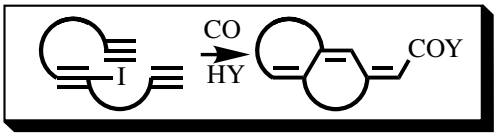

IV.3.3 Palladium-Catalyzed Tandem and Cascade Carbopalladation of Alkynes and 1,1-Disubstituted Alkenes Terminated by Carbonylative Reactions

EI-ICHI NEGISHI and CHRISTOPHE COPÉRET

A. INTRODUCTION

As discussed in the two preceding sections, the living two-stage (tandem) and multistage (cascade) carbopalladation processes generally involving the use of alkynes and 1,1-disubstituted alkenes can be terminated by (i) Heck alkene substitution (**Sect. IV.3.1**) and (ii) various nucleophilic substitution processes including hydride reduction, cross-coupling with organometals, and reactions with heteronucleophiles (**Sect. IV.3.2**). Interesting and potentially useful variants of these processes involve incorporation of CO only in the termination stage. Since acylpalladium species can much more readily react with a variety of nucleophiles, especially with alcohols, amines, and other heteroatom nucleophiles, than simple organopalladium species containing alkyl, aryl, alkenyl, and alkynyl, termination of the tandem and cascade carbopalladation processes via trapping of acylpalladium intermediates with nucleophilic reagents might be expected to be very favorable. However, such carbopalladation–carbonylative trapping processes would be feasible and synthetically attractive only if CO does not interfere with the tandem and cascade carbopalladation and participates in the reaction only after the carbopalladation process is complete in each catalytic cycle.

The feasibility of such a sequential process was accidentally discovered in 1989[1] in an unsuccessful attempt to achieve cyclic acylpalladation (**Sect. VI.4**) of **1a** (**Scheme 1**) with 40 atm of CO, 1.5 equiv of NEt_3, and 4 equiv of MeOH in the presence of 3 mol % of $Pd(PPh_3)_4$ at 100 °C. Whereas none of the desired cyclic acylpalladation product **2a** was formed, the reaction gave an unexpected carbopalladation product **3a** in 42% yield along with an uncyclized premature esterification product **4a** formed in 28% yield. Similarly, **1b** provided **3b** and **4b** in 18% and 42% yields, respectively, rather than the desired **2b** (**Scheme 1**). Since formation of seven-membered ketones via cyclic acylpalladation has never been observed, the results are perhaps not surprising. Later optimization of the reaction conditions including the use of 1 atm pressure of CO has

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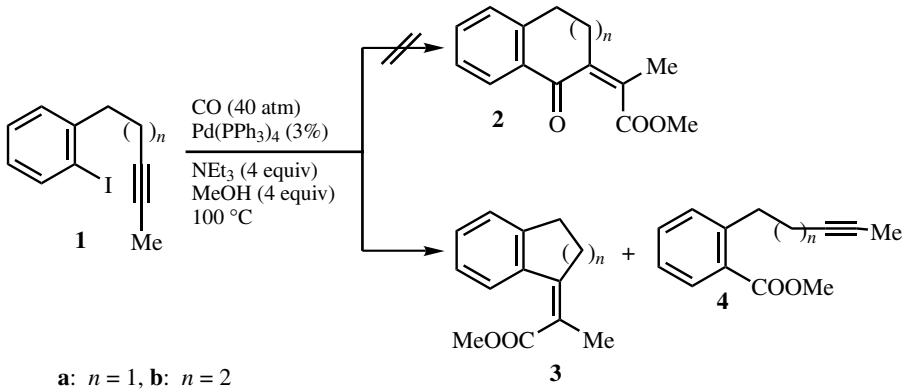


n	**3**	**4**
1	42%	28%
2	18%	42%

Scheme 1

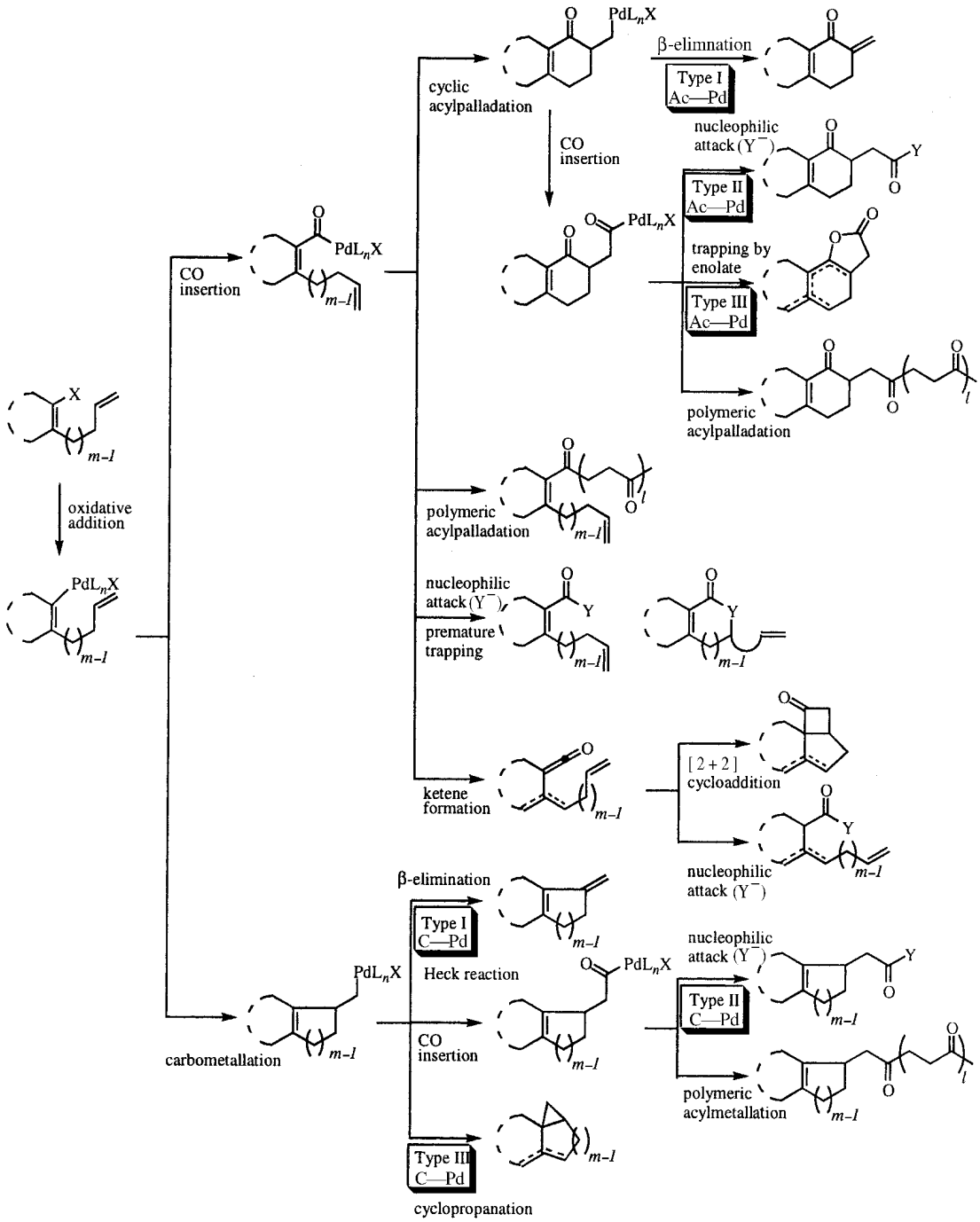
led to the development of the carbopalladation–carbonylative trapping process as a synthetically attractive tool as discussed below.

