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Communications

The First Palladium(0) Complex of a Linear 1,6,11-Triyne. A Reactive Intermediate in the Catalytic Cyclotrimerization of a Triyne

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Summary: The reaction of $Pd_2(dba)_3$·$CHCl_3$ with dimethyl 4,9-dioxatrideca-2,7,12-triyne-1,13-dioate gave the first palladium(0) triyne complex in good yield. The triyne complex was confirmed to be an efficient catalyst precursor for the cyclization of the triyne ligand.

Transition-metal alkyne complexes have received considerable attention as intermediates in a wide variety of alkyne oligomerizations.[1] Low-valent late-transition-metal complexes bearing two or more alkyne ligands, however, are hardly found in the literature, although such polyalkyne complexes are implicated in the cyclooligomerizations of alkynes. This is because coordinated alkynes readily undergo oxidative cyclization to give metallacyclopentadienes, which can finally be converted into cyclobutadiene complexes via reductive C−C coupling or arenes via coupling with an extra alkyne. A few bis-alkyne platinum(0) complexes have been reported, but in these examples, two alkyne ligands cannot be cyclized around the metal center because their alkyne ligands are mutually *trans* and approximately perpendicular to each other.[2,3] In addition to the alkyne complexes, *ortho*-arene cyclyne nickel(0) complexes have been synthesized as cyclic triyne complexes by Youngs.[4] The rigid *ortho*-arene cyclynes cannot be easily converted into highly strained metallacyclopentadienes, although the three alkyne moieties are placed in the same plane. On the other hand, less rigid macrocyclic triynes or linear triynes are more readily cyclized into a metallacyclopentadiene or further into an arene product. Actually, Volhardt has recently synthesized the first metallacyclopentadiene(alkyne) complexes from the reaction of $Cp'Co(C_2H_4)_2$

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(2) (a) Rochon, F. D.; Theophanides, T. *Can. J. Chem.* **1972**, *50*, 1325. (b) Dubey, R. J. *Acta Crystallogr.* **1975**, *B31*, 1860. (c) Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1976**, 759.

(3) Many Mo(II) and W(II) bis- or tris-alkyne complexes have been reported. In these examples, 4*e*-donor alkyne ligands are placed perpendicular to the plane containing the metal atom and the alkyne ligand centers. For a review, see: Templeton, J. L. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1989; Vol. 29, p 1.

(4) For a review, see: Youngs, W. J.; Tessier, C. A.; Bradshaw, J. D. *Chem. Rev.* **1999**, *99*, 3153.

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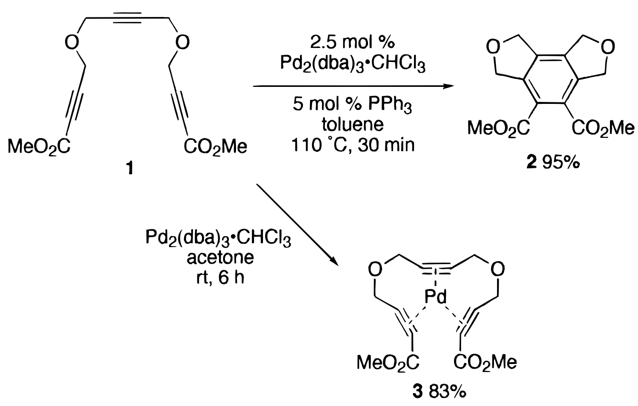
Scheme 1



and aryl-tethered acyclic triynes.[5] In addition, transition-metal-mediated transformations of silicon-tethered cyclotriynes into tricyclic benzene derivatives have been reported by Sakurai et al.[6] In this context, we have investigated the reaction of a palladium(0) complex with a more flexible linear triyne, dimethyl 4,9-dioxatrideca-2,7,12-triyne-1,13-dioate. As a result, we could obtain a palladium(0) triyne complex at ambient temperature and successfully characterized its structure by X-ray analysis. Herein we wish to report the structure and reactivity of the novel palladium(0) triyne complex.

