Preparation, Structures, and Thermal Reactivity of Alkoxycarbonyl(cyano)palladium(II) Complexes *trans*-Pd(COOR)(CN)(PPh$_3$)$_2$ (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{t}Bu, and Bn) as Intermediates of the Palladium-Catalyzed Cyanoesterification of Norbornene Derivatives

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Alkoxycarbonyl(cyano)palladium(II) complexes *trans*-Pd(COOR)(CN)(PPh$_3$)$_2$ (**1**, R = Me; **2**, R = Et; **3**, R = ^{n}Pr; **4**, R = ^{i}Pr; **5**, R = ^{n}Bu; **6**, R = ^{t}Bu; **7**, R = Bn) are prepared via oxidative addition of the corresponding cyanoformates to Pd(PPh$_3$)$_4$ in toluene at room temperature or 50 °C and characterized by means of NMR (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) and IR spectroscopy as well as elemental analyses. X-ray crystallography of **3**, **4**, and **6** showed a square-planar coordination around the Pd center that is bonded to alkoxycarbonyl and cyano ligands in the *trans* configuration. The Pd−CN and Pd−COOR bonds in **1**, **3**, **4**, and **6** are similar to those of the cyanopalladium(II) and alkoxycarbonylpalladium(II) complexes reported to date. On reaction of Pd(PPh$_3$)$_4$ with phenyl cyanoformate a thermally induced ligand exchange takes place to afford the dicyanopalladium(II) complex, *trans*-Pd(CN)$_2$(PPh$_3$)$_2$ (**8**). Complex **2** is able to catalyze the reaction of norbornadiene with ethyl cyanoformate to produce (2*R**,3*S**)-ethyl 3-cyanobicyclo-[2.2.1]hept-5-ene-2-carboxylate (**13**) and is recovered after the reaction. This observation supports the identification of alkoxycarbonyl(cyano)palladium(II) complexes as intermediates in the catalytic cycle of cyanoesterification of norbornene derivatives.

Introduction

The activation of carbon−carbon σ-bonds promoted by transition metal complexes has been one of the most prominent challenges in both synthetic organic and organometallic chemistry.[1−3] For instance, transition metal hydrido complexes can affect C−C bond-breaking or -forming processes for simple dienes to afford branched dienes.[4] Owing to their high ring strain, small-membered ring molecules are easily converted into their ring-opened products via C−C bond cleavage mediated by transition metal complexes.[5,6] However, in most cases, the carbon−carbon σ-bond cleavage reaction is limited to the ring-opening, intramolecular rearrangement reactions or formation of the stable metal complexes as the intermediates.[7] On the other hand, although the double functionalization of unsaturated organic molecules via C−C σ-bond cleavage and the subsequent addition to unstrained molecules have been reported,[8] much less attention has been paid to the mechanism of the catalytic reactions. In particular, the roles of the metal center, which promote the C−C σ-bond activation and the subsequent bond-forming reactions to produce the functionalized products are not clear. Recently we reported the addition reaction of

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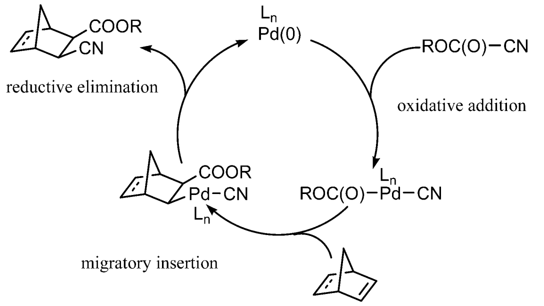
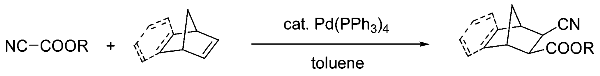
Scheme 1. Plausible Catalytic Cycle of Cyanoesterification of Norbornenes



cyanoformates (cyanoesterification) to norbornene derivatives catalyzed by $Pd(PPh_3)_4$, as shown in eq 1, which leads ultimately to the formation of the corresponding double-functionalized products with high *exo*-selectivity.[9] The present catalysis most likely proceeds via three fundamental processes, as shown in Scheme 1: the initial oxidative addition of the C−C σ-bond of cyanoformates to a Pd(0) center, followed by insertion of norbornenes into the resulting Pd−C bond and subsequent C−C reductive elimination to form the corresponding adducts.



(1)

Recently several research groups have published transition metal complexes-promoted synthetic organic reactions via C−C σ-bond cleavage of unstrained molecules. They propose that these reactions proceed via oxidative addition of substrates to the metal center as the first step.[10,11] However, no report has appeared which describes the isolation of any intermediate complexes after oxidative addition. For this reason, the stoichiometric reactions of cyanoformates with Pd(0) complexes are important since they would provide a clue to the above reaction mechanisms. Indeed, the structure and chemical properties of palladium complexes containing cyano or alkoxycarbonyl groups as ancillary ligands have attracted attention in conjunction with mechanisms of Pd-catalyzed synthetic organic reactions such as cyanation[12] and esterification[13] of unsaturated organic molecules reported to date.

