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Isocyanide insertion across the Pd–C bond of allenyl and propargyl palladium complexes bearing phosphoquinoline as a spectator ligand. Synthesis of a palladium complex bearing a coordinated cyclobutenyl fragment†

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We have studied the insertion of *p*-toluenesulfonylmethyl isocyanide (TosMIC) on selected allenyl and propargyl complexes of palladium bearing diphenylphosphine quinoline as a spectator ligand. The fast process gives different products depending on the tautomer involved in the reaction. Thus, the unsubstituted allenyl species yields an insertion complex with the isocyanide coordinated between the metal and the first allenyl carbon. On the other hand, a mixture of phenyl substituted allenyl and propargyl palladium complexes yields a novel species characterized by a cyclo-butenyl fragment directly coordinated to palladium. The solid state structure of such a complex together with an exhaustive kinetic study of the whole process is reported.

Introduction

The importance of η^1-allenyl or -propargyl palladium(II) tautomers as intermediates in numerous catalytic processes involving cross-[1,2] or hetero cross-coupling[3,4] reactions is well recognized. In these processes, the allenyl or propargyl fragments usually undergo nucleophilic attack,[5] whereas the insertion of small molecules through the metal–carbon bond is more rare since the presence of a triple or double carbon–carbon bond may promote easier pathways.[1d]

We have chosen isocyanides (CNR) as inserting molecules because among the unsaturated molecules they are comparatively less studied (considerably less than the isoelectronic C≡O)[6] although their steric and electronic characteristics can be easily modulated by taking advantage of the nature of the substituent R.[4]

Moreover, we have recently published some studies related to the insertion of isocyanides across the metal–carbon bond in palladium–alkyl, –aryl[7] and –allyl[8] complexes. Therefore, for the sake of completeness, we have tried to extend our investigation also to the insertion of isocyanides across the allenyl and propargyl palladium–carbon bond since to the best of our knowledge only one study on such a topic is available in the literature to date.[9]

Results and discussion

We have taken into consideration the reaction of the fully characterized allenyl and propargyl palladium phosphoquinoline derivatives **1**, **2** and **3** reported in Scheme 1 with *p*-toluenesulfonylmethyl isocyanide (TosMIC). We decided to study these complexes and this isocyanide since (i) the ligand phosphoquinoline imparts a sometimes but not always predictable reactivity to its palladium derivatives,[10] (ii) the different reactivities of the tautomers might be worth investigating and (iii) TosMIC is one of the most reactive species among the commercially available isocyanides.[7]

Complex **1** was obtained by oxidative addition of 3-chloro-1-propyne to the derivative [(DPPQ)Pd(η^2-dmfu)] (DPPQ = 8-(diphenylphosphino)quinoline; dmfu = dimethylfumarate), whereas the reaction of 3-chloro-1-phenyl-propyne with the same Pd(0) derivative yields an almost equimolecular equilibrium mixture of **2** and **3** at RT.[11] We have firstly monitored the reaction of complex **1** with an equimolecular amount of

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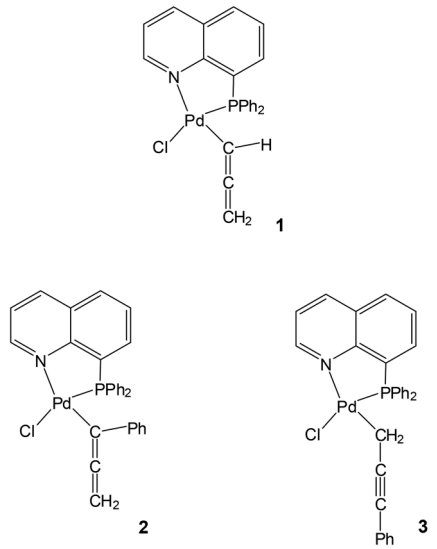
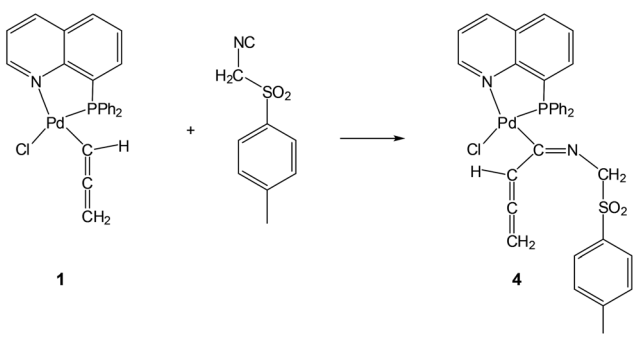


Scheme 1 Allenyl (**1**, **2**) and propargyl (**3**) palladium complexes bearing 8-(diphenylphosphino)quinoline (DPPQ) as a spectator ligand.

