ates. These results provide significantly important information about the dioxygen-activation mechanism in biological and industrial systems.

Experimental Section

Synthetic procedures of ligands L2 and TEPA, as well as the copper(II) complex of L2 have been reported elsewhere.[18,20]

L1: 2,2-Diphenylethylamine (1.97 g, 10 mmol) and 2-vinylpyridine (5.25 g, 50 mmol) were heated to reflux in CH_3OH (20 mL) containing acetic acid (3.01 g, 50 mmol) for 10 days. The solvent was removed by evaporation, and the resulting viscous material was dissolved in H_2O (200 mL) and extracted with $CHCl_3$ (3×200 mL). After drying over anhydrous K_2CO_3, evaporation of the organic solvent gave yellow oily material, from which L1 was isolated by SiO_2 column chromatography ($CHCl_3$/AcOEt as eluent) in 54% yield (2.21 g); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.76$–2.96 (m, 8H; $-CH_2-CH_2-Py$), 3.16 (d, $J = 7.5$ Hz, 2H; $-CH_2-CH-Ph_2$), 4.09 (t, $J = 7.5$ Hz, 1H; $-CH-Ph_2$), 6.76 (d, $J = 7.8$ Hz, 2H; $H_{py\text{-}5}$), 7.03–7.26 (m, 12H; C_6H_4 and $H_{py\text{-}3}$), 7.43 (td, $J = 1.8$ and 7.8 Hz, 2H; $H_{py\text{-}4}$), 8.50 ppm (ddd, $J = 0.9$, 1.8, and 4.8 Hz, 2H; $H_{py\text{-}6}$); FAB-HRMS (positive ion): calcd for $C_{28}H_{29}N_3$: *m/z* 406.2283; found: *m/z* 406.2289 [M^+].

[$Cu^{II}(L1)(ClO_4)_2]\cdot H_2O$: Ligand L1 (122.3 mg, 0.3 mmol) was treated with $Cu^{II}(ClO_4)_2\cdot 6H_2O$ (111.2 mg, 0.3 mmol) in CH_3OH (10 mL) for 30 min at room temperature. Addition of Et_2O (200 mL) to the mixture gave blue solids that were isolated by decantation, washed three times with Et_2O, and dried (83% yield). Single crystals were obtained by vapor diffusion of Et_2O into a solution of the complex in CH_3OH. FTIR (KBr): $\tilde{\nu} = 1130$, 1043, 621 cm^{-1} (ClO_4^-); FAB-MS (positive ion): *m/z* 569.2 [M^+]; elemental analysis for [$Cu^{II}(L1)(ClO_4)_2]\cdot H_2O$, calcd (%) for $C_{28}H_{31}O_9N_3CuCl_2$: C 48.88, H 4.54, N 6.11; found: C 48.72, H 4.48, N 6.06.

[$Cu^{II}(TEPA)(ClO_4)]ClO_4$: The TEPA ligand (332.5 mg, 1.0 mmol) was treated with $Cu^{II}(ClO_4)_2\cdot 6H_2O$ (370.5 mg, 1.0 mmol) in CH_3CN (10 mL) for 30 min at room temperature. Addition of Et_2O (200 mL) to the mixture gave a blue oily material that was isolated by decantation and redissolved into CH_3OH (10 mL). Addition of the CH_3OH solution into Et_2O (200 mL) gave blue solids that were isolated by decantation, washed with Et_2O three times, and dried (95% yield). Single crystals were obtained by vapor diffusion of Et_2O into a solution of the complex in CH_3OH. FTIR (KBr): $\tilde{\nu} = 1143$, 1081, 625 cm^{-1} (ClO_4^-); FAB-MS (positive ion): *m/z* 494.07 [M^+]; elemental analysis for [$Cu^{II}(TEPA)(ClO_4)](ClO_4)$, calcd (%) for $C_{21}H_{28}O_8N_4CuCl_2$: C 39.98, H 4.47, N 8.88; found: C 40.18, H 4.16, N 8.87.

Caution! The perchlorate salts in this study are all potentially explosive and should be handled with care.