Table 1. Reaction Temperature, Time, and Yields of Complexes 1−7

complex	temp (°C)	time (h)	yield (%)[a]
trans-$Pd(CN)(COOMe)(PPh_3)_2$ (**1**)	25	24	98
trans-$Pd(CN)(COOEt)(PPh_3)_2$ (**2**)	25	48	97
trans-$Pd(CN)(COO^nPr)(PPh_3)_2$ (**3**)	25	72	89
trans-$Pd(CN)(COO^iPr)(PPh_3)_2$ (**4**)	50	24	95
trans-$Pd(CN)(COO^nBu)(PPh_3)_2$ (**5**)	50	24	94
trans-$Pd(CN)(COO^tBu)(PPh_3)_2$ (**6**)	50	48	89
trans-$Pd(CN)(COOBn)(PPh_3)_2$ (**7**)	25	48	96

[a] Yields are before recrystallization, but their purity was confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectra.

In this paper we report the preparation of alkoxycarbonyl(cyano)palladium(II) complexes with various substituents in the alkoxycarbonyl group. The synthesis involves the reactions of cyanoformates with $Pd(PPh_3)_4$, in which oxidative addition takes place via C−C bond cleavage. Thermal properties and catalytic activity for cyanoesterification of norbornadiene of the formed complexes were investigated. Part of this work was reported in a preliminary form.[9a]

Results and Discussion

Reactions of Alkyl and Benzyl Cyanoformates with $Pd(PPh_3)_4$. The initial experiment to confirm oxidative addition was elucidated using $Pd(PPh_3)_4$ with methyl cyanoformate at room temperature. Methyl cyanoformate reacts readily with $Pd(PPh_3)_4$ even at room temperature to produce *trans*-Pd(CN)-$(COOMe)(PPh_3)_2$ (**1**) in 98% isolated yield. This oxidative addition is completed more rapidly than the whole catalytic reaction conducted at 110 °C. Analogously, $Pd(PPh_3)_4$ reacts with various cyanoformates, NC−COOR (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{t}Bu, and Bn), at room temperature or 50 °C to produce the corresponding alkoxycarbonyl(cyano)palladium(II) complexes *trans*-$Pd(CN)(COOR)(PPh_3)_2$ (**2**, R = Et; **3**, R = ^{n}Pr; **4**, R = ^{i}Pr; **5**, R = ^{n}Bu; **6**, R = ^{t}Bu; and **7**, R = Bn), respectively, in excellent yields (eq 2). Table 1 shows reaction temperatures, reaction times, and yields of the complexes formed via oxidative addition reactions. The magnitude of the difference in the reaction temperatures increases significantly with an increase in the bulk of the alkyl groups in the ester moieties: the reactivity becomes lower in the order **1** < **2** < **3** < **4**, **5** < **6**, **7**, in the cyanoformates. Table 2 summarizes the $^{13}C\{^1H\}$ NMR data of the COOR and CN groups in the employed cyanoformates for synthesis of complexes **1**−**7**. The $^{13}C\{^1H\}$ NMR peak positions vary little depending on the alkyl substituents in the ester groups. This obviously indicates that the reactivity of the

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Table 2. $^{13}C\{^1H\}$ NMR Data of Cyanoformates

R	*C*O	*C*N
Me	144.6	109.1
Et	144.2	109.3
^{n}Pr	144.2	109.3
^{i}Pr	143.8	109.5
^{n}Bu	144.3	109.3
^{t}Bu	142.9	109.9
Bn	144.0	109.2

[a] 75.3 MHz at 25 °C in chloroform-d_1.

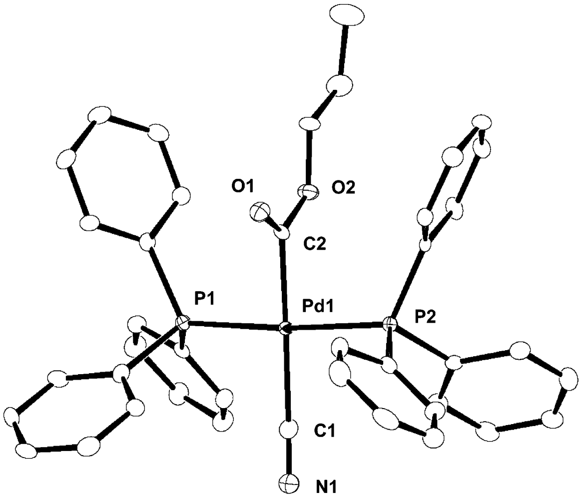
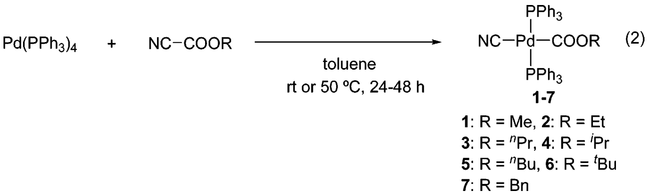


