Palladium(0)-Catalyzed Intramolecular [2+2+2] Alkyne Cyclotrimerizations with Electron-Deficient Diynes and Triynes

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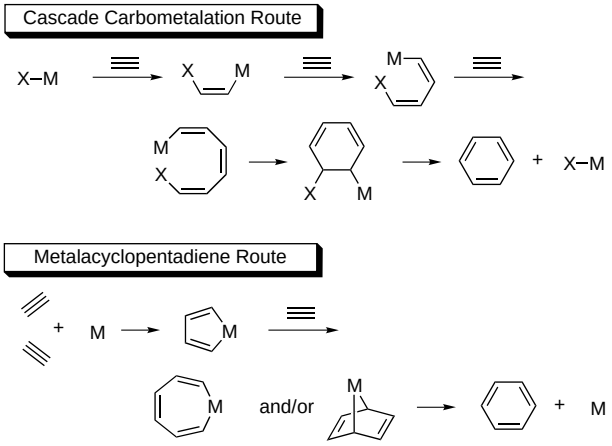
Abstract: In the presence of 2.5 mol% of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) and 5 mol% of PPh_3, nearly equimolar amounts of dimethyl nona-2,7-diyne-1,9-dioate derivatives (diyne diesters) and dialkyl acetylenedicarboxylates were allowed to react in toluene at 110 °C to afford [2+2+2] cycloadducts in moderate-to-good yields. Similarly, dimethyl trideca-2,7,12-triyne-1,13-dioate derivatives (triyne diesters) were catalytically transformed into phthalic acid ester analogues in excellent yields. To gain insight into the mechanism of these intramolecular alkyne cyclotrimerizations, stoichiometric reactions of $[Pd_2(dba)_3]$ with a diyne diester and a triyne diester bearing ether tethers were conducted in acetone at room temperature to furnish an oligomeric bicyclopalladacyclopentadiene and a Pd^0 triyne complex, respectively. The structures of these novel complexes were unequivocally determined by X-ray structure analysis. The isolated triyne complex was heated at 50 °C or treated with PPh_3 in acetone at room temperature to afford the arene product. Furthermore, the same complex catalyzed the triyne cyclization with or without PPh_3.

Keywords: alkynes · cyclotrimerization · homogeneous catalysis · metallacycles · palladium

Introduction

The transition-metal-mediated cyclotrimerization of alkynes is a powerful method to synthesize highly substituted benzene derivatives.[1] The atom-economical[2] and convergent cyclotrimerization approach has found extensive application, including natural product synthesis,[3] materials science,[4] and the construction of theoretically or biologically interesting molecules.[5, 6] Since the first discovery by Reppe and Schweckendiek,[7] various transition-metal catalysis reactions have been found to date, and they can be formally categorized into two reaction types: one is a cascade carbometalation[8] and the other is a [2+2+2] cycloaddition involving a metallacyclopentadiene intermediate (the "common mechanism")[9] (Scheme 1). With respect to palladium catalysis, the cascade carbopalladation triggered by a palladium(II) chloride species has been pioneered by Maitlis and co-workers.[10] Subsequently, Maitlis et al. and Ishii et al. have independently reported that the formation of oligomeric tetracarboalkoxypalladacyclopentadiene (TCPC) from a palladium(0) dibenzylideneacetone (dba) complex and two molecules of dimethyl acetylenedicarboxylate (DMAD), and hexamethyl mellitate was obtained from the reaction of TCPC with DMAD (Scheme 2).[11] TCPC was also found to



Scheme 1. Possible mechanisms of alkyne cyclotrimerization.

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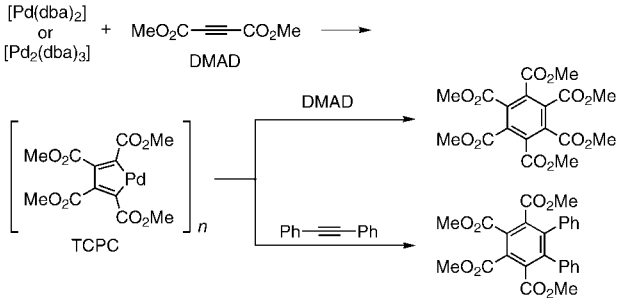
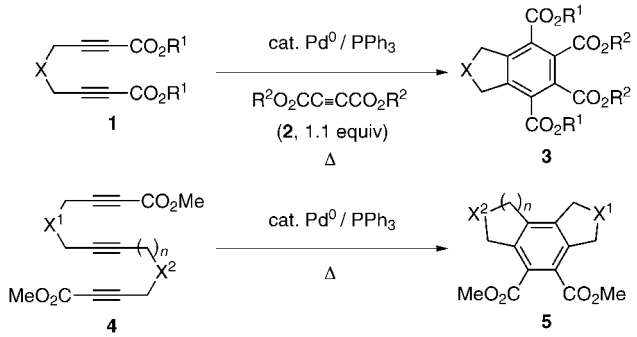


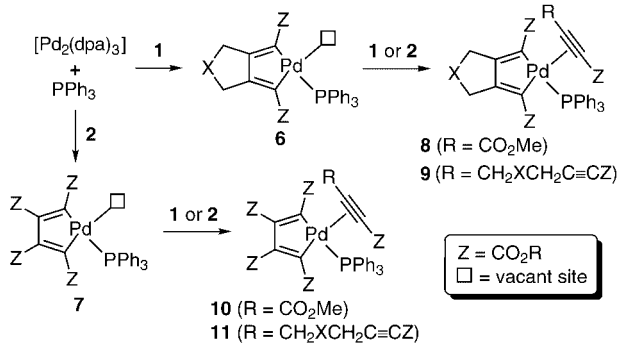
Scheme 2. Pd^0-catalyzed cyclotrimerization of dimethyl acetylenedicarboxylate.

catalyze the cyclotrimerization of DMAD leading to hexamethyl mellitate. Whereas TCPC also reacted with an electronically neutral diphenylacetylene to give a coupling product, the cyclo-cotrimerization of these alkynes never proceeded under catalytic conditions.[11a,b, 12] This fact clearly shows that the electron-deficient DMAD selectively undergoes oxidative cyclization on the electron-rich palladium(0) center to produce the palladacycle intermediate (i.e. TCPC), which predominantly reacted again with DMAD. This is why palladium catalysis via the palladacycle mechanism has been confined to the reaction with a single electron-deficient alkyne component. To address such a limitation and to expand the synthetic scope, we developed the palladium(0)-catalyzed intramolecular [2+2+2] annulation of electron-deficient diynes and triynes, as outlined in Scheme 3.[13, 14] Whereas the palladium-catalyzed formation of polycyclic benzenes



Scheme 3. Pd^0-catalyzed cycloadditions of diyne diesters and triyne diesters.

from diynes or triynes has already been accomplished by the cascade carbometallation protocol,[15] the alternative palladacycle approach utilizing electron-deficient polyalkynes was unknown.[16] The diyne diesters **1** were expected to be suitable substrates for the cycloaddition with DMAD, because the formation of bicyclopalladacycle key intermediates **6** from the diyne **1** might be entropically more favorable than that of the TCPC–PPh_3 complex **7** from DMAD **2** (Scheme 4). In turn, **6** might predominantly react with **2** activated by two ester groups rather than less electrophilic **1** (**8** over **9**). As a result, highly chemoselective cycloaddition between **1** and **2** would be achieved, suppressing the competitive side reactions via other intermediates **9**–**11**. The palladium(0) catalyst system was further extended to a completely intramolecular



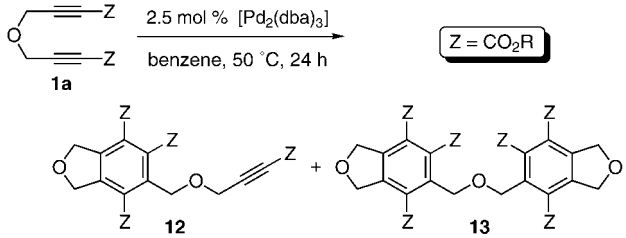
Scheme 4. Possible palladacycle intermediates.

variant, the [2+2+2] cyclization of triyne diesters, furnishing tricyclic benzene derivatives in strictly chemo- and regioselective manner. Herein, we report the full details of our study of palladium(0)-catalyzed intramolecular [2+2+2] alkyne cyclotrimerization with electron-deficient diynes and triynes.[17]

Results and Discussion

Catalyzed oligomerization of diyne diester: Prior to the exploration of the coupling between the diyne diesters and the monoalkyne diesters, we first examined the reactivity of diyne diester **1a** under palladium catalysis (Table 1). In the presence of 2.5 mol% $[Pd_2(dba)_3]$ (5 mol% palladium atom), **1a** was heated at 50 °C in benzene (0.5 M) for 24 h; however, the diyne was hardly consumed and was recovered to 81% after silica gel column chromatography (Table 1, run 1). The result was dramatically improved by the addition of 5 mol% triphenylphosphine (1 equiv relative to Pd atoms). The expected cycloadducts **12** and **13** were obtained in 39% and 27% yields, respectively (Table 1, run 2). A similar promoting effect of triphenylphosphine was observed in the [2+2+2] cyclocotrimerization of DMAD with cycloalkenes.[18] Cyclopen-

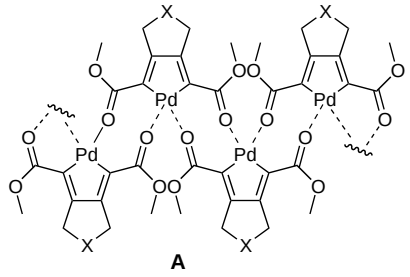
Table 1. Catalyzed oligomerization of diyne diester **1a**.



Run	Additive	Amount [mol%]	Yield **12**/**13**[a] [%]	Recovered **1a** [%]
1	none		trace/trace	81
2	PPh_3	5	39/27	
3	PPh_3	10	20/14	
4	$P(o\text{-tolyl})_3$	5	31/trace	45
5	PEt_3	5	39/19	
6	PBu_3	5	28/20	
7	PCy_3	5	trace/trace	30
8	$P(OPh)_3$	5	trace/trace	48
9	$P(OMe)_3$	5	0/0	76

[a] Yield of isolated product.

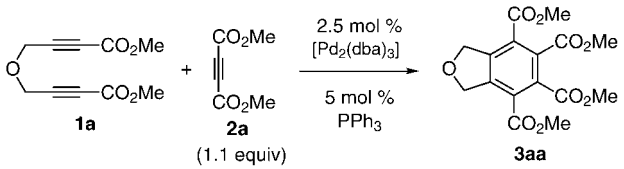
tene or cyclohexene underwent the cyclo-cotrimerization with two molecules of **2a** in the presence of TCPC and PPh_3, but no cycloadduct was formed in the absence of the phosphine. On the basis of the X-ray crystallographic analysis of a dimeric palladacyclopentadiene complex, [{Pd[$C_4(CO_2Me)_4$]L}$_2$], such a promoting effect was ascribed to the *trans* labilizing influence of the donor ligand L, which elongates the Pd–C bond *trans* to L and makes it more susceptible to the insertion of the coordinated olefin. Similarly, triphenylphosphine activated the Pd–C bond at its *trans* position in a plausible intermediate **9** (Scheme 4). The phosphine might also prevent the formation of palladacyclopentadiene oligomer complexes **A**, which are hardly soluble in common solvents, such as acetone, benzene, and dichloromethane.