TosMIC ([**1**] ≈ [TosMIC] ≈ 1.5×10^{-2} mol dm^{-3} in CD_2Cl_2, RT) by ^{1}H-NMR. The reaction was complete in *ca.* 30 min and the insertion product was stable for several hours (Scheme 2).

From the NMR spectra of the isolated complex **4** (see the NMR spectra in Fig. S1 and S2, ESI†) it is possible to infer its structure. As can be seen in the top insert of Fig. S1† only one isomer is present in solution. Furthermore, in the ^{1}H-NMR and $^{31}P\{^1H\}$-NMR spectra all the signals of the phosphoquinoline fragment can be observed (Fig. S1, ESI†). In particular, the low field resonance of the H^2 quinoline proton (9.90 ppm) clearly indicates that the initial structure of complex **1** with the chloride *cis* to the quinoline nitrogen is maintained.[12] The resonances ascribable to the protons of the organic fragment (C<u>H</u> at 5.72 ppm; C<u>H</u>$_2$ at 4.40 and 4.86 ppm) suggest the maintenance of the allenyl structure in complex **4** (the lower stability of the propargyl tautomer **4′**, *ca.* 2 kcal mol^{-1}, is confirmed by DFT calculations; see DFT Scheme 1 in the ESI†). Finally, the observed multiplicity of the signals related to the C<u>H</u>$_2$S and C=C<u>H</u>$_2$ protons indicates that the steric congestion of the molecule strongly disfavors the fluxionality of the sterically demanding organic fragment. Such a structural hypothesis is also confirmed by $^{13}C\{^1H\}$-NMR (Fig. S2, ESI†). In particular, the signal at 185.2 is ascribable to the –<u>C</u>=N carbon, whereas the characteristic signals of the allenyl group are clearly detected at 77.6 ppm (=<u>C</u>H$_2$), 100.8 ppm (<u>C</u>H=) and 217.1 ppm (C=<u>C</u>=C). As for the $^{31}P\{^1H\}$-NMR spectrum only one signal indicating the presence of only one compound in solution is detectable at 28.7 ppm.



Scheme 2 Insertion reaction of TosMIC on complex **1**.

The reactivity displayed by the mixture of complexes **2** and **3** with the isocyanide TosMIC is somehow more intriguing. The reaction progress detected by NMR after the addition of the isocyanide to the solution of the isomers entails the disappearance of the starting species within a few minutes and the appearance of a novel derivative **5** the spectrum of which is very similar to that of complex **4**, as can be deduced from the resonance within 4.5 and 5 ppm of the two methylene fragments in ^{1}H- and the signal at *ca.* 28 ppm in $^{31}P\{^1H\}$-NMR spectra, respectively. At variance with the previously described formation of complex **4**, in this case the reaction proceeds further and in about a couple of hours complex **5** rearranges to give the new derivative **6** (see Fig. 1 and Scheme 3).

However, the disappearance of the signals related to the insertion product **5**, the collapse into a singlet of both the methylenic protons (=C<u>H</u>$_2$ and –C<u>H</u>$_2$–SO_2) in the ^{1}H-NMR and the appearance of a novel signal in the $^{31}P\{^1H\}$-NMR spectrum at 34 ppm are not sufficient for a univocal structural interpretation of the newly formed species (see Fig. S3 and S4 in the ESI†).

The solid state structure of complex **6** was therefore determined by an X-ray diffractometric study as can be seen in the ORTEP[13] representation shown in Fig. 2. The geometry around the Pd centre is a slightly distorted square planar where the four positions are occupied by a halogen atom Cl, the N and the P of the phosphoquinoline ligand, and the C22 carbon of the 3-imino-2-phenyl substituted cyclobutenyl ring. The phosphoquinoline plane is rotated by 10.80(6)° with respect to the Pd coordination plane.