In principle, ω-haloalkenes and ω-haloalkynes can undergo either carbonylative cyclization, that is, *acylpalladation* or Ac—Pd process, or noncarbonylative cyclization, that is, sample *carbopalladation* or C—Pd process, in the presence of CO and a Pd catalyst. Various possibilities with ω-halo alkenes as representative substrates are shown in **Scheme 2**.[2] Those processes that incorporate CO in the cyclization processes are discussed in **Part VI** including **Sects. VI.4–VI.6**. In this section, those cases that do not incorporate CO during the cyclization processes but do so only after cyclization will be discussed. Such cyclic carbopalladation–carbonylative termination tandem and cascade processes are represented by the Type II C—Pd process in **Scheme 2**, which may take place in competition with the other processes shown in **Scheme 2**, especially the cyclic Heck reaction (Type I C—Pd process) and cyclic carbopalladation involving cyclopropanation (Type III C—Pd process).

The process-initiating groups may be a variety of organic electrophiles including halides, usually iodides and bromides, and other related electrophiles capable of undergoing oxidative addition to Pd. Aryl and alkenyl electrophiles have so far been used most extensively. In principle, however, benzyl, allyl, propargyl, and other types of organic electrophiles may also be employed. π-Functional groups participating in the cyclic carbopalladation processes may, in principle, be alkenes, alkynes, and even arenes as well as their oligomeric combinations, such as allenes, conjugated and nonconjugated dienes, oligoenes, enynes, diynes, and oligoynes, even though some such compounds may not have been tested in the past.

In the cyclic carbopalladation of 1,1-disubstituted alkenes, one asymmetric carbon center is generated unless the process leads to the formation of symmetrical structures lacking chirality. Such reactions are subject to asymmetric induction in both diastereomeric and enantiomeric senses.

A couple of recent reviews[2],[3] have described some of the reactions discussed in this section.



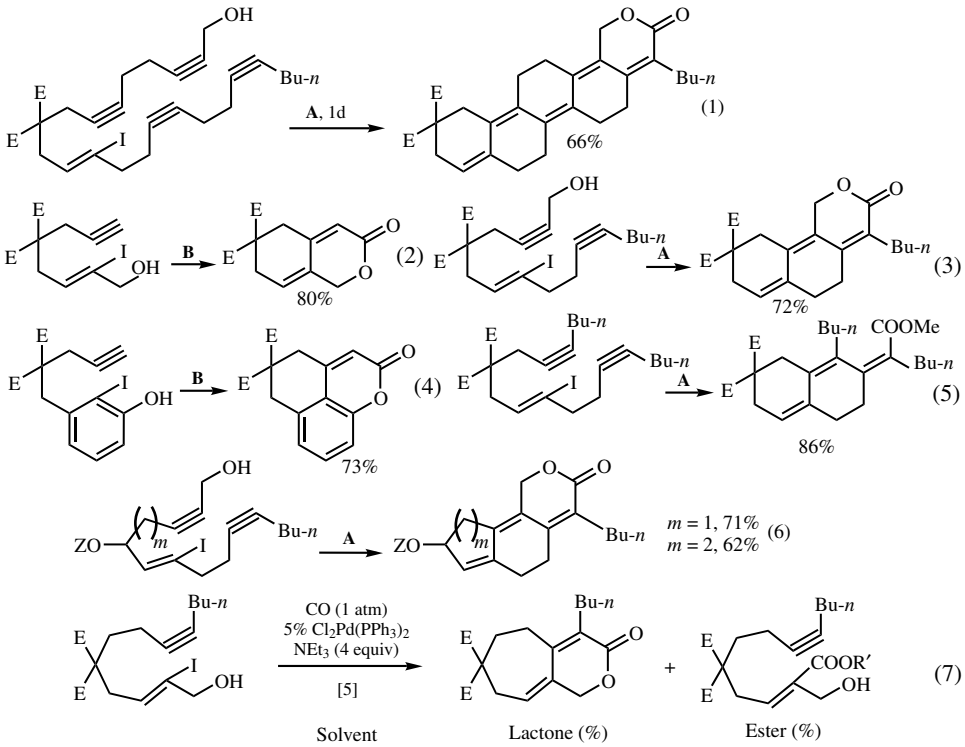
X = I Br, OTf, etc. Y$^-$ = nucleophiles centered at H, C, N, O etc. *l,m,n* = integers

Scheme 2

B. Pd-CATALYZED TANDEM AND CASCADE CARBOPALLADATION OF ALKYNES TERMINATED BY CARBONYLATION

B.i. Termination by Carbonylative Esterification and Lactonization

The catalytic cyclic carbopalladation of alkynes can proceed to produce five- and six-membered rings at 1.0–1.1 atm of CO without premature incorporation of CO, and *in situ* regeneration of Pd–phosphine catalysts can be achieved in high yields by termination of the cyclic carbopalladation via deferred carbonylative esterification and lactonization, as suggested by the results shown in **Scheme 1**. One key to observing the formation of the desired products in high yields is to employ 1.0–1.0 atm of CO. Some representative examples are summarized in **Scheme 3**.