The increased amount of PPh_3 (10 mol %), however, lowered the yield (Table 1, run 3), and tri(*o*-tolyl)phosphine possessing a larger cone angle (194°) than PPh_3 (145°) slowed the reaction (Table 1, run 4). In addition to triarylphosphines, more strongly electron-donating trialkylphosphines, such as triethylphosphine and tributylphosphine, were found to effectively promote the cycloaddition (Table 1, runs 5 and 6), while a bulkier tricyclohexylphosphine was totally ineffective (Table 1, run 7). On the contrary, more electron-accepting triphenyl and trimethyl phosphites gave poor results (Table 1, runs 8 and 9).

Catalyzed cycloaddition of diyne esters with acetylenedicarboxylic acid esters: Encouraged by the above results, we subsequently examined the cycloaddition of the diyne diester **1a** with DMAD (Table 2). The desired coupling product, phthalan derivative **3aa**, however, was obtained only in a trace amount under the same reaction conditions as those optimized above (Table 2, run 1). It is noteworthy that the expected cycloaddition hardly proceeded; however, neither the diyne oligomers nor hexamethyl mellitate was detected in the crude reaction mixture. This observation suggested that the strongly coordinated **2a** cannot be substituted by the less electron-deficient **1a**. In addition, the insertion of **2a** into the Pd–C_{sp^2} single bond of the palladacycle seemed to require higher temperature, at least under the catalytic conditions (vide infra). Actually, the cycloaddition proceeded at 80 °C. Upon heating for 19 h, **3aa** was obtained in 45 % isolated yield (Table 2, run 2). Whereas the yield was increased in halogenated polar solvents, such as chlorobenzene and 1,2-dichloroethane, the concomitant formation of the mellitate was observed (Table 2, runs 3 and 4). Lewis-basic solvents were also tested. A similar yield was obtained in 1,4-dioxane

Table 2. Catalyzed cycloaddition of diyne diester **1a** with DMAD **2a**.

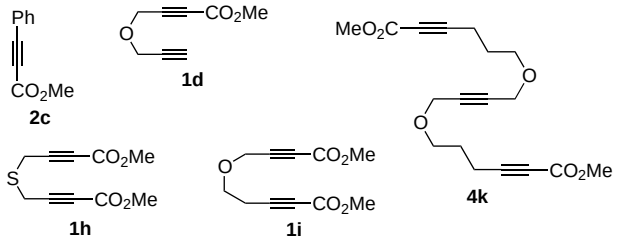


Run	Solvent	Conc. [M]	T [°C]	Time [h]	Yield **3aa** [%][a]
1	benzene	0.5	50	24	trace
2	benzene	0.5	80	19	45
3	chlorobenzene	0.5	80	19	52[b]
4	1,2-dichloroethane	0.5	80	17	66[b]
5	1,2-dioxane	0.5	80	17	51
6	DMF	0.5	80	17	14
7	toluene	0.5	110	1	61
8	toluene	0.1	110	0.5	73
9	toluene	0.01	110	1	66

[a] Yield of isolated product. [b] Hexamethyl mellitate was obtained in yields of 15 % (run 3) and 31 % (run 4).

(Table 2, run 5), but the yield was significantly decreased in DMF (Table 2, run 6). At higher temperature (110 °C) in toluene, the reaction was completed after only 1 h to afford **3aa** in 61 % yield (Table 2, run 7). The yield was further increased to 73 % by performing the reaction at 0.1 M concentration (Table 2, run 8). At lower concentration of 0.01 M, however, a longer reaction time was required for the complete consumption of **1a** and the yield was slightly decreased to 66 % (Table 2, run 9).

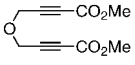
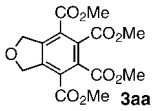
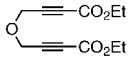
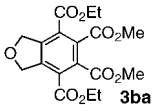
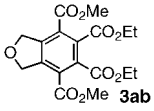
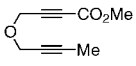
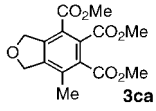
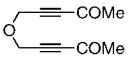
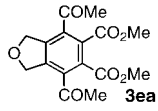
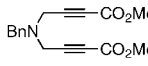
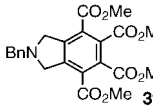
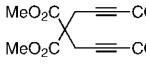
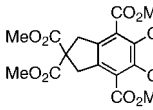
The scope of the present coupling was examined with respect to a series of diyne and monoalkyne substrates (Table 3). In the same manner as above (Method A), a diethyl ester **1b** reacted with **2a** to afford **3ba** with a similar yield (Table 3, run 2). Diethyl acetylenedicarboxylate (DEAD, **2b**) also participated in the cycloaddition (Table 3, run 3). In contrast, a less electron-deficient monoester **2c** (Scheme 5) hardly reacted with **1a**, indicative of the two



Scheme 5. Electron-deficient alkynes that failed to undergo cycloaddition

electron-withdrawing groups on the monoalkyne component being indispensable for the present cycloaddition. Similarly, the ester substituents on the diynes play an important role. The yield was decreased to 54 % for the reaction of a diyne monoester **1c** (Table 3, run 4). A diyne monoester bearing a terminal alkyne **1d** (Scheme 5) hardly gave the corresponding cycloadduct as well as the mellitate. Moreover, diketone **1e** gave **3ea** only in 17 % yield (Table 3, run 5). The product yields also varied with the substituent at the 4-position in the diyne. A dipropargylamine derivative **1f** could be used as a

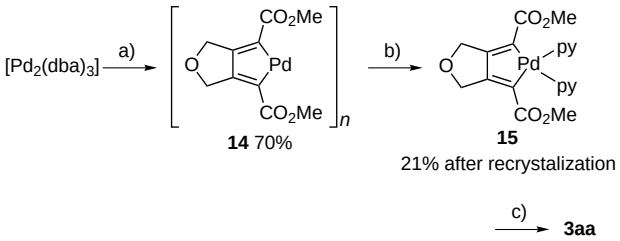
Table 3. Catalyzed cycloaddition of diynes **1a–g** with acetylenedicarboxylic acid esters **2a**,**b**.[a]

Run	Diyne	2	Product	Method	Time [h]	Yield [%][b]
1	 **1a**	**2a**	 **3aa**	A B	1 0.5	73 67
2	 **1b**	**2a**	 **3ba**	A B	1 0.5	72 66
3	**1a**	**2b**	 **3ab**	A B	1 1	71 61
4	 **1c**	**2a**	 **3ca**	A B	3 1	54 43
5	 **1e**	**2a**	 **3ea**	A B	1 1	17 13
6	 **1f**	**2a**	 **3fa**	A B	1 0.5	40 53
7	 **1g**	**2b**	 **3gb**	A B	5 5	49 79

[a] Method A: A solution of a diyne **1**, an acetylenedicarboxylic acid ester **2** (1.1 equiv), $[Pd_2(dba)_3]$ (2.5 mol%), and PPh_3 (5 mol%) in toluene (0.1M) was stirred at 110°C for the specified time. Method B: An acetylenedicarboxylic acid ester **2** (1.1 equiv) was added to the premixing solution of a diyne **1**, $[Pd_2(dba)_3]$ (2.5 mol%), and PPh_3 (5 mol%) in toluene (0.1M), and the solution was stirred at 110°C for the specified time. [b] Yield of isolated product.

diyne component; however, an isoindolin derivative **3fa** was obtained only in 40% yield (Table 3, run 6). The cycloaddition of a malonate-derived diyne **1g** with **2b** required a longer reaction time of 5 h, although **1g** was expected to be a superior diyne substrate compared to other diynes because of the kinetic Thorpe–Ingold effect[19] induced by the quaternary center on the tether chain. An indane derivative **3gb** was obtained in 49% yield (Table 3, run 7). These results show that Lewis-basic functionalities, such as amine or ester carbonyl group, interfere with the cycloaddition by coordinating to the palladium center. In fact, a sulfide **1h** proved to be totally ineffective because of the catalyst poisoning by the strong coordination with the sulfur atom. Interestingly, the order of addition of the catalyst precursor and the substrates affected the product yields. The yields of **3fa** and **3gb** were improved by the addition of an acetylenedicarboxylate into the premixing solution of a diyne and the catalyst precursor (Method B). The reason for such an improvement is not clear. Finally, a diyne diester **1i**, in which two alkyne moieties were connected with a 4-atom tether, failed to react with **2a** under the same reaction conditions (Scheme 5).

Synthesis of bicyclopalladacycle complex from diyne diester and $[Pd_2(dba)_3]$: As described above, the cycloaddition of the diyne diester **1** is envisioned to start with the formation of the bicyclopalladacycle intermediate **6**, which subsequently reacts with **2** to form **3** (Scheme 4). To confirm this scenario, we attempted the synthesis and isolation of the palladacycle intermediate. As outlined in Scheme 6, $[Pd_2(dba)_3]$ was treated with the diyne diester **1a** (1.2 equiv per Pd atom) in acetone at room temperature for 6 h to give an oligomeric palladacyclopentadiene **14** as a green powder in 70% yield. The formation of **14** was supported by the absence of the alkyne absorption and the reduced carbonyl stretching frequency (1705 cm^{-1}) in the IR spectrum. Further detailed inspection was impossible on account of the insolubility of **14** in common organic solvents. Therefore, **14** was converted into the corresponding monomeric bispyridine complex **15** upon treatment with excess pyridine in CH_2Cl_2 at room temperature. In the IR spectrum, no alkyne absorption was again observed



Scheme 6. Synthesis of bicyclopalladacycle complexes: a) **1a** (1.2 equiv), acetone, RT, 6 h; b) pyridine, CH_2Cl_2, RT, 3 h; c) **2a**, $[D_6]$DMSO, RT

and the carbonyl stretching appeared at 1670 cm^{-1}. The absence of the acetylenic carbon atoms was also confirmed by ^{13}C NMR spectroscopy; however, two C_{sp^2} signals corresponding to the palladacyclopentadiene unit were observed at $\delta = 141.8$ and 171.4 ppm. The bicyclopalladacycle structure was unequivocally determined by X-ray structure analysis of the single crystal of **15**·CH_2Cl_2 (Figure 1). The palladium(II) center has a square-planar geometry and the pyridine ligands are accommodated in such a way that they are perpendicular to the palladacycle moiety. The Pd1–C3 and Pd1–C4 bond lengths of 2.041(3) Å are similar to those of Pd^{II}–C_{sp^2} single

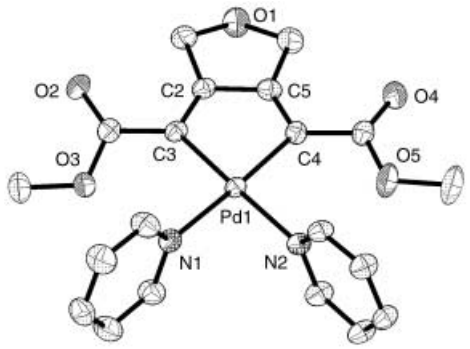
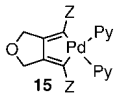
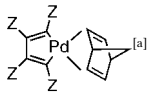
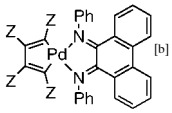
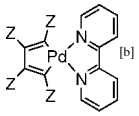


Figure 1. Structure of **15** (ORTEP diagram; all hydrogen atoms are omitted for clarity). Selected bond lengths[Å] and angles[°]: Pd1–C3 2.041(3), Pd1–C4 2.041(3), C2–C3 1.351(4), C2–C5 1.446(4), C4–C5 1.354(4), Pd1–N1 2.103(2), Pd1–N2 2.098(3); Pd1-C3-C2 112.62(19), Pd1-C4-C5 112.81(19), C3-C2-C5 116.9(2), C2-C5-C4 116.3(2), C3-Pd1-C4 81.29(10), N1-Pd1-N2 85.35(8), C3-Pd1-N1 96.23(9), C4-Pd1-N2 97.13(9).

