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Benzene ring assembly promoted by a camphor derived palladium complex

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Abstract

Trans-[$PdCl_2L_2$] (**1**, L = 3-$NNMe_2C_{10}H_{14}O$), under mild reaction conditions, acts as a catalyst for the cyclic trimerization of alkynes. The best performance is achieved for the reaction with PhC≡CMe that affords 1,3,5-trimethyl-2,4,6-triphenyl benzene with high activity and selectivity (ca. 99%). As a general trend the catalytic activity is higher for internal (PhC≡CMe, PhC≡CPh) than for terminal alkynes (HC≡CPh, HC≡C^{t}Bu, HC≡CCO_2Me). Under more drastic experimental conditions the reaction of **1** with PhC≡CPh yields *trans*-[$PdCl_2$(PhC≡CPh)$_2$] and no catalytic activity is observed. The molecular structure of 1,3,5-trimethyl-2,4,6-triphenyl benzene was confirmed by X-ray diffraction analysis. The molecules were characterized by ^{1}H- and ^{13}C-NMR spectroscopies, FAB-MS and, in some cases, elemental analyses.

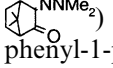
Keywords: Catalysis; Cyclotrimerization; Palladium complexes; Camphorimine; C–C coupling; Alkynes

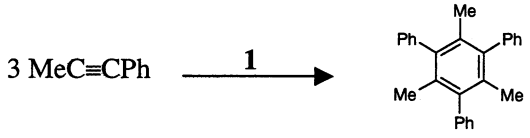
1. Introduction

The relevance of cyclo oligomerization processes to organic syntheses encourages the search for efficient catalysts and reinforces the interest in the study of the mechanisms of alkyne trimerization in order to get higher chemo- and regio-selectivity or to obtain multifunctional aromatic compounds. Modern applications of the Reppe's alkyne cyclo-oligomerization [1] include the syntheses of tetra-substituted benzenes by sequential cycloaddition [2] or the selective synthesis of fulvenes [3].

The ability of some Pd(II) complexes to promote the activation of alkynes towards cyclo-trimerization [4–8] is known for more than 50 years, although the efficiency of most of the processes is not very high, from the point of view of practical applications. During our research we verified that platinum and palladium camphor derived species are efficient in promoting C–C coupling processes that lead to ring expansion [9]. We now wish to report the catalytic promotion of cyclic trimerization of terminal alkynes mediated by camphorimine palladium complexes.

2. Results and discussion

Under mild conditions (room temperature and relatively short reaction times) *trans*-[$PdCl_2L_2$] (L = ) (**1**) catalyses the cyclic trimerization of 1-phenyl-1-propyne (MeC≡CPh) affording 1,3,5-trimethyl-2,4,6-triphenyl benzene (**i**), Eq. (1)



(1)

(i)

The formulation of **i** was based on data obtained by ^{1}H-NMR, ^{13}C-NMR, DEPT and FAB Mass Spectrometry. The structure was confirmed by X-ray diffraction analysis, although the low number of observed reflections precluded a final *R* value lower than 0.079. The asymmetric unit plus the twofold axis generated mole-

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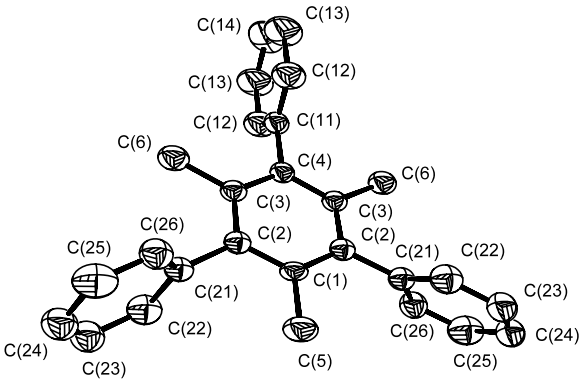

Fig. 1. X-ray structure of 1,3,5-trimethyl-2,4,6-triphenyl benzene (**i**) showing the atom labelling scheme.

cule is depicted in Fig. 1. The X-ray structure shows that the phenyl groups occupy perpendicular positions to the plane of the benzene ring and are approximately parallel to each other.