Kinetic measurements for the reaction of copper(II) complexes (0.2 mM) and H_2O_2 were performed by using a multi-scan double mixing stopped-flow spectrophotometer designed for low-temperature measurements (RSP-1000, Unisoku Co., Ltd.) in CH_3OH at −90°C. The reaction of [$Cu^{II}(L1)(ClO_4)_2$] and H_2O_2 at the higher concentration (Figure S10 in the Supporting Information) was followed using the previously reported[18] Hewlett Packard HP8453 diode array spectrophotometer with a Unisoku thermostated cell holder designed for low-temperature measurements.

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Indenol Ether Formation from Aryl Alkynes Bearing *ortho*-Acetals: An Unprecedented Rearrangement in Palladium-Catalyzed Carboalkoxylation

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Yuya Mizushima, and Yoshinori Yamamoto*

The catalytic addition reaction to a C–C multiple bond is one of the most important processes for organic synthesis, because this process can construct new chemical bonds in an efficient and atom-economic manner. A wide variety of transition-metal-catalyzed (TM-catalyzed) addition reactions of pronucleophiles ($H-CR_3$,[1] $H-NR_2$,[2] H–OR,[3] H–OC(O)R,[4] H–SR,[5] $H-PR_2$,[6] etc.) and hydrides (H–B,[7]

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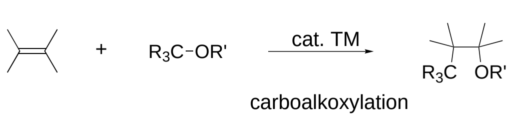
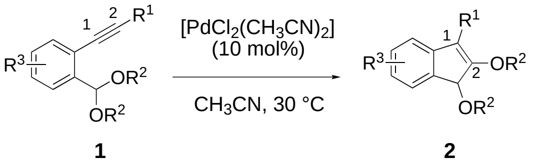
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

H–Si,[8] H–Sn,[9] etc.) have been developed and become a powerful method to construct various kinds of carbon–carbon and carbon–heteroatom bonds. More recently, transition-metal-catalyzed addition of other types of bonds, such as B–B,[10] B–Si,[11,12] Si–Si,[8a,11,13] Si–Sn,[11,14] Sn–Sn,[15] etc., have been reported. However, catalytic addition of a carbon–oxygen bond to carbon–carbon multiple bonds, so-called carboalkoxylation, has rarely been investigated, perhaps because of the lower reactivity of ether C–O bonds,[16] although this process is useful to construct both carbon–carbon and carbon–oxygen bonds simultaneously [Eq. (1)]. It occurred to us that an acetal C–O bond would be more reactive than that in ethers. We now report that the palladium-catalyzed reaction of the aryl alkynes bearing *ortho*-acetals **1** gives the indenol ether **2** in high to moderate yields [Eq. (2)]. The mechanistic investigation of this unprecedented rearrangement[17] reveals that R^1 migrates from the C-2 atom to the C-1 atom under the palladium-catalysis conditions.



(1)



(2)

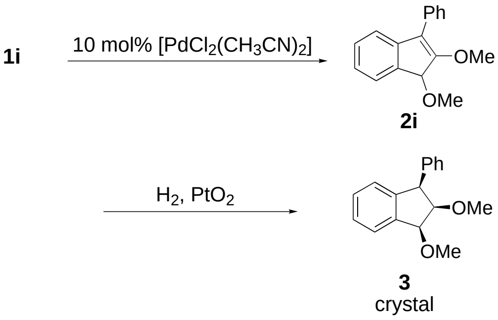
The results of our study are summarized in Table 1. In the presence of 10 mol% of $[PdCl_2(CH_3CN)_2]$, the reaction of 2-(1-pentynyl)benzaldehyde dimethyl acetal (**1a**) proceeded smoothly at 30 °C, and the corresponding 1,2-dimethoxyindene derivative **2a** was obtained in 75% yield (entry 1). Other transition-metal compounds, such as $[Pd(PPh_3)_4]$, $Pd(OAc)_2$, $NiCl_2$, and $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene), didn't promote the reaction at all. The reaction of **1a** proceeded even at room temperature and produced **2a** in 63% yield, although the reaction took slightly longer. The reaction of the corresponding diethylacetal **1b** and dibutylacetal **1c** gave **2b** and **2c** in 87% and 80% yield, respectively (entries 2 and 3). The reaction of the dimethylacetal **1d** and diethylacetal **1e** of 2-(1-octynyl)benzaldehyde also proceeded very smoothly (entries 4 and 5). Chloro, bromo, and ester substituents were tolerated in this reaction (entries 6 and 7). The steric bulk of R^1 exerted significant influence on the speed of the reaction. The reaction of 2-(cyclohexylethynyl)-benzaldehyde dimethylacetal **1h** proceeded at 60 °C, producing **2h** in 52% yield after 15 h (entry 8). The presence of the *tert*-butyl group (R^1 = *t*Bu) totally halted the reaction and the starting material was recovered under the reaction conditions described above. The reaction of 2-(2-phenylethynyl)benzaldehyde dimethylacetal **1i** gave the corresponding 3-aryl indenol ether **2i** in a moderate yield (entry 9). The reaction of **1j**, **1k**, and **1l** with substituents on the initial aromatic ring, proceeded in a similar manner (entries 10–12). On the contrary, the reaction of **1m** and **1n**, which had a methoxy group at the 4 and 5-positions, respectively, did not proceed at all.