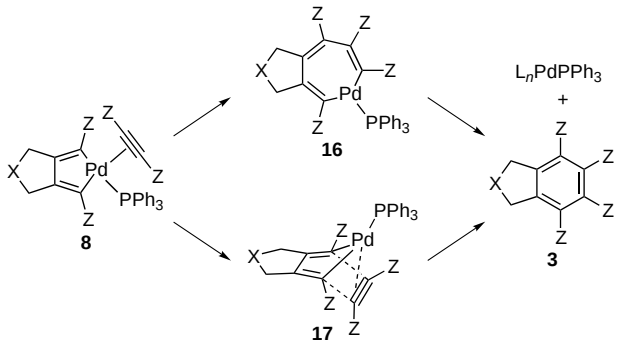
bonds.[20] The C2–C3 and C4–C5 bond lengths of 1.351(4) and 1.354(4) Å, respectively, are similar to the expected C_{sp^2}–C_{sp^2} double bond length of 1.32 Å, while the C2–C5 bond length of 1.446(4) Å is close to that of the typical C_{sp^2}–C_{sp^2} single bond (1.48 Å).[21] Compared to previously reported TCPC complexes (Table 4),[18a, 22] the Pd–C_{sp^2} single bonds (a and a′) are longer, but in turn, the C_{sp^2}–C_{sp^2} single bond (c) is shorter by 0.027 – 0.042 Å. The formation of the cycloadduct **3aa** from **15** and **2a** was also observed by ^{1}H NMR spectroscopy ([D$_6$]DMSO), even at room temperature.

Cycloaddition mechanism: Whereas the intermediacy of the bicyclopalladacycle complex was rationalized by the formation of **14** from **1a**, the detailed mechanism for the conversion of the palladacycle into an arene product is still not clear at this stage. The insertion/reductive elimination sequence can be assumed to be a plausible route to **3** according to the "common mechanism",[9] although a palladacycloheptatriene intermediate **16** was not detected (Scheme 7). On the other hand, Bercaw, Bergman, and McAlister previously claimed[23a] that the arene formation from a coordinatively saturated cobaltacyclopentadiene(trimethylphosphine) complex and DMAD occurs with the direct Diels – Alder cycloaddition mechanism on the basis of an observed second-order rate.[23] In this case, the combination of the electron-rich metallacyclopentadiene moiety and the highly electron-deficient DMAD as an excellent dienophile is indispensable. Such a direct cycloaddition mechanism, however, seems less likely for the palladacycle complexes, because its diene moiety is deactivated by the electron-withdrawing ester substituents. In addition, the increased loading of triphenylphosphine slowed the reaction rate, indicative of the pre-coordination of DMAD being necessary. An indirect [4+2] cycloaddition mechanism involving a palladacyclopentadiene(alkyne) complex intermediate, however, cannot be ruled out (i.e. **8** → **17** → **3**). A recent density functional study showed that this type of transformation from a cobaltacyclopentadiene(alkyne) complex into a η-arene cobalt complex occurs with a very small activation energy ($\Delta H^{\ddagger} = 0.5$ kcal mol^{-1}) in the CpCo-catalyzed acetylene cyclotrimerization.[24]

Table 4. Bond lengths[Å] in monomeric palladacyclopentadiene complexes.

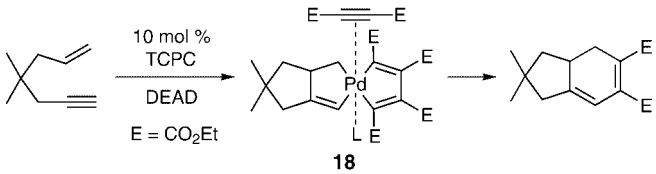
	a	a′	b	b′	c
 **15**	2.041(3)	2.041(3)	1.351(4)	1.354(4)	1.446(4)
 [a]	2.019(3)	2.026(3)	1.347(4)	1.339(4)	1.479(3)
 [b]	2.008(7)	2.008(7)	1.347(10)	1.347(10)	1.488(10)
 [b]	2.003(8)	2.024(9)	1.352(12)	1.329(13)	1.473(12)

[a] Ref. [18a]. [b] Ref. [20].



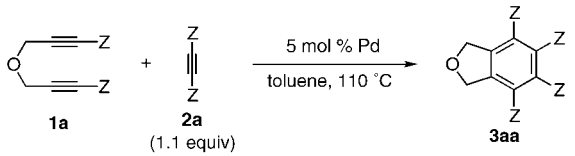
Scheme 7. Possible pathways from the bicyclopalladacycle to the arene product.

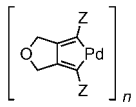
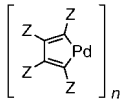
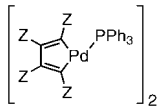
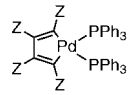
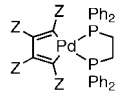
Moreover, the cycloaddition mechanism becomes obscure with respect to the possibility of a palladium(IV) intermediate.[25] Trost and Tanoury claimed that a palladium(IV) spirocyclic complex **18** is involved in the [2+2+2] cycloaddition of a 1,6-enyne with DEAD and TCPC as a catalyst precursor (Scheme 8).[26] To see whether such a Pd^{II} – Pd^{IV} redox cycle operates or not in our case, we conducted both catalytic and stoichiometric cycloaddition reactions with palladacycle complexes as catalyst precursors. As summarized in Table 5, the oligomeric complexes **14** and **19** exhibited similar activities, despite having different palladacyclopentadiene moieties (Table 5, runs 1 and 2). The reaction time was shortened and the yield of **3aa** was improved by employing a



Scheme 8. Trost's cycloaddition of enyne with DEAD.

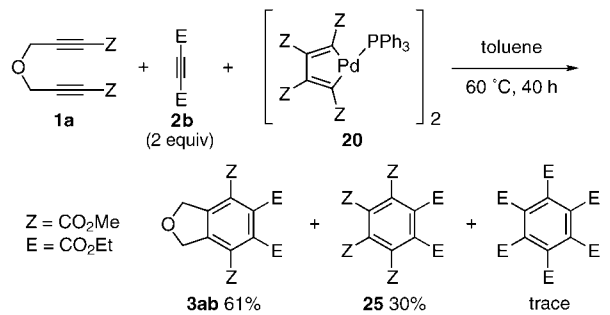
Table 5. Catalyzed cycloaddition of diyne diester **1a** with DMAD **2a** with palladacyclopentadienes as the catalyst precursor.[a]



Run	Palladacycle		Time [h]	**3aa** [%][b]	Hexamethyl mellitate [%][b]
1		**14**	9	48	18
2		**19**	17	36	8
3		**20**	1	68	13
4		**21**	3	72	14
5[c]		**22**	18	40	14

[a] Z = CO_2Me. [b] Yield of isolated product. [c] The reaction was carried out in xylene at 140 °C.

more soluble dimeric triphenylphosphine complex **20** (Table 5, run 3). A monomeric bisphosphine complex **21** gave a comparable result, albeit with a longer reaction time (Table 5, run 4). This shows again that the predissociation of the phosphine ligand is needed for the cycloaddition. In accordance with this observation, a complex bearing bis(diphenylphosphino)ethane, which forms a stable chelate, considerably deactivated the palladacycle (Table 5, run 5). To obtain more insight into the fate of the diene moiety in these palladacycles, equimolar amounts of the dimeric complex **20** and the diyne **1a** were treated with excess DEAD **2b** (Scheme 9). Upon heating at 60 °C in toluene for 40 h, the diyne- and palladacycle-derived products **3ab** and **25** were obtained in 61 and 30% yields, respectively. The palladacycle **20** was not recovered and hexaethyl mellitate was hardly obtained. These

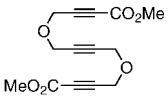
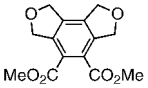
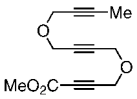
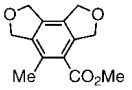
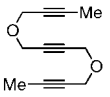
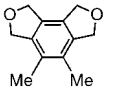
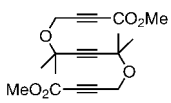
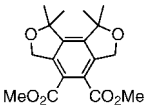
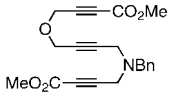
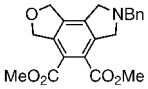
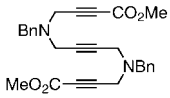
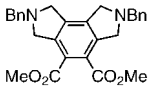
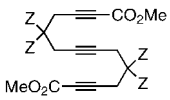
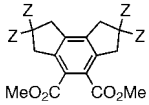
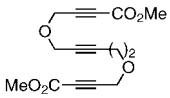
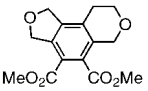
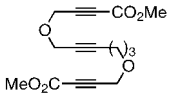
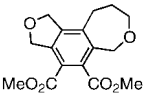
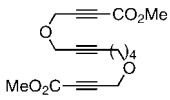
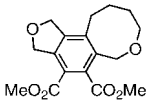


Scheme 9. Stoichiometric reaction of diyne diester **1a**, DEAD **2b**, and [{TCPC(PPh_3)}$_2$] (**20**).

results revealed that **20** first reacted with DEAD to furnish **25** and a [$PdPPh_3$] fragment, which was predominantly trapped by the diyne **1a** leading to **3ab**. Accordingly, the mechanism based on the Pd^{II}/Pd^{IV} redox cycle seems unlikely in the cycloaddition of the diyne diesters with acetylenedicarboxylic acid esters.