The selected bond distances and angles are displayed on Table 1.

In order to study the interaction of 1-phenyl-1-propyne with **1** the reaction was followed by ^{1}H-NMR. Soon after the addition of the alkyne to the $CDCl_3$ solution of **1**, new signals were detected at δ values (0.95, 0.99 and 1.09) that are slightly different from those of the original methyl groups (0.97, 1.03 and 1.10) of the camphor skeleton. Concomitantly, a new signal (δ 3.03) appeared in the region attributed to the methyl signal of the hydrazone group on complex **1** (δ 3.25). However, on a preparative scale, the only complex recovered is the starting complex **1**. The reaction is complete within 2 h.

Table 1
Selected bond lengths and angles for compound 1,3,5-trimethyl-2,4,6-triphenyl benzene (**i**)

Bond lengths (Å)		Bond angles (°)	
C1–C2	1.388(7)	C2–C1–C5	119.3(6)
C1–C5	1.512(11)	C2–C3–C4	120.6(5)
C3–C2	1.399(8)	C2–C3–C6	118.6(5)
C3–C4	1.389(7)	C4–C3–C6	120.8(5)
C3–C6	1.521(9)	C2–C21–C22	120.7(6)
C21–C2	1.496(9)	C2–C21–C26	120.8(6)
C21–C22	1.378(9)	C22–C21–C26	118.5(6)
C21–C26	1.372(10)	C1–C2–C3	118.9(5)
C4–C11	1.487(11)	C1–C2–C21	119.9(5)
C11–C12	1.366(8)	C3–C2–C21	121.2(5)
C22–C23	1.380(10)	C3–C4–C11	120.2(6)
C26–C25	1.379(10)	C4–C11–C12	120.9(6)
C12–C13	1.391(10)	C21–C22–C23	119.9(6)
C23–C24	1.367(12)	C21–C26–C25	120.6(7)
C25–C24	1.361(10)	C11–C12–C13	121.8(7)
C13–C14	1.378(11)	C22–C23–C24	121.6(7)
C6–H6A	0.960(9)	C26–C25–C24	121.3(6)
C6–H6B	0.960(8)	C23–C24–C25	118.1(7)
C6–H6C	0.960(8)	C12–C13–C14	118.9(7)
C22–H22	0.930(11)		
C26–H26	0.930(9)		
C12–H12	0.930(10)		
C5–H5A	0.960(4)		
C5–H5B	0.960(4)		
C5–H5C	0.960(4)		
C23–H23	0.930(10)		
C25–H25	0.930(11)		
C24–H24	0.930(10)		
C13–H13	0.930(13)		
C14–H14	0.94(4)		

The catalytic activity (A) of complex **1**, *per* hour (2 h were considered as the average effective reaction time), towards the cyclic trimerization of 1-phenyl-1-propyne was tentatively calculated [1.1×10^4 gT/(mol [Pd] × [(C≡C)] × h)] on the basis of the mass (g) of cyclic trimer species (gT) *per* mol of palladium *per* molar concentration of alkyne. Since the catalytic experimental conditions were not optimized this is a promising value. In addition, the reaction is very selective, since, just traces ($< 1\%$) of other organic products were detected.

The reactions of **1** with other internal alkynes [e.g. diphenyl acetylene (PhC≡CPh), dimethyl acetylenedicarboxylate ($MeCO_2C{\equiv}CCO_2Me$)] or terminal [phenyl acetylene (PhC≡CH), methyl propiolate ($MeCO_2C{\equiv}$CH), 3,3-dimethyl-1-butyne (^{t}BuC≡CH)] followed by ^{1}H-NMR display a pattern similar to that mentioned for 1-phenyl-1-propyne. However, the isolated yield and selectivity are dependent on the alkyne.

The reaction of complex **1** with diphenyl acetylene affords hexaphenyl benzene (**ii**) as the main product, although other species also form. The yield (46%) calculated relative to the alkyne is lower than that obtained in the reaction with 1-phenyl-1-propyne (74%), but the catalytic activity is similar [1.1×10^4 gT/(mol [Pd] × [(C≡C)] × h)].