Solvent	Lactone (%)	Ester (%)
i-PrOH	66	11 (R′ = Pr-*i*)
MeOH	28	57 (R′ = Me)
DMF	11	—

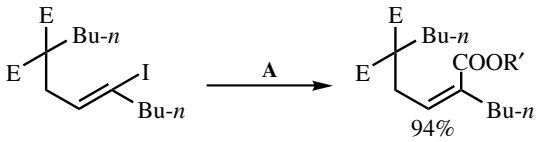
E = COOMe, Z = $SiMe_2Bu$-*t*
A = CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (2 equiv), MeOH
B = CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (2 equiv), DMF

Scheme 3

The results shown in **Scheme 3** indicate the following:

1. Cyclic carbopalladation producing five- and six-membered rings can proceed in good yields despite the fact that the expected carbonylative esterification does take

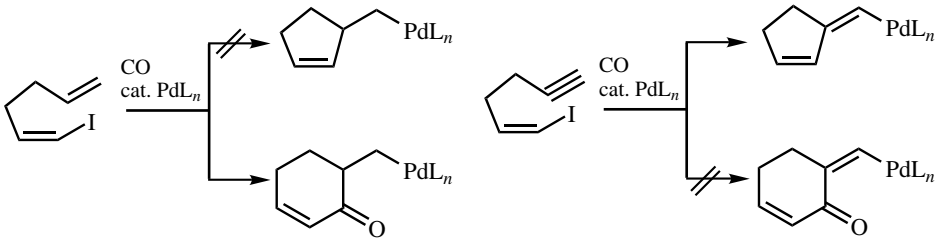
place in the absence of strategically positioned alkyne groups[4] (**Scheme 4**). Surprisingly, MeOH is a satisfactory solvent, which is superior to others, such as DMF, THF, MeCN, and benzene. This indicates that cyclic carbopalladation of alkynes producing five- and six-membered rings must be much faster than carbonylative esterification. In the formation of the pentacyclic product in Eq. 1 of **Scheme 3**, partially cyclized products containing mono-, di-, tri-, and/or tetracyclic frames were not formed to significant extents. The results suggest that, once the cascade cyclic carbopalladation is initiated, it must proceed rapidly to complete the tetracyclization process



A: see **Scheme 3**

Scheme 4

2. The formation of cyclic ketones via acylpalladation does not seriously compete in the reactions shown in **Scheme 3**. This is in contrast with the corresponding reaction of *ω*-iododienes, which preferentially undergo cyclic acylpalladation in cases where six-membered cyclic ketones can be formed via cyclic acylpalladation.[6]–[8] These contrasting behaviors may be summarized as shown in **Scheme 5**.[4] There has been no indication that the formation of five- or six-membered rings by either cyclic carbopalladation or acylpalladation is reversible, even though the formation of three-membered rings by carbopalladation has been shown to be readily reversed.[9]



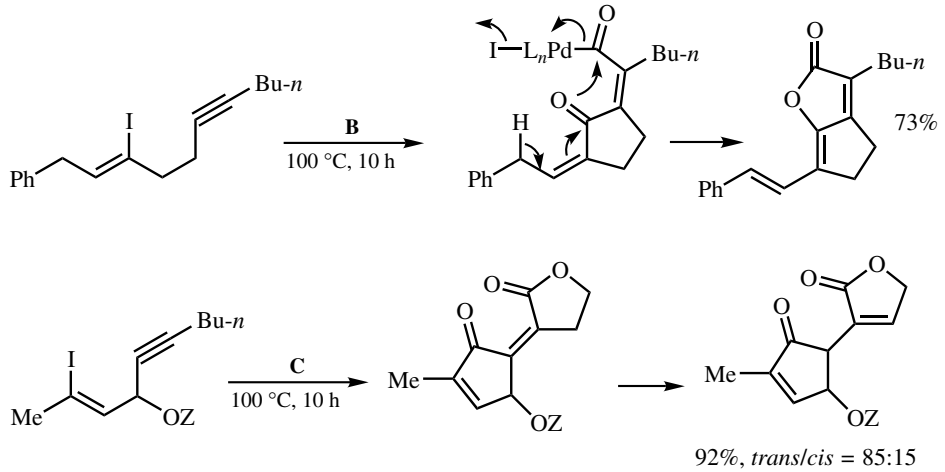
Scheme 5

As the formation of seven-membered ketones has never been observed with either alkenes or alkynes, it may tentatively be concluded that cyclic carbopalladation producing six-membered rings is favored over acylpalladation producing seven-membered ketones. All of the above-mentioned results can be taken as an indication that alkynes might be generally reluctant to undergo acylpalladation, but this does not appear to be an accurate statement. Thus, in the competition between cyclic carbopalladation producing four-membered rings and cyclic acylpalladation producing five-membered ketones, the latter indeed wins out, as indicated by the results shown in **Scheme 6**.[4]

The results shown in **Schemes 3–6** lead to the summary shown in **Table 1** concerning the effects of tether length or ring size on the competition between C—Pd and Ac—Pd processes in the presence of CO.

TABLE 1. Effects of Ring Size on the Competition Between Cyclic Carbopalladation and Cyclic Acylpalladation in the Presence of Co

Ring Size	Substrate	Cyclic C—Pd	Cylic Ac—Pd
4 vs. 5	Alkenes and alkynes	Not observed	Favored
5 vs. 6	Alkenes	Can be competitive at 1 atm of Co	Can be dominant
	Alkynes	Favored	Not observed
6 vs. 7	Alkenes and alkynes	Favored	Not observed

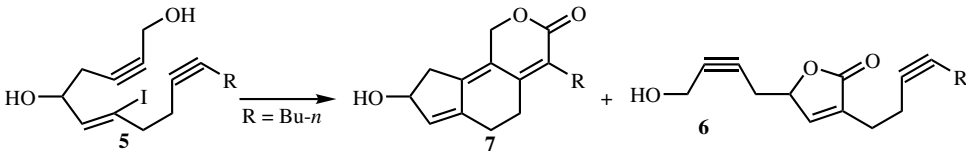


B = CO (1 atm), 5% $Cl_2Pd(Ph_3)_2$, NEt_3 (2 equiv), DMF
C = same as B except that C_6H_6 was used in place of DMF

Scheme 6

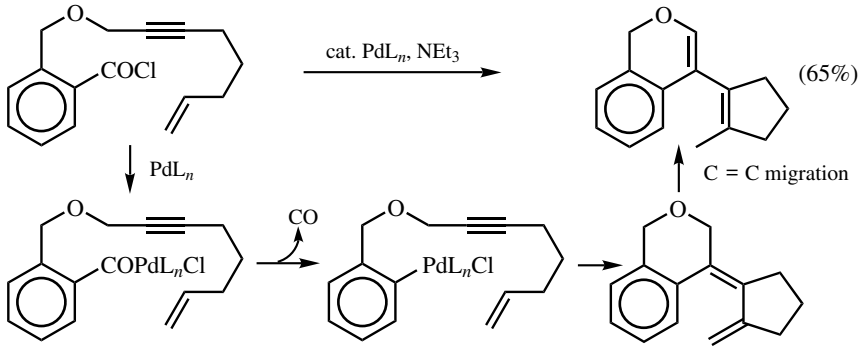
The relative rates of carbopalladation and CO insertion represent a very delicate issue, which is, to a considerable extent, dependent on the reaction conditions. The reaction of PhI with even 1 atm of CO in the presence of 1-octyne and MeOH under the influence of 5 mol % of $Cl_2Pd(PPh_3)_2$ gives only methyl benzoate (73%) without the sign of either intermolecular carbopalladation or acylpalladation.[4] One may conclude that intermolecular C—Pd and Ac—Pd processes are, in general, decidedly slower than the CO insertion–methanolysis tandem process.

