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Stable N-Heterocyclic Carbene (NHC)–Palladium(0) Complexes as Active Catalysts for Olefin Cyclopropanation Reactions with Ethyl Diazoacetate

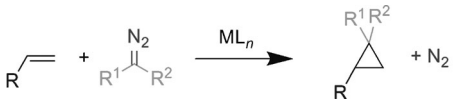
Carmen Martín,[a] Francisco Molina,[a] Eleuterio Alvarez,[b] and Tomás R. Belderrain*[a]

Abstract: The Pd^0 complexes [(NHC)PdL_n] (NHC = N-heterocyclic carbene ligand; L = styrene for $n=2$ or PR_3 for $n=1$) efficiently catalyse olefin cyclopropanation by using ethyl diazoacetate (EDA) as the carbene source with activities that improve on previously described catalytic systems based on this metal. Mechanistic studies have shown that all of these catalyst precursors deliver the same catalytic species in solution, that is, [(IPr)Pd(sty)], a $14e^-$ unsaturated intermediate that further reacts with EDA to afford [(IPr)Pd(=$CHCO_2Et$)(sty)], from which the cyclopropane is formed.

Keywords: cyclopropanation · diazo compounds · homogeneous catalysis · palladium

Introduction

Cyclopropanes are widespread in nature and constitute the building blocks of many biologically active compounds.[1] Among the various methods used for their preparation, the transition-metal-catalysed cyclopropanation of olefins with diazo reagents has attracted great interest [Eq. (1)].[2] Many transition-metal complexes, especially those containing rhodium,[3] copper,[2e,4] cobalt,[5] iron,[5f,k,6] or ruthenium,[7] have been employed to induce this type of transformation. Interestingly, one of the most commonly employed metals in homogenous catalysis, palladium, has scarcely been described as a catalyst for this process, in spite of the discovery of its application for this purpose in the mid sixties.[8] During the last decade, a number of contributions relating to the use of diazomethane as a carbene reagent with palladium-based catalysts have appeared,[9] a topic recently reviewed by Wang and Zhang.[10] However, such catalysts seem to fail with alkyl diazoacetates as the reactant,[9a,b,11] in spite of the fact that they are stable and either commercially available or easy-to-prepare reagents, in contrast to diazomethane, which is known to be unstable.



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The already-described Pd^0-based catalysts for these transformations contain phosphanes or olefins as ancillary ligands.[9d,11c] On the other hand, Pérez and co-workers have reported that group 11 metal complexes containing N-heterocyclic carbene (NHC) ligands are active catalysts towards carbene transfer from ethyl diazoacetate (N_2CHCO_2Et; EDA) to several saturated or unsaturated substrates.[4q,12] Although Pd^0–NHC compounds have been successfully employed as catalysts in several reactions, such as C–C and C–N coupling reactions, oxidations, telomerisations and hydrogenations,[13] to the best of our knowledge there have not been any reports of the use of these compounds in olefin cyclopropanation.[14] In addition, there is still debate[15] about the oxidation state of the palladium catalytic species in these compounds.

On the basis of this, we decided to prepare a series of novel (NHC)Pd^0 complexes and investigate their potential as catalysts for the olefin cyclopropanation reaction with alkyl diazoacetate reagents. We have found that they are quite active catalysts for the olefin cyclopropanation reaction. A detailed mechanistic study, including kinetic and thermodynamic data, has led to the proposal of a mechanism for this transformation.

Results and Discussion

Synthesis and characterisation of complex [(IPr)$Pd^0$$(sty)_2$] (1): Although several methods have been employed for the synthesis of mono-NHC–Pd^0–alkene complexes,[16,17] we have prepared complex **1** in good yields by following a method reported by Nolan and co-workers for the prepara-

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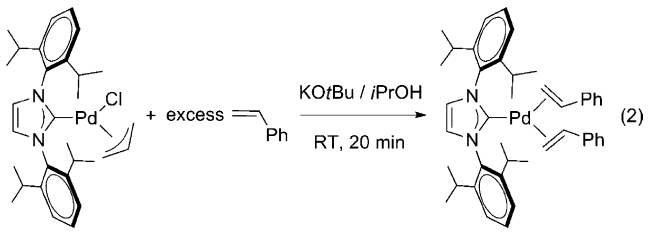
tion of mono-NHC–Pd^0–PR_3 complexes from [(NHC)Pd-(allyl)Cl].[18] Thus, the reaction of [(IPr)Pd(allyl)Cl] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with KO*t*Bu (1 equiv) in *i*PrOH in the presence of an excess of styrene [sty; Eq. (2)] led to the formation of **1** in high yields (80%). This complex is stable in the solid state and can be kept for an unlimited period of time under an inert atmosphere.