The molecular structure of **ii** (see Fig. 2) obtained by X-ray analysis is in full agreement with that previously reported [10,11].

Hydrolysis, possibly due to traces of moisture in the alkyne, conceivably accounts for the formation of 1,3,5-trihydroxy-2,4,6-triphenyl benzene (**iii**) as a by-product. The high melting point (283 °C) suggests extended hydrogen bonding through the unit cell.

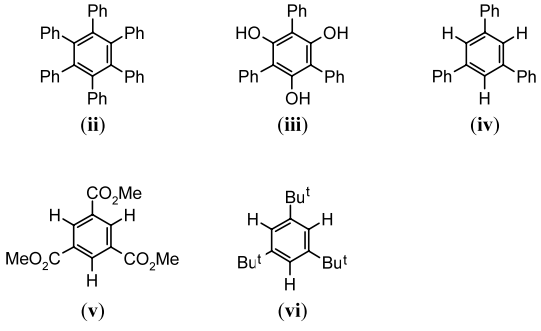

Fig. 2. Trimerization products.

As with 1-phenyl-1-propyn, compound **1** is the only complex recovered from the reaction at room temperature. However, under reflux conditions, the replacement of the camphor derived ligand by the alkyne affords a dark red compound that is formulated as $[PdCl_2(PhC{\equiv}CPh)_2]$ (**2**) based on elemental microanalyses, conductivity measurements and NMR spectroscopic data (see Section 3). Under these experimental conditions, just traces of the cyclic trimer **ii** were detected and no other organic products were obtained.

In CH_2Cl_2, complex **2** displays by cyclic voltammetry a reversible reduction wave ($E^{red}_{1/2} = -0.28$ V) but no oxidation process was found within the available potential range, in contrast with the behaviour reported for complex **1** [13] which exhibits irreversible cathodic and anodic processes.

The reaction of complex **1** with dimethyl acetylenedicarboxylate was followed by ^{1}H-NMR which reveals a pattern comparable to that observed for the aromatic alkynes. However, no cyclic or other organic products were detected. This result was unexpected for two reasons. First, there is evidence by NMR for the interaction of the alkyne with the metal centre; second, the reaction of dimethyl acetylenedicarboxylate with $[PdCl_2(NCPh)_2]$ proceeds towards cyclic trimerization, although through a different intermediate [4]. Hence, the catalytic activity of our system is strongly dependent on the characteristics of the alkyne.

Terminal alkynes such as PhC≡CH, $MeCO_2C{\equiv}CH$ or ^{t}BuC≡CH react with complex **1** affording the corresponding cyclic trimer, species **iv**, **v** or **vi**, that were formulated on the basis of FAB-MS and ^{1}H- or ^{13}C-NMR spectroscopies. The ^{1}H- or ^{13}C-NMR spectra were not fully conclusive in the case of **iv** and **v**. As expected, in compound **iv** the resonances appear as a complex multiplet in the aromatic region from which a few signals emerge but no clear structure could be ascertained. By FAB-MS, compound **iv** displays an intense signal (m/z (%) = 306 (100)) that is attributed to the molecular ion of the cyclic trimer. The fragmentation pattern suits this formulation. The isolated yield for compound **iv** is low (20%, relative to the alkyne) and the catalytic activity [$(3.1 \times 10^3$ gT/(mol [Pd] × [(C≡C)] × h)] is one order of magnitude lower than that measured for the internal alkynes. The selectivity is also lower and species with higher molecular weight such as (m/z (%) = 408 (2)), possibly a tetrameric species, are detected by FAB-MS.

In the reaction of $MeCO_2C{\equiv}CH$ with **1** at least two products are formed. One is whitish, poorly soluble in common solvents and formulated as the cyclic trimer **v** based mostly on FAB-MS (m/z (%) = 252 (26)). The NMR data mentioned in Section 3 were obtained in solution during the reaction, previously to precipitation. The activity was calculated as 1.8×10^3 gT/(mol [Pd] × [(C≡C)]) × h). The other species is a dark brownish-grey product, highly soluble in all common solvents, that appears to be paramagnetic in view of the ^{1}H-NMR spectrum. In this case, the FAB-MS data were inconclusive.

