Palladium-Complex-Catalyzed Cyanation of Allylic Carbonates and Acetates Using Trimethylsilyl Cyanide

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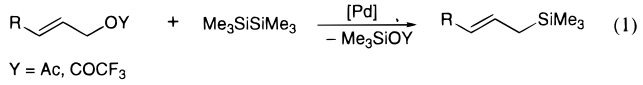
Allylic carbonates are cyanated in high yields to β,γ-unsaturated carbonitriles using trimethylsilyl cyanide in the presence of a catalytic amount (5 mol %) of $Pd(PPh_3)_4$ in THF under reflux. In the reaction, cinnnamyl methyl carbonate affords cinnamyl cyanide in 98% yield. Allylic acetates also provide the corresponding carbonitriles, but often in lower yields. The cyanations of several *cis*- and *trans*-alicyclic substrates proceed cleanly (stereoselectivity > 99%) with overall retention. Characterization and reaction of palladium complexes relevant to the present catalysis indicate that transmetalation of an η^3-allyl palladium complex with trimethylsilyl cyanide is facile, while the resulting cyano(η^3-allyl)palladium complexes afford the corresponding allylic cyanides only when excess trimethylsilyl cyanide is present. Stereochemistry of the product indicates that the CN attacks the η^3-allyl moieties from the palladium side.

Introduction

One of the most important aspects of η^3-allylpalladium chemistry might be its intermediacy in palladium-catalyzed reactions of allylic compounds with nucleophiles.[1,2] Formation of the η^3-allylpalladium species by oxidative addition of the allylic compounds to Pd(0) and subsequent reaction with nucleophiles are imperative in the catalysis. As the nucleophiles, stabilized carbanions,[3] enolates,[4] organotin reagents,[5] and nitrogen nucleophiles[6] can be successfully employed in the presence of strongly coordinating ligands such as phosphines. However, the reaction will be more promising if untried functionalities can be introduced to the allylic system.

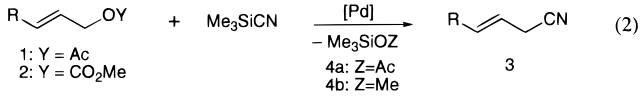
We have been developing catalytic silylation and/or stannylation reactions using group 14 compounds[7] and found palladium-catalyzed functionalizations of allylic esters by utilizing silicon compounds. That is, we recently explored general silylation reaction of allylic esters using organodisilanes as a silylating reagent, which is catalyzed by a palladium complex and involves a cleavage of the Si−Si σ-bond (eq 1).[8] The strong



(1)

oxophilicity of silicon would facilitate the silylation reaction.

In addition, we found the first example of cyanation of allylic esters catalyzed by a palladium complex and reported the preliminary results (eq 2).[9] In the reaction,



(2)

trimethylsilyl cyanide (Me_3SiCN) is very efficient as a cyanide source and afforded β,γ-unsaturated carbonitriles.[10,11] Here, we describe details of the cyanation,

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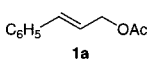
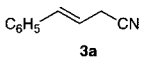
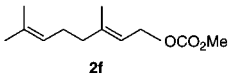
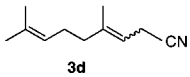
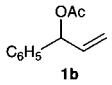
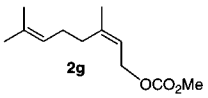
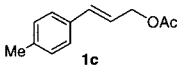
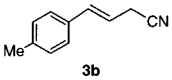
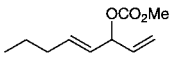
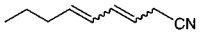
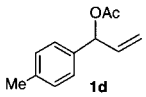
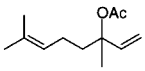
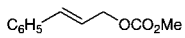
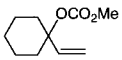
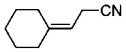
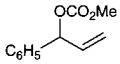
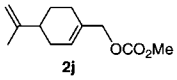
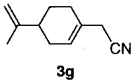
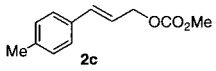
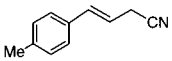
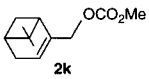
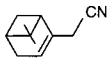
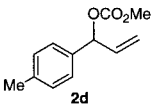
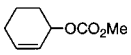
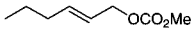
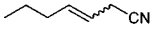
Table 1. Cyanation of Allylic Acetates (1) or Carbonates (2)[a]

entry	allylic compd (**1** or **2**)	product (**3**)	yield[b]/%	entry	allylic compd (**1** or **2**)	product (**3**)	yield[b]/%
1	 **1a**	 **3a**	(98)	10[c]	 **2f**	 **3d**	89[e]
2	 **1b**	**3a**	82	11[c]	 **2g**	**3d**	80[e]
3	 **1c**	 **3b**	88	12[h]	 **2h**	 **3e**	75[g]
4	 **1d**	**3b**	86	13[c]	 **1e**	**3d**	65[f]
5	 **2a**	**3a**	92(98)	14[h]	 **2i**	 **3f**	60
6	 **2b**	**3a**	92(99)	15[h]	 **2j**	 **3g**	81
7	 **2c**	 **3b**	91	16[i]	 **2k**	 **3h**	93
8	 **2d**	**3b**	92	17	 **2l**	 **3i**	88
9[c]	 **2e**	 **3c**	78[d]				