Catalyzed cyclization of triynes: In the above diyne–monoyne cycloadditions, the electron-withdrawing ester substituents were essential for all the alkyne components to maintain cycloaddition efficacy. In this regard, the [2+2+2] cyclization of triyne diesters such as **4a** is a fascinating variant in which the two electron-deficient alkynes and the neutral one might be coupled together (Table 6, run 1). In the presence of 2.5 mol% [$Pd_2(dba)_3$] and 5 mol% PPh_3, a 0.1M solution of **4a** in toluene was heated at 110 °C for 0.5 h to afford the desired tricyclic phthalate derivative **5a** in excellent isolated yield. In

Table 6. Catalyzed cyclization of triynes **4a–j**.[a]

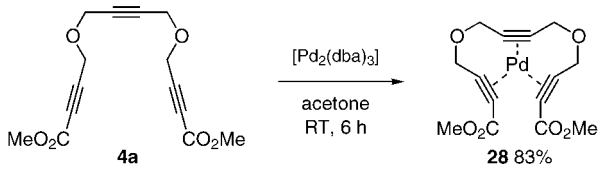
Run	Triyne	Time [h]	Product	Yield [%][b]
1		**4a** 0.5		**5a** 95
2		**4b** 0.5		**5b** 61
3		**4c** 1		**5c** 35
4		**4d** 1		**5d** 61
5		**4e** 0.5		**5e** 91
6		**4f** 0.5		**5f** 98
7[c]		**4g** 5		**5g** 95
8		**4h** 0.25		**5h** 87
9		**4i** 1.5		**5i** 77
10		**4j** 1.5		**5j** 16

[a] Conditions: [$Pd_2(dba)_3$] (2.5 mol%), PPh_3 (5 mol%), toluene (0.1M), 110 °C. [b] Yield of isolated product. [c] Z = CO_2Me.

sharp contrast to the diyne–monoalkyne cycloaddition, the cyclization of **4a** also proceeded in the absence of triphenylphosphine to give **5a** albeit in slightly lower yield (72%) after heating for 5 h. Moreover, a triyne monoester **4b** gave a benzoate derivative **5b** in 61% yield (Table 6, run 2). However, the cyclization of triynes having no ester substituent **4c** resulted in a lower yield (Table 6, run 3). The generality with respect to the triyne structure was further disclosed as summarized in Table 6. The steric hindrance around the central alkyne moiety slowed the rate of conversion from **4d** into **5d** (Table 6, run 4). Amine tethers did not interfere with the cyclization of **4e** and **4f** (Table 6, runs 5 and 6). Consequently, **5e** and **5f** containing one or two 3-pyrroline rings were obtained in high yields under the same reaction conditions with **4a**. These results are in striking contrast to the cycloaddition of the amine-tethered diyne diester **1f** (Table 3, run 6). The retardation of the cyclization by malonate tethers in **4g** (Table 6, run 7) is quite similar to the cycloaddition of the malonate-derived diyne **1g** with **2b** (Table 3, run 7). The yield of **5g** was excellent as opposed to that of **3gb** under the similar conditions.

The palladium(0) catalysis failed to promote the cycloaddition of the diyne with a 4-atom tether **1i** (Scheme 5). This is probably because the formation of a palladacyclopentadiene intermediate similar to **14** from **1i** is unfavorable in terms of entropy, and, as a result, the competitive cyclotrimerization of **2a** became predominant over the desired cycloaddition between **1i** and **2a**. On the contrary, an unsymmetrical triyne **4h** possessing both 3- and 4-atom tethers was heated in toluene for 0.25 h to afford the desired product **5h** in 87% yield (Table 6, run 8). Similarly, a triyne **4i** containing a five-atom tether was converted into **5i** in 77% yield, but the corresponding eight-membered-ring product **5j** was obtained only in 16% yield from **4j** (Table 6, runs 9 and 10). In these triyne cyclizations, one of the two tethers must be a three-atom chain because **4k** gave no cyclization product (Scheme 5).

Synthesis of the palladium(0) triyne complex from triyne diester and $[Pd_2(dba)_3]$: The implication of a palladacyclopentadiene intermediate is also expected for the triyne cyclizations. The necessity of a diyne unit connected by a three-atom tether implies that the cyclization might start with the formation of the bicyclopalladacycle intermediate **26** shown in Scheme 10. Alternatively, the formation of palladacycle **27** only with the electron-deficient alkyne terminals is also possible. Such a metallacyclopentadiene complex that bears a π-bound alkyne ligand has long been the missing link between a metallacyclopentadiene intermediate and an arene product in the alkyne cyclotrimerization. Only recently, Vollhardt and co-workers successfully isolated the first cobaltacyclopentadiene(alkyne) complexes by reacting $[Cp'Co(C_2H_4)_2]$ with *ortho*-arene-tethered triynes at $-20\,^{\circ}C$.[27] On the other hand, the more flexible triyne **4a** was anticipated to be readily converted into the final arene product. In contrast to this expectation, the treatment of **4a** with $[Pd_2(dba)_3]$ in acetone at room temperature for 5 h gave the unexpected triyne complex **28** as well as a trace amount of **5a** (Scheme 11). The structure of this novel complex was



Scheme 11. Synthesis of palladium(0) triyne complex **28**.

elucidated as follows: in the IR spectrum, the absorption of the coordinated 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. ^1H NMR spectroscopy 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 $\delta = 3.88$, 4.58, and 4.66 ppm, respectively. Furthermore, three different C_{sp} signals appeared at $\delta = 72.9$, 75.6, and 89.7 ppm in the ^{13}C NMR spectrum. These facts enabled us to assign the structure of **28**. Finally, the structure of **28** was unequivocally confirmed by X-ray analysis (Figure 2). The palladium atom

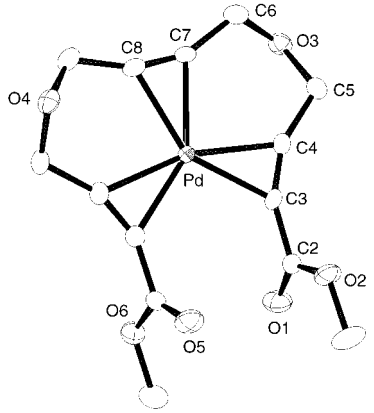
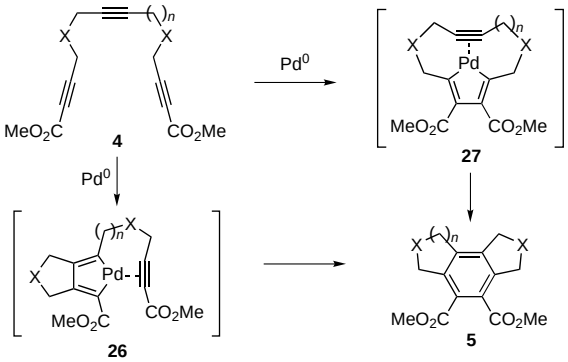


Figure 2. Structure of **28** (ORTEP diagram; all hydrogen atoms are omitted for clarity).

and the three alkyne moieties are placed almost in the same plane. The acetylenic triple bond lengths are C3–C4 = 1.239(2) 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-



Scheme 10. Palladacyclopentadiene(alkyne) intermediate complexes.

C8 = 157.1(2)°. The distances from the Pd atom to the centers of alkynes are 2.11 and 2.05 Å. These values show that the backdonations from the Pd^0 to each alkyne moiety are not very significant compared to known Pd^0 alkyne complexes[28] (e.g. $[Pd(PPh_3)_2(dmad)]$: triple bond length 1.279 Å, bond angle 144.9°, Pd–alkyne distance 1.96 Å).[28a] Such a weak backdonation might be ascribed to the dispersion of the backbonding electrons into the three alkyne moieties.

Cyclization of the triyne ligand in the palladium(0) triyne complex: Transition metal alkyne complexes have received considerable attention as intermediates in a wide variety of alkyne oligomerizations.[29] 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 by reductive C–C coupling or arenes by coupling with an extra alkyne. A few bisalkyne platinum(0) complexes have been reported, but in these examples, two alkyne ligands cannot be cyclized around the metal center, because the alkyne ligands are mutually *trans* and approximately perpendicular to each other.[30] Many Mo^{II} and W^{II} bis- or trisalkyne complexes have also been reported, in which 4e-donor alkyne ligands are placed perpendicular to the plane containing the metal atom and the alkyne ligand centers.[31]

In addition to those alkyne complexes, *ortho*-arene cyclyne nickel(0) complexes have been synthesized as cyclic triyne complexes by Youngs and co-workers.[32] The rigid *ortho*-arene cyclynes, however, cannot be easily converted into highly strained metallacyclopentadienes, although the three alkyne moieties are placed in the same plane. In striking contrast, the flexible linear triyne complex **28** proved sensitive to heat and impact.[33] The isolated complex **28** was heated at 50 °C in acetone for 30 min to furnish **5a** in 50% yield. Moreover, **28** was cleanly converted into **5a** in 97% yield at room temperature upon treatment with an equimolar amount of PPh_3 in acetone. This observation indicates that the coordination of the phosphine triggered the spontaneous cyclization of the triyne ligand with or without formation of the palladacycle intermediates. Whereas the conversion of **28** into **5a** was also observed for the 0.1–0.2 M $CDCl_3$ solutions of **28**, even at 25 °C, no intermediate, such as **26a** (X = O, n = 1) or **27a** (X = O, n = 1) was detected by ^{1}H NMR spectroscopy (Figure 3). Interestingly, the conversion rate was dependent on the initial concentration of **28**. The complete consumption of **28** required 2.5 and 5 h at 0.2 M and 0.1 M concentrations, respectively. This fact suggests that the decomposition of **28** in a solution might be induced by the coordination of an ether or ester carbonyl oxygen atom of **28** or the resultant phthalate **5a**. Unfortunately, detailed kinetic information is not available because the NMR resolution is gradually lowered as the palladium mirror decomposes. The isolation of any intermediate complex from the unsymmetrical triyne diesters would give further information about the cyclization mechanism, but the reaction of $[Pd_2(dba)_3]$ with higher triyne homologues **4h** or **4i** failed.

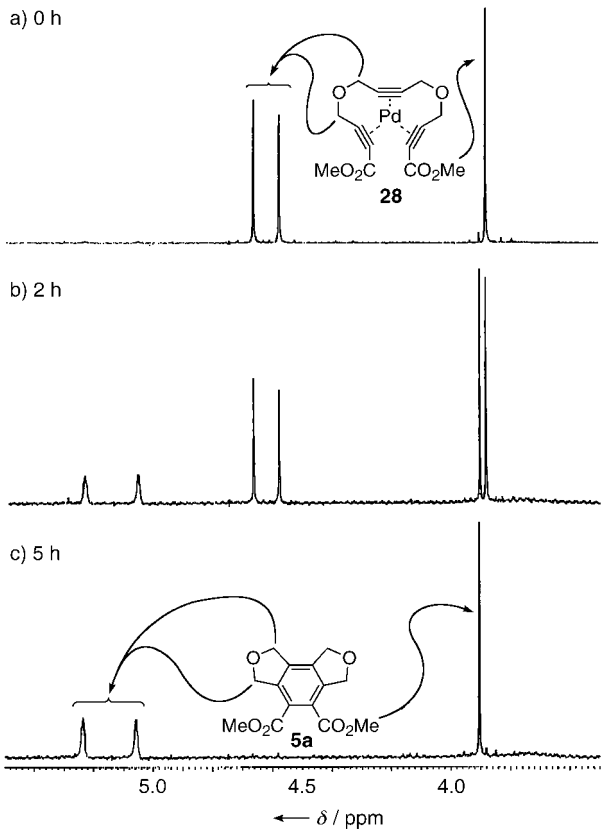


Figure 3. ^{1}H NMR (300 MHz) spectra of 0.10 M solution of **28** in $CDCl_3$ at 25 °C.

We then investigated the possible structures and the relative thermodynamic stability of palladacyclopentadiene(alkyne) complexes **26a** and **27a** by means of B3LYP hybrid density functional calculations.[34] Prior to the structure optimizations of these intermediates, we first attempted the full optimization of stationary geometries of the triyne complex **28** with various basis sets, and the obtained structural parameters were compared with those from the X-ray analysis. The selected bond lengths and angles were summarized in Table 7. Initially, the structural optimization of **28** was carried out with the LanL2DZ[35] basis set including a double ζ basis set with the relativistic effective core potential of Hay and Wadt for Pd, the 6–31G(d)[36] basis set for C and O, and the 3–21G[37] basis set for H (BS1). A similar structure to that from the X-ray analysis was obtained with this basis set;

Table 7. Selected bond lengths [Å] and angles [deg] in the X-ray and calculated structures of Triyne Complex **28**.