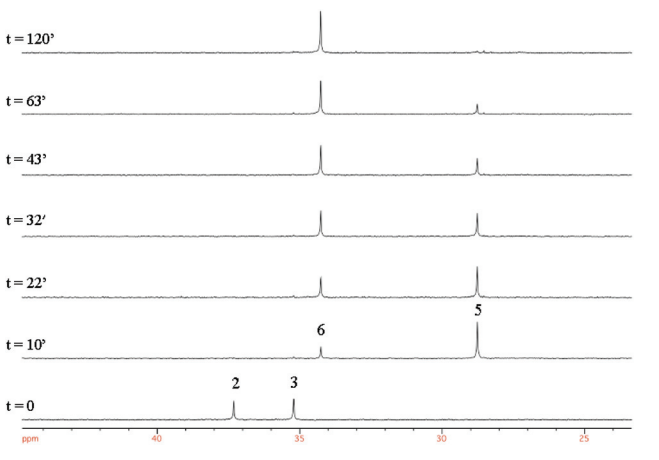
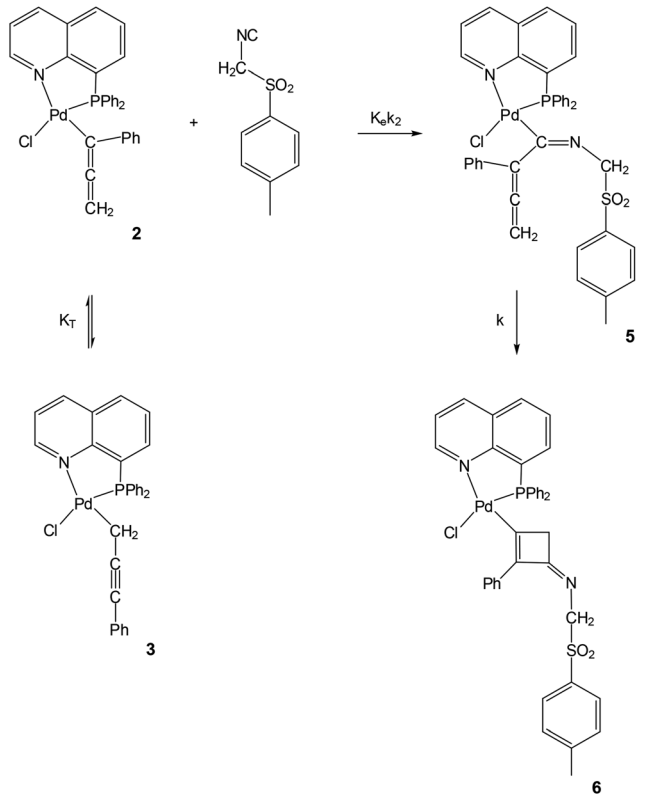


Fig. 1 $^{31}P\{^1H\}$NMR spectra in CD_2Cl_2 at 298 K for the reaction: **2** + **3** + TosMIC → **5** → **6**.



Scheme 3 Isocyanide insertion and rearrangement of the inserted complex **5** into complex **6**.

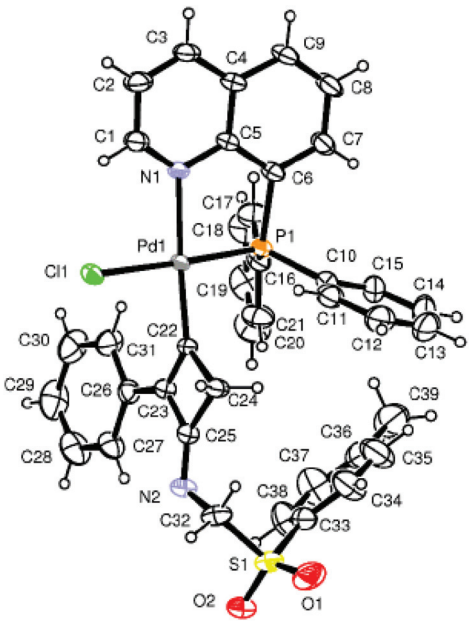


Fig. 2 ORTEP view of the complex **6**. A selection of bond distances and angles is given in Table S2 (ESI†).

It is now easy to interpret the relevant features of the NMR spectra of complex **6**. In this respect, the $^{13}C\{^1H\}$-NMR experiment coupled with the two-dimensional HMBC and HMQC experiments allows the identification of the cyclobutenyl carbons whereas all the signals ascribable to the phosphoquinoline fragment are now clearly detectable. In particular, the ^{1}H-NMR experiment identifies the signal at low field (10.07 ppm) related to the quinolinic H^2 which again is due to the presence of a chloride *cis* to the quinoline nitrogen.[12]

Finally, the shift to higher field of the methylenic protons $\underline{CH}_2$ (from 4.9–5.0 to 3.0 ppm) indicates their acquired alkyl character whereas the collapse of the tosyl doublet into a singlet is evidence of an easier fluxionality of the tosyl fragment in the less bulky complex **6**.

At this point an interpretation of the observed phenomenon is in order. In this respect we have to consider the following facts:

(i) The NMR spectra of the intermediate **5** are very similar to those of the complex **4** which was obtained by insertion of the isocyanide through the palladium–carbon bond of the allenyl tautomer **1**.