[a] Conditions: **1** (1.5 mmol), Me_3SiCN (3.0 mmol), $Pd(PPh_3)_4$ (0.075 mmol), THF (6.0 mL), under reflux for 18 h. [b] Isolated yields. Numbers in parentheses show GLC yields determined by the internal standard method. [c] For 5 h. [d] *E*/*Z* = 80:20. [e] *E*/*Z* = 71:29. [f] *E*/*Z* = 70:30. [g] (3*E*,5*E*)/(3*Z*/5*E*)/(3*E*/5*Z*)/(3*Z*/5*Z*) = 70:14:14:2. [h] In benzene (6.0 mL) under reflux. [i] In toluene (6.0 mL) under reflux.

including stereochemistry of the reaction, characterization of palladium complexes relevant to the catalysis, and results of enantioselective cyanation.

Results and Discussion

Cinnamyl acetate (**1a**) reacts with 2 equiv of Me_3SiCN in the presence of 5 mol % $Pd(PPh_3)_4$ to afford cinnnamyl cyanide (**3a**) regio- and stereoselectively (entry 1, Table 1). The same product **3a** was obtained from **1b**, suggesting a η^3-allyl palladium intermediacy (entry 2). Similarly, **1c** and **1d** afforded the corresponding cyanated product **3b** in high yields (entries 3 and 4). The corresponding allylic carbonates were also smoothly cyanated with Me_3SiCN: **3a** was obtained from **2a** or **2b** (entries 5 and 6), and **3b** from **2c** or **2d** in high yields (entries 7 and 8). Aliphatic allylic carbonates **2e**−**2h** readily gave the corresponding β,γ-unsaturated carbonitriles regioselectively in high yields, but with modest stereoselectivity (entries 9−12). The *E*/*Z* ratio did not depend on conversion of **2**, indicating *E*/*Z* isomerizations during the reaction were unlikely. Compared with the allylic carbonates **2**, the corresponding aliphatic acetates such as (*E*)-2-hexenyl, geranyl, and neryl acetates showed only lower conversions (10%−50%), whereas tertiary acetates such as **1e** reacted somewhat faster to afford better yields (entry 13). Accordingly, for the present cyanation reaction, allylic carbonates **2** are more suitable substrates than the corresponding acetates **1**. Alicyclic allylic carbonates also afforded the corresponding carbonitriles in high yields (entries 14−17). Although almost no **2k** was consumed under the standard conditions (reflux in THF), the cyanation readily proceeded at higher reaction temperature, under reflux in toluene (entry 16) or 110 °C in diglyme. As the catalyst precursors, $Pd(PPh_3)_4$ and $Pd(CO)(PPh_3)_3$ show high catalytic activity. However, other representative catalyst precursors were not effective; yields of **3a** from **2a** under otherwise the same reaction conditions as entry 5 were as follows: $Pd(OAc)_2$ 4%, $PdCl_2(PPh_3)_2$ trace, $Pd(DBA)_2$ (DBA = dibenzylideneacetone) 5%, $PdCl_2(PhCN)_2$ 5%, $Pt(PPh_3)_4$ 0%, $Ru_3(CO)_{12}$[12a,b] 4%, $Mo(CO)_6$[12c] 3%.

(11) For transition metal-catalyzed cyanation of allylic acetals using Me_3SiCN, see: (a) Mukaiyama, T.; Soga, T.; Takenoshita, H. *Chem. Lett.* **1989**, 997. (b) Mukaiyama, T.; Takenoshita, H.; Yamada, M.; Soga, T. *Chem. Lett.* **1990**, 229.

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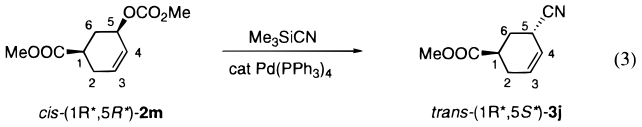
Trimethylsilyl cyanide is a potent cyanation reagent[13] and was used so far in cyanations of aryl halides[14a] and alkynes[14b] catalyzed by a palladium complex. On the other hand, KCN and NaCN could be used for cyanation of iodobenzene in the presence of a palladium complex.[15] Therefore, efficiency of KCN and NaCN as cyanation reagents for the allylic carbonates (**2**) and acetates (**1**) was investigated. When KCN was employed in place of Me_3SiCN with **1a** under the standard reaction conditions (entry 1), the acetate **1a** did not convert at all. If Me_3SiCN was replaced with KCN in entry 5, the carbonate **2a** was consumed completely, but only afforded cinnamyl methyl ether in 40% yield by palladium-catalyzed decarboxylation.[16] Employment of NaCN rather than Me_3SiCN in entry 5 lowered conversion of **2a** (<20%). In all the cases with KCN or NaCN as the cyanide source, no cyanated product **3a** was obtained.