The relative rates of CO insertion and intramolecular carbopalladation producing five- and six-membered rings are more difficult to assess. However, the results summarized in **Scheme 7**[4] indicate that the CO insertion–lactonization tandem process of **5** producing **6** is competitive with the intramolecular C—Pd process producing a five-membered ring (**7**) and that their relative rates depend on CO pressure. One may conclude that CO insertion can be at least as fast as or possibly faster than favorable intramolecular carbopalladation. This, in turn, indicates that CO insertion must readily be reversible for favoring the cyclic C—Pd process over premature esterification. The ready reversibility of CO insertion is clearly indicated by the results shown in **Scheme 8**.[4] In summary, the relative rates of various processes in decreasing order of rates are as shown in **Scheme 9**.



Conditions	7 (%)	6 (%)
CO (1 atm), cat. $Cl_2Pd(PPh_3)_2$, NEt_3 (4 equiv), MeOH (100 equiv)	59	19
CO (20 atm), cat. $Cl_2Pd(PPh_3)_2$, NEt_3 (4 equiv), MeOH (100 equiv)	0	46

Scheme 7



Scheme 8

> 5-*exo*- or 6-*exo*-Alkyne carbopalladation
> 5-*exo*-Alkyne acypalladation
> Acylpalladium trapping with MeOH
> Intermolecular carbopalladation or acylpalladation

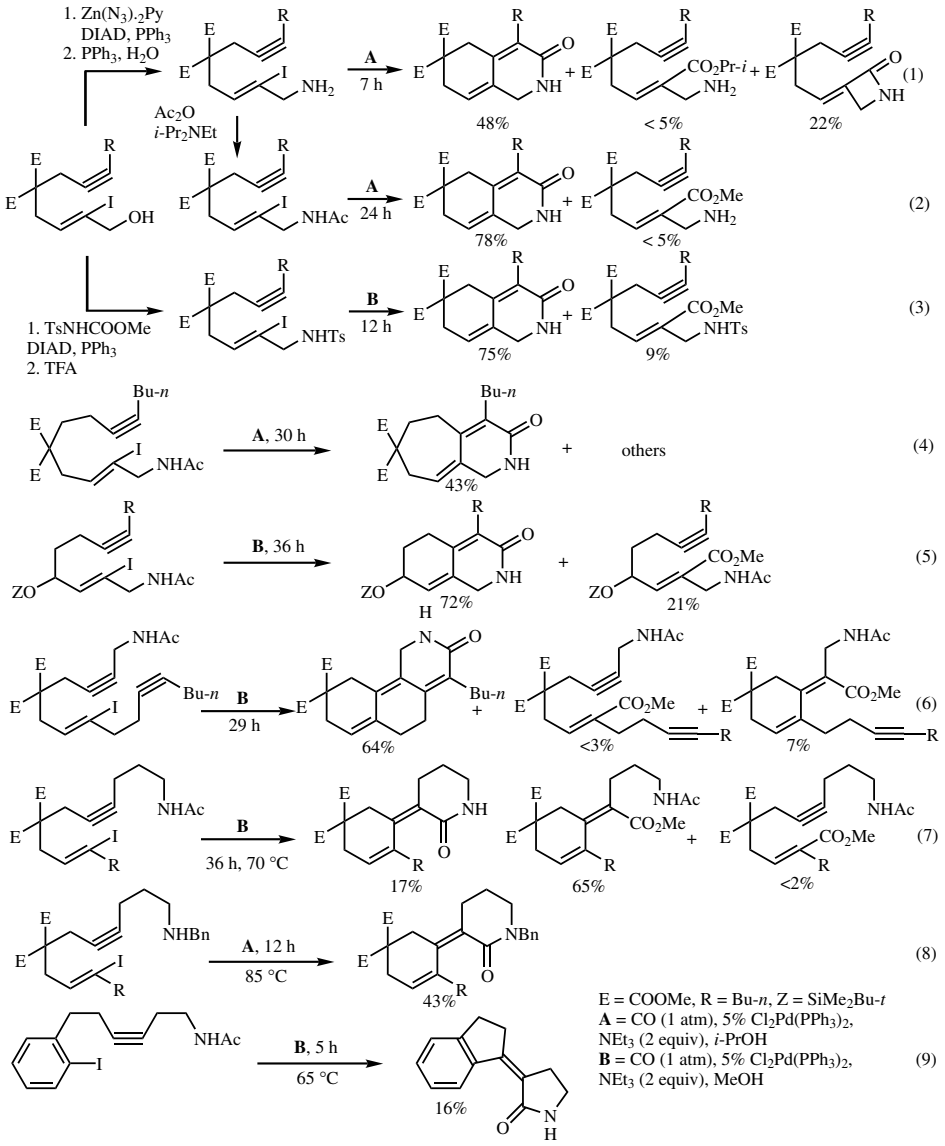
Scheme 9 CO insertion (and five- and six-membered lactone formation).

B.ii. Termination by Carbonylative Lactamization

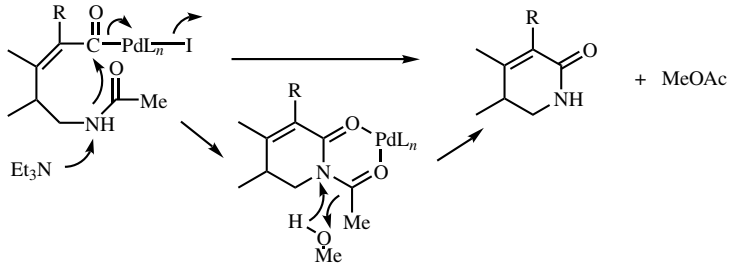
As might be expected, cyclic carbopalladation of alkynes can also be terminated by carbonylative lactamization. Some representative experimental results[10],[11] are summarized in **Scheme 10**, and the following features are noteworthy.

1. Free amines, carboxamides, and sulfonamides have all been shown to participate in the tandem process. However, free amines generally lead to less satisfactory results than amides.[10],[11] Catalyst poisoning may be suspected.

2. The reaction of acetamides to give lactams proceeds with deacetylation, even though formation of nonlactam by-products does not involve deacetylation.[10],[11] Although this point needs to be clarified further, it is tempting to consider a chelation-promoted lactamization involving deacetylation shown in **Scheme 11**.