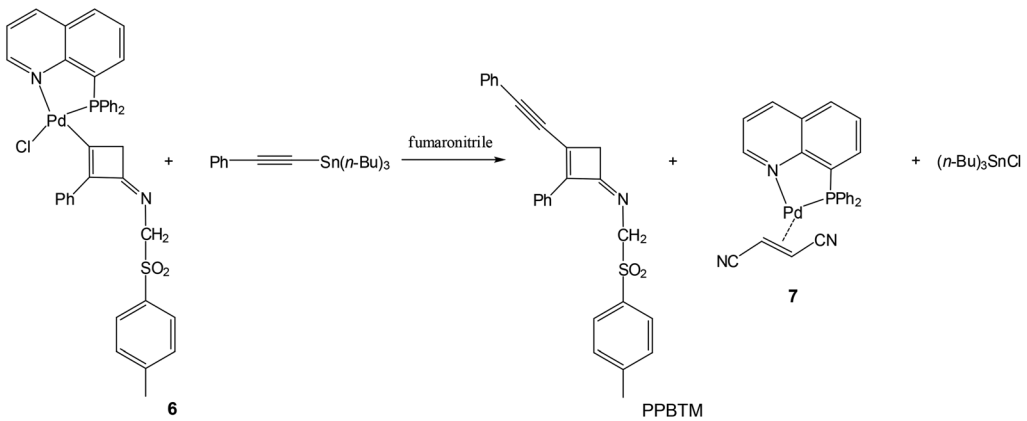
(ii) At variance with what was observed in the case of the complexes **4** and **4′**, it appears from DFT calculations that the inserted allenyl complex **5** is less stable than its propargylic counterpart **5′** by about 3 kcal mol^{-1}.

(iii) The inserted intermediate **5** does not revert to the more stable propargylic species but rather gives the final cyclobutenyl complex **6** (Scheme 3).

From points (i) and (ii) it can be deduced that only the allenyl tautomer **2** is the reacting species and consequently the formation of the thermodynamically disfavored intermediate **5** is kinetically governed. Moreover, since the propargyl tautomer **3** is no longer detectable in the ^{1}H-NMR spectra after the addition of the isocyanide to the initial tautomeric mixture, we think that a fast equilibrium between the two isomers is operative at R.T. and the reversible conversion of tautomer **2** into **3** is faster than the reaction yielding complex **5**. As for point (iii) we think that the formation of the propargylic inserted compounds **5′** is kinetically disfavored (high energy transition state) whereas the reactivity of complex **5** compared with the inertness of **4** might be interpreted on the basis of the long-chain electronic conjugation favored by the electron withdrawing phenyl group which lowers the transition state energy.

Since it was recognized that cyclobutenones are synthetically equivalent to vinylketenes and can be used as precursors in the formation of novel cyclic compounds *via* intermolecular [4 + 2]-[14] and [4 + 1]-cycloaddition[15] or intramolecular cyclization[16,17] we have investigated the feasibility of the displacement of the organic fragment from complex **6** which can eventually be easily hydrolyzed to its corresponding cyclobutenone.[18]

As reported in Scheme 4 the displacement of the compound (2-phenyl-3-(phenylethynyl)cyclobut-2-enylidene)-1-tosylmethanamine (PPBTM) by transmetallation with tributyl(phenylethynyl)stannane is achievable. The reaction was carried out in CD_2Cl_2 in an NMR test tube by mixing a stoichiometric quantity of complex **6** (~10^{-2} mol dm^{-3}) with an equimolecular amount of tributyl(phenylethynyl)stannane (PhC≡CSn



Scheme 4 Displacement of the fragment PPBTM from complex **6** by PhC≡CSn $(n\text{-Bu})_3$.

$(n\text{-Bu})_3$) and a slight excess of fumaronitrile (fn) to stabilize the ensuing Pd(0) complex. The reaction proceeds smoothly and is over in *ca.* one hour and the solution is dried under vacuum. The organic compounds were separated from complex **7** (see Fig S7 ESI†) by extraction with diethylether from the mixture of the reaction products and subsequent drying. No fumaronitrile was detected in the separated organic fraction since it was removed by sublimation in the drying process. The NMR spectra fully confirm the nature of the formed species and in particular the alkyl protons of the PPBTM at 3.36, 4.81 and 2.50 ppm related to =C$\underline{H}_2$, C$\underline{H}_2$$SO_2$ and tol–C$\underline{H}_3$ protons, respectively, are clearly distinguishable from the *n*-butyl protons of the stannane moiety within 0.9 and 1.8 ppm (Fig. S5–S7 ESI†). As for the ^{13}C NMR, the signals at 42.3, 74.0 and 21.4 are again ascribable to the alkyl carbons =$\underline{C}H_2$, $\underline{C}H_2SO_2$ and tol–$\underline{C}H_3$ groups, whereas the $\underline{C}$=N, Ph$\underline{C}$= and =$\underline{C}$–C≡ resonate at 169.6, 146.7 and 130.7 ppm, respectively (Fig. S8 ESI†). In particular, the last mentioned signal substitutes that of the corresponding =$\underline{C}$–Pd of complex **6** at 181.3 ppm. Finally, it is noteworthy that the PPBTM and $(n\text{-Bu})_3$SnCl derivatives can be easily separated by classical chromatographic techniques (see Experimental).