^{29}Si NMR spectra of resulting reaction mixtures were measured to elucidate the fate of the trimethylsilyl moiety of Me_3SiCN. After the reaction with allylic acetates (**1**) (entry 1), the comparable amount of Me_3SiOAc (**4a**) (22.06 ppm; lit.[17a] 22.0 ppm) was found in the reaction mixture along with excess Me_3SiCN (−12.30 ppm; lit.[17b] −12.12 ppm). In the reaction with allylic carbonates (**2**) (entry 5), comparable formation of Me_3SiOMe (**4b**) (17.66 ppm; lit.[17c] 17.75 ppm) was confirmed similarly. The strong oxophilicity of the trimethylsilyl functionality (bond dissociation energy:[18] Si−O 430−530 kJ mol^{-1}) may favor the reaction via effective trapping of the oxygen-containing leaving group.

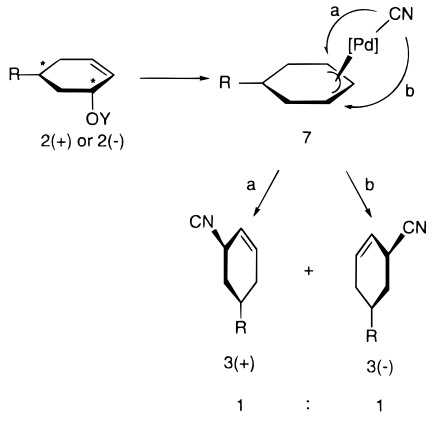
In an effort to determine the stereochemistry of the present cyanation reaction, the reactions with several *cis*- and *trans*-alicyclic substrates were examined. The cyanation of a racemic mixture of *cis*-(1*R**,5*R**)-**2m**[19] under the standard reaction condition afforded *trans*-(1*R**,5*S**)-**3j** (*trans* > 99%) stereoselectively in 94% yield (eq 3). The *trans*-stereochemistry of the product could



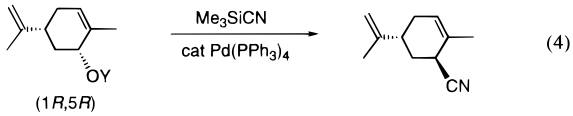
cis-(1R*,5*R**)-**2m** *trans*-(1R*,5*S**)-**3j** (3)

be readily confirmed on the basis of their vicinal couplings (axial−axial and axial−equatorial) for the axial H6 proton[19,20] at δ 2.02. Similar overall inversion

Scheme 1

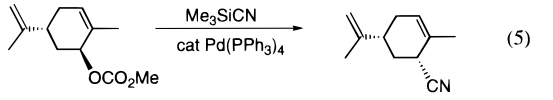


cyanation from a *cis*-substrate to a *trans*-product was observed with optically pure *cis*-(1*R*,5*R*)-**2n**, which provides *trans*-(1*R**,5*S**)-**3k** (*trans* > 99%) in 73% yield (eq 4). A chiral gas chromatograph analysis (on CP-



(1*R*,5*R*) (4)
cis-**2n**: Y=CO_2Me *trans*-(1*R**,5*S**)-**3k**
cis-**1f**: Y=Ac

Chirasil Dex CB, CHROMPACK) showed the *trans*-product **3k** was a 1:1 mixture of the two enatiomers, even if the optically pure *cis*-**2n** was employed. The corresponding acetate, *cis*-(1*R*,5*R*)-**1f**, also gave *trans*-(1*R**,5*S**)-**3k** (*trans* > 99%) stereoselectively, but conversion of the reaction and the yield (12%) were very low. Again, the acetate was less reactive in the present cyanation. Furthermore, starting from a *trans*-substrate, the similar overall inversion cyanation was observed: optically pure *trans*-(1*S*,5*R*)-**2o** afforded a 1:1 racemic mixture of *cis*-(1*R**,5*R**)-**3l** (*cis* > 99%) in 86% yield (eq 5). In this manner, the cyanation with the



trans-(1*S*,5*R*)-**2o** *cis*-(1*R**,5*R**)-**3l** (5)

clean overall inversion proceeded from both *cis*- and *trans*-substrates.

While the present cyanation is highly stereoselective (overall inversion), optically active substrates such as *cis*-(1*R*,5*R*)-**2n**, *cis*-(1*R*,5*R*)-**1f**, and *trans*-(1*S*,5*R*)-**2o** afforded only racemic mixtures (eqs 4 and 5). Apparently, regiochemistry of the CN attack (a or b) cannot be regulated without a chiral auxiliary (Scheme 1). To realize enantioselective cyanation, the reaction should be carried out in the presence of a chiral phosphine ligand. As a catalyst precursor for the enantioselective cyanation, $[(C_3H_5)PdCl]_2$ (5 mol % as Pd atom) combined with (*S*)-(−)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl ((*S*)-MeO-MOP)[21] was employed. When the cyanation of *trans*-(1*S*,5*R*)-**2o** was carried out with the