Figure 1. Structure of complex **3** determined by X-ray crystallography with 50% thermal ellipsoidal plotting. Hydrogen atoms were omitted for simplicity.

added cyanoformates was affected by the steric demands and not the electronic factors. Reaction of methyl cyanoformate with the once isolated **2** or **7**, respectively, in CD_2Cl_2 at room temperature and even at 40 °C did not show the formation of **1**, indicating that this oxidative addition is irreversible.



$$\mathrm{Pd(PPh_3)_4} + \mathrm{NC{-}COOR} \xrightarrow[\text{rt or 50 °C, 24-48 h}]{\text{toluene}} \mathrm{NC{-}\overset{PPh_3}{\underset{PPh_3}{Pd}}{-}COOR} \quad (2)$$

1: R = Me, **2**: R = Et
3: R = ^{n}Pr, **4**: R = ^{i}Pr
5: R = ^{n}Bu, **6**: R = ^{t}Bu
7: R = Bn

Careful recrystallization of the complexes **3**, **4**, and **6** from CH_2Cl_2−hexane furnished colorless crystals and unequivocal confirmation of the structure was obtained by X-ray crystallography. Figures 1−3 depict molecular structures of complexes **3**, **4**, and **6** and Table 3 summarizes selected bond distances and angles of the complexes. The molecules exhibit square-planar coordination at the metal center with the cyano ligand and the alkoxycarbonyl ligand in *trans* configurations. The exclusive formation of square-planar complexes with PPh_3 as ancillary ligands is ascribed to the steric bulk of the PPh_3 ligands dominating the large *trans* effect of the cyano and ester ligands. Although oxidative addition of ethyl cyanoformate with Ni(0) is known to afford Ni(CN)(COOEt)(triphos) (triphos = MeC-$(CH_2PPh_2)_3$),[14] to the best of our knowledge, no precedent for the structure of *trans*-Pd(CN)(COOR)$(PPh_3)_2$ has been reported. The structures of palladium complexes **3**, **4**, and **6** are very similar to that of **1**.[9a] The minor differences in bond angles result from the longer Pd−CN or Pd−COOR bond lengths. The

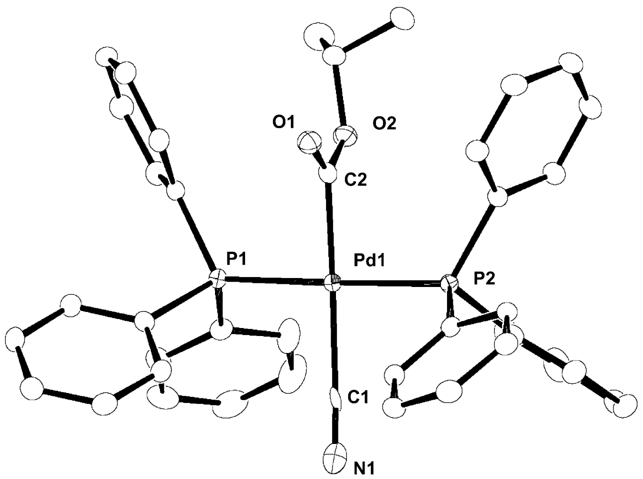


Figure 2. Structure of complex **4** determined by X-ray crystallography with 50% thermal ellipsoidal plotting. Hydrogen atoms and solvated CH_2Cl_2 were omitted for simplicity.

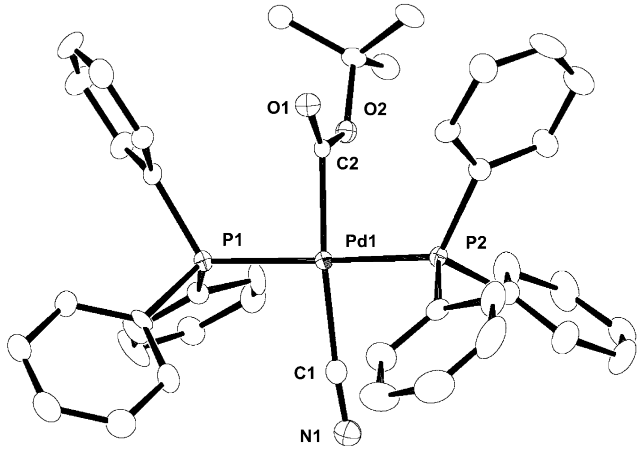


Figure 3. Structure of complex **6** determined by X-ray crystallography with 50% thermal ellipsoidal plotting. Hydrogen atoms and solvated CH_2Cl_2 were omitted for simplicity. One of the two crystallographically independent molecules is shown.

structures of the three new complexes are closely comparable to those of other square-planar Pd(II) complexes containing Pd−CN[15] and Pd−COOR[12g,13d,16] bonds.