Kinetic studies

Determination of the second order rate constant (see point 4, ESI†)

In order to measure the rate constant and obtain clues to the reaction mechanism, we have used UV-Vis spectrophotometry which is comparatively faster and more precise than NMR spectrometry with regard to adequate reaction rates and absorbance changes. In the case of complex **1** reacting with TosMIC the analysis of spectral changes *vs.* time in the 460–280 nm interval provided the experimental conditions whereas non-linear regression of absorbance changes at a fixed wavelength *vs.* time based on the monoexponential model:

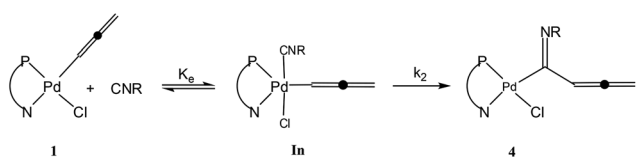
$$A_t - A_\infty = (A_0 - A_\infty)e^{-k_{obs}t}$$

with A_0, A_∞ and A_t as the initial, the final and the absorbance at time t, respectively, yielded the observed rate constant at every pseudo-first order concentration of TosMIC in excess.

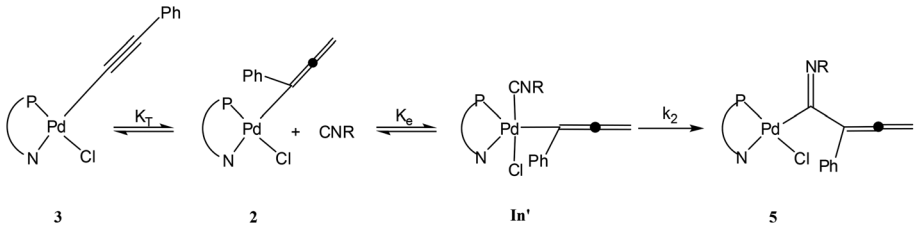
The measured k_{obs} are linearly dependent on the concentration of the isocyanide and therefore suggest an overall second order rate law. Such dependence is not unprecedented and was already observed in the case of the insertion of isocyanides across the Pd–alkyl[3] and Pd–aryl[7] bonds. It can be interpreted on the basis of a mechanism involving a fast pre-equilibrium formation of an intermediate bearing the isocyanide coordinated to palladium which undergoes a subsequent slow rearrangement into the reaction product. In this case the k_{obs} is given by the relationship $k_{obs} = K_e k_2[\text{TosMIC}]/(K_e + 1)$ where K_e is the pre-equilibrium constant related to the reaction (Scheme 5).

Eventually, owing to the negligible value of K_e (no intermediate in the NMR experiments nor immediate UV-Vis absorbance changes upon TosMIC addition are detectable, *i.e.* $K_e \ll 1$), the slope of the linear regression of the observed rate constants *vs.* [TosMIC] gives the overall second order rate constant for the complex studied ($K_e k_2$ = 1.8 ± 0.1 mol^{-1} dm^3 s^{-1}).

The kinetic study of the reaction of the tautomeric mixtures **2** and **3** can be carried out independently of the subsequent much slower rearrangement (**5** → **6**) and displays a trend similar to that described above. However, in this case the observed rate constant would assume the form $k_{obs} = K_T K_e k_2[\text{TosMIC}]/(K_e + 1)(K_T + 1)$ according to the reaction shown in Scheme 6.



Scheme 5 Mechanism of the insertion reaction of TosMIC in complex **1**.



Scheme 6 Mechanism of the insertion reaction of TosMIC in complex **2**.

The resulting linear regression of k_{obs} *vs.* TosMIC concentration yields the value of 3.5 ± 0.2 mol^{-1} dm^3 s^{-1} for the overall second order rate constant. Under the hypothesis that the attack of the isocyanide involves only the allenyl tautomer[19] with $K_e \ll 1$ the overall second order rate constant determined by the linear regression becomes $K_T K_e k_2/(K_T + 1)$. However, since at RT $K_T \approx 1$ (the concentrations of **2** and **3** are almost the same) the resulting value for $K_e k_2$ becomes ≈7 mol^{-1} dm^3 s^{-1}. Despite the enhanced steric requirements complex **2** reacts faster than **1** bearing the unsubstituted allenyl fragment (Scheme 1). We think that such an increase in the reaction rate might be traced back to the distortion induced by the phenyl group of the allenyl fragment on the main molecular plane of complex **2**, thereby rendering the formation of the five-coordinate intermediate **In′** easier and therefore increasing the K_e value.[12a] An alternative intermediate bearing the allenyl and isocyanide groups bound to a square planar palladium complex with the uncoordinated chloride forming an ion-pair could not easily explain the steric effect observed.[8] In our opinion other hypothetical mechanisms involving an η^3-allenyl intermediate can be ruled out safely, since at variance with some cases observed with allyl species,[8] the formation of this three-hapto derivative requires a preliminary dechloridation of the propargyl complex.[11b]