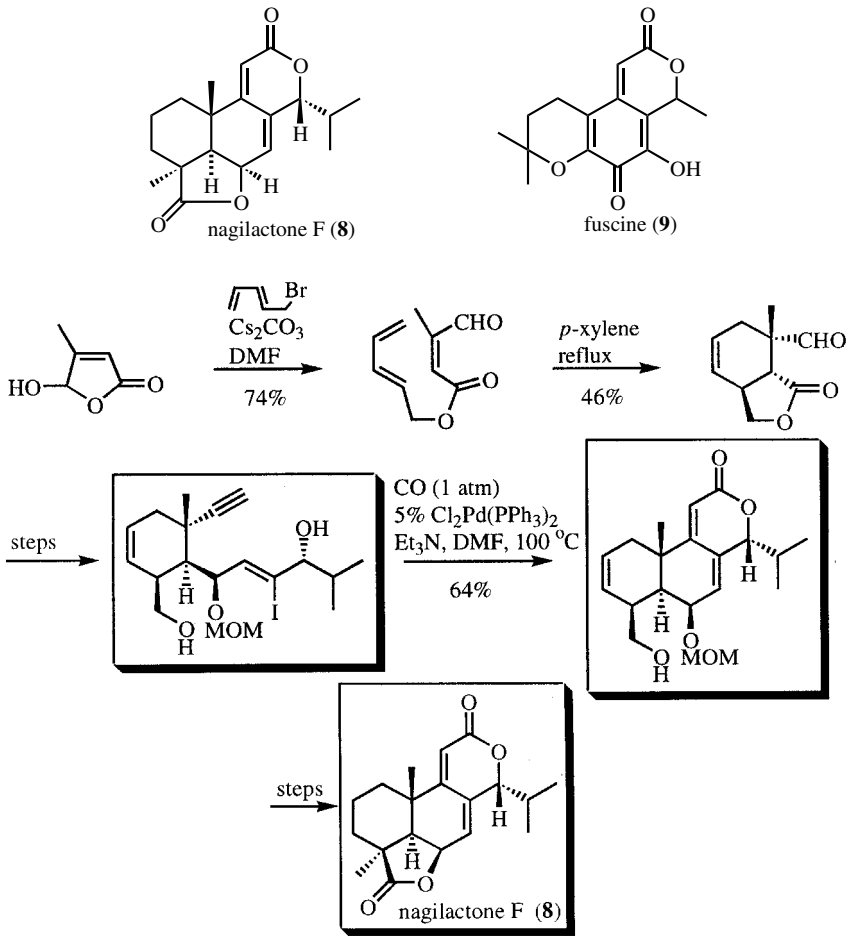
Scheme 10



Scheme 11

B.iii. Applications to Natural Products Synthesis

Although the possibility of synthesizing natural products using the cyclic carbopalladation–carbonylative lactonization process has been suggested,[3] there has as yet been no report on this topic. However, progress made toward the synthesis of nagilactone F (**8**)[12] and fuscin (**9**)[13] are very promising,[14] and the synthesis of other natural products using this methodology as a key component appears very likely. Some key steps in the synthesis of nagilactone F are shown in **Scheme 12**.



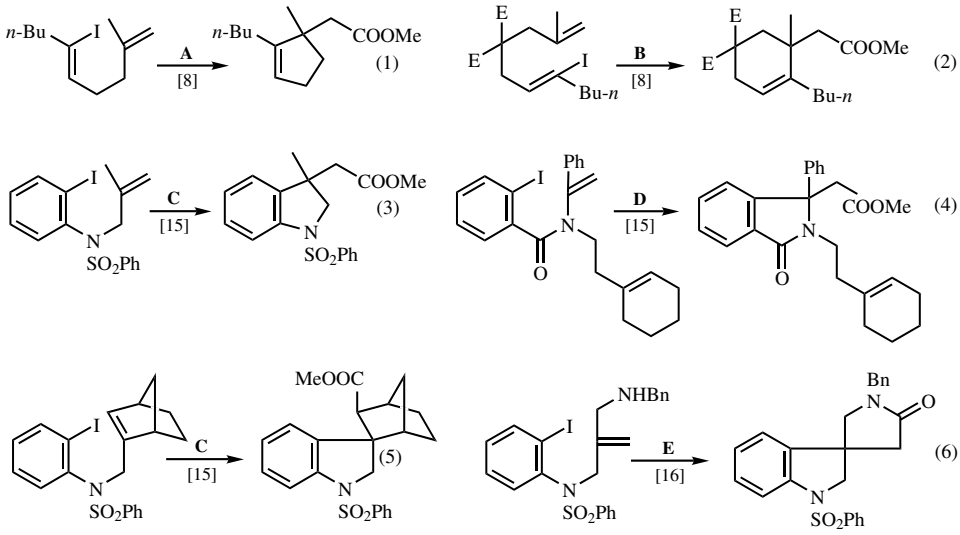
Scheme 12

C. Pd-CATALYZED TANDEM AND CASCADE CARBOPALLADATION OF ALKENES TERMINATED BY CARBONYLATION

C.i. Termination by Carbonylative Esterification, Lactonization, Amidation, and Lactamization

1,1-Disubstituted alkenes and other alkenes that can undergo "living" carbopalladation (e.g., norbornene) can participate in the carbopalladation–carbonylative termination

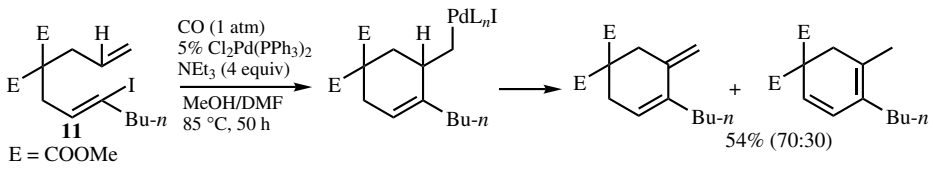
tandem process discussed in the previous section. Some representative examples are shown in **Scheme 13**.[8],[15],[16] Note that the *syn*-carbopalladation product derived from norbornene does not have any H atom β and *syn* to Pd. The use of 1 atm of CO and boiling MeOH as the solvent favors the desired tandem process.



A = CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (4 equiv), MeOH/DMF, 100 °C, 4 h.
B = CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (4 equiv), MeOH/DMF/H_2O (1/2/0.1), 85 °C, 1 h.
C = CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, TlOAc(3 equiv), MeOH, 65 °C.
D = CO (20 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (4 equiv), MeOH, 106 °C, 4 h.
E = CO (1 atm), 10% $Pd(OAc)_2$, 20% PPh_3, Tl(OAc) (1.2 equiv), MeCN, 80 °C.