Table 1. Palladium-catalyzed carboalkoxylation of the *o*-alkynylbenzaldehyde dialkylacetals **1**.[a]

Entry	**1**	R^1	R^2	R^3	**2**	Yield [%][b]
1	**1a**	*n*Pr	Me	H	**2a**	75
2	**1b**	*n*Pr	Et	H	**2b**	87
3	**1c**	*n*Pr	Bu	H	**2c**	80
4	**1d**	*n*Hex	Me	H	**2d**	65
5	**1e**	*n*Hex	Et	H	**2e**	54
6	**1f**	$(CH_2)_4Cl$	Me	H	**2f**	45
7	**1g**	$(CH_2)_4OCO(p\text{-}BrC_6H_4)$	Me	H	**2g**	45
8[c]	**1h**	cyclohexyl	Me	H	**2h**	52
9	**1i**	Ph	Me	H	**2i**	40
10	**1j**	*n*Pr	Me	4-CF_3	**2j**	57
11	**1k**	*n*Pr	Me	5-CF_3	**2k**	52
12	**1l**	*n*Pr	Me	4-Me	**2l**	51

[a] The reaction of **1** was carried out in the presence of 10 mol% of $[PdCl_2(CH_3CN)_2]$ in CH_3CN at 30 °C for 15 h. [b] Yield of product isolated. [c] The reaction was carried out at 60 °C.

The structure of **2** was confirmed by spectroscopic methods (especially by NOE analysis, see Supporting Information). Furthermore, the structure of **2i** was determined unambiguously by an X-ray crystallographic analysis of **3**, which was obtained through the hydrogenation of the double bond of **2i** [Eq. (3)]. The ORTEP structure of **3** is shown in Figure 1. It is clear that the phenyl group of **1i** is at the benzylic position (C-1) of **2i** and the two methoxy groups at the C-2 and C-3 positions.



(3)

Plausible mechanisms of this reaction are illustrated in Scheme 1. The acetal group of **1** coordinates to an electron deficient Pd^{II} center as shown in **4** (route **A**). A carbon–oxygen bond would be cleaved to generate the oxonium cation **5** and the palladium alkoxide species. Nucleophilic attack of the oxonium cation by the alkynyl group would produce the five-membered ring species **6**. Alkoxypalladation of the C–C double bond of **6** would form the palladium–carbene complex **7**.[18] Migration of R^1 followed by elimination of $PdCl_2$ would produce the carboalkoxylation product **2**. Alternatively, it is conceivable that coordination of the alkynyl moiety of **1** to Pd^{II} (as shown in **8**) occurs at the beginning of catalytic cycle (route **B**). Nucleophil-