Determination of the rate constant of the intramolecular cyclization

Finally, the last process involving the rearrangement of complex **5** into **6** is comparably slower than the previously described insertion reactions and is characterized by an unfavorable absorbance change. Therefore, it was investigated by a ^{1}H NMR technique. The process under study obeys the following equations whereas the concentration *vs.* time profiles for **5** with its related best fit are reported in Fig. 3:

$$[\mathbf{5}]_0 = [\mathbf{5}] + [\mathbf{6}]$$

$$-\frac{d[\mathbf{5}]}{dt} = k[\mathbf{5}] \quad [\mathbf{5}] = [\mathbf{5}]_0 e^{-k\times t} \quad [\mathbf{6}] = [\mathbf{5}]_0(1 - e^{-k\times t})$$

$$k = (3.96 \pm 0.01) \times 10^{-4}\ s^{-1}$$

These experimental pieces of evidence can be interpreted on the basis of an intramolecular rearrangement involving two distinct steps according to the mechanisms recently suggested by Iwasaki and co-workers in the case of the CO insertion through the Pd–C bond of an allenyl derivative.[20] As depicted in Scheme 7 the first step can be represented as a 1,3-shift of the palladium (formally an allenyl ketenimino-vinyl ketenimino rearrangement)[21] followed by an intramolecular [2 + 2] cyclization of the vinyl ketenimino fragment generating the final cyclobutenyl complex **6**.[21b] The progress of the reaction, which is described by a monoexponential decay, suggests that the rate determining step is the allenyl ketenimino-vinyl ketenimino rearrangement since no vinylketenimino species is experimentally detected.

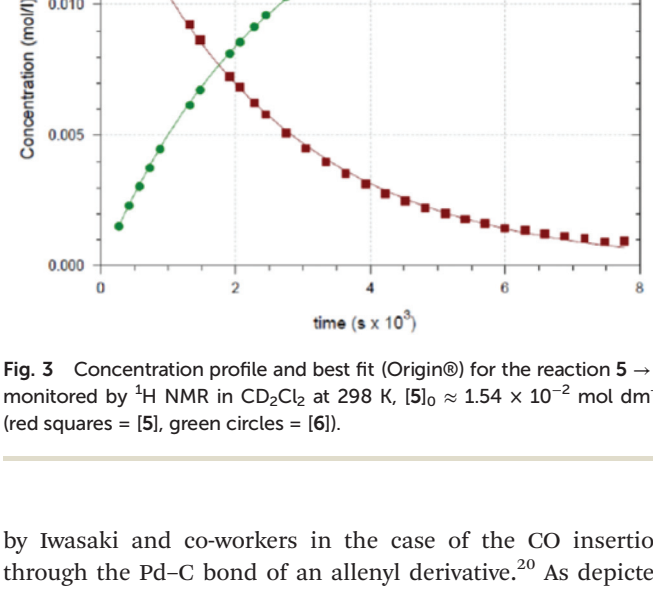
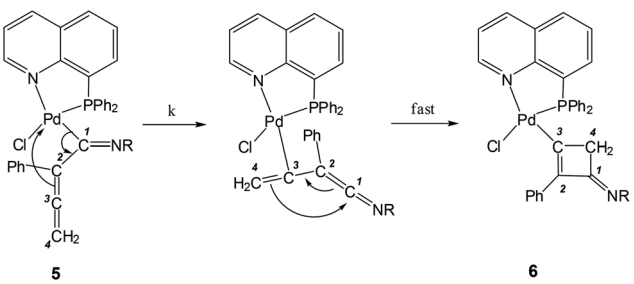


Fig. 3 Concentration profile and best fit (Origin®) for the reaction **5** → **6** monitored by ^{1}H NMR in CD_2Cl_2 at 298 K, $[\mathbf{5}]_0 \approx 1.54 \times 10^{-2}$ mol dm^{-3} (red squares = [**5**], green circles = [**6**]).



Scheme 7 Proposed mechanism for the cyclic rearrangement **5** → **6**.

Conclusion

The palladium allenyl complex **1** bearing 8-(diphenylphosphino)quinoline as a spectator ligand reacts with *p*-toluenesulfonylmethyl isocyanide to give the expected insertion product **4** whereas the mixture of allenyl and propargyl complexes **2** and **3** reacting with the same isocyanide yields a different species. In particular, the palladium derivative **6**, to the best of our knowledge, is the first example of a cyclobutenyl bound to this metal promoted by the insertion of an isocyanide through the Pd–C bond. We have shown that such a cyclobutenyl fragment can be easily removed by transmetallation. We report the structure of complex **6** together with a complete kinetic study and propose mechanisms for the insertion and the cyclization reactions.

Experimental

Solvents and reagents

All the distillation processes were carried out under an inert atmosphere (argon). CH_2Cl_2 was distilled over CaH_2 whereas all other chemicals were commercially available grade products and were used as purchased.