The yellow oily species **vi** obtained from reaction of ^{t}BuC≡CH with complex **1** was characterized by ^{1}H-NMR and ^{13}C-NMR as the cyclic trimer. The attribution of the ^{13}C-NMR chemical shifts was confirmed by DEPT. In this case, the yield and catalytic activity could not be accurately calculated. However, the selectivity is high i.e. comparable with that observed in the case of **i**.

The benzene ring assembly catalysed by palladium(II) is not unique. More than 20 years ago it was reported that $PdCl_2$ or $[PdCl_2(NCPh)_2]$ could promote the catalytic cyclization of alkynes [4,12].

The step forward provided by this research is that, in contrast with the former systems, complex **1** provides good catalytic activity and high selectivity (ca. 100%, in some cases) under mild conditions. The turnover number for **i** (TON = 7.4) is not very high, but under the experimental conditions used (30-fold molar excess of alkyne) the maximum value that could be reached is 10. Moreover, TON is calculated on the basis of the weight of the isolated product and would have a large error in this present case due to the small quantities used in the reactions.

One favourable characteristic of this system for scaling up is that in the solvent, CH_2Cl_2, the aryl derived trimers, separate out thus making their separation easy.

In order to try to ascertain the generality of the alkyne cyclization process using palladium camphor-type derived complexes we studied the reaction of *cis*-$[PdCl_2L'_2]$ (L′ = ) (**3**) with MeC≡CPh and ^{t}BuC≡CH under similar experimental conditions to those used for complex **1**. In the case of 1-phenyl-1-propyne no trimerization was detected. However, in the reaction of **3** with 3,3-dimethyl-1-butyne there is evidence for the formation of an organic product that was tentatively characterized by FAB-MS ($m/z = 789$ (< 1)) as an oligomeric species. The NMR data, although not fully conclusive, support the formulation. In this reaction, traces of the oily cyclic trimer **vi** were also detected.

The linear oligomerization of 3,3-dimethyl-1-butyne could in-principle involve the formation of an intermediate of the type $\{Pd{-}C(^t Bu){=}CHCH{=}C(^t Bu)Cl\}$ formerly proposed [4] for the reaction of $HC{\equiv}C^t Bu$ with $[PdCl_2(NCPh)_2]$.

The substantial differences observed for the apparently similar complexes **1** and **3** for benzene ring assembly possibly result from both geometric and electronic factors. In **1** the *trans* geometry and the lower dimension of L compared to L′ in **3** can impose lower steric constraints. Moreover, a previously reported

cyclic voltammetry study [13] revealed that the electronic properties of the camphorimine and camphorsulphonimine in complexes **1** and **3**, respectively, are considerably different, i.e., camphorimine is a weak net electron donor whereas camphorsulphonimine is a slightly π-electron withdrawing ligand.

Apart from the different reactivities of complexes **1** and **3**, the specific characteristics of the alkyne also play a role in the activity and selectivity towards cyclic trimerization. In terms of activity, internal alkynes provide better results than terminal ones and aryl groups apparently favour the process. The relevance of the presence of an aryl group at the alkyne for the promotion of alkyne C–C insertion was formerly stressed [14] in the case of a ruthenium azavinylidene trinuclear system. Furthermore, in that system the M–N bound ligand was not completely innocent [14], allowing the stabilization of the system. That could also be the case, in our system, although the detailed mechanism of cyclization of alkynes has not been elucidated.

3. Experimental

All the manipulations were carried out under dinitrogen atmosphere using standard Schlenk glassware techniques. The solvents were dried before use by standard methods. Palladium(II) chloride was purchased from Aldrich and the camphor derived complexes were prepared by published methods [13].