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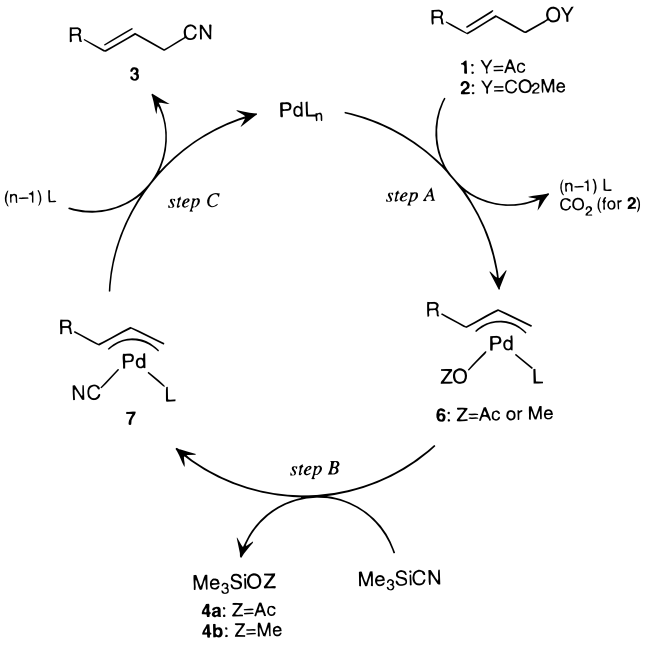
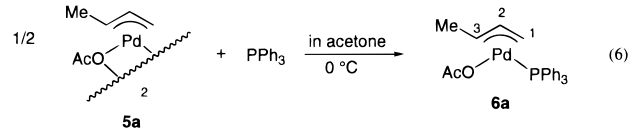
Scheme 2



chiral catalyst system in benzene at 60 °C, *cis*-**3l** was obtained in 63% ee and 89% yield; *trans*-**3l** was also obtained in 3% yield. A racemic mixture of *trans*-**2o** also gave the identical result under the same reaction conditions. Using the same catalyst system in benzene at 35 °C, **2l** provided **3i** in 19% ee and 99% yield. As for other chiral auxiliaries, (*R*)-BINAP[22] and (*S*)-(*R*)-PPFA[23] only afforded intractable mixtures in benzene, while (+)-NMDPP[24] did not show any enantioselectivity in the cyanation.

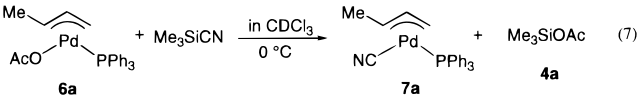
A possible catalyst cycle for the present cyanation is shown in Scheme 2. The catalyst cycle would consist of three representative steps: oxidative addition of the allylic esters to palladium(0) catalyst species (step A), transmetalation of allylpalladium species (**6**) with Me_3SiCN (step B), and reductive elimination to afford the products (step C). The oxidative addition of allylic esters to palladium(0) complexes has been well-studied.[25] However, the transmetalation with Me_3SiCN (step B) and reductive elimination of the cyano(η^3-allyl)-palladium species **7** (step C) are totally unprecedented.[26] Therefore, these two steps were explored using model complexes.

As a model complex for the step B, η^3-crotylpalladium complex (**6a**: R = Me, Z = Ac, L = PPh_3) was prepared from the corresponding known acetate dimer **5a**[27] and PPh_3 in acetone at 0 °C (eq 6). The reaction is highly



(6)

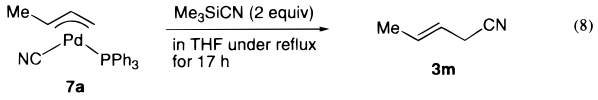
selective and afford **6a** as a single isomer regio- and stereoselectively. The product **6a** was fully characterized with ^1H and ^{13}C NMR, DEPT, and C−H COSY spectra. As for the π-allyl system of **6a**, only H_3 and C_3 resonances have spin−spin couplings to the phosphorus ($^3J_{H3-P} = 8.4$ Hz and $^2J_{C3-P} = 24.7$ Hz), indicating *trans* disposition of the PPh_3 to the C_3 carbon. Syn η^3-allyl structure of **6a** is evident by $^3J_{H3-H2}$ vicinal coupling (12.8 Hz). As a model reaction for the transmetalation, **6a** was allowed to react with 1.5 equiv of Me_3SiCN in $CDCl_3$ at 0 °C for 1 h (eq 7). Instantaneous color change



(7)

from clear orange to yellow showed the reaction is fast. ^1H and ^{13}C NMR spectra of the resulting solution indicated that all the **6a** was consumed and the known cyano complex **7a**[28] formed quantitatively, which was isolated in 74% yield from the reaction mixture. In addition, the ^{29}Si NMR spectrum of the same reaction mixture showed a comparable formation of Me_3SiOAc (**4a**) (22.47 ppm, lit.[17a] 22.0 ppm). These results clearly indicate that the transmetalation between **6a** and Me_3SiCN occurs readily and regioselectively, affording **7a** and **4a**. For the cyanation, the complex **7a** itself showed high catalytic activity. When 5 mol % of **7a** was used as a catalyst precursor in place of $Pd(PPh_3)_4$ in entry 5, **3a** was obtained in 98% yield, indicating **7a** could be involved in the catalytic cycle and is not an inactive species extruded from the catalysis.