IR, NMR, UV-Vis measurements and elemental analysis

The IR, ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a PerkinElmer Spectrum One spectrophotometer and on a Bruker 300 Avance or Bruker 400 spectrometer, respectively.

The ^{1}H NMR reactivity tests were carried out by dissolving the complex under study in 0.8 ml of CD_2Cl_2 ([Complex] $\approx 1.2 \times 10^{-2}$ mol dm^{-3}) and adding microaliquots of a concentrated CD_2Cl_2 solution (*ca.* 1.2×10^{-1} mol dm^{-3}) of propargyl chloride and monitoring the signals for the disappearance of the starting and intermediate complex and the appearance of the final products.

A UV-Vis preliminary study was carried out by placing 3 ml of freshly prepared CH_2Cl_2 solution of the complex under study ($[\text{Complex}]_0 = 1 \times 10^{-4}$ mol dm^{-3}) in the thermostated (298 K) cell compartment of the UV-Vis spectrophotometer. Microaliquots of solutions containing the isocyanide at adequate concentrations ([TosMIC] $\geq 1 \times 10^{-3}$ mol dm^{-3}) were added and the absorbance changes were monitored in the 280–460 nm wavelength interval or at an optimized fixed wavelength.

The elemental analysis of the synthesized complex was carried out using an Elementar CHN "CUBO micro Vario" analyzer.

Synthesis of the complexes

The allenyl **1**, **2** and propargyl **3** complexes were synthesized according to a published procedure[11] and confirmed by comparison of their NMR spectra with the original ones.

Synthesis and NMR characterization of complex 4

0.0400 g (0.0809 mmol) of **1** and 0.01176 g (0.0901 mmol) of TosMIC were sequentially introduced under an inert atmosphere (Ar) into a two necked flask containing 8 ml of anhydrous CH_2Cl_2. The solution was stirred for 10 min and evaporated under vacuum to a reduced volume. Addition of diethylether induces the precipitation of the title complex which was filtered off on a Gooch, washed with diethylether and dried under vacuum. 0.0443 g (0.064 mmol; yield 79%) of **4** as a light orange microcrystalline solid was obtained.

^{1}H-NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.47 (s, 3H, Tos-CH_3), 4.31 (d, 1H, J = 15.1 Hz, CH_2SO_2), 4.40 (dd, 1H, J = 13.0, 6.5 Hz, CH_2═), 4.86 (dd, 1H, J = 13.0, 6.5 Hz, CH_2═), 5.19 (d, 1H, J = 15.1 Hz, CH_2SO_2), 5.72 (td, 1H, J = 6.5, 3.1 Hz, CH═), 7.30–7.33 (m, 2H, Tos-Aryl), 7.42–7.79 (m, 19H, Ph, PPh_2, Tos-aryl H^3, H^6), 7.88 (d, d, d, 1H, J = 10.1, 7.2, 1.3 Hz, H^7), 8.17 (dt, 1H, J = 8.1, 1.3 Hz, H^5), 8.53 (dt, 1H, J = 8.4, 1.6 Hz, H^4), 9.83 (dd, 1H, J = 4.9, 1.6 Hz, H^2).

^{13}C{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 21.6 (CH_3, Tos-CH_3), 77.6 (CH_2, ═CH_2), 77.7 (CH_2, CH_2SO_2), 100.8 (d, CH, J_{CP} = 10.3 Hz, CH═), 123.3 (CH, C^3), 131.8 (CH, C^6), 135.2 (CH, C^5), 137.3 (CH, C^7), 139.4 (CH, C^4), 149.9 (d, C, J_{CP} = 19.6 Hz, C^9), 153.1 (CH, C^2), 185.2 (C, C═N), 217.1 (C, ═C═).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 28.7.

Anal. Calcd for $C_{33}H_{28}ClN_2O_2PPdS$: C 57.48, H 4.09, N 4.06. Found: C 57.52, H 3.97, N 4.13.

Synthesis and NMR characterization of complex 6

0.0363 g (0.0636 mmol) of an equimolecular mixture of **2** and **3** and 0.0138 g (0.10 mmol) of TosMIC were sequentially introduced under an inert atmosphere (Ar) into a two necked flask containing 8 ml of anhydrous CH_2Cl_2. The solution was stirred for 4 h and then cooled in an ice/water bath. The solution was evaporated to a reduced volume under vacuum and the title complex precipitated with diethylether, filtered off on a Gooch, washed with diethylether and dried under vacuum. 0.0419 g (0.055 mmol) (yield 86%) of a light brown solid was obtained.