Previously, we have reported that in the presence of 2.5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$ and 5 mol % PPh_3, the triyne **1** was heated at 110 °C for 30 min to afford a tricyclic arene product, **2**, in good yield (Scheme 1).[7] To gain further insight into the mechanism of the triyne cyclization, we investigated the stoichiometric reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ and **1**. The triyne **1** was treated with $Pd_2(dba)_3{\cdot}CHCl_3$ in acetone at room temperature for 6 h to afford a white solid. In the IR spectrum of this solid, the absorption of the alkyne was observed at 1977 cm^{-1} together with the absorption of the ester carbonyl group at 1712 cm^{-1}. This shows that at least one alkyne moiety remained intact. The ^1H NMR revealed that the compound has a highly symmetrical structure; only three singlets corresponding to the methoxy group and a pair of methylenes α to the ether oxygen atom were observed at δ 3.88, 4.58, and 4.66 ppm, respectively. Furthermore, three different sp-carbon signals appeared at δ 72.9, 75.6, and 89.7 ppm in the ^{13}C NMR spectrum. These facts allowed us to assign the obtained compound to a trialkyne complex **3**. Finally, the structure was unequivocally confirmed by X-ray analysis as shown in Figure 1. The palladium atom and the three alkyne moieties are placed almost in the same plane. The acetylenic triple-bond lengths are C3−C4 = 1.239(2) Å and C7−C8 = 1.222(3) Å, and the alkyne bond angles are C2−C3−C4 = 153.5(1)°, C3−C4−C5 = 157.0(2)°, and C6−C7−C8 = 157.1(2)°. The distances from the Pd atom to the centers of the central and terminal alkynes are ca. 2.11 and 2.05 Å, respectively. These values show that the back-donations from the Pd(0) to each alkyne moiety are not very significant compared to the known Pd(0) alkyne complexes[8] [e.g., $Pd(PPh_3)_2(dmad)$: triple bond length 1.279 Å, bond angle 144.9°, Pd−alkyne distance 1.96 Å].[8a] Such a weak back-donation might be ascribed to the dispersion of the back-bonding electrons into the three alkyne moieties (vide infra).

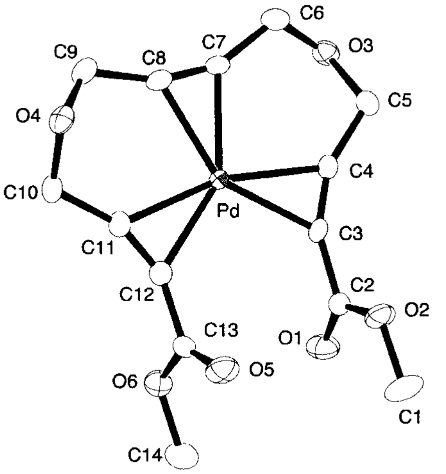


Figure 1. ORTEP diagram of the structure of **3**. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd−C3, 2.134(1); Pd−C4, 2.145(1); Pd−C7, 2.191(2); C3−C4, 1.239(2); C7−C8, 1.222(3); Pd−C3−C4, 73.64(9); Pd−C4−C3, 72.69(9); Pd−C7−C8, 74.0(1); C2−C3−C4, 153.5(1); C3−C4−C5, 157.0(2); C6−C7−C8, 157.1(2).

Another significant feature of the triyne complex **3** is its chemical behavior toward the [2 + 2 + 2] cyclotrimerization of the triyne **1**.[9] The isolated complex **3** was heated at 50 °C in acetone for 30 min to afford **2** in 50% yield. Furthermore, PPh_3 was found to effectively promote the conversion of **3** into **2** at ambient temperature. In acetone, the treatment of **3** with an equimolar amount of PPh_3 for 10 min gave **2** in 97% yield. Encouraged by these results, we next developed the catalytic cyclization of **1** using **3** as a catalyst precursor. In the presence of **3** (5 mol %), the triyne **1** was heated in toluene at 110 °C for 5 h to afford the desired product **2** in 92% yield. In this case, phosphine additives were not required. Thus, the net catalyst is the naked palladium atom itself.