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Complex **1** was characterised by NMR spectroscopy and by X-ray crystallography. It shows fluxional behaviour, as inferred from the line broadening observed in the variable temperature (VT) NMR spectra (see the Supporting Information). At room temperature the resonances corresponding to the C*H* protons of *i*Pr and the vinyl protons of the olefin appear as three broad peaks at $\delta = 3.07$, 3.19 and 3.89 ppm in the ^{1}H NMR spectrum (Figure 1 I), which may result from 1) fast (on the NMR timescale) exchange processes with the free olefin, and/or 2) fast rotation of the olefin around the palladium–olefin bond axis. At low temperatures (−40 °C; Figure 1 II), the resonances of the methine C*H* of the *i*Pr groups split into two signals at $\delta = 2.83$ (heptet, $J = 6.5$ Hz, 2H) and 3.43 ppm (heptet, $J = 6.5$ Hz, 2H), whereas the olefinic protons appear as three signals at 2.94 (d, $J = 9.0$ Hz, 2H), 3.07 (d, $J = 12.4$ Hz, 2H) and 3.75 ppm (dd, $J = 9.3$, $J = 12.4$ Hz, 2H), at much higher field than for free styrene ($\delta = 5.00$, 5.59 and 6.55 ppm in C_6D_6), indicating strong back donation of electron density from the palladium metal into the π* orbitals of the alkene. Accordingly, in the ^{13}C{^{1}H} NMR spectrum of **1** at −40 °C, the olefin carbon atoms resonate at $\delta = 74.7$ (s, olefin *C*H) and 53.0 ppm (s, olefin CH_2; $\delta = 135.5$ and 112.0 ppm for the free olefin).[19]

Since we could not extract conclusions from the VT NMR studies of the complex alone, we studied the effect of the presence of excess olefin on the ^{1}H NMR spectrum at room temperature (Figure 1, bottom). Thus, the addition of free olefin (6 equiv) afforded even broader peaks for the protons of the coordinated olefin. Although this behaviour is expected for an associative olefin-exchange process at the metal center,[20] we could not discard the dissociative mechanism since at 60 °C only one set of signals was observed for the methine and the methyl protons of the *i*Pr groups of the NHC ligand. Furthermore, an Eyring plot obtained by use of this VT ^{1}H NMR study (monitoring the change in the signals corresponding to the methyl groups of the IPr ligand)