^{1}H-NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.46 (s, 3H, Tos-CH_3), 3.00 (s, 2H, CH_2CN), 4.57 (s, 2H, CH_2SO_2), 7.05–7.86 (m, 21H, Ph, PPh_2, Tos-aryl H^3, H^6), 8.01 (d, d, d, 1H, J = 10.2, 7.2, 1.3 Hz, H^7), 8.11 (dt, 1H, J = 8.1, 1.4 Hz, H^5), 8.57 (dt, 1H, J = 8.4, 1.6 Hz, H^4), 10.07 (dd, 1H, J = 5.0, 1.6 Hz, H2).

^{13}C{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 21.5 (CH_3, Tos-CH_3), 46.0 (CH_2, CH_2CN), 73.8 (CH_2, CH_2SO_2), 123.3 (CH, C^3), 125.9 (CH, C^6), 132.5 (CH, C^5), 137.1 (CH, C^7), 139.4 (CH, C^4), 150.7 (d, C, J_{CP} = 20.0 Hz, C^9), 152.7 (C, PhC═), 153.6 (CH, C^2), 167.6 (C, C═N), 181.3 (C, PdC═).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 34.3.

Anal. Calcd for $C_{39}H_{32}ClN_2O_2PPdS$: C 61.18, H 4.21, N 3.66. Found: C 61.31, H 4.15, N 3.57.

Displacement of PPBTM from complex 6

The reaction was carried out in CD_2Cl_2 at 298 K and the reaction progress was followed by ^{1}H NMR. To 8.2 mg of complex **6** dissolved in *ca.* 0.8 ml of CD_2Cl_2, 9 mg of fumaronitrile and 4.2 mg of tributyl(phenylethynyl)stannane were added. The reaction progress was followed for *ca.* one hour with a Bruker 400 Avance 3 spectrometer. Tributylchlorostannane and PPBTM were extracted from the dried mixture of the reaction

products with diethylether and characterized by ^{1}H and ^{13}C NMR (Fig. S5–S7 ESI†). Owing to the favorable R_f ratio ($R_{f\ PPBTM}$ = 0.25; $R_{f\ (n\text{-}Bu)_3SnCl}$ = 0.75 in 0.2 mm layer, silica gel 60), tributylchlorostannane and PPBTM can be easily separated with flash chromatography using CH_2Cl_2 as the eluent. The NMR data reported below are related to PPBTM.

^{1}H-NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.50 (s, 3H, Tos-CH_3), 3.36 (s, 2H, CH_2CN), 4.81 (s, 2H, CH_2SO_2), 7.41–7.48 (m, 8H, Ph, Tos-aryl), 7.61–7.65 (m, 2H, Ph), 7.84–7.87 (m, 2H, Tos-aryl), 8.08–7.11 (m, 2H, Ph).

$^{13}C\{^{1}H\}$-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 21.4 (CH_3, Tos-CH_3), 42.3 (CH_2, CH_2CN), 74.0 (CH_2, CH_2SO_2), 84.2 (C, =C–*C*≡), 108.2 (C, ≡CPh), 127.1 (CH, Ph), 128.5 (CH, Tos-aryl), 128.6 (CH, Tos-aryl), 129.1 (CH, Ph), 129.3 (CH, Ph), 129.6 (CH, Ph), 129.9 (CH, Ph), 130.7 (C, =*C*–C≡), 131.9 (CH, Ph), 145.2 (C, Tos-aryl), 146.7 (C, PhC=), 169.6 (C, C=N).

Computational details

The geometrical optimization of the complexes was carried out by the Gaussian 09 program[22] without symmetry constraints, using the hyper-GGA functional MO6,[23,24] in combination with polarized triple-ζ-quality basis sets (LAN2TZ(f))[25,26] and relativistic pseudopotential for the Pd atoms, polarized double-ζ-quality basis sets (LANL2DZdp)[27] with diffuse functions for the halogen atoms and polarized double-ζ-quality basis sets (6-31G(d,p)) for the other elements. Solvent effects (CH_2Cl_2, ε = 9.93) were included using CPCM.[28,29]

The "restricted" formalism was applied in all the calculations. The zero-point vibrational energies and thermodynamic parameters were obtained[30] by means of the stationary points characterized by IR simulation.

All the computational work was carried out on Intel based x86-64 workstations.

X-ray diffractometric details

The crystal data of compound **6** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation. The data sets were integrated with the Denzo-SMN package[31] and corrected for Lorentz, polarization and absorption effects (SORTAV).[32] The structures were solved by direct methods using the SIR97[33] system of programs and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions, riding on their carrier atoms.

The crystal contains molecules of solvent in the asymmetric unit: a molecule of CH_2Cl_2 in a general position and a molecule of CH_2Cl_2 in a special position on a twofold axis.

All calculations were performed using SHELXL-2014/6[34] and PARST[35] implemented in the WINGX[36] system of programs. The crystal data are given in Table S1 (ESI†) and a selection of bond distances and angles is given in Table S2 (ESI†).

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1509243.

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