Next, thermolysis of **7a** was carried out under various reaction conditions as a model reaction for step C. Simply heating **7a** in refluxing THF did not afford expected (*E*)-2-butenyl cyanide **3m** at all. In sharp contrast, in the presence of 2 equiv of Me_3SiCN under otherwise identical conditions, **7a** provided **3m** smoothly in 68% yield (eq 8). Although various reaction condi-



(8)

tions were examined, **3m** was afforded from **7a** only when Me_3SiCN was present with **7a**: addition of 4 equiv of maleic anhydride, PPh_3, *tert*-butyl isocyanide, or CO (40 kg/cm^2), which are all known to accelerate the reductive elimination,[29] was not effective to afford **3m**. To gain more information on a role of the Me_3SiCN, ^{13}C-labeled Me_3SiCN ($Me_3Si^{13}CN$) was prepared[30] and employed in the reaction. Using 2 equiv of $Me_3Si^{13}CN$ under the same reaction conditions as eq 8, **3m** and **3m*** (**3m** containing ^{13}CN moiety) were provided in 6:4 ratio (total yield: 66%), while with 4 equiv of $Me_3Si^{13}CN$ the

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(26) (a) Reductive elimination of allylnickel cyanide was concluded to proceed with retention from stereochemical studies on nickel-catalyzed deuteriocyanation of 1,3-cyclohexadiene.[26b,c] (b) Bäckvall, J.-E.; Andell, O. S. *J. Chem. Soc., Chem. Commun.* **1984**, 260. (c) Bäckvall, J.-E.; Andell, O. S. *Organometallics* **1986**, *5*, 2350.
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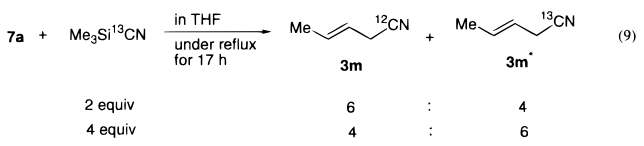
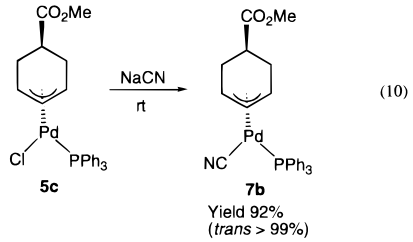
two products were obtained in 4:6 ratio (total yield: 71%) (eq 9). Even though excess $Me_3Si^{13}CN$ was used,

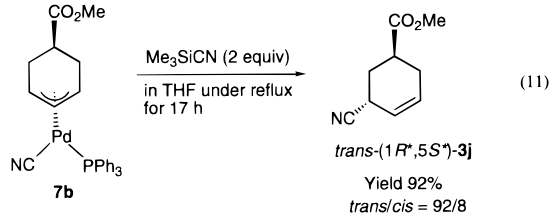


a substantial amount of **3m** was formed together with **3m***. Hence, direct attack of the ^{13}CN onto the π-allyl moiety from outside of the coordination sphere might be unlikely. In any event, involvement of Me_3SiCN was essential for the formation of **3m** from **7a**. Then, **7a** was treated with 1 equiv of $Me_3Si^{13}CN$ in a NMR tube for 1 h at room temperature, and the ^{13}C NMR spectrum was measured. In the reaction mixture, no reductive elimination products (**3m** or **3m***) were formed due to the lower reaction temperature. The spectrum of the resulting solution showed a large broad resonance (the width at half-height $\nu_{1/2} = 180$ Hz) at 142.1 ppm, which is close to the CN resonance of **7a** (141.3 ppm, lit.[28] 141.0 ppm), while the CN resonance of $Me_3Si^{13}CN$ at 126.9 ppm ($^1J_{C-Si} = 52$ Hz) decreased considerably. Apparently, Me_3SiCN interacts with **7a** substantially via exchange of the CN ligand.

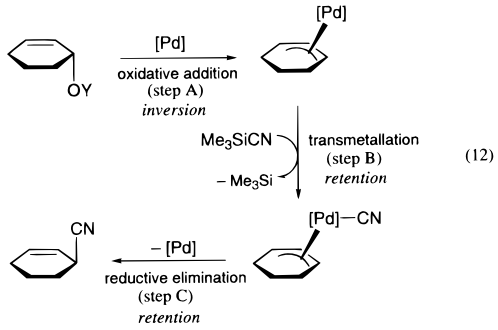
Since the reductive elimination of **7a** was rather complicated due to the involvement of Me_3SiCN as mentioned above, another model complex, **7b**, was prepared from the known complex **5c**[31] by applying the reported procedure[28] (eq 10). The *trans*-structure of **7b**



was confirmed by X-ray crystallographic analysis (Figure 1),[32] and Table 2 lists selected bond distances and angles for **7b**. The reductive elimination (thermolysis) of **7b** was carried out, but its behavior was very reminiscent of **7a**: **7b** would not afford **3j** by simply heating it in refluxing THF or even in refluxing toluene. Only heating **7b** with Me_3SiCN (2 equiv) provided **3j** in 92% yield (eq 11). Noteworthy is that **7b** afforded *trans*-



(1*R**,5*S**)-**3j** stereoselectively (*trans*/*cis* = 92:8), indicating the CN attacks the η^3-allyl moiety from the palladium side. Despite the function of Me_3SiCN, the reductive elimination process was stereoselective retention.[26] Accordingly, the stereochemical path of the catalysis will be as shown in eq 12. Reactions with some



stabilized anions are likely to occur by external attack from the face opposite the metal and afforded overall retention products.[1] On the other hand, several nucleophiles afford the overall inversion products[33] via initial attack on the metal followed by stereoselective reductive elimination. In the present cyanation, two factors might be responsible for the clean overall inver-