The IR peaks of the ν(CN) vibration of complexes **1**−**7** in the solid state are observed at 2127−2124 cm^{-1} with frequencies

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Table 3. Selected Bond Distances (Å) and Angles (deg) of 1, 3, 4, and 6

	1 (R = Me)	**3** (R = ^{n}Pr)	**4** (R = ^{i}Pr)	**6** (R = ^{t}Bu)	
Pd(1)−P(1)	2.3268(5)	2.3388(10)	2.3271(6)	2.3281(18)	2.3360(17)
Pd(1)−P(2)	2.3225(5)	2.3268(10)	2.3183(6)	2.3140(18)	2.320(17)
Pd(1)−CN	2.106(2)	2.067(4)	2.130(2)	2.057(7)	2.064(8)
Pd(1)−COOR	2.015(2)	2.014(4)	2.008(2)	2.037(6)	2.009(6)
C(1)−N(1)	1.056(3)	1.123(6)	1.066(3)	1.153(10)	1.132(10)
C(2)−O(1)	1.217(3)	1.205(4)	1.209(2)	1.178(7)	1.214(7)
C(2)−O(2)	1.311(3)	1.359(4)	1.354(3)	1.373(7)	1.362(7)
O(2)−C(3)	1.563(3)	1.442(5)	1.468(3)	1.430(9)	1.533(9)
P(1)−Pd(1)−P(2)	177.09(2)	174.90(3)	177.35(2)	173.63(5)	171.14(5)
P(1)−Pd(1)−C(1)	92.62(5)	93.55(12)	90.13(6)	92.8(2)	90.2(2)
P(1)−Pd(1)−C(2)	86.72(7)	90.12(11)	89.40(7)	89.3(2)	92.6(2)
P(2)−Pd(1)−C(1)	89.90(5)	91.04(12)	90.94(6)	89.7(2)	90.1(2)
P(2)−Pd(1)−C(2)	90.80(7)	85.72(11)	89.58(7)	89.31(19)	80.8(2)
C(1)−Pd(1)−C(2)	178.42(7)	169.74(17)	178.50(7)	169.4(2)	168.8(2)
Pd(1)−C(1)−N(1)	178.0(2)	174.3(3)	175.80(19)	175.1(7)	175.9(7)
Pd(1)−C(2)−O(1)	125.0(2)	121.8(3)	125.38(18)	132.1(4)	131.3(4)
Pd(1)−C(2)−O(2)	113.8(2)	115.8(2)	111.46(15)	103.0(3)	105.2(3)
O(1)−C(2)−O(2)	121.1(2)	122.3(3)	123.1(2)	124.9(6)	123.5(5)
	ref 9a	this work	this work	this work	

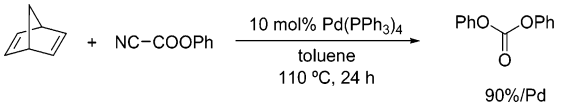
Table 4. Melting Points, Analytical Results, and IR Data of Complexes 1−8

		anal. (%)[b]			IR[c]	
complex	mp[a]	C	H	N	ν(CN)	ν(CO)
1	163−164	65.46 (65.42)	4.61 (4.65)	1.84 (1.96)	2124	1663
2	131−132	65.78 (65.81)	4.75 (4.83)	1.88 (1.92)	2126	1638
3	123−125	66.57 (66.18)	4.96 (5.01)	1.59 (1.88)	2125	1632
4	115−117	66.17 (66.18)	4.97 (5.01)	1.87 (1.88)	2124	1643
5	114−117	66.57 (66.54)	5.18 (5.18)	1.65 (1.85)	2126	1652
6	108−109	66.92 (66.54)	5.11 (5.18)	2.04 (1.85)	2126	1654
7	133−135	68.25 (68.23)	4.67 (4.71)	1.91 (1.77)	2127	1646
8	240−242	66.46 (66.82)	4.36 (4.43)	3.91 (4.10)	2132	

[a] Decomposed. [b]Calculated values are in parentheses. [c]cm^{-1} in KBr disks.

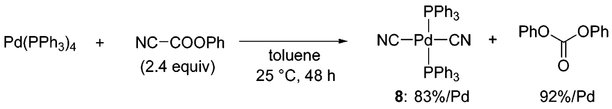
nearly independent of the substituents in the ester group (Table 4). On the contrary, the wavenumbers of ν(COOR) for the series of complexes decrease in the order, **1** > **6** > **5** > **7** > **4** > **2** > **3**, corresponding to decreased carbonyl stretching frequency on introduction of the alkyl group in the ester groups. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}NMR data of complexes **1**−**7** are listed in Tables 5 and 6. The square-planar coordination with the phosphine ligands in *trans* positions is dominant also in solution. The ^{1}H NMR spectra of **1**−**4** show a characteristic alkoxycarbonyl signal at δ 2.44−3.71. The ^{13}C{^{1}H} NMR signal of the ipso carbons of PPh$_3$ ligands of the complexes appears as apparent triplets due to virtual coupling. The Pd−P moiety in **1**−**7** displayed a singlet at δ 20.7−22.3 in the ^{31}P{^{1}H} NMR spectrum. These data indicate that the two PPh$_3$ ligands are situated in mutually *trans* positions.