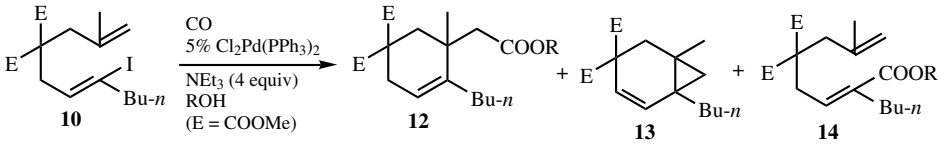
Scheme 13

A detailed investigation with **10** summarized in **Table 2**[8] indicates that premature esterification and cyclopropanation (Type III C—Pd process in **Scheme 2**) can occur as dominant side reactions but that, under the optimized conditions (entry 7), both can be suppressed to insignificant levels ($\leq$3%). It is also important to note that, in marked contrast with the cyclic acylpalladation (Type II Ac—Pd) discussed in **Sect. VI.4.1.1**, monosubstituted alkenes that can readily participate in dehydropalladation (e.g., 11) cannot undergo the cyclic carbopalladation–carbonylative esterification tandem process (Type II C–Pd) since they merely undergo the cyclic Heck reaction (Type I C—Pd process in **Scheme 14**).[8] The contrasting behavior mentioned above may be attributable to a chelation effect exerted by the carbonyl group in the acylpalladation (**Scheme 15**), which is lacking in the carbopalladation shown in **Scheme 14**.

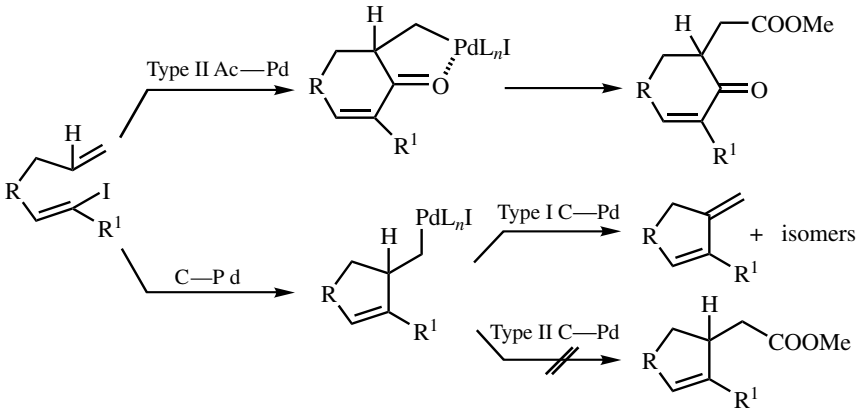


Scheme 14

TABLE 2. Pd-Catalyzed Reaction of Iododiene 10 with CO and Alcohols

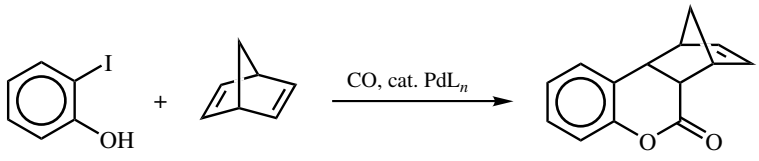


Entry	ROH and Solvent	CO (atm)	Temperature (°C)	Time (h)	Product Yield (%) 12	13	14
1	MeOH	1	65	40	18	<1	82
2	MeOH	1	Reflux	30	52	23	22
3	EtOH	1	Reflux	24	30	2	59
4	*i*-PrOH	1	85	24	53	3	27
5	*i*-PrOH	1	Reflux	24	64	10	6
6	MeOH/DMF	1	85	1	63		<3
7	MeOH/DMF/H_2O (1:2:0.1)	1	85	1	81	3	<3
8	MeCN	0	Reflux	48	—	75	—



Scheme 15

With specially structured alkenes, such as norbornadiene, it is feasible to observe the intermolecular version of the carbopalladation–carbonylative lactonization tandem process, as shown in **Scheme 16**.[17] This also represents a rare example in which the termination step involves lactonization. Although a single example of termination by lactamization is shown in Eq. 6 of **Scheme 13**, there does not appear to be any example in which termination involves intermolecular amidation.



Scheme 16

C.ii. Diastereoselective Cyclic Carbopalladation of 1,1-Disubstituted Alkenes Terminated by Carbonylative Esterification

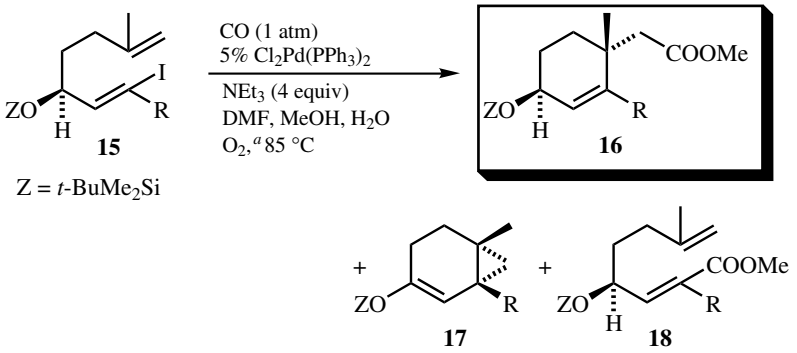
Under optimized conditions, iododiene **15** undergoes a highly diastereoselective Type II C–Pd process, as shown in **Table 3**.[18] Formation of both cyclopropanation and premature esterification products (i.e., **17** and **18**) can be kept at the ≤5% levels.

The diastereoselectivity of the Type II C—Pd process significantly depends on the nature of the chiral group in the substrates, as exemplified by the results shown in **Scheme 17**.[18] The results can be explained by assuming (i) a coplanar arrangement of the C—Pd and the participating C═C bond and (ii) a boat-like transition state for the transition state of the *exo*-mode cyclic carbopalladation.[19] The overall outcome may be determined by both steric and electronic (especially chelation) effects. Steric effects favor placement of substituents in pseudoequatorial positions, whereas chelation effects can favor pseudoaxial arrangements.

As indicated by entry 3 in **Table 3**, the diastereoselectivity of the Type II C—Pd process can be influenced by other achiral groups as well. It is also influenced by the reaction conditions, as exemplified by the results shown in **Scheme 18**, in which the substrate is the same as in entry 3 of **Table 3**.