	X-ray	BS1	BS2	BS3	BS4
Pd–C3	2.134 (1)	2.214	2.185	2.170	2.178
Pd–C4	2.145 (1)	2.199	2.175	2.162	2.167
C3–C4	1.239 (2)	1.247	1.249	1.251	1.244
Pd–C7	2.191 (2)	2.266	2.229	2.216	2.226
C7–C8	1.222 (3)	1.240	1.243	1.244	1.237
Pd–C3–C4	73.64 (9)	72.942	72.889	72.851	72.905
Pd–C4–C3	72.69 (9)	74.239	73.804	73.851	72.905
C2–C3–C4	153.5 (1)	157.236	155.956	155.432	155.551
C3–C4–C5	157.0 (2)	157.058	156.551	156.205	156.250
Pd–C7–C8	74.0 (1)	74.123	73.809	73.700	73.874
C6–C7–C8	157.1 (2)	160.679	159.537	159.109	159.613

however, the bond lengths between the palladium center and the alkyne carbon atoms (Pd–C3, Pd–C4, and Pd–C7) were longer than those in the solid-state structure by ≈0.05–0.08 Å. These discrepancies improved with the SDD[38] basis set that involves the Stuttgart–Dresden–Bonn energy-consistent pseudopotential (SDB ECP28MWB ECP) for Pd instead of the LanL2DZ basis set (BS 2). A satisfactory result was obtained by adding two f-type and one g-type polarization functions[39] to the SDD basis set (BS 3), exhibiting the shortest Pd–alkyne bond lengths. The use of the valence triple-ζ 6–311G(d)[40] basis set for C and O instead of the 6–31G(d) basis set (BS 4) gave a similar result.

On the basis of these results, the structure optimizations of **26a** and **27a** were performed with the BS 3 basis set consisting of the SDD basis set with the f- and g-functions for Pd, the 6–31G(d) basis set for C and O, and the 3–21G basis set for H. The optimization of **26a** afforded a 16-electron bicyclopalladacycle complex **26a′** in which the carbonyl oxygen atom O5 as well as the C11–C12 triple bond is coordinated by the palladium center (Figure 4). As a result, the Pd^{II} center has a

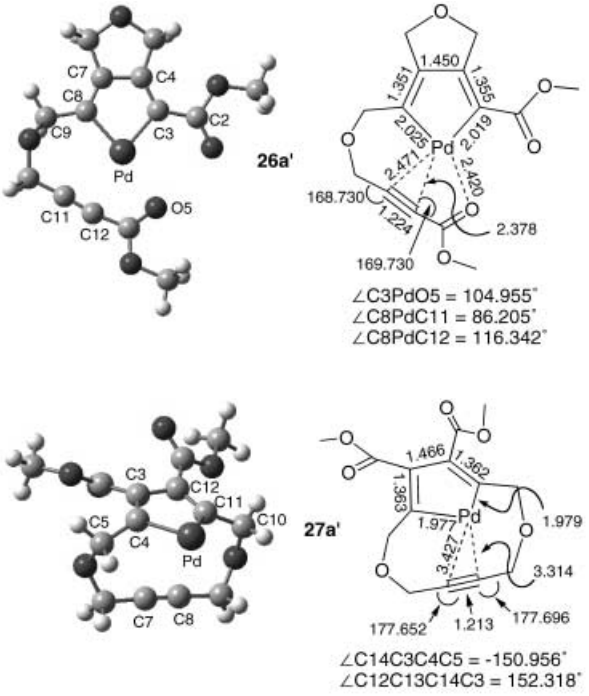


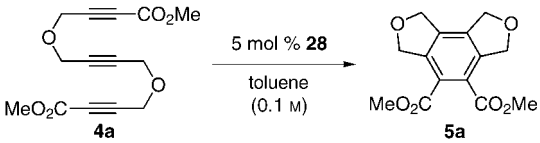
Figure 4. Optimized structures of palladacyclopentadienes of **26a′** and **27a′** at the B3LYP/BS 3 level with selected bond lengths [Å] and angles [°].

square-planar geometry. The bond lengths in the palladacyclopentadiene moiety are very similar to those of the palladacyle bispyridine complex **15**. The Pd–C11 and Pd–C12 bond lengths of 2.471 and 2.378 Å, respectively, are considerably longer than those in the parent triyne complex **28**. In addition, the distance between the Pd^{II} center and the carbonyl group (Pd–O5 2.420 Å) is also much longer than that observed in the TCPC(2,6-lutidine) dimer complex (≈2.16 Å).[18b] Such a weak coordination of the ynoate moiety might be ascribed to the tether chain connecting the palladacycle with the alkyne terminal. The shortening of the dative bonds caused unfavorable strain on the tether moiety.

The palladacycle **27a** was then optimized at the same level of theory. However, the anticipated palladacyclopentadiene(alkyne) structure was not obtained, but instead, a coordinatively unsaturated palladacyclopentadiene complex with a free alkyne moiety **27a′** resulted (Figure 4). The strain of the dioxapalladacyclododecyne ring apparently caused the dissociation of the internal alkyne. As a consequence, the coordinatively unsaturated **27a′** is ≈12 kcal mol^{-1} thermodynamically less stable than the parent triyne complex **28**. This is in sharp contrast to the fact that the bicyclopalladacycle(alkyne) structure **26a′** is estimated to be ≈15 kcal mol^{-1} more stable than **28**. Consequently, the transformation of the triyne complex **28** into the phthalate derivative **5a** was considered to proceed via a bicyclopalladacycle intermediate complex, such as **26a′** rather than **27**.

Catalytic cyclization of the triyne diester with the palladium(0) triyne complex: With the above results in hand, we next examined the catalytic behavior of **28** with respect to the present [2+2+2] cyclization of **4a** (Table 8). In the presence of 5 mol% **28**, **4a** was heated at 110 °C in toluene for 5 h to afford **5a** in 88% yield (Table 8, run 1). In this case, no phosphine additive was required. Accordingly, the net catalyst

Table 8. Catalyzed cyclization of triyne diester **4a** with Pd^0 triyne complex **28**.



Run	Additive	T [°C]	Time [h]	Yield **1a** [%]
1	none	110	5	88
2	PPh_3 (5 mol%)	110	0.5	92
3	PPh_3 (5 mol%)	50	7	80

is the naked palladium atom itself. Furthermore, the catalytic cyclization was completed within only 10 min to give **5a** in 92% yield, when 5 mol% triphenylphosphine was used with **28** (Table 8, run 2). At a lower temperature of 50 °C, 7 h was required for the consumption of **4a**, and **5a** was obtained in 80% yield (Table 8, run 3).

Conclusion

In conclusion, the highly chemoselective cycloaddition of the diyne diesters with acetylenedicarboxylates was achieved by use of $[Pd_2(dba)_3]$ as a catalyst precursor along with the phosphine additive, PPh_3. The corresponding monoester, diketone, or higher homologue having a four-atom tether proved to be less effective as a diyne substrate. The intermediate bicyclic palladacyclopentadiene complex was obtained as an insoluble oligomer by reacting the diyne diester **4a** and $[Pd_2(dba)_3]$ at room temperature. The bicyclopalladacycle structure was successfully confirmed by X-ray structure analysis as the bispyridine complex. This palladium

catalysis was further extended to the high-yield cyclization of triyne esters. In contrast to the diyne diester **1a**, the triyne diester **4a** formed the novel palladium(0) trisalkyne complex from the reaction with $[Pd_2(dba)_3]$. The novel triyne complex was also characterized by X-ray diffraction. These different behaviors between the diyne diester and the triyne diester might be ascribed to the number of coordinated alkynes which accept the backbonding electrons from the Pd^0 center.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury 300 NMR spectrometer as $CDCl_3$ solutions. Chemical shifts are given relative to $CDCl_3$. Mass spectra were recorded on a JEOL JMS-AX 505 HA mass spectrometer. Elemental analyses were performed by the Microanalytical Center of Kyoto University (Japan). Melting points were obtained by a Büchi Melting Point B-540 and are uncorrected. Flash chromatography was performed with a silica gel column (Merck Silica gel 60) eluted with mixed solvents (hexane/AcOEt). Benzene, chlorobenzene, toluene, 1,2-dichloroethane, 1,4-dioxane, and *N*,*N*-dimethylformamide were dried over CaH_2 and distilled. Acetone was dried over $CaCl_2$ and distilled.

Starting materials: $[Pd_2(dba)_3]\cdot CHCl_3$ was prepared according to the established procedure.[41] The palladacyclopentadiene complexes **19**,[11] **20**,[18b] **21**,[11] and **22**[11b] were reported in the literature. The alkynoate substrates were synthesized by the treatment of the corresponding lithium acetylides of the parent diynes and triynes with methyl chloroformate.[42] The diyne **1d** has been reported in the literature.[43]

Analytical data for 1a: M.p. 74.2–74.4 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2240, 1717, 1259 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.79 (s, 6H), 4.41 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 52.92, 56.61, 78.71, 81.80, 153.09 ppm; MS (FAB): *m*/*z* (%): 211 (100) $[M+H]^+$, 154 (78) $[M-CO_2Me+3H]^+$; elemental analysis calcd (%) for $C_{10}H_{10}O_5$ (210.05): C 57.14, H 4.80; found: C 57.27, H 4.67.

Analytical data for 1b: M.p. 29–30 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2239, 1714, 1249 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.30 (t, *J* = 7.2 Hz, 6H), 4.23 (q, *J* = 7.2 Hz, 4H), 4.39 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.02, 56.58, 62.24, 78.95, 81.33, 152.63 ppm; MS(FAB): *m*/*z* (%): 239 (100) $[M+H]^+$, 193 (20) $[M-OEt]^+$, 165 (32) $[M-CO_2Et]^+$, 154 (54) $[M+H-C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{12}H_{14}O_5$ (238.24): C 60.50, H 5.92; found: C 60.44, H 6.11.

Analytical data for 1c: IR ($CHCl_3$): $\tilde{\nu}$ = 2239, 1716, 1258 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.86 (t, *J* = 2.4 Hz, 3H), 3.79 (s, 3H), 4.22 (q, *J* = 2.4 Hz, 2H), 4.37 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 3.68, 52.83, 55.87, 57.69, 73.72, 77.91, 83.16, 83.91, 153.30 ppm; MS (FAB): *m*/*z* (%): 165 (78) $[M-H]^+$, 152 (44) $[M+H-CH_3]^+$, 137 (100) $[M+H-2CH_3]^+$; elemental analysis calcd (%) for $C_9H_{10}O_3$ (166.17): C 65.05, H 6.07; found: C 64.98, H 6.13.

Analytical data for 1e: IR ($CHCl_3$): $\tilde{\nu}$ = 2210, 1682, 1226 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.37 (s, 6H), 4.43 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 32.59, 56.85, 85.44, 86.32, 183.45 ppm; MS (FAB): *m*/*z* (%): 179 (100) $[M+H]^+$, 149 (58) $[M+H-CO]^+$; elemental analysis calcd (%) for $C_{10}H_{10}O_3$ (178.18): C 67.41, H 5.66; found: C 67.21, H 5.86.