Reaction of Phenyl Cyanoformate with Pd(PPh$_3$)$_4$. The reaction of phenyl cyanoformate with norbornadiene in the presence of 10 mol % of Pd(PPh$_3$)$_4$ was reported to afford diphenylcarbonate as an organic product in 90% yield, based on the added catalyst (eq 3).[9a]



(3)

Since this result was quite puzzling to us, we conducted the stoichiometric reaction of phenyl cyanoformate (2.4 equiv) with Pd(PPh$_3$)$_4$ without addition of norbornadiene. As shown in eq 4, *trans*-Pd(CN)$_2$(PPh$_3$)$_2$ (**8**) was formed in 90% yield. Tanaka et al. have reported the structure of **8** by X-ray analysis.[15k] Formation of **8** was also confirmed by measuring the ^{31}P{^{1}H} NMR spectrum, whose signal appears at δ 24.6 as a singlet, as well as elemental analysis.



(4)

A proposed mechanism for the formation of **8** is summarized in Scheme 2. When phenyl cyanoformate reacts with Pd(PPh$_3$)$_4$, complex **9** might be formed via oxidative addition, analogously to the formation of complexes **1**−**7**. But, due to the high basicity of phenoxide ion as opposed to the alkoxide ion in complexes **1**−**7**, once formed **9** causes decarbonylation to give **10**. As a result of both **9** and **10** in the reaction mixture, a ligand exchange initiated by nucleophilic attack of phenyloxopalladium complex **10**[17] to **9** occurs to generate **8** and **11**. Our assignment of these compounds to the oxidative addition product **9** and phenyloxo complex **10** must be tentative as the complexes could not be fully characterized. However, reaction of *trans*-PdCl(COOPh)(PPh$_3$)$_2$ with NaOPh, presumably giving rise to in situ formation

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(16) For examples: (a) Del Piero, G.; Cesari, M. *Acta Crystallogr., Sect. B Struct. Crystallogr. Cryst. Chem.* **1979**, *35*, 2411−2413. (b) Sacco, A.; Vasapollo, G.; Nobile, C. F.; Piergiovanni, A.; Pellinghelli, M. A.; Lanfranchi, M. *J. Organomet. Chem.* **1988**, *356*, 397−409. (c) Smith, G. D.; Hanson, B. E.; Merola, J. S.; Waller, F. J. *Organometallics* **1993**, *12*, 568−570. (d) Garrone, R.; Romano, A. M.; Santi, R.; Millini, R. *Organometallics* **1998**, *17*, 4519−4522. (e) Santi, R.; Romano, A. M.; Garrone, R.; Millini, R. *J. Organomet. Chem.* **1998**, *566*, 37−43. (f) Gallo, E.; Ragaini, F.; Cenini, S.; Demartin, F. *J. Organomet. Chem.* **1999**, *586*, 190−195. (g) Dervisi, A.; Edwards, P. G.; Newman, P. D.; Tooze, R. P.; Coles, S. J.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1999**, 1113−1119. (h) Ruiz, J.; Martinez, M. T.; Florenciano, F.; Rodriguez, V.; Lopez, G.; Perez, J.; Chaloner, P. A.; Hitchcock, P. B. *Inorg. Chem.* **2003**, *42*, 3650−3661. (i) Yasuda, H.; Maki, N.; Choi, J.-C.; Sakakura T. *J. Organomet. Chem.* **2003**, *682*, 66−72. (j) Campora, J.; Palma, P.; Del Rio, D.; Alvarez, E. *Organometallics* **2004**, *23*, 1652−1655.

(17) The aryloxo ligand of **10** might be highly basic and nucleophilic, similar to the aryloxo ligand of Pd(II) and Pt(II) complexes; see: (a) Kim, Y. J.; Osakada, K.; Takenaka A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096−1104. (b) Kapteijn, G. M.; Dervisi, A.; Grove, D. M.; Kooijman, H.; Lakin, M. T.; Spek A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 10939−10949.

Table 5. ^{1}H NMR Data for Complexes 1−7^a

	OCH_n	others		Ph
1	2.44 (s, 3H, OCH_3)			7.39−7.55 (m, 18H) 7.67−7.79 (m, 12H)
2	2.73 (q, (7), 2H, OCH_2)	0.52 (t, (7), 3H, CH_3)		7.38−7.51 (m, 18H) 7.66−7.78 (m, 12H)
3	2.62 (t, (7), 2H, OCH_2)	0.90 (q, (8), 2H, CH_2)	0.52 (t, (8), 3H, CH_3)	7.40−7.51 (m, 18H) 7.66−7.72 (m, 12H)
4	3.68 (sep, (6), 1H, OCH)	0.28 (d, (6), 6H, CH_3)		7.38−7.50 (m, 18H) 7.64−7.71 (m, 12H)
5	2.66 (t, (7), 2H, OCH_2)	0.80−0.95 (m, 4H, $2CH_2$)	0.69 (t, (7), 3H, CH_3)	7.34−7.51 (m, 18H) 7.65−7.76 (m, 12H)
6		0.45 (s, 9H, CH_3)		7.39−7.49 (m, 18H) 7.67−7.74 (m, 12H)
7	3.71 (s, 2H, OCH_2)	6.70−6.73 (m, 2H)	7.19−7.22 (m, 3H)	7.31−7.50 (m, 18H) 7.64−7.70 (m, 12H)