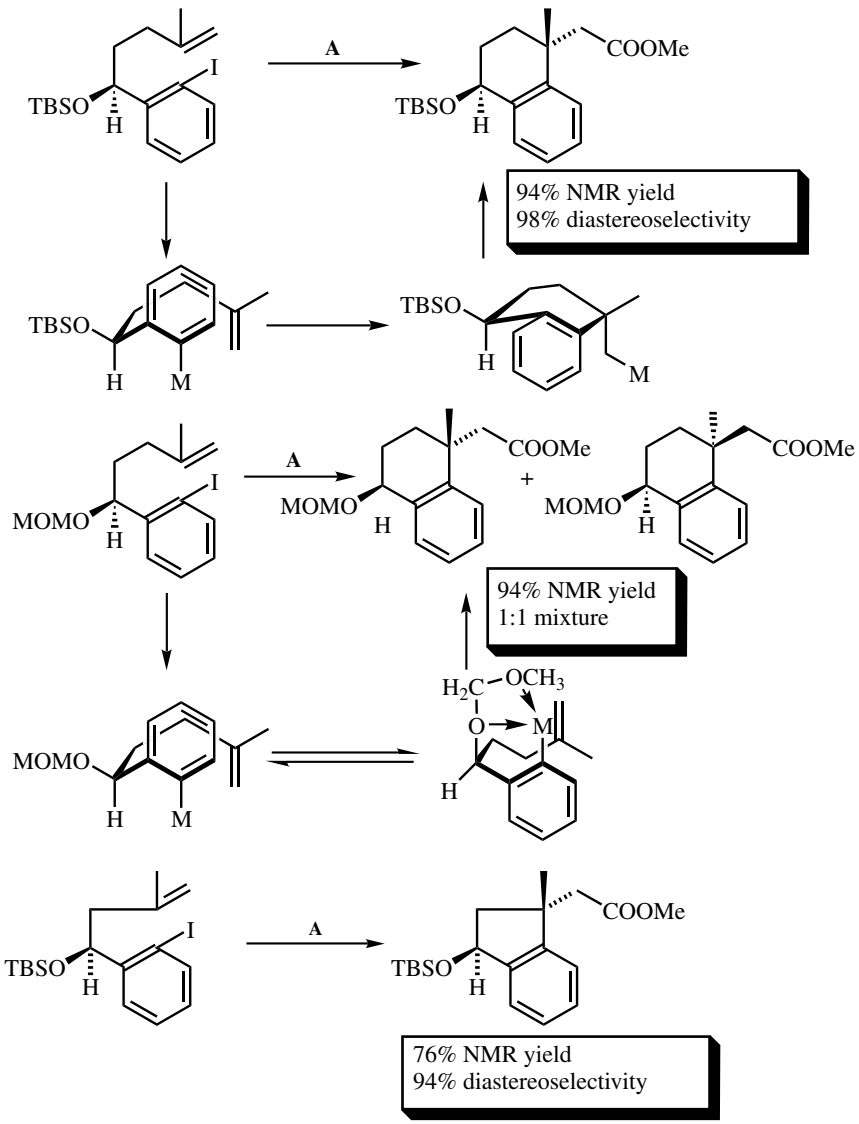
Although little effort has been made to apply the diastereoselctive process discussed above to the synthesis of natural products, the feasibility of an asymmetric synthesis of the Colvin–Raphael lactone (**19**)[20] used as a key intermediate in the synthesis of natural products, such as trichodermin and tricholdiene, has been demonstrated as shown in **Scheme 19**.[18]

TABLE 3. Pd-Catalyzed Diasteroselective Cyclic Carbopalladation–Carbonylation Termination of Iododiene 15 with CO and Methanol



		Product Yield (diastereoselectivity) (%)		
Entry	R	**16**[b]	**17**	**18**
1	H	91 (94)	<2	<3
2	*n*-Bu	84 (95)	<2	5
3	—$(CH_2)_2CH{=}CH_2$	65 (85)	<2	<2
4	—$(CH_2)_2CH{=}CMe_2$	80 (93)	<2	<2

[a] After mixing all compounds, the reaction mixture was exposed to air for 20–30 seconds, flushed again with CO, and stirred until the mixture turned black over 0.5–1 h.
[b] The number in parentheses indicates diastereoselectivity.



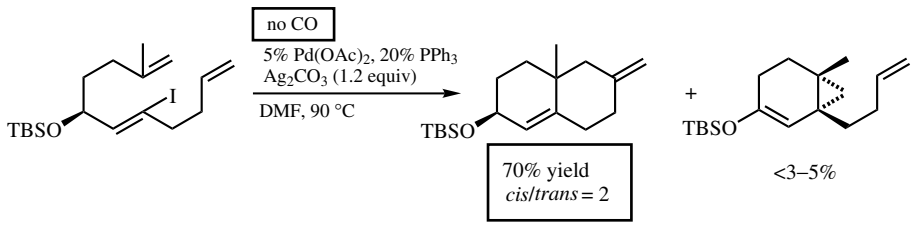
A = CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, O_2, DMF, MeOH, H_2O, 85 °C
M = PdL_nI

Scheme 17

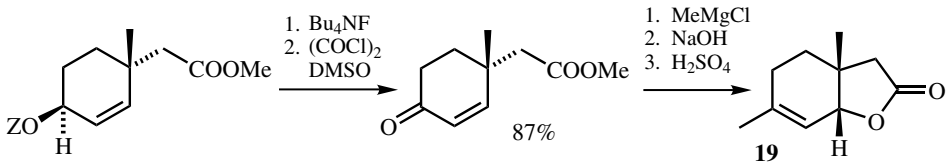
Some other Type II C—Pd processes, such as those shown in **Scheme 20**, have been reported to give single diastereoisomers.[15],[21] As yet, there does not appear to be any report on an enantioselective Type II C—Pd process.

C.iii. Termination by Other Carbonylative Processes

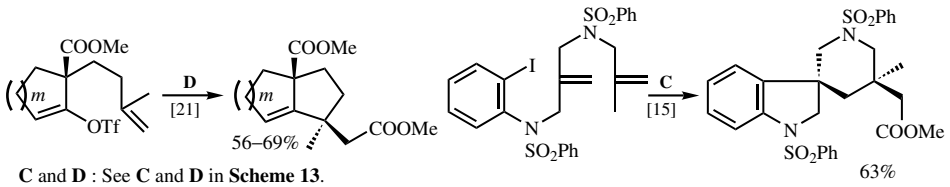
Cyclic carbopalladation processes can also be terminated by various other carbonylative derivatization reactions for recycling Pd as a catalyst. Use of organometals of relatively low



Scheme 18



Scheme 19

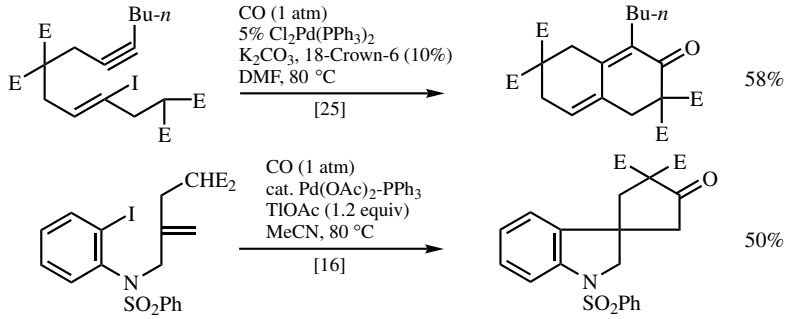


C and **D** : See **C** and **D** in **Scheme 13**.