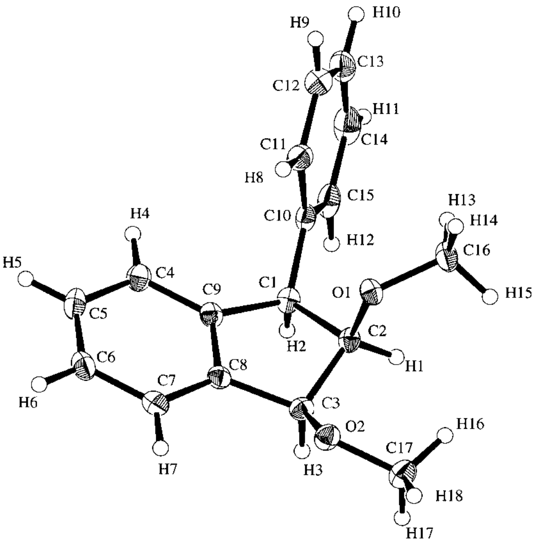
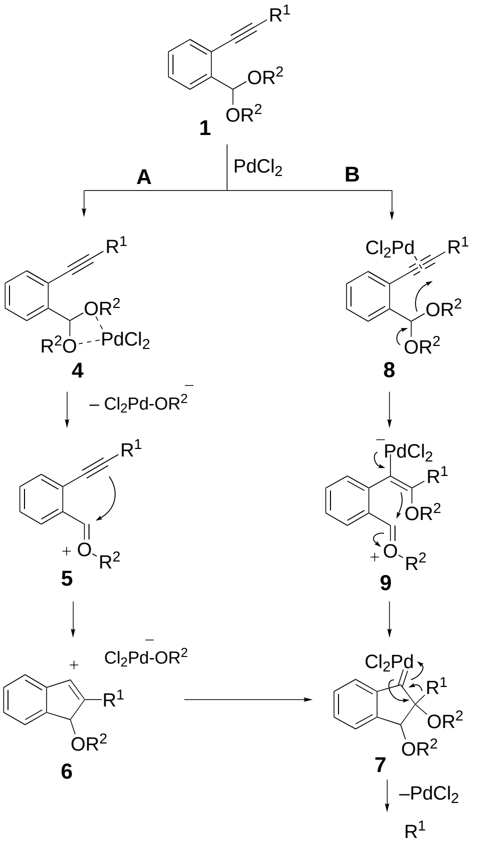


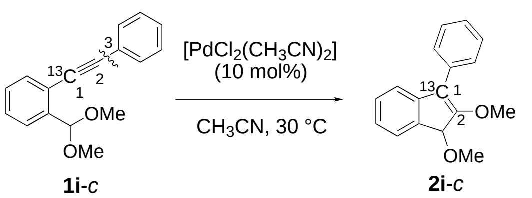
Figure 1. ORTEP drawing of **3** (thermal ellipsoids set at 50 % probability).



Scheme 1. Plausible mechanisms which lead to the formation of **2**.

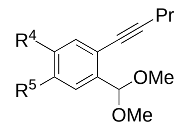
ic attack of the electron-deficient carbon–carbon triple bond by an alkoxide would give the vinylpalladium species **9**, which subsequently undergoes the ring-closing C–C bond formation to produce the palladium carbene species **7**.

To confirm the proposed step from **7** to **2** in Scheme 1, we carried out a ^{13}C labeling experiment [Eq. (4)]. In the



(4)

presence of catalytic amounts of $[PdCl_2(CH_3CN)_2]$, the reaction of **1i**-*c*, which has a ^{13}C carbon atom at the C-1 position, gave **2i**-*c* in 40 % yield along with a trace amount of unknown byproducts. This result clearly indicates that the bond cleavage occurred between the C-2 and C-3 positions of **1i**-*c*.



1j (R^4 = CF_3, R^5 = H)
1k (R^4 = H, R^5 = CF_3)
1l (R^4 = Me, R^5 = H)
1m (R^4 = MeO, R^5 = H)
1n (R^4 = H, R^5 = MeO)

The palladium-catalyzed hydrolysis of acetals and ketals, which lead to the corresponding carbonyl compounds, was reported by Lipshutz et al.,[19] and the rhodium-catalyzed substitution reaction of acetals with TMSCN (TMS = trimethylsilyl) to produce α-alkoxycyanides was reported by Mukaiyama and co-workers.[20] To our knowledge, however, catalytic addition of an acetal carbon–oxygen bond to carbon–carbon multiple bonds is not known. The structural framework of indenol derivatives is often found in naturally occurring compounds,[21] and the alkenyl ether functionality may be synthetically elaborated by reaction with a variety of electrophiles.