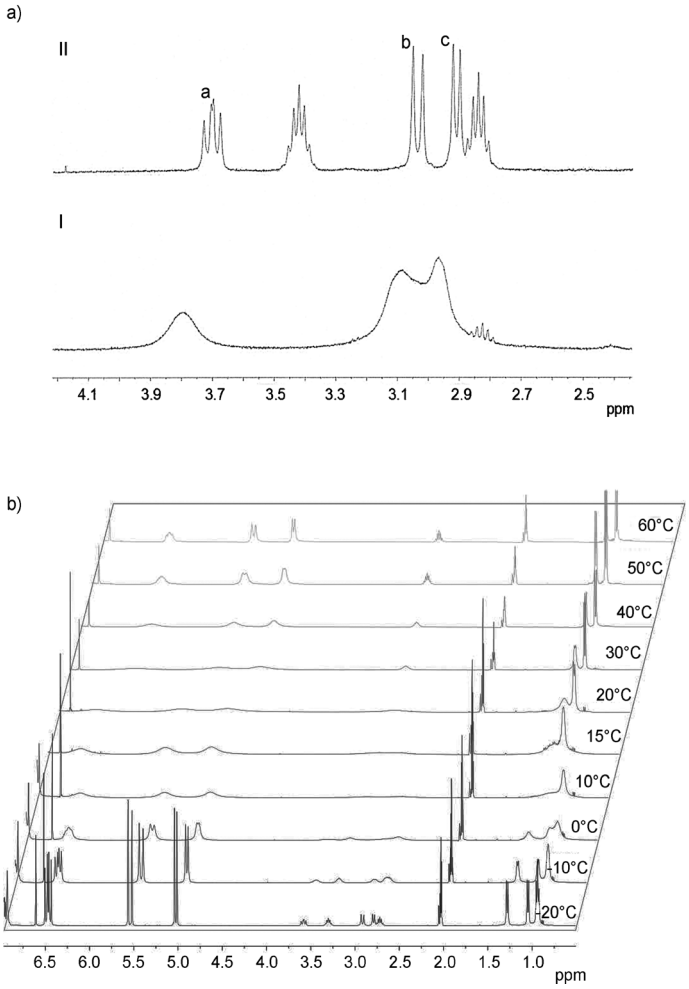


Figure 1. Top: Olefinic resonances (labelled as a, b and c) in the ^{1}H NMR spectrum of **1** at low (II) and room temperature (I). Bottom: VT ^{1}H NMR spectra of **1** in the presence of six equivalents of styrene. Sample conditions: [Pd] = 14 mM and [sty] = 84 mM in [D_8]toluene.

in the presence of the olefin (Figure 2) enabled the determination of activation parameters: $\Delta H^{\neq} = 22.4 \pm 1.6$ Kcal/mol and $\Delta S^{\neq} = 31 \pm 5$ ue. This positive value for the activation

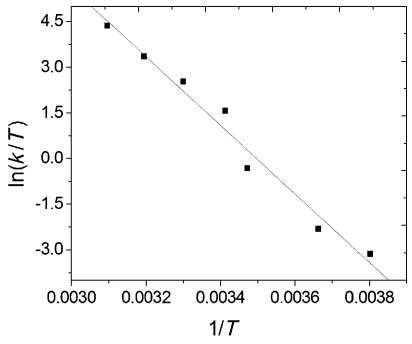


Figure 2. Eyring plot of the temperature-dependent behaviour of the olefin exchange reaction. Sample conditions: [Pd] = 14 mM and [sty] = 84 mM in [D_8]toluene.

entropy supports the proposal of a dissociative mechanism. Such a pathway would involve the formation of the unsaturated 14e$^-$ species [(IPr)Pd(sty)] in a similar manner to that proposed by Elsevier and co-workers in the (NHC)Pd-catalysed transfer hydrogenation of alkynes.[21]

The proposed structure of complex **1** has been confirmed by single-crystal X-ray analysis (recrystallised by using toluene as the solvent). An ORTEP diagram of **1** is shown in Figure 3. The asymmetric unit of the structure in the crystal

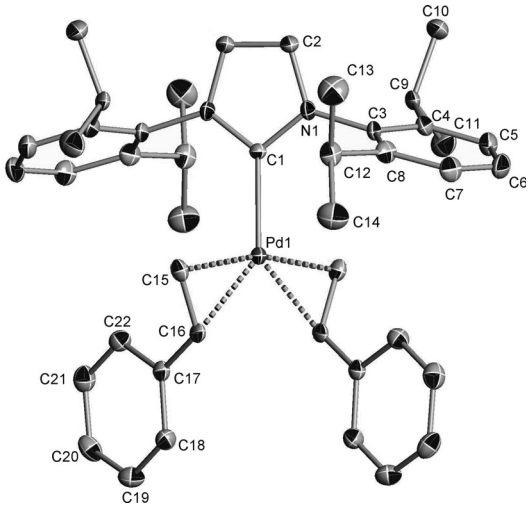
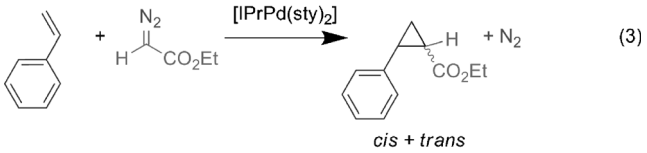


Figure 3. ORTEP diagram of [(IPr)Pd(sty)$_2$] (**1**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°] for **1**: Pd–C1 2.101(7), C15–C16 1.397(8), Pd–C15 2.147(6), Pd–C16 2.189(6), C1-Pd-C15 97.89(17), C1-Pd-C16 135.23(15), N1-C1-N′1 104.6(6).