Analytical data for 1f: IR ($CHCl_3$): $\tilde{\nu}$ = 2240, 1715, 1254 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.57 (s, 4H), 3.72 (s, 2H), 3.79 (s, 6H), 7.25–7.40 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 42.11, 56.76, 57.46, 77.40, 82.88, 127.66, 128.44, 128.94, 136.61, 153.40 ppm; MS (FAB): *m*/*z* (%): 299 (100) $[M]^+$, 216 (66) $[M-C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{17}H_{17}NO_4$ (299.32): C 68.21, H 5.72, N 4.68; found: C 68.12, H 5.91, N 4.57.

Analytical data for 1g: IR ($CHCl_3$): $\tilde{\nu}$ = 2244, 1742, 1715 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.15 (s, 4H), 3.75 (s, 6H), 3.80 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 23.18, 52.73, 53.59, 55.74, 75.78, 82.15, 153.17, 167.76 ppm; MS (FAB): *m*/*z* (%): 325 (85) $[M+H]^+$, 293 (77) $[M-OMe]^+$, 265 (100) $[M+H-CO_2Me]^+$, 233 (97) $[M+H-3OMe]^+$, 195 (78) $[M-H-OMe-C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{15}H_{16}O_8$ (324.78): C 55.56, H 4.97; found: C 55.35, H 4.98.

Analytical data for 1h: M.p. 34–35 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2242, 1714, 1266 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.65 (t, *J* = 6.6 Hz, 2H), 3.71 (t, *J* = 6.6 Hz, 2H), 3.76 (s, 3H), 3.79 (s, 3H), 4.32 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 19.93, 52.59, 52.79, 57.95, 67.10, 73.64, 78.01, 82.75, 85.49, 153.14, 153.62 ppm; MS (FAB): *m*/*z* (%): 225 (100) $[M+H]^+$, 193 (70) $[M-OMe]^+$, 163 (66) $[M+H-2OMe]^+$; elemental analysis calcd (%) for $C_{11}H_{12}O_5$ (224.21): C 58.93, H 5.39; found: C 58.95, H 5.37.

Analytical data for 4a: M.p. 34–35 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2239, 1714, 1258 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.79 (s, 6H), 4.32 (s, 4H), 4.39 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 52.62, 56.02, 57.04, 78.03, 82.02, 82.45, 153.13 ppm; MS (FAB): *m*/*z* (%): 279 (100) $[M+H]^+$, 154 (70) $[M+H-CO-CH_2C{\equiv}CCO_2Me]^+$, 137 (84) $[M+H-CO_2Me-C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{14}H_{14}O_6$ (278.26): C 60.43, H 5.07; found: C 60.37, H 5.13.

Analytical data for 4b: IR ($CHCl_3$): $\tilde{\nu}$ = 2240, 1716, 1261 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.86 (t, *J* = 2.4 Hz, 3H), 3.79 (s, 3H), 4.20 (q, *J* = 2.4 Hz, 2H), 4.28 (t, *J* = 1.8 Hz, 2H), 4.32 (t, *J* = 1.8 Hz, 2H), 4.39 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 3.53, 52.69, 55.92, 56.23, 57.10, 57.13, 74.00, 77.97, 80.95, 82.57, 83.00, 83.09, 153.05 ppm; MS (FAB): *m*/*z* (%): 235 (95) $[M+H]^+$, 135 (100) $[M-CO_2Me-HC{\equiv}CMe]^+$; elemental analysis calcd (%) for $C_{13}H_{14}O_4$ (234.25): C 66.66, H 6.02; found: C 66.57, H 6.11.

Analytical data for 4d: M.p. 33–34 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2245, 1714, 1263 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.49 (s, 12H), 3.78 (s, 6H), 4.36 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 28.76, 52.22, 52.69, 71.70, 76.77, 84.78, 86.16, 153.35 ppm; MS (FAB): *m*/*z* (%): 335 (15) $[M+H]^+$, 221 (23) $[M-OCH_2C{\equiv}CCO_2Me]^+$, 191 (100) $[M-OMe-OCH_2C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{18}H_{22}O_6$ (334.36): C 64.66, H 6.63; found: C 64.55, H 6.39.

Analytical data for 4e: IR ($CHCl_3$): $\tilde{\nu}$ = 2240, 1715, 1262 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.48 (t, 2H, *J* = 1.8 Hz), 3.55 (s, 2H), 3.70 (s, 2H), 3.78 (s, 3H), 3.79 (s, 3H), 4.32 (t, 2H, *J* = 1.8 Hz), 4.40 (s, 2H), 7.25–7.36 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 41.86, 42.58, 52.73, 52.83, 56.40, 57.38, 77.22, 78.10, 79.97, 82.47, 82.74, 83.41, 127.48, 128.35, 128.95, 137.03, 153.21, 153.50 ppm; MS (FAB): *m*/*z* (%): 368 (100) $[M+H]^+$, 284 (15) $[M-CO_2Me]^+$, 216 (24) $[M-C{\equiv}CCH_2OCH_2C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{21}H_{21}NO_5$ (367.40): C 68.65, H 5.76, N 3.81; found: C 68.60, H 5.89, N 3.73.

Analytical data for 4f: M.p. 69–70 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2239, 1714, 1257 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.47 (s, 4H), 3.56 (s, 4H), 3.71 (s, 4H), 3.78 (s, 6H), 7.25–7.38 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 41.93, 42.75, 52.73, 57.45, 77.19, 80.23, 83.65, 127.48, 128.37, 129.02, 137.23, 153.57 ppm; MS (FAB): *m*/*z* (%): 457 (100) $[M+H]^+$, 216 (30) $[M-C{\equiv}CCH_2N(Bn)CH_2C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{28}H_{28}N_2O_4$ (456.53): C 73.66, H 6.18, N 6.14; found: C 73.66, H 6.25, N 6.16.

Analytical data for 4g: M.p. 101–102 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2243, 1741, 1714, 1269 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.94 (s, 4H), 3.08 (s, 4H), 3.74 (s, 6H), 3.77 ppm (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 22.93, 23.36, 52.71, 53.38, 56.19, 75.39, 77.77, 83.12, 153.40, 168.44 ppm; MS (FAB): *m*/*z* (%): 507 (100) $[M+H]^+$, 475 (20) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_{12}$ (506.46): C 56.92, H 5.17; found: C 56.62, H 5.12.

Analytical data for 4h: IR ($CHCl_3$): $\tilde{\nu}$ = 2239, 1708, 1279 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = (tt, *J* = 6.6, 2.1 Hz, 2H), 3.65 (t, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 3.79 (s, 3H), 4.25 (t, *J* = 2.1 Hz, 2H), 4.31 (s, 2H), 4.37 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 19.90, 52.71, 52.72, 55.80, 57.44, 57.79, 68.21, 75.75, 77.77, 77.81, 82.90, 83.07, 84.35, 153.13 ppm; MS (FAB): *m*/*z* (%): 293 (66) $[M+H]^+$, 179 (100) $[M-OCH_2C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{15}H_{16}O_6$ (292.28): C 61.64, H 5.52; found: C 61.69, H 5.57.

Analytical data for 4i: IR ($CHCl_3$): $\tilde{\nu}$ = 2239, 1715, 1263 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.80 (ddd, *J* = 13.2, 7.2, 6 Hz, 2H), 2.34 (tt, *J* = 7.2, 2.4 Hz, 2H), 3.61 (t, *J* = 6 Hz, 2H), 3.79 (s, 6H), 4.25 (t, *J* = 2.4 Hz, 2H), 4.27 (s, 2H), 4.38 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 15.51, 27.00, 28.35, 52.80, 55.81, 57.62, 57.91, 68.90, 74.94, 77.62, 77.87, 83.05, 83.63, 87.25, 153.25, 153.32 ppm; MS (FAB): *m*/*z* (%): 307 (100) $[M+H]^+$,

193 (78) $[M-OCH_2C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{16}H_{18}O_6$ (306.31): C 62.74, H 5.92; found: C 62.61, H 6.05.

Analytical data for 4j: IR ($CHCl_3$): $\tilde{\nu}=2239$, 1715, 1263 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.57-1.75$ (m, 4H), 2.67 (tt, $J=6.3$, 2.4 Hz, 2H), 3.55 (t, $J=6.3$ Hz, 2H), 3.79 (s, 6H), 4.25 (t, $J=2.4$ Hz, 2H), 4.26 (s, 2H), 4.37 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=18.21$, 24.80, 26.69, 28.27, 52.47, 55.48, 57.32, 57.47, 69.65, 74.58, 77.24, 77.55, 82.82, 83.55, 87.54, 152.90, 152.99 ppm; MS (FAB): *m/z* (%): 321 (100) $[M+H]^+$, 207 (52) $[M-OCH_2C{\equiv}CCO_2Me]^+$, 179 (64) $[M-CO_2Me-C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{17}H_{20}O_6$ (320.34): C 63.74, H 6.29; found: C 63.64, H 6.27.

Pd-catalyzed oligomerization of diyne diester 1a to dimer 12 and trimer 13: A solution of the diyne diester **1a** (105 mg, 0.5 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (13 mg, 0.0125 mmol), and PPh_3 (6.5 mg, 0.025 mmol) in dry degassed benzene (1 mL) was stirred under argon at 50 °C for 24 h. The resultant solution was concentrated in vacuo and the residue was purified by silica gel chromatography (hexane/AcOEt 1:1) to afford the dimer **12** (41 mg, 39%) as a colorless solid. Further elution (hexane/AcOEt 1:2) gave the trimer **13** (28 mg, 27%) as a colorless solid.

Analytical data for 12: M.p. 114–115 °C; IR ($CHCl_3$): $\tilde{\nu}=2240$, 1727, 1259 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.79$ (s, 3H), 3.91 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 4.20 (s, 2H), 4.83 (s, 2H), 5.21 (s, 2H), 5.32 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=52.74$, 52.83, 52.87, 52.98, 57.39, 66.56, 73.45, 74.58, 78.03, 82.80, 124.06, 129.48, 134.23, 135.82, 142.57, 142.78, 153.19, 164.66, 166.28, 168.12 ppm; MS (FAB): *m/z* (%): 419 (30) $[M-H]^+$, 389 (17) $[M-OMe]^+$, 305 (100) $[M-H-OMe-C{\equiv}CCO_2Me]^+$; elemental analysis calcd (%) for $C_{20}H_{20}O_{10}$ (420.37): C 57.14, H 4.80; found: C 57.13, H 4.81.

Analytical data for 13: M.p. 196–197 °C; IR ($CHCl_3$): $\tilde{\nu}=1731$, 1225 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.83$ (s, 6H), 3.86 (s, 6H), 3.89 (s, 6H), 4.67 (s, 4H), 5.17 (s, 4H), 5.30 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=52.52$, 52.76, 52.85, 67.23, 73.50, 74.61, 123.95, 129.49, 135.28, 135.42, 142.18, 142.27, 164.83, 166.21, 168.10 ppm; MS (FAB): *m/z* (%): 631 (50) $[M+H]^+$, 460 (98) $[M-5OMe-CH_3]^+$, 391 (100) $[M-2OMe-3CO_2Me]^+$; elemental analysis calcd (%) for $C_{30}H_{30}O_{15}$ (630.55): C 57.14, H 4.80; found: C 57.17, H 4.77.