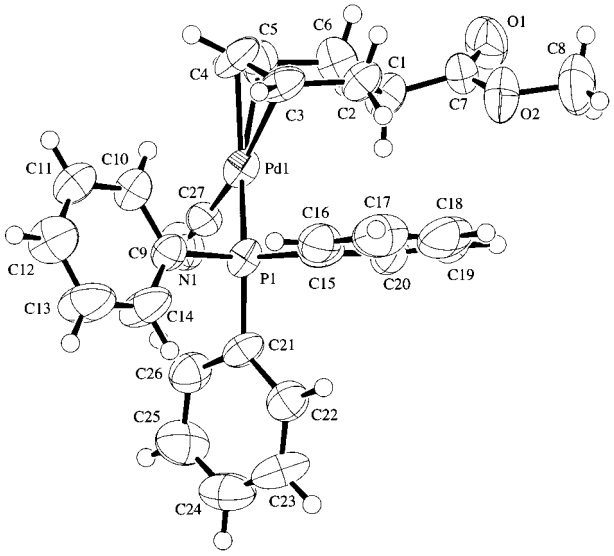


Figure 1. Perspective ORTEP drawing of the molecular structure of complex **7b**. All non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 50% probability, and hydrogen atoms are deleted for ease of viewing.

Table 2. Selected Bond Distances and Angles for 7b

Distances (Å)			
Pd(1)−P(1)	2.323(3)	Pd(1)−C(3)	2.20(1)
Pd(1)−C(4)	2.12(1)	Pd(1)−C(5)	2.25(1)
Pd(1)−C(27)	2.02(1)	C(3)−C(4)	1.40(2)
C(4)−C(5)	1.43(2)	N(1)−C(27)	1.14(1)
C(5)−C(6)	1.49(2)	C(2)−C(3)	1.52(2)
C(1)−C(6)	1.52(2)	C(1)−C(2)	1.53(2)
Angles (deg)			
P(1)−Pd(1)−C(3)	95.8(3)	P(1)−Pd(1)−C(4)	127.5(4)
P(1)−Pd(1)−C(5)	160.8(3)	P(1)−Pd(1)−C(27)	102.1(4)
C(3)−Pd(1)−C(5)	65.5(5)	C(5)−Pd(1)−C(27)	96.7(5)
C(2)−C(3)−C(4)	120(1)	C(3)−C(4)−C(5)	117(1)
C(4)−C(5)−C(6)	120(1)	C(1)−C(2)−C(3)	113(1)
C(1)−C(6)−C(5)	114(1)	C(2)−C(1)−C(7)	111(1)
C(6)−C(1)−C(7)	111(1)	Pd(1)−C(27)−N(1)	177(1)

(31) Kurosawa, H.; Kajimaru, H.; Ogoshi, S.; Yoneda, H.; Miki, K.; Kasai, N.; Murai, S.; Ikeda, I. *J. Am. Chem. Soc.* **1992**, *114*, 8417.

(32) Crystal data of **7b**: monoclinic, space group $P2_1/n$, colorless, $a = 12.717(2)$ Å, $b = 9.881(2)$ Å, $c = 19.846$ Å, $\beta = 104.01(1)°$, $V = 2419.7(7)$ Å^3, $Z = 4$, $T = 23.0$ °C, $d_{calcd} = 1.465$ g/cm^3, μ(Mo Kα) = 8.57 cm^{-1}, $R = 0.069$, $Rw = 0.065$, GOF = 1.56.

sion reaction: (i) facile Pd−CN bond formation via the fast transmetalation (step B) and (ii) attack of the CN ligand from the palladium side by the stereoselective reductive elimination prompted by Me_3SiCN (step C).

In conclusion, Me_3SiCN is an efficient cyanation reagent for allylic carbonates in the presence of a catalytic amount (5 mol %) of $Pd(PPh_3)_4$. The cyanation proceeds with overall inversion in high yields. Characterizations and reactions of some palladium complexes relevant to the catalysis revealed that transmetalation of η^3-allylpalladium with Me_3SiCN is facile to afford cyano(η^3-allyl)palladium, and Me_3SiCN is indispensable for formal reductive elimination.

Experimental Section

General Procedure and Materials. All manipulations were performed under an argon atmosphere in conventional Schlenk-type glassware on a dual-manifold Schlenk line or in a nitrogen-filled glovebox (UNICO, UN-650F). NMR spectra were recorded in $CDCl_3$ on a JEOL-α 400 and a Varian Inova-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz). The ^{29}Si NMR (79.3 MHz) measurements was carried out with an INEPT pulse sequence, and chemical shifts were referred to external Me_4Si. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Trimethylsilyl cyanide was purchased from Tokyo Kasei. The reagents and the solvents were dried and purified before use by usual methods.[34] The following compounds were prepared by the published methods: *cis*-**2m**,[19] **5a**,[27] **5c**,[31] **7a**,[28] $Pd(PPh_3)_4$,[35a] $Pd(CO)(PPh_3)_3$,[35b] $PdCl_2(PPh_3)_2$,[35c] $Pd(DBA)_2$,[35d,e] $PdCl_2(PhCN)_2$,[35f] and $Pt(PPh_3)_4$.[35g] For preparation of **2i**, the corresponding alcohols was first converted to their lithium salt using *n*-BuLi and then reacted with methyl chloroformate. Allylic esters **2n**, **1f**, and **2o** were obtained from the corresponding carveols.[36]