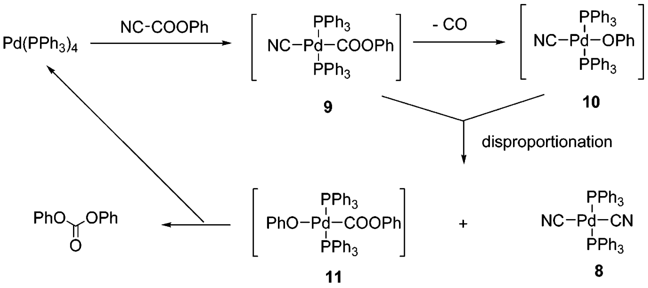
^{a} 300 MHz at 25 °C in dichloromethane-d_2.

Table 6. ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR Data of Complexes 1−7

	^{13}C{^{1}H} NMR^a							
	COO*R*	*C*O	*C*N	ortho^c	meta^c	para	ipso^d	^{31}P{^{1}H} NMR^b
1	50.0	192.9 (2)	136.8 (20)	127.8 (5)	133.8 (7)	130.2	130.9 (24)	21.8
2	13.2, 59.6	192.6 (3)	137.2 (20)	127.8 (5)	133.8 (7)	130.1	131.0 (24)	21.6
3	10.5, 21.9, 66.5	193.6	138.2	128.7 (5)	134.7 (6)	131.0	131.9 (24)	22.3
4	21.6, 68.2	192.5	138.5	128.7 (5)	134.8 (7)	131.0	131.9 (24)	21.9
5	14.0, 19.5 30.8, 64.8	193.6	138.1 (20)	128.7 (5)	134.7 (6)	131.0	131.9 (24)	22.2
6	27.4, 81.0	190.9 (5)	138.7 (21)	128.5 (5)	134.8 (6)	130.8	131.8 (24)	20.7
7	66.7	193.7	137.5	128.8 (5)	134.7 (6)	131.1	131.8 (24)	22.3

^{a} 150.6 MHz at 25 °C in dichloromethane-d_2. ^{b}121 MHz at 25 °C in dichloromethane-d_2. ^{c}Observed splitting of the signals (Hz) is given in parentheses. ^{d}Apparent triplet due to virtual coupling. Observed splitting of the signals (Hz) is given in parentheses.

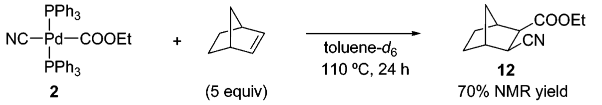
Scheme 2



of complex **11**, was reported to afford diphenylcarbonate at 100 °C.[16i] The total amount of the Ph group of the product diphenylcarbonate (90%) based on Pd in the catalytic reaction using 10 mol % of $Pd(PPh_3)_4$ in eq 3 is reasonable, because reductive elimination from **11** regenerates Pd(0), which repeatedly leads to the formation of complex **8** and diphenylcarbonate until the Pd(0) species is completely consumed.

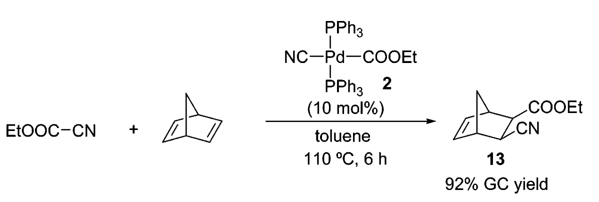
We succeeded in isolating complexes **1** and **2** but each isolated complexe gradually converts into **8** in solution. The relative facility for formation of complex **8** by disproportionation is **2** > **1** and is not directly related to the acidity of the alkoxy group in the complexes.

Reactivity of Complex 2 toward Cyanoesterification of Norbornenes. The different reactivities of cyanoformates in the parent catalytic reactions leading to the corresponding adducts makes the insertion of norbornenes into the Pd-COOR bond (alkoxycarbonylpalladation) very likely. However, cyanopalladation cannot be ruled out as an alternative possibility for the insertion process as shown in Scheme 1. To gain insight into the intermediate after migratory insertion, we conducted the reaction of the isolated **2** with 5 equiv of norbornene at 110 °C for 24 h. However, due to the fast reductive elimination affording (2*R**,3*S**)-ethyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (**12**) in 70% NMR yield, the detection of the intermediate before reductive elimination failed (eq 5).