Typical procedure for Pd-catalyzed cycloaddition of diynes with acetylenedicarboxylic acid esters: cycloaddition of diyne diester 1a with DMAD (2a)

Method A: A solution of the diyne diester **1a** (60 mg, 0.29 mmol), DMAD (45 mg, 0.32 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (7.4 mg, 0.007 mmol), and PPh_3 (3.7 mg, 0.014 mmol) in toluene (2.9 mL) was stirred under argon at 110 °C for 1 h. The resultant brown solution was concentrated in vacuo and the residue was purified by silica gel chromatography (hexane/AcOEt 4:1) to afford the phthalan **3aa** (79 mg, 78%) as a colorless solid; M.p. 133–134 °C; IR ($CHCl_3$): $\tilde{\nu}=1734$, 1235 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.90$ (s, 6H), 3.91 (s, 6H), 5.32 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=53.08$, 53.18, 74.06, 126.26, 133.55, 144.00, 164.57, 166.64 ppm; MS (FAB): *m/z* (%): 351 (23) $[M-H]^+$, 321 (100) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{16}H_{16}O_9$ (352.29): C 54.55, H 4.58; found: C 54.29, H 4.56.

Method B: A solution of the diyne diester **1a** (60 mg, 0.29 mmol) and $[Pd_2(dba)_3]\cdot CHCl_3$ (7.4 mg, 0.007 mmol) in toluene (2.9 mL) was stirred under argon for 30 min at room temperature. To the resultant green solution was added PPh_3 (3.7 mg, 0.014 mmol) and the solution was stirred for 30 min. Finally, DMAD (45 mg, 0.32 mmol) was added and the reaction mixture was heated at 110 °C for another 30 min. The resultant brown solution was concentrated in vacuo and the residue was purified by silica gel chromatography (hexane/AcOEt 4:1) to afford the phthalan **3aa** (73 mg, 67%).

The cycloaddition of **1a** with **2a** and palladacyclopentadienes **14**, **19**–**22** as catalyst precursors were carried out in a similar manner.

Analytical data for 3ab: M.p. 63–65 °C; IR ($CHCl_3$): $\tilde{\nu}=1734$, 1236 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.34$ (t, $J=7.0$ Hz, 6H), 3.89 (s, 6H), 4.34 (q, $J=7.0$ Hz, 4H), 5.29 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=13.99$, 52.88, 62.28, 74.00, 126.17, 133.69, 143.72, 164.62, 166.08 ppm; MS (FAB): *m/z* (%): 379 (50) $[M-H]^+$, 335 (35) $[M-OEt]^+$, 289 (95) $[M-H-2OEt]^+$, 273 (100) $[M-OEt-2OMe]^+$; elemental analysis calcd (%) for $C_{18}H_{20}O_9$ (380.35): C 56.84, H 5.30; found: C 56.82, H 5.32.

Analytical data for 3ba: M.p. 111–112 °C; IR ($CHCl_3$): $\tilde{\nu}=1729$, 1233 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.36$ (t, $J=7.2$ Hz, 6H), 3.89 (s, 6H), 4.36 (q, $J=7.2$ Hz, 4H), 5.32 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=14.13$, 53.06, 62.39, 74.07, 126.41, 133.50, 143.90, 164.09, 166.70 ppm; MS (FAB): *m/z* (%): 379 (35) $[M-H]^+$, 349 (100) $[M-OMe]^+$, 261 (45) $[M-H-OEt-CO_2Et]^+$; elemental analysis calcd (%) for $C_{18}H_{20}O_9$(380.35): C 56.84, H 5.30; found: C 56.78, H 5.33.

Analytical data for 3ca: M.p. 126–127 °C; IR ($CHCl_3$): $\tilde{\nu}=1731$, 1242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=2.31$ (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 3.88 (s, 3H), 5.11 (m, 2H), 5.32 ppm (t, $J=2$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=17.24$, 52.61, 52.68, 52.86, 72.93, 75.23, 121.19, 131.88, 134.16, 134.44, 141.96, 142.58, 165.17, 167.07, 167.93 ppm; MS (FAB): *m/z* (%): 307 (52) $[M-H]^+$, 277 (100) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{15}H_{16}O_7$ (308.28): C 58.44, H 5.23; found: C 58.50, H 5.17.

Analytical data for 3ea: M.p. 89–92 °C; IR ($CHCl_3$): $\tilde{\nu}=1737$, 1700, 1222 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=2.45$ (s, 6H), 3.89 (s, 6H), 5.15 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=29.96$, 53.25, 72.84, 130.64, 135.99, 141.03, 166.48, 199.47 ppm; MS (FAB): *m/z* (%): 320 (25) $[M]^+$, 289 (100) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{16}H_{16}O_7$ (320.29): C 60.00, H 5.04; found: C 59.71, H 5.32.

Analytical data for 3fa: M.p. 95–97 °C; IR ($CHCl_3$): $\tilde{\nu}=1733$, 1232 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.85$ (s, 6H), 3.87 (s, 6H), 3.92 (s, 2H), 4.18 (s, 4H), 7.27–7.42 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=52.85$, 53.02, 58.58, 59.61, 127.28, 128.41, 128.51, 128.89, 132.15, 137.90, 144.40, 165.24, 166.65 ppm; MS (FAB): *m/z* (%): 442 (100) $[M+H]^+$, 394 (96) $[M--OMe-CH_3]^+$; elemental analysis calcd (%) for $C_{23}H_{23}NO_8$ (441.43): C 62.58, H 5.25, N 3.17; found: C 62.80, H 5.12, N 3.09.

Analytical data for 3gb: M.p. 123–126 °C; IR ($CHCl_3$): $\tilde{\nu}=1736$ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.33$ (t, $J=7.2$ Hz, 6H), 3.76 (s, 6H), 3.81 (s, 4H), 3.90 (s, 6H), 4.32 ppm (q, $J=7.2$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=14.01$, 40.57, 52.78, 53.33, 59.23, 62.20, 129.24, 132.49, 143.61, 165.68, 166.11, 170.98 ppm; MS (FAB): *m/z* (%): no molecular ion peak 449 (50) $[M-OEt]^+$, 389 (100) $[M-H-OMe-CO_2Et]^+$; elemental analysis calcd (%) for $C_{23}H_{26}O_{12}$ (494.45): C 55.87, H 5.30; found: C 55.83, H 5.34.

Synthesis of palladacyclopentadiene complex 15: A solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (81 mg, 0.078 mmol) and the diyne **1a** (40 mg, 0.19 mmol) in dry degassed acetone (1.0 mL) was stirred at room temperature under an argon atmosphere for 6 h. The resultant green suspension was filtered and the residue was washed with acetone. The filtrate was concentrated to give complex **14** (40 mg, 70%) as a dark green solid; M.p. 157 °C(decomp.); IR (Nujol): $\tilde{\nu}=1705$ cm^{-1}; ^1H NMR (300 MHz, [D$_6$]DMSO, 25 °C): $\delta=3.52$ (s, 6H), 4.13 ppm (s, 4H); elemental analysis calcd (%) for $[C_{10}H_{10}O_5Pd]_n$: C 37.94, H 3.19, found: C 37.98, H 3.31.

To a suspension of **14** (32 mg, 0.10 mmol) in dry degassed CH_2Cl_2 (5.0 mL) was added pyridine (57 mg, 0.72 mmol) and the reaction mixture was stirred at room temperature under an argon atmosphere for 3 h. The resultant brown solution was concentrated under reduced pressure. The residue was purified by recrystallization from CH_2Cl_2/diethyl ether to give **15** (11 mg, 21%) as a yellowish green needle; M.p. 136 °C(decomp.); IR ($CHCl_3$): $\tilde{\nu}=1670$ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.16$ (s, 6H), 4.49 (s, 4H), 7.65–7.78 (m, 2H), 8.65 ppm (d, $J=4.8$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=50.13$, 67.24, 124.53, 137.15, 141.83, 150.70, 171.39, 173.47 ppm; MS (FAB): *m/z* (%): 474 (25) $[M]^+$, 460 (78) $[M+H-CH_3]^+$, 395 (100) $[M-C_5H_5N]^+$; elemental analysis calcd (%) for $C_{20}H_{20}N_2O_5Pd$ (474.80): C, 50.59; H, 4.25; N, 5.90; found: C, 50.66; H, 4.20; N, 5.87.

Stoichiometric reaction of diyne diester 1a, palladacyclopentadiene triphenylphosphine complex 20, and DEAD 2b: A solution of **1a** (105 mg, 0.5 mmol), **20** (330 mg, 0.25 mmol), and **2b** (170 mg, 1.0 mmol) in dry degassed toluene (5 mL) was heated at 60 °C under Ar. The reddish reaction mixture changed to brown to dark brown. After stirring for 40 h, the insoluble materials were filtered off and the filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (hexane/AcOEt 4:1) to afford **3ab** (116 mg, 61%) and diethyl tetramethyl mellitate (68.4 mg, 30%).

Typical procedure for Pd-catalyzed cyclization of triynes: cyclization of triyne diester 4a: A solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (18.5 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol), and the triyne diester **4a** (198 mg, 0.71 mmol) in dry degassed toluene (7.1 mL) was heated at 110 °C under an Ar

atmosphere for 30 min. The solvent was removed and the residue was purified by silica-gel flash column chromatography (hexane/AcOEt 3:1) to give **5a** (187 mg, 94%) as a colorless solid; m.p. 143.5–144.2 °C; IR ($CHCl_3$): $\tilde{\nu}=1724\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.89$ (s, 6H), 5.05 (s, 4H), 5.22 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=$ 52.59, 71.82, 73.34, 124.74, 135.88, 140.29, 166.60 ppm; MS (FAB): *m/z* (%): 279 (96) $[M+H]^+$, 247 (100) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{14}H_{14}O_6$ (278.26): C 60.43, H 5.07; found: C 60.30, H 4.99.

Analytical data for 5b: M.p. 186–187 °C; IR ($CHCl_3$): $\tilde{\nu}=1719\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=2.44$ (s, 3H), 3.89 (s, 3H), 5.00 (s, 2H), 5.07 (s, 2H), 5.12 (s, 2H), 5.26 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=17.80$, 51.72, 71.71, 72.90, 73.30, 74.94, 123.28, 130.27, 132.44, 135.05, 139.60, 141.85, 167.06 ppm; MS (FAB): *m/z* (%): 235 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{13}H_{14}O_4$ (234.25): C 66.66, H 6.02; found: C 66.73, H 5.95.

Analytical data for 5c: M.p. 207–208 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=2.15$ (s, 6H), 5.03 (s, 4H), 5.09 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=15.45$, 72.80, 73.24, 128.35, 128.61, 137.95 ppm; MS (FAB): *m/z* (%): 189 (100) $[M-H]^+$; elemental analysis calcd (%) for $C_{12}H_{14}O_2$ (190.24): C 75.76, H 7.42; found: C 75.77, H 7.40.

Analytical data for 5d: M.p. 106–107 °C; IR ($CHCl_3$): $\tilde{\nu}=1731\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.62$ (s, 12H), 3.89 (s, 6H), 5.10 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=27.94$, 52.65, 69.59, 85.97, 124.80, 141.63, 143.59, 166.81 ppm; MS (FAB): *m/z* (%): 333 (58) $[M-H]^+$, 303 (100) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{18}H_{22}O_6$ (334.36): C 64.66, H 6.63; found: C 64.57, H 6.68.