Cyanation Procedure. A typical procedure is as follows: A 20 mL flask was charged with $Pd(PPh_3)_4$ (87 mg, 0.075 mmol; 5.0 mol %), THF (6.0 mL), cinnamyl methyl carbonate (**2a**; 288 mg, 1.5 mmol), and Me_3SiCN (298 mg, 3.0 mmol) under an argon flow. The reaction was carried out under reflux for 18 h. After the reaction, the whole mixture was passed through a short Florisil column (8 mm i.d. × 70 mm) to give a clear yellow solution. GLC analysis (OV-17 or PEG-HT) with naphthalene as an internal standard showed cinnamyl cyanide (**3a**) was formed in 98% yield. The product was isolated by Kugelrohr distillation in 92% yield (198 mg).

The products **3a**, **3c**, **3d**, **3h**, and **3i** were identified as reported.[9]

3b: ^{1}H NMR δ 2.33 (s, 3H), 3.22 (d, J = 6 Hz, 2H), 5.96 (dt, J = 16 Hz, 6 Hz, 1H), 6.66 (d, J = 16 Hz, 1H), 7.11−7.28 (m, 4H); ^{13}C NMR δ 20.6, 21.1, 115.6, 117.3, 126.2, 129.3, 132.8, 134.3, 138.1. Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05. Found: C, 84.15; H, 6.87.

3e: Isolated as a mixture of (3*E*,5*E*), (3*Z*,5*E*), (3*E*,5*Z*), and (3*Z*,5*Z*) isomers. (3*E*,5*E*): ^{1}H NMR δ 0.91 (t, J = 7 Hz, 3H), 1.43 (sext, J = 7 Hz, 2H), 2.07 (q, J = 7 Hz, 2H), 3.14 (d, J = 6 Hz, 2H), 5.41 (dt, J = 15 Hz, 6 Hz, 1H), 5.76 (dt, J = 15 Hz, 7 Hz, 1H), 6.02 (dd, J = 15 Hz, 10 Hz, 1H), 6.33 (dd, J = 15 Hz, 10 Hz, 1H); ^{13}C NMR δ 13.67, 20.37, 22.26, 34.65, 117.1, 117.5, 128.5, 135.1, 136.8. (3*Z*,5*E*): ^{13}C NMR δ 13.67, 20.58, 22.23, 29.82. (3*E*,5*Z*): ^{13}C NMR δ 13.70, 15.93, 22.70, 34.97. (3*Z*,5*Z*): ^{13}C NMR δ 13.70, 15.84, 22.56, 29.72. Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 79.84; H, 9.91.

3f: ^{1}H NMR δ 1.52−1.59 (m, 6H), 2.09−2.15 (m, 4H), 3.05 (d, J = 7 Hz, 2H), 5.10 (t, J = 7 Hz, 1H); ^{13}C NMR δ 15.5, 26.4, 27.3, 28.1, 28.8, 36.6, 108.4, 118.8, 146.4. Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 79.81; H, 9.89.

3g: ^{1}H NMR δ 1.46−1.59 (m, 1H), 1.74 (s, 3H), 1.82−1.90 (m, 1H), 1.91−2.22 (m, 5H), 3.01 (s, 2H), 4.71−4.72 (m, 1H), 4.73−4.75 (m, 1H), 5.78−5.84 (m, 1H); ^{13}C NMR δ 20.8, 25.4, 27.3, 28.5, 30.5, 40.4, 109.1, 117.7, 125.8, 126.8, 149.0. Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38. Found: C, 81.85; H, 9.57.

trans-(1*R**,5*S**)-**3j**: ^{1}H NMR δ 2.02 (ddd, J = 13.6 Hz, 10.8 Hz, 5.7 Hz, 1H), 2.26−2.34 (m, 2H), 2.39−2.43 (m, 1H), 2.83−2.92 (m, 1H), 3.35−3.42 (m, 1H), 3.73 (s, 3H), 5.64−5.70 (m, 1H), 5.92−5.99 (m, 1H); ^{13}C NMR δ 25.6, 26.9, 27.8, 36.0, 52.1, 120.4, 130.3, 174.4. IR 2238 cm^{-1} (ν_{CN}); MS *m*/*e* 165 (M^+). Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71. Found: C, 65.35; H, 6.93.

cis-(1*R**,5*R**)-**3j**: ^{1}H NMR δ 1.96 (ddd, J = 13.3 Hz, 12.4 Hz, 11.2 Hz, 1H), 2.54−2.62 (m, 1H), 3.73 (s, 3H); ^{13}C NMR δ 26.6, 27.0, 28.3, 37.9, 52.1, 120.8, 129.5, 173.9.

trans-(1*R**,5*S**)-**3k**: ^{1}H NMR δ 1.74 (ddd, J = 13.2 Hz, 12.6 Hz, 6.0 Hz, 1H), 1.76 (m, 3H), 1.83 (m, 3H), 1.85−1.98 (m, 1H), 2.11 (dm, J = 13 Hz, 1H), 2.17−2.78 (m, 1H), 2.36−2.46 (m, 1H), 3.13 (m, 1H), 4.74 (m, 1H), 4.80 (m, 1H), 5.66 (m, 1H); ^{13}C NMR δ 20.7, 21.8, 30.1, 30.8, 31.6, 37.1, 109.7, 120.9, 126.2, 126.9, 147.5; IR 2234 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38. Found: C, 81.79; H, 9.69.