(5)

On the other hand, the cyanoesterification of ethyl cyanoformate with norbornadiene proceeded in the presence of complex **2** (10 mol %) as the catalyst gives **13** in 92% GC yield (eq 6). We can thus conclude that the cyano(alkoxycarbonyl)-palladium complexes **1**−**7** are involved in the catalytic cycle of the cyanoesterification reaction of norbornenes as indicated in Scheme 1.



(6)

In addition, neither decarboxylation[18] from complex **2** nor double cyanation of norbornene derived from **8** was observed in either GC-MS or NMR studies of the reaction mixtures.

Table 7. Crystal Data and Details of the Structure Refinement of 3, 4, and 6

	3	4	6
formula	$C_{41}H_{37}NO_2P_2Pd$	$C_{41}H_{37}NO_2P_2Pd \cdot CH_2Cl_2$	$C_{42}H_{39}NO_2P_2Pd \cdot 0.5CH_2Cl_2$
mol wt	744.10	829.03	800.59
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
a (Å)	12.148(5)	11.288(3)	16.125(3)
b (Å)	12.420(5)	12.435(4)	15.318(3)
c (Å)	13.138(7)	15.926(6)	17.591(3)
α (deg)	92.116(18)	68.424(14)	90
β (deg)	105.123(17)	89.252(15)	115.382(6)
γ (deg)	116.199(13)	68.756(12)	90
V (Å^3)	1690.4(13)	1918.8(10)	3947.6(10)
Z	2	2	4
μ (mm^{-1})	0.6817	0.7430	0.6544
F(000)	764	848	822
D_{calcd} (g cm^{-3})	1.462	1.435	1.347
cryst size (mm^3)	0.35 × 0.30 × 0.05	0.45 × 0.37 × 0.10	0.45 × 0.40 × 0.40
2θ range (deg)	5.0−54.9	5.0−55.0	5.0−60.0
no. of unique reflns	16 720	18 709	47 549
no. of used reflns	13 578	8699	22 759
no. of variables	461	452	893
$R1$ ($I > 2.00\sigma(I)$)	0.062	0.030	0.068
R	0.062	0.036	0.075
wR_2[a]	0.092	0.085	0.213
GOF	1.004	1.127	1.024

[a] Weighting scheme $[\sigma(F_o)^2]^{-1}$.

Conclusion

A series of *trans*-Pd(COOR)(CN)$(PPh_3)_2$ prepared by oxidative addition provides new information on the reactivity of cyanoformates towards Pd(0) as influenced by the substituents in the alkoxycarbonyl ligands and chemical properties of the complexes. Oxidative addition of cyanoformates bearing bulky substituents took place at elevated temperatures. The facile cleavage of the C−C σ-bond of cyanoformates with a palladium center, which was suggested to account for the results of Pd-catalyzed cyanoesterification reactions, has been realized by the present study.

Experimental Section

General Procedures. All reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven and heated under reduced pressure before use.

Measurements. NMR spectra (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) were recorded on Varian INOVA 600 (600 MHz) or Mercury 300 (300 MHz) spectrometers at ambient temperature with the chemical shifts being expressed in parts per million. Residual peaks of solvent were used as the reference for ^{1}H NMR (chloroform-d_1, δ 7.26; dichloromethane-d_2, δ 5.32; toluene-d_8, δ 2.09). ^{13}C{^{1}H} NMR signals were referenced with the solvent signals, while 85% H_3PO_4 (δ 0) was used as an external standard for ^{31}P{^{1}H} NMR measurement. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using a Shimadzu capillary column (CBP1-M25-025) and a Shimadzu C-R6A-Chromatopac integrator. The evolution of CO gas was analyzed on a mass spectrometer, HIDEN HALO-100, connected to the vacuum-line assembly via a turbomolecular pump. Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Osaka City University.

Materials. Methyl cyanoformate, ethyl cyanoformate, and norbornadiene were purchased from Aldrich and used as received. $Pd(PPh_3)_4$[19] and cyanoformates (R = ^{n}Pr,[20] ^{i}Pr,[20] ^{n}Bu,[20] ^{t}Bu,[21] Bn,[20] and Ph[22]) were prepared according to the literature procedures. Dehydrated toluene, dichloromethane, hexane, and diethyl ether were purchased from Kanto Chemicals. CH_2Cl_2 was dried over activated molecular sieves and stored in a Schlenk tube after three freeze−pump−thaw cycles were performed. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using silica gel 60 N (spherical, neutral, 40−100 μm) from Kanto Chemicals.

General Procedure for Complexes 1−7 (eq 2): Preparation of 1. To a toluene (20 mL) dispersion of $Pd(PPh_3)_4$ (693 mg, 0.60 mmol) was added methyl cyanoformate (114 μL, 1.44 mmol) at room temperature. The dispersed pale yellow solid was gradually dissolved on stirring to give a deposition of white solid after 24 h. The solvents were evaporated under vacuum. The resulting off-white solid was washed with hexane (20 mL × 2 times) and dried under vacuum to give **1** as a white solid (416 mg, 0.58 mmol, 97%). Recrystallization from CH_2Cl_2−hexane afforded colorless crystals of **1** suitable for X-ray crystallography. Complexes **2**−**7** were prepared analogously.