Analytical data for 5e: IR ($CHCl_3$): $\tilde{\nu}=1724\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.85$ (s, 2H), 3.87 (s, 3H), 3.87 (s, 3H), 3.92 (s, 2H), 4.06 (s, 2H), 4.99 (s, 2H), 5.24 (s, 2H), 7.28–7.40 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=52.53$, 52.62, 56.99, 57.86, 59.93, 71.92, 74.19, 122.53, 127.27, 128.31, 128.43, 128.56, 128.90, 136.16, 137.67, 138.18, 140.28, 140.43, 166.25, 167.89 ppm; MS (FAB): *m/z* (%): 368 (100) $[M+H]^+$, 336 (26) $[M-OMe]^+$, 276 (11) $[M-CH_2Ph]^+$, 234 (29) $[M-CH_2N(Bn)CH_2]^+$; elemental analysis calcd (%) for $C_{21}H_{21}NO_5$ (367.40): C 68.65, H 5.76, N 3.81; found: C 68.84, H 5.61, N 3.77.

Analytical data for 5f: M.p. 69–71 °C; IR ($CHCl_3$): $\tilde{\nu}=1723\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.78$ (s, 4H), 3.84 (s, 6H), 3.89 (s, 4H), 4.10 (s, 4H), 7.24–7.39 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=$ 52.36, 56.88, 58.69, 59.96, 124.89, 127.10, 128.33, 128.50, 137.90, 138.47, 140.35, 167.40 ppm; MS (FAB): *m/z* (%): 457 (100) $[M+H]^+$, 425 (14) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{28}H_{28}N_2O_4$ (456.53): C 73.66, H 6.18, N 6.14; found: C 74.15, H 5.83, N 5.99.

Analytical data for 5g: M.p. 177–178 °C; IR ($CHCl_3$): $\tilde{\nu}=1734\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.52$ (s, 4H), 3.71 (s, 4H), 3.74 (s, 12H), 3.86 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=38.93$, 40.41, 52.44, 53.19, 59.80, 126.98, 139.31, 139.68, 167.45, 171.30 ppm; MS (FAB): *m/z* (%): 507 (10) $[M+H]^+$, 475 (100) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_{12}$ (506.46): C 56.92, H 5.17; found: C 56.64, H 5.17.

Analytical data for 5h: M.p. 129–130 °C; IR ($CHCl_3$): $\tilde{\nu}=1724\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=2.72$ (t, $J=6$ Hz, 2H), 3.87 (s, 3H), 3.91 (s, 3H), 3.98 (t, $J=6$ Hz, 2H), 4.76 (s, 2H), 5.07 (s, 2H), 5.33 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=26.26$, 52.41, 52.60, 63.96, 65.89, 72.08, 75.14, 119.82, 131.24, 132.16, 132.25, 139.02, 140.18, 165.35, 168.29 ppm; MS (FAB): m/z (%): 291 (100) $[M-H]^+$, 261 (99) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{15}H_{16}O_6$ (292.28): C 61.64, H 5.52; found: C 61.34, H 5.55.

Analytical data for 5i: M.p. 118–119 °C; IR ($CHCl_3$): $\tilde{\nu}=1725\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.86$ (q, $J=5.6$ Hz, 2H), 2.89 (dd, $J=5.6$, 5.4 Hz, 2H), 3.86 (s, 3H), 3.94 (s, 3H), 4.04 (t, $J=5.4$ Hz, 2H), 4.64 (s, 2H), 5.14 (s, 2H), 5.34 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=28.76$, 31.26, 52.47, 52.81, 69.72, 72.67, 75.01, 75.77, 119.26, 134.69, 137.35, 140.02, 141.13, 141.44, 165.21, 169.36 ppm; MS (FAB): *m/z* (%): 305 (83) $[M-H]^+$, 275 (100) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{16}H_{18}O_6$ (306.31): C 62.74, H 5.92; found: C 62.44, H 5.91.

Analytical data for 5j: IR ($CHCl_3$): $\tilde{\nu}=1724\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=1.56-1.64$ (m, 2H), 1.73–1.82 (q, $J=6.6$ Hz, 2H), 3.01 (t, $J=6.6$ Hz, 2H), 3.73 (t, $J=5.4$ Hz, 2H), 3.87 (s, 3H), 3.94 (s, 3H), 4.77 (s, 2H), 5.15 (t, $J=2$ Hz, 2H), 5.35 ppm (t, $J=2$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=26.60$, 26.71, 29.34, 52.48, 52.75, 67.46, 70.69, 72.74, 75.78, 119.63, 134.65, 137.15, 139.67, 140.54, 140.91, 169.35 ppm; MS (FAB): *m/z* (%): 319 (65) $[M-H]^+$, 289 (100) $[M-OMe]^+$; elemental analysis calcd (%) for $C_{17}H_{20}O_6$ (320.34): C 63.74, H 6.29; found: C 63.66, H 6.37.

Procedure for the synthesis of palladium triyne complex 28: A solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (168 mg, 0.16 mmol) and the triyne **4a** (99 mg, 0.36 mmol) in dry degassed acetone (3.3 mL) was stirred at room temperature under an argon atmosphere for 6 h. The resultant green suspension was concentrated under reduced pressure. The residue was suspended in ether and the insoluble materials were filtered off. The residue was washed with AcOEt and the filtrate was concentrated to give the triyne complex **28** (103 mg, 83%) as a off-white solid; m.p. 84 °C (decomp.); IR ($CHCl_3$): $\tilde{\nu}=$ 1977, 1712 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=3.88$ (s, 6H), 4.58 (s, 4H), 4.66 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta=52.74$, 55.16, 55.37, 72.90, 75.57, 89.69, 160.80 ppm; MS (FAB): *m/z* (%): 384 (100) $[M]^+$, 353 (64) $[M-OMe]^+$; elemental analysis (%) calcd for $C_{14}H_{14}O_6Pd$ (384.68): C 43.71, H 3.67; found: C 43.70, H 3.68.

Thermolysis of triyne complex 28: A solution of **28** (15.9 mg, 0.041 mmol) in dry degassed acetone (1.6 mL) was heated at 50 °C under an argon atmosphere for 30 min. The solvent was removed and the residue was purified by silica-gel flash column chromatography (hexane/AcOEt 3:1) to give **5a** (5.7 mg, 50%) as a white solid.

PPh_3-promoted conversion of triyne complex 28 into benzene 5a: A solution of PPh_3 (5.8 mg, 0.022 mmol) in acetone (1.0 mL) at room temperature under an argon atmosphere was added to a solution of **28**

Table 9. Summary of the crystallographic data for **15**·CH_2Cl_2 and **28**.

	15·CH_2Cl_2	**28**
formula	$C_{21}H_{20}Cl_2N_2O_5Pd$	$C_{14}H_{14}O_6Pd$
M_r	557.69	384.66
crystal size [mm]	0.7 × 0.1 × 0.1	0.75 × 0.20 × 0.10
crystal system	monoclinic	monoclinic
a [Å]	9.2747(4)	8.1278(2)
b [Å]	21.1519(10)	8.118(1)
c [Å]	11.7468(5)	21.6687(4)
β [°]	99.1720(10)	94.7869(7)
space group	$P2_1/n$	$P2_1/c$
Z	4	4
V [Å^3]	2274.99(17)	1424.89(4)
ρ_{calcd} [g cm^{-3}]	2.035	1.793
T [K]	173	173
λ ($Mo_{K\alpha}$) [Å]	0.71073	0.71069
μ ($Mo_{K\alpha}$) [cm^{-1}]	0.1356	13.27
θ range [°]	1.93–29.15	
$2\theta_{max}$ [°]	–	55.1
no. reflections observed	17738	3179
no. of ind reflns	6125 [R(int) = 0.0281]	–
no. of parameters	–	190
absorption correction	SADABS	
refinement method	full-matrix least-squares on F^2	full-matrix (TEXSAN)
GOF	0.743	1.83
R[a]	0.0387	0.020
R_W[b]	0.1043	0.041
residual electron density [e Å^{-3}]	1.310 and −1.251	0.85 and −0.47

[a] $R=\Sigma\,|\,(F_o-F_c)\,|\,/\Sigma(F_o)$. [b] $R_W=\Sigma[(\omega(F_o-F_c)^2)]/\Sigma(\omega F_o^2)^{1/2}$.

(8.5 mg, 0.022 mmol) in dry degassed acetone (1.0 mL). After the mixture had been stirred for 10 min, the solvent was removed and the residue was purified by silica-gel flash column chromatography (hexane/AcOEt 3:1) to give **5a** (5.9 mg, 97%) as a colorless solid.

Crystallographic structural determinations

Palladacyclopentadiene(bispyridine) complex 15: A single crystal of **15**·CH_2Cl_2 suitable for X-ray structure analysis was obtained by the recrystallization from CH_2Cl_2/diethyl ether at $-15\,^{\circ}C$. A crystal of the dimensions $0.70 \times 0.10 \times 0.10$ mm was mounted on a quartz fiber, and diffraction data was collected in a θ range of 1.93–29.15° at 173 K on a Brucker SMART APEX CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The absorption correction was made with SADABS. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 with SHELXTL. A total of 17738 reflections were measured and 6125 were independent. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. A summary of the fundamental crystal and refinement data is given in Table 9.

Palladium triyne complex 28: A single crystal of **28** suitable for X-ray analysis was obtained by recrystallization from CH_2Cl_2/diethyl ether at $-15\,^{\circ}C$. A crystal of the dimensions $0.75 \times 0.20 \times 0.10$ mm was mounted on a quartz fiber. The crystal was transferred to an Rigaku AFC7 equipped with a MSC/ADSC Quantum1 CCD detector with $Mo_{K\alpha}$ radiation and cooled to $-100\,^{\circ}C$ under a cold nitrogen stream previously calibrated by a thermocouple placed in the same position. After the crystal had been carefully optically centered within the X-ray beam, four data frames measured at 0.5° increments of ω were collected to assess the crystal quality. In order to correct for high-energy background events in the images, data frames were collected as the sum of two 15-s exposures and non-correlating events were eliminated. A total of 149 reflections with $I > 3\sigma(I)$ were selected and utilized to calculate a preliminary unit cell. The intensity images were measured at 0.5° intervals of ω for a duration of 82 s each. Frame data were integrated with the d*TREK program package, and an absorption correction was performed with the REQAB program. The 3196 integrated reflections were averaged in point group 2/*m* to give 3179 unique reflections. All calculations were performed with TEXSAN. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located at calculated positions. A summary of the fundamental crystal and refinement data is given in Table 9.

CCDC-195393 (**15**) and CCDC-148170 (**28**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Computational methods: All calculations were performed with the Gaussian 98 package.[44] The 3–21G,[37] 6–31G(d),[36] 6–311G(d),[40] LanL2DZ,[35] and SDD[38] basis sets were used as stored in the Gaussian program. The f and g exponents for Pd were used as reported in the literature.[39] The density functional calculations were carried out at the B3LYP level with the following combinations of the basis sets: BS 1: LanL2DZ for Pd, 6–31G(d) for C and O, 3–21G for H; BS 2: SDD for Pd, 6–31G(d) for C and O, 3–21G for H; BS 3: SDD with f- and g-polarization functions for Pd, 6–31G(d) for C and O, 3–21G for H; BS 4: SDD with f- and g-polarization functions for Pd, 6–311G(d) for C and O, 3–21G for H.

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