cis-(1*R**,5*R**)-**3l**: ^{1}H NMR δ 1.74 (s, 3H), 1.81 (q, J = 12.0 Hz, 1H), 1.87 (m, 3H), 1.95−2.04 (m, 1H), 2.08−2.18 (m, 2H), 2.25 (ddd, J = 12.0 Hz, 5.6 Hz, 2.4 Hz, 1H), 3.26−3.36 (m, 1H), 4.74 (m, 1H), 4.78 (m, 1H), 5.65 (m, 1H); ^{13}C NMR δ 20.5, 21.4, 30.1, 32.1, 32.7, 39.9, 110.0, 120.7, 125.7, 126.2, 147.5; IR 2234 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38. Found: C, 81.82; H, 9.57.

Preparation of 6a (Eq 6). A 30 mL flask was charged with **5a** (121 mg, 0.27 mmol) in acetone (5.0 mL). At 0 °C, PPh_3 (142 mg, 0.54 mmol) in acetone (1.5 mL) was added to the **5a** in acetone over 10 min, and the resulting solution was stirred for 4 h at 0 °C. Then, the solvent was evaporated off in vacuo to give **6a** quantitatively.

6a: ^{1}H NMR δ 1.63 (dd, J = 8.4 Hz, 6.4 Hz, 3H), 1.78 (s, 3H), 2.60 (br, 2H), 4.83 (ddq, J = 12.8 Hz, 8.4 Hz, 6.4 Hz, 1H), 5.37 (dt, J = 12.8 Hz, 9.2 Hz, 1H), 7.1−7.8 (m, 15H); ^{13}C NMR δ 17.6, 24.0, 48.6, 97.8 (d, J = 24.7 Hz), 116.2, 128.5 (d, J = 9.8 Hz), 130.2, 132.4 (d, J = 41.1 Hz), 133.8 (d, J = 41.1 Hz), 133.8 (d, J = 14.8 Hz).

Reaction of 6a with Me_3SiCN (Eq 7). At 0 °C, Me_3SiCN (95 mg, 0.96 mmol) was added to **6a** (309 mg, 0.64 mmol) in degassed $CDCl_3$ (3.6 mL). Instantaneous color change from clear orange to yellow occurred. ^{1}H and ^{13}C NMR measurements showed that the known cyano complex **7a** formed quantitatively. Addition of ether (40 mL) to the solution precipitated **7a** as yellow powder in 74% yield (213 mg).

Thermolysis of 7a (Eq 8) or 7b (Eq 11). Under an argon atmosphere, **7a** (90 mg, 0.20 mmol) and naphthalene (13 mg, 0.10 mmol, as an internal standard for GC analysis) were dissolved in THF (8.0 mL). Me_3SiCN (40 mg, 0.40 mmol) was added to the **7a**, and the solution was stirred under reflux for 16 h. GC analysis showed **3m** was formed in 68% yield (0.14 mmol). Similar reaction of **7b** afforded **3j** in 92% yield (eq 11).

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Preparation of 7b (Eq 10) and X-ray Structure Determination. Cyanation of known complex **5c**[31] (300 mg, 0.55 mmol) by the reported procedure[28] afforded **7b** in 81% yield (238 mg). Slow diffusion of hexane into a toluene solution of **7b** afforded single crystals suitable for X-ray analysis. The cell dimensions were determined by least-squares refinement of diffractometer angles for 25 automatically centered reflections. Structure was solved and refined using the teXsan crystallographic software package. Scattering factors for neutral atoms were from Cromer and Waber,[37] and anomalous dispersion[38] was used. The structure was solved by direct methods (SHELXS86[39]) and expanded by DIRDIF.[40] The weighting scheme was $w = [\sigma^2(F_o) + 0.0001F_o^2]^{-1}$. The final full-matrix least-squares cycle included non-hydrogen atoms with anisotropic thermal parameters and hydrogen atoms at fixed positions with isotropic thermal parameters that were 1.2 times the connected atoms.

7b: ^{1}H NMR δ 1.24−1.37 (m, 1H), 1.71−1.79 (m, 1H), 2.06−2.16 (m, 1H), 2.31−2.40 (m, 1H), 2.79 (ddd, J = 14.8 Hz, 8.6 Hz, 6.8 Hz, 1H), 3.52 (s, 3H), 4.32 (br, 1H), 5.22−5.27 (m, 1H), 5.72 (br, 1H), 7.36−7.52 (m, 15H); ^{13}C NMR δ 28.7, 29.8, 36.9, 51.8, 81.7, 82.0 (d, J = 29.6 Hz), 109.8, 128.8 (d, J = 10.7 Hz), 130.6, 132.4 (d, J = 40.5 Hz), 133.6 (d, J = 13.3 Hz), 137.4 (d, J = 19.7 Hz), 173.8. IR 2120 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{27}H_{26}NO_2PPd$: C, 60.74; H, 4.91. Found: C, 60.92; H, 4.85.

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Supporting Information Available: Tables of crystal data and refinement details, atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles of **7b** (8 pages). See any current masthead page for ordering information and Internet access instructions.

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