Reaction of Norbornadiene with Phenyl Cyanoformate in the Presence of a Catalytic Amount of $Pd(PPh_3)_4$ (eq 3). To a solution $Pd(PPh_3)_4$ (23 mg, 0.02 mmol, 10 mol %) in toluene (2 mL) were added phenyl cyanoformate (29.2 mg, 0.2 mmol) and norbornadiene (21 μL, 0.2 mmol) at room temperature. The reaction mixture was stirred for 24 h at 110 °C. GC yield was calculated using commercially available **8** as an authentic sample to be 90% (0.18 mmol), based on Pd. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 7.25−7.32 (m, 3H, aromatic), 7.39−7.46 (m, 1H, aromatic).

Reaction of $Pd(PPh_3)_4$ with Phenyl Cyanoformate: Formation of *trans*-$Pd(CN)_2(PPh_3)_2$(8) (eq 4). To a toluene (20 mL) dispersion of $Pd(PPh_3)_4$ (347 mg, 0.30 mmol) was added phenyl cyanoformate (106 mg, 0.72 mmol) at room temperature. The dispersed pale yellow solid was gradually dissolved on stirring to give a deposition of white solid after 48 h. The resulting off-white solid was filtered, washed with hexane (20 mL × 2 times), and

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[18] M−COOR species (M = Ni, Pd) have been known to undergo decarbonylation in polar solvents. See: (a) Jones, F. N. *J. Org. Chem.* **1968**, *33*, 4290−4292. (b) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180−3188.

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[20] Childs, M. E.; Weber, W. P. *J. Org. Chem.* **1976**, *41*, 3486−3487.

[21] Carpino, L. A. *J. Am. Chem. Soc.* **1960**, *82*, 2725−2727.

[22] Hoffmann, H. M. R.; Iranshahi, L. *J. Org. Chem.* **1984**, *49*, 1174−1176.

dried in vacuo to give **8** as a white solid (173 mg, 0.25 mmol, 83%). The ^{1}H and ^{31}P{^{1}H} NMR spectroscopies showed *trans*-Pd(CN)$_2$(PPh$_3$)$_2$ (**8**).[23] ^{1}H NMR (300 MHz, dichloromethane-d_2): δ 7.39−7.57 (m, 18H, Ph), 7.61−7.74 (m, 12H, Ph). ^{31}P{^{1}H} NMR (121 MHz, dichloromethane-d_2): δ 24.6 (s). The filtrates were evaporated under vacuum to give a colorless oil. Bulb-to-bulb distillation gave diphenylcarbonate (59 mg, 0.28 mmol, 92% yield, based on Pd) as a colorless oil. Decarbonylation was confirmed by detection of CO gas on a mass spectrometer.

Stoichiometric Reaction of Norbornene with 2 (eq 5). To a solution of the isolated **2** (36.5 mg, 0.05 mmol) in toluene-d_8 (0.6 mL) were added an excess (5 equiv) of norbornene (24 mg, 0.25 mmol) and mesitylene (7 μL, 0.05 mmol) as an internal standard. An NMR tube was heated at 110 °C for 24 h to afford (2*R**,3*S**)-ethyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (**12**) in 70% NMR yield.

Reaction of Ethyl Cyanoformate with Norbornadiene Catalyzed by 2 (eq 6). To a solution of **2** (15 mg, 0.02 mmol, 10 mol %) in toluene (2 mL) were added ethyl cyanoformate (20 μL, 0.2 mmol), norbornadiene (19 mg, 0.2 mmol), and dodecane (46 μL, 0.2 mmol) as an internal standard. The reaction mixture was heated at 110 °C for 6 h to afford (2*R**,3*S**)-ethyl 3-cyanobicyclo[2.2.1]-hept-5-ene-2-carboxylate (**13**) in 92% GC yield.

X-ray Crystallography. Single crystals of **3**, **4**, and **6** suitable for X-ray diffraction studies were grown from CH$_2$Cl$_2$−hexane. Crystallographic data and details of refinement are summarized in Table 7. The crystals were sealed in glass capillary tubes and mounted, and the X-ray data were collected at −180 °C with a Rigaku R-AXIS RAPID II imaging plate area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Calculations were carried out by using the CrystalStructure crystallographic software package.[24] A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. CCDC-643360 (**3**), -643361 (**4**), and -643362 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Table of crystallographic data and complete tables of non-hydrogen and selected hydrogen parameters, bond lengths and angles, calculated hydrogen atom parameters, anisotropic thermal parameters, and intermolecular contacts for **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700343Y

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[23] Uson, R.; Fornies, J.; Uson, M. A.; Lalinde, E. *J. Organomet. Chem.* **1980**, *185*, 359−366.

[24] *Crystal Structure Analysis Package*; Rigaku and MSC, 2001.