In striking contrast to the triyne **1**, a diyne, dimethyl 5-oxahepta-2,7-diyne-1,9-dioate (**4**), gave an oligomeric palladacyclopentadiene, **5**, instead of the corresponding bis-alkyne complex (Scheme 2).[10] In this case, the back-bonding electrons were shared by the only two alkyne moieties, and as a result, the well-reduced alkynes underwent facile oxidative cyclization to form the bicyclopalladacycle **5** (vide supra). The formation of **5** was

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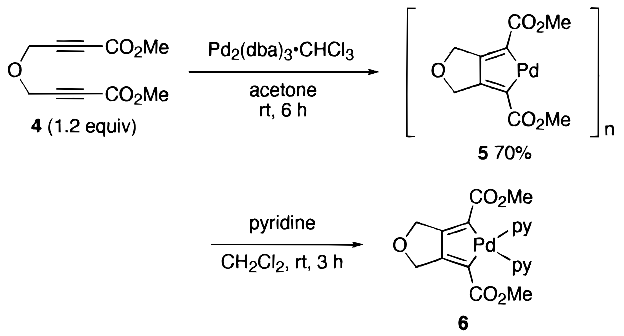
(9) Related catalytic cyclizations of 4,5-dioxadodeca-1,6,11-triyne have been reported: (a) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1357. (b) Peters, J.-U.; Blechert, S. *Chem. Commun.* **1997**, 1983. (c) Ojima, I.; Vu, A. T.; McCullagh, J. V.; Kinoshita, A. *J. Am. Chem. Soc.* **1999**, *121*, 3230.

(10) Related palladacyclopentadienes have been synthesized: (a) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169. (b) Ito, T. S.; Hasegawa, S.; Takahashi, Y.; Ishii, Y. *J. Organomet. Chem.* **1974**, *73*, 401. (c) Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8494. (d) Brown, L. D.; Itoh, K.; Suzuki, H.; Hirai, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 8232. (e) tom Dieck, H.; Munz, C.; Müller, C. *J. Organomet. Chem.* **1990**, *384*, 243. (f) van Belzen, R.; Klein, R. A.; Kooijman, H.; Veldman, N.; Spek, A. L.; Elsevier, C. J. *Organometallics* **1998**, *17*, 1812.

Scheme 2



supported by the absence of the alkyne absorption and the reduced carbonyl stretching frequency (1705 cm^{-1}) in the IR spectrum. Further detailed inspections of the metallacyclic structure were carried out for the monomeric bis-pyridine complex **6**. In the IR spectrum, the absorption of the alkyne triple bond was not observed and the carbonyl stretching appeared at 1670 cm^{-1}. The absence of an sp-carbon was also confirmed by ^{13}C NMR, but instead, two sp^2 signals corresponding to the palladacyclopentadiene unit were observed at δ 141.8 and 171.4 ppm. These spectroscopic measurements and satisfactory elemental analyses clearly confirmed the formation of the palladacyclopentadiene **5** from the diyne **4**.

In conclusion, we have obtained a palladium(0) trisalkyne complex from $Pd_2(dba)_3$•$CHCl_3$ and a linear triyne, dimethyl 4,9-dioxatrideca-2,7,12-triyne-1,13-dioate. The structure of the novel triyne complex was unequivocally determined by X-ray diffraction. The triyne complex was confirmed to be an efficient catalyst precursor for the cyclization of the triyne ligand. Therefore, this is the first example of a low-valent transition-metal complex bearing a cyclizable triyne ligand and its catalytic reaction. In sharp contrast to the triyne, the corresponding diyne, dimethyl 5-oxahepta-2,7-diyne-1,9-dioate, was reacted with $Pd_2(dba)_3$•$CHCl_3$ at room temperature to afford the corresponding oligomeric palladacyclopentadiene. These different behaviors of the polyalkynes might be ascribed to the number of coordinated alkynes that accept the back-bonding electrons from the Pd(0) center.

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Supporting Information Available: Analytical data for **1**–**6**, tables of crystallographic data and data collection details, positional parameters with *B*(eq), anisotropic displacement parameters, bond distances and angles, and a figure containing the atom-numbering scheme for **3**. This material is available free of charge via the Internet at http://pubs.asc.org.

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