Experimental Section

Synthesis of **2a**: **1a** (109.2 mg, 0.5 mmol) in acetonitrile (1 mL) was added to $[PdCl_2(CH_3CN)_2]$ (12.9 mg, 0.05 mmol) in acetonitrile (1 mL) under an Ar atmosphere, in a pressure vial. After heating at 30 °C for 15 h, the reaction mixture was filtered through a short silica-gel column using ethyl acetate as an eluent. Separation by silica-gel column chromatography using hexane/EtOAc as an eluent afforded the product **2a**. IR (neat): $\tilde{\nu} = 3067$–2823, 1648, 1607, 1469, 1350, 1332, 1249, 1164, 1099, 1060, 1035, 933, 758, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.3$ Hz, 3H), 1.58 (m, 2H), 2.39 (m, 2H), 3.10 (s, 3H), 3.96 (s, 3H), 5.18 (s, 1H), 7.06–7.03 (m, 2H), 7.31–7.21 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.07$, 21.22, 25.11, 51.44, 57.85, 78.33, 117.68, 119.70, 123.23, 123.55, 128.64, 136.19, 144.53, 156.89 ppm; elemental analysis (%) calcd for $C_{14}H_{18}O_2$ (218.30): C 77.03, H 8.31; found: C 76.78, H 8.37; HRMS (EI) calcd for $C_{14}H_{18}O_2$: *m*/*z* 218.1306, found: *m*/*z* 218.1307.

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Monodisperse Surface Micelles of Nonpolar Amphiphiles in Langmuir Monolayers**

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There are several examples of surface micelles (hemimicelles) formed by self-assembly of small molecules and macromolecules that are adsorbed on solid surfaces and in equilibrium with aqueous solutions.[1] On the other hand, reports on surface micelles in Langmuir monolayers are essentially limited to copolymers.[2] Although their existence has long been predicted,[3,4] so far only one example of surface micelles made from small amphiphilic molecules exists.[5] These surface micelles were made from *strongly polar* surfactants. Furthermore no rule for predicting the size of the hemimicelles has been found. We report here on novel surface micelles made of a nonpolar amphiphile, namely, the semifluorinated alkane $C_8F_{17}C_{16}H_{33}$ (F8H16), their structure, and a model that accounts for their size.

Since the pioneering work of Gaines demonstrated that semifluorinated alkanes $C_nF_{n+1}C_mH_{2m+1}$ (F*n*H*m* diblocks) form Langmuir monolayers,[6] their structure has remained controversial. A primary issue was the orientation of the F*n*H*m* molecules at the air–water interface. Grazing-incidence X-ray diffraction (GIXD) and X-ray reflectivity (GIXR) studies on F12H18 concluded that the most probable arrangement was a monolayer in which the H*m* segments are in contact with water and the F*n* segments extend upwards from the surface.[7] However, a bilayer structure in which the diblocks are antiparallel, with tilted F8 segments outside and interleaved H18 segments inside, was recently proposed on the basis of X-ray reflectivity measurements.[8] In the bulk, F*n*H*m* molecules crystallize in a large number of different stable smectic phases, depending on temperature and on *n* and *m* block lengths.[9–11] F*n*H*m* were instrumental in allowing reversible vertical phase separation from phospholipids upon compression of Langmuir monolayers.[12] They allowed substantial stabilization of fluorocarbon-in-water emulsions and control over particle size.[13,14]

F8H16[15] was thoroughly purified by column chromatography, and its purity (> 99 %) determined by GC, TLC, NMR spectroscopy, and elemental analysis. Monolayers were spread from a 1 mM solution of F8H16 in chloroform onto pure water from a milli-Q system. Surface pressure P_s (Wilhelmy plate method) versus molecular area isotherms were recorded at 22.0 ± 0.5 °C on a Langmuir trough (Riegler & Kirstein, Germany) equipped with two movable barriers.

F8H16 formed a monolayer that remained stable up to about 8 $mN\,m^{-1}$ (Figure 1) with a limiting area of about 30 $Å^2$ that corresponds to the cross section of a perfluorinated chain, which is larger than that of a typical hydrocarbon chain (ca.

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