is formed of two structually equivalent, symmetrically independent half molecules of the carbene complexes, with the others halfs generated by a crystallographic twofold axis of symmetry (see the Supporting Information). The Pd–C1 bond length, 2.101(7) Å, is somewhat longer than those found for other NHC–palladium olefin complexes,[16a–c] but is similar to that reported for [(IMes)Pd(DMF)$_2$] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; DMF = dimethyl fumarate).[16d] The C=C double bonds in the coordinated styrenes, C15=C16 1.397(8) Å, are longer than in free styrene (1.346(20) Å).[22] This distance is similar to that reported for the Rh^I complex [(PNP)Rh(sty)]X (PNP = 2,6-bis[(diphenylphosphino)methyl]pyridine; X = BF_4^-) and longer than that for Pt^{II} and Pd^{II} complexes.[23] This is again consistent with significant metal to olefin π back donation. The NHC plane is oriented at an angle of 59.87(26)° to the coordination plane of the styrenes (C15-Pd-C′15), in a similar manner to the complex [(IMes)Pd(DMF)$_2$]. The Pd–C15 separation, 2.147(6) Å, is shorter than the Pd–C16 separation 2.189(6) Å, as already reported for other styrene complexes.[24] The dihedral angle between the coordination planes of the two styrenes (Pd-C15-C16 and Pd-C24-C25) is 11.23(35)° (only slightly higher than in the case of [(IMes)Pd(DMF)$_2$]),[16d] and therefore the two styrene molecules are coordinated to the metal in an almost planar fashion.

Catalytic cyclopropanation reaction of styrene by using NHC–Pd^0 complexes as catalysts: Once complex **1** was characterised, it was tested as the catalyst precursor in the styrene cyclopropanation reaction by using EDA as the carbene source. A solution of the Pd^0 complex (0.01 mmol) in dichloromethane was charged with styrene (5 mmol) and EDA (1 mmol) to give a [Pd]/[EDA]/[styrene] ratio of 1:100:500. The reaction was monitored by GC, which showed the gradual disappearance of EDA and appearance of cyclopropanes. After 4 h, no diazo compound was detected in the reaction mixture, the analysis of the crude products (after volatles had been removed) showed the formation of a mixture of the *cis*- and *trans*-cyclopropanes [Eq. (3)] in 98% yield based on the remaining EDA. The remaining initial diazoacetate was converted into a mixture of diethyl fumarate and maleate, a process also catalysed by complex **1** [Eq. (4)].



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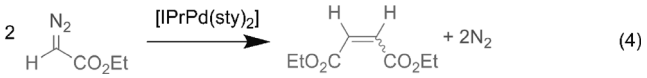

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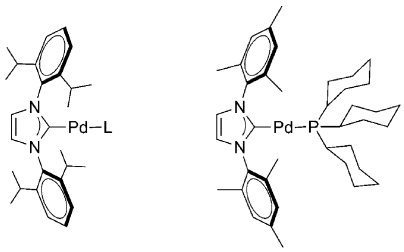
After determining the catalytic capability of [(IPr)Pd(sty)$_2$] towards styrene cyclopropanation with EDA, we decided to screen a series of related complexes of composition [(NHC)PdL] in this test reaction (see the Experimental Section for their preparation or in situ generation procedures). Complexes **2**–**4** contain IPr, as well as a PR_3 ligand; complex **5** corresponds to a biscarbene Pd^0 complex, whereas complex **6** contains an IMes ligand, along with PCy_3 (Cy = cyclohexane). The data in Table 1 show that complexes **1**–**4** and **6** display nearly identical catalytic behaviour in terms of activity and diastereoselectivity, with only the biscarbene complex [IPr$_2$Pd] (**5**) being ineffective. Table 1, entries 1, 3 and 5 correspond to experiments carried out with a [Pd]/[EDA]/[styrene] ratio of 1:100:500, that is, 1 mol% of the Pd catalyst, and provided nearly quantitative conversion into the desired cyclopropanes. Interestingly, the *cis*:*trans* ratio was also identical, providing what could be considered to be an indication of the existence of a common catalytic species, at least for catalysts **1**–**4**. A second series of experiments carried out with 0.5 mol% of the catalyst ([Pd]/[EDA]/[styrene] = 1:200:1000; Table 1, entries 2 and 4 produced similar conversions, yields and diastereoselectivities, although longer reaction times were required.

Table 1. Styrene cyclopropanation by using the NHC–Pd^0 complexes **1**–**6** as the catalysts.



