladium and aroylpalladium centers, $[(bpy)(L)Pd\{C_6H_4(OCH_2CH_2)_4OC_6H_4COPd(L)(bpy)\}]^{2+}(BF_4^-)_2$ (**6**).[9] Intramolecular transmetalation of the aryl ligand to the other palladium center forms a palladacyclic intermediate that causes ensuing reductive elimination of **4a**. The minor product **3a** is attributed to further decarbonylation of **6** and intramolecular coupling of the two aryl ligands of the cationic dinuclear arylpalladium complex. Formation of the crown ether having a dicarbonyl group is not observed in the reaction of $AgBF_4$ with **2a** either under Ar or under CO due to difficulty of transmetalation of the aroyl ligand. Transmetalation of the aryl ligand of **6** is more rapid than the decarbonylation of the remaining aroyl ligand, because **4a** is the major product, even under Ar. In the reaction under CO, coordination of CO to the palladium center prevents the decarbonylation of the aroyl complex, which results in the low yields of **3a** and **4a**.



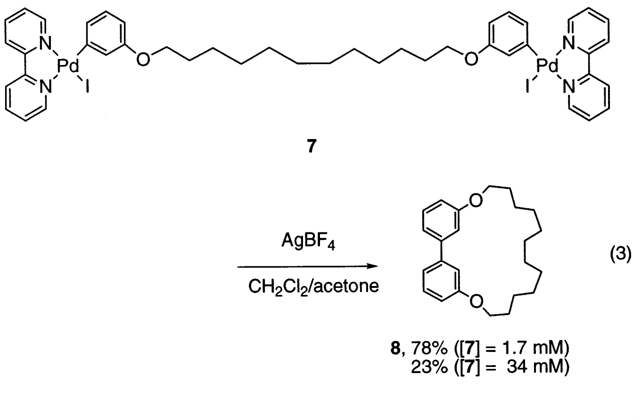
4a, 94%
3a, 6%

Scheme 3



2a
5 (L = acetone or CO)
6 (L = acetone or CO)
(L = acetone or CO)

A dinuclear palladium(II) complex with a polymethylene tether, $[(bpy)(I)Pd\{C_6H_4O(CH_2)_6\}]_2$ (**7**), reacts with $AgBF_4$ to give the cyclophane **8** (eq 3). Yields of the product vary depending on the initial concentration of the palladium(II) complex **7**; the reactions with [**7**] =



7

8, 78% ([**7**] = 1.7 mM)
23% ([**7**] = 34 mM)

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[8] Selected data for **4a**: $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 67.3 (CH_2), 69.8 (CH_2), 70.1 (CH_2), 70.7 (CH_2), 117.8, 118.8, 121.9, 130.1, 138.4, 157.5, 195.7(CO); GC-MS *m/z* 372.

[9] Decarbonylation of aroylpalladium(II) complexes with diimine ligands: Cinellu, M. A.; Gladiali, S.; Minghetti, G. *J. Organomet. Chem.* **1989**, *363*, 401.

1.7 and 34 mM produces **8** in 78% and 23% yields, respectively. The latter reaction is accompanied by the formation of byproducts with high molecular weights (M_n = 5000 by GPC)[10] due to polycondensation via intermolecular transfer of the aryl ligand.

The above results suggest an interaction between the oligo(ethylene oxide) group of the complex and Ag^+ cation during the cyclization reactions. Ag^+ in the reaction mixture plays a dual role, abstraction of the iodo ligand from Pd to produce the cationic intermediates and formation of a template by coordination of the oligo(ethylene oxide) chain, which enhances the cyclization rather than intermolecular coupling.[11] The 1:2 reaction of **1a** with $AgBF_4$ in DMF with and without addition of KBF_4, however, does not show a difference the yield of the macrocyclic product (41−46%), indicating that the potassium cation is ineffective for the formation of the template.

In conclusion, we found that the cyclization of dinuclear arylpalladium complexes as well as of aryl(aroyl)dipalladium complexes produces the crown ethers with aryl groups effectively. The reactions are triggered by the formation of cationic dipalladium complexes which cause easy aryl ligand transfer between the metal centers.

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Supporting Information Available: Text giving full details of the experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] The molecular weight was determined by GPC in THF vs polystyrene standard.

[11] Complexation of Ag^+ with crown ethers: Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475.