Scheme 20

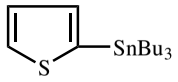
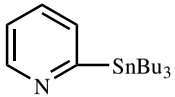
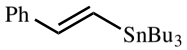
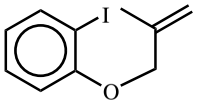
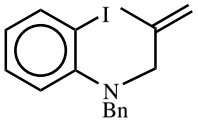
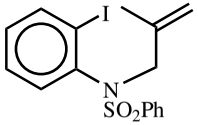
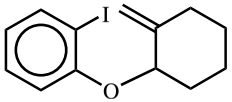
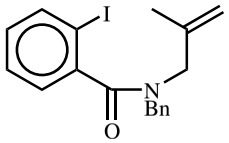
intrinsic reactivity permits the formation of ketones via C—C bond formation.[22] More reactive organometals, such as organozincs, may preferentially participate in premature ketonization or noncarbonylative cross-coupling[23] before carbopalladation and may therefore be less well suited for this purpose. Closely related to the C—C bond formation mentioned above is the C—H bond formation producing aldehydes.[24] Diphenylmethylsilane has been used successfully as a hydride source, whereas sodium formate leads to noncarbonylative hydrogenolysis after cyclic carbopalladation.[24] Some representative examples of the synthesis of ketones and aldehydes containing heterocycles are summarized in **Table 4**.[22],[24]

Trapping of acylpalladium intermediates can also be achieved with enolates (**Sect. VI.2.3**), as exemplified by the results shown in **Scheme 21**.[16],[25]



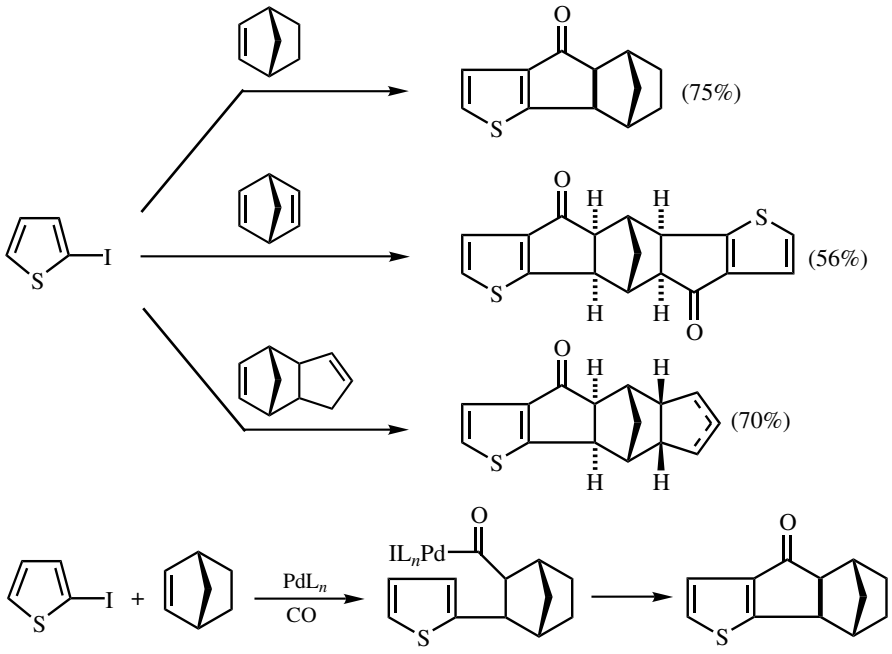
Scheme 21

TABLE 4. Pd-Catalyzed Synthesis of Ketones and Aldehydes Via Cyclic Carbopalladation–Carbonylative Trapping with Carbanion and Hydride Sources [a]

	Trapping Agent[b] (Product Yield, %)				
Aryl Iodide	$NaBPh_4$				Ph_2MeSiH
	80	88	83	61	61
	—	87	71	78	54
	82	—	—	—	61
	84	—	—	—	—
	60	—	—	—	54

[a] CO (1 atm), 10 mol % $Pd(OAc)_2$, 20 mol % PPh_3, Et_4NCl, toluene, 110 °C.
[b] See Ref. [22] for ketone syntheses and Ref. [24] for aldehyde synthesis.

As in the cases of termination by lactonization and lactamization, some specially structured alkenes, such as norbornene and related alkenes, can participate in intermolecular carbopalladation–carbonylative ketonization tandem processes. In the reactions shown in **Scheme 22**, the acylpalladium intermediates undergo intramolecular acylpalladation with arenes to provide ketones.[26]



Scheme 22

D. SUMMARY

1. Cyclic carbopalladation of alkynes and 1,1-disubstituted alkenes that produces "living" alkenyl- and alkylpalladiums containing common rings, mostly five- and six-membered, can be terminated for recycling Pd catalysts via carbonylative derivatization leading to the formation of C—O, C—N, C—C, and C—H bonds.

2. Although some competition may be expected for the cases where cyclic carbopalladation producing five-membered rings and cyclic acylpalladation producing six-membered ketones are possible, the latter process can be suppressed through the use of 1 atm of CO. Cyclic carbopalladation producing six- or seven-membered rings does not appear to be in competition with seven- or eight-membered ketone formation, respectively. On the other hand, cyclic carbopalladation producing four-membered rings cannot compete with acylpalladation producing five-membered ketones.

3. Alkenes that can provide hydrogen atoms β and *syn* to Pd, such as monosubstituted alkenes, may not be used in the cyclic carbopalladation–carbonylative trapping process, as the reaction is dominated by the cyclic Heck reaction. The difference between this process and the Type II Ac—Pd process (**Sect. VI.4.1.1**) may be attributable to a chelation effect in the latter preventing otherwise competitive dehydropalladation.

4. Two other possible side reactions, that is, premature trapping of organopalladium intermediates before cyclic carbopalladation and cyclopropanation of homoallylic organopalladium intermediates, must be avoided. The results presented in this section indicate that, in many cases, suitable conditions may be found to achieve this goal.

5. Although there has been no report on the application of the cyclic carbopalladation–carbonylative termination process of alkynes to the natural product synthesis, very promising results have been obtained.

6. With 1,1-disubstituted alkenes, diastereoselective and/or enantioselective cyclic carbopalladation can, in principle, be achieved. Whereas the latter has not yet been demonstrated for the cyclic carbopalladation–carbonylative termination processes, its diastereoselective version promises to provide an attractive method for the synthesis of chiral natural products.

7. Although attempts to use allenes in the cyclic carbopalladation–carbonylative termination process have not been successful,[27] various types of dienes, oligoenes, enynes, and other π-compounds may prove to be worth exploring.

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