The compounds were dissolved in $CDCl_3$ and the NMR spectra were recorded on a Varian UNITY 300 spectrometer. FAB-Mass spectra were measured with Varian CH5 (EI mode, 70 eV) and LCQ Finnigan (ESI) instruments using 4-nitrobenzyl alcohol as matrix. Conductivity measurements were made using a Schott Konduktometer CG 855 provided with a Cell Schott Gerate LF 1100. Melting and sublimation points were measured using a Leica Galen III Microscope.

3.1. X-ray crystallographic analysis

X-ray data were collected from white crystals mounted in thin-walled glass capillaries at room temperature on Enraf–Nonius MACH3 diffractometer with graphite-monochromatized Mo–K_α radiation, using an $\omega-2\theta$ scan mode. The data and refinement parameters are displayed in Table 2. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections. The crystal was found to crystallise in the monoclinic $I2_1/a$ space group with $a = 10.557(5)$, $b = 14.882(2)$, $c = 12.818$ Å, $\beta = 99.80(2)^\circ$, $V = 1984(10)$ Å^3, $Z = 4$, $D_c = 1.17$ g cm^{-3}, $\mu(\text{Mo–K}_\alpha) = 33$ cm^{-1}. The data were corrected [15] for Lorentz-polarization effects and linear decay. The structure was solved by direct methods using SHELXS 86 [16], and was found to have a binary axis bisecting the molecule and passing through one methyl group and two carbon atoms of the central six membered ring. The atomic positions and thermal parameters were refined by least-squares on F^2 using SHELXL 93 [17], with all the non-hydrogen atoms refining with anisotropic thermal motion parameters. The hydrogen atoms were included in calculated positions, constrained to ride at fixed distances of the parent carbon atom. Atomic scattering factors and anomalous dispersion terms were as in SHELXL 93 [17]. The ORTEP drawings were made with ORTEX [18].

Table 2
Crystallographic data for compound 1,3,5-trimethyl-2,4,6-triphenyl benzene (**i**)

Empirical formula	$C_{27}H_{24}$
Formula weight	348.46
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$I2_1/a$
Unit cell dimensions	
a (Å)	10.557(5)
b (Å)	14.882(2)
c (Å)	12.818(2)
α (°)	90.00
β (°)	99.80
γ (°)	90.00
Volume (Å^3)	1984.4(10)
Z	4
D_{calc} (g cm^{-3})	1.166
Absorption coefficient (mm^{-1})	0.066
$F(0\,0\,0)$	744
Crystal size (mm^3)	$0.25 \times 0.25 \times 0.40$
θ Range for data collection (°)	25
Index ranges	$-12 \le h \le 0$, $0 \le k \le 17$, $-15 \le l \le 15$
Reflections collected/unique	1750
Refinement method	Full-matrix least-squares on F^2
Data/restraint/parameters	1291/1/127
Final R (observed)	0.0788

3.2. Catalytic reactions

As a typical procedure for the catalytic experiments, the reaction of complex **1** with 1-phenyl-1-propyne is indicated as follows: PhC≡CCH$_3$ (0.65 cm^3, 5.2 mmol) was added to a solution of complex **1** (0.10 g, 0.17 mmol) in CH_2Cl_2 (44 cm^3) and stirred for ca. 20 h, although the process is complete within 2 h (as verified by NMR). The solvent was then evaporated approximately to 1/3 to afford a yellowish abundant precipitate that flocculates from the solution. Upon filtration and washing with Et_2O (2×5 cm^3), ((**i**) 0.45 g, 1.29 mmol; 74% yield relatively to the alkyne) a white precipitate is obtained. ^{1}H-NMR: δ 7.47–6.95 (m, 15H, C_6H_5), 2.04 (s, 3H, CH_3), 1,72 (s, 6H, CH_3). ^{13}C-NMR: δ 142.2,

139.8, 133.2 (s, quaternary), 130.3, 129.4, 128.5, 127.3, 126.5, 125.7 (s, C_6H_5), 19.4 (s, CH_3). FAB-MS: m/z (%) = 348 (62). Sublimation point: 192 °C. The sharp and weak (1600 cm^{-1}) and the sharp and strong (702 cm^{-1}) IR bands are characteristics of the product.

From the mother-liquor traces of the starting complex and of other organic products (< 1%) were obtained.

Under similar experimental conditions the main organic product of the reaction of complex **1** with PhC≡CPh is hexaphenyl benzene (**ii** = 46% yield relatively to the alkyne). ^{1}H-NMR: δ 6.82 (s, C_6H_5). ^{13}C-NMR: δ 140.5, 140.2 (s, quaternary), 131.3, 126.4, 125.0 (s, C_6H_5). FAB-MS: m/z (%) = 360 (100). In the process, 1,3,5-trihydroxy-2,4,6-triphenyl benzene (**iii**, 2% yield relatively to the alkyne) also forms (m.p. = 283 °C). ^{1}H-NMR: δ 7.51 (s, 6H, C_6H_5), 7.32 (s, 9H, C_6H_5), 1.54 (s, 3H, OH). ^{13}C-NMR: δ 162.2, 153.7, 101.0 (s, quaternary), 131.4, 129.1 (s, C_6H_5). $C_{24}H_{18}O_3$ (354): Calc. C, 81.4; H, 5.1. Found: C, 81.2; H, 5.2%. FAB-MS: m/z (%) = 354 (5).

Reaction of complex **1** with ca. 30-fold molar excess of HC≡CPh affords 1,3,5-triphenyl benzene (**iv**, 20% yield relatively to the alkyne). ^{1}H-NMR: δ 7.72–7.16 (m, 18H, CH, $C_6H_3R + C_6H_5$). ^{13}C-NMR: δ 129.7–125.6 (m, CH, $C_6H_3R + C_6H_5$). FAB-MS: m/z (%) = 306 (100). In the same reaction conditions, HC≡CCO_2Me affords 1,3,5-trimethylcarboxylate benzene (**v**, 21% yield relatively to the alkyne) in addition to a mixture of not characterized species. ^{1}H-NMR: δ 7.31 (s, 3H, C_6H_3R), 3.5–3.4 (s, br, 9H, CH_3CO_2). ^{13}C-NMR: δ 165.1 (s, CO_2Me), 140.8 (s, quaternary), 134.3 (s, CH, C_6H_3R), 52.4 (m, br, OCH_3). The reaction of compound **1** with HC≡C^{t}Bu affords 1,3,5-tri-*tert*-butyl benzene (**vi**) as the sole organic species. FAB-MS: m/z (%) = 252 (29). ^{1}H-NMR: δ 7.28 (s, 3H, C_6H_3R), 1.31 (s, 27H, ^{t}Bu). ^{13}C-NMR: δ 149.8 (s, quaternary), 119.4 (s, CH, C_6H_3R), 34.9 (s, CMe_3), 31.5 (s, CH_3).

The reaction of complex **3** with ^{t}BuC≡CH affords traces of **vi** and oligomeric species, FAB-MS: m/z = 789 (< 1).

3.3. Syntheses of the complexes

[$PdCl_2$(PhC≡CPh)$_2$] (**2**)—Complex **1** (100 mg, 0.17 mmol) reacts with diphenyl acetylene (300 mg, 1.7 mmol) under reflux in CH_2Cl_2 (20 cm^3) for 2 days affording an orange solution that upon evaporation of the solvent to half the volume and addition of Et_2O (3 cm^3) affords **2** (40 mg, 44% yield). Further addition of Et_2O to the solution leads to the precipitation of traces of a mixture of **2** and cyclic trimer. ^{1}H-NMR: δ 7.84 (d, 8.0 Hz, 2H), 7.68 (t, 8.0, 1H), 7.53–7.43 (m, 2H); ^{13}C-NMR δ 167.3, 131.6, 130.7, 129.8, 128.4, 128.3.

$PdCl_2C_{28}H_{20}$. 1/20 ($C_{14}H_{10}$): Calc. C, 63.5; H, 3.8. Found: C, 63.6; H, 4.2%. Conductivity: 2.4 Ω^{-1} cm^2 mol^{-1} (in CH_2Cl_2).

3.4. Crystallographic data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 208927 for compound **i**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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