	Catalyst precursor	Time [h]	Conversion [%][c]	Yield [%][d]	*cis*/*trans*
1	[(IPr)Pd(sty)$_2$], **1**[a]	4	99	98	38:62
2	[(IPr)Pd(sty)$_2$], **1**[b]	24	98	98	37:63
3	[(IPr)PdL], **2**–**4**[a]	4	99	98	37:63
4	[(IPr)PdL], **2**–**4**[b]	24	99	93	37:63
5	[(IPr)$_2$Pd], **5**[a]	48	2	n.d.[e]	n.d.[e]
6	[(IMes)Pd(PCy$_3$)], **6**[a]	24	99	90	37:63

[a] [Pd]/[EDA]/[olefin] = 1:100:500. [b] [Pd]/[EDA]/[olefin] = 1:200:1000. [c] Conversions were determined by ^{1}H NMR spectroscopy. [d] The percentage yield of the cyclopropane at the end of the reaction determined by using 1,4-dimethoxybenzene as the internal standard (diethyl fumarate and maleate accounted for the rest of the EDA). [e] n.d. = not determined.

As mentioned above, very few examples of the use of palladium-based catalysts for olefin cyclopropanation with diazoacetates have been described most of which employ a Pd^{II} precursor. Seminal work was described by Noels and co-workers and utilised $Pd(OAc)_2$ as the catalyst precursor.[11c] Styrene and EDA were employed in a 15:1 ratio to give 98% conversion into the cyclopropane. They also reported the use of [$Pd(PPh_3)_4$] as the catalyst for the same reaction, although only a 57% yield of the cyclopropane was achieved. In our case, Pd^0 complexes **1**–**4** and **6** improved on this activity, with the added advantage of employing only a 5:1 ratio of [styrene]/[EDA]. Importantly, high yields of the cyclopropane (80% in 4 h) were obtained even if the reaction was carried out by using only a 1:1 ratio of [styrene]/[EDA]. This is a remarkable result since previous palladium-based catalytic systems have required an excess of the olefin. It seems that the replacement of phosphine ligands with IPr is the key to this success. However, these systems are less active than those reported for other transition metals. For instance, the group of Pérez has reported that the turnover frequency (TOF) for the [$Tp^{Ms}Cu$] (Tp^{Ms} = hydrotris(3-mesitylpyrazolyl)borate) complex is 250 mmol h^{-1}, whereas in the case of **1**, the TOF is 24 mmol h^{-1}.[4s]

Unusually, our system also extends to other usually less reactive olefins, such as 1-hexene and cyclooctene. As shown in Table 2, both the olefin in 1-hexene and cyclooctene can be converted into the corresponding cyclopropane in high (95%) or moderate (58%) yield, respectively. These yields are much higher than those reported with $Pd(OAc)_2$ for the same olefins (30% for 1-hexene and 20% for cyclooctene), providing evidence that the Pd^0-based catalysts reported herein are quite active.[11c] Competition experiments carried out with styrene, 1-hexene and cyclooctene have established the relative reactivity of these three olefins to be 3.80:1.20:1.00, respectively. This trend is similar to that found by Noels and co-workers with $Pd(OAc)_2$ as the catalyst (2.36:1.31:1.00), with the aforementioned differences in activity favouring the NHC–Pd^0-based system.

Table 2. Cyclopropanation of 1-hexene and cyclooctene by using EDA and [(IPr)Pd(PPh_3)] (**3**) as the catalyst precursor.[a]

	Olefin	Time [h]	Conversion [%][b]	Yield [%][c]	*cis*/*trans*
1	1-hexene	24	98	95	40:60
2	cyclooctene	24	63	58	13:87

[a] [Pd]/[EDA]/[olefin] = 1:100:500. [b] Conversions were determined by ^{1}H NMR spectroscopy. [c] The percentage yield of the cyclopropane at the end of the reaction determined by using 1,4-dimethoxybenzene as the internal standard (diethyl fumarate and maleate accounted for the rest of the EDA).

Mechanistic studies

Kinetics: Having demonstrated the unprecedented catalytic activity of the aforementioned Pd^0 complexes towards the olefin cyclopropanation reaction with diazoacetates as the carbene source, we focussed on the elucidation of the reaction mechanism. To gain information about this, we first monitored the evolution of nitrogen in the decomposition of EDA in the abscense and presence of styrene with [(IPr)Pd(sty)$_2$] (**1**) as the catalyst precursor. Figure 4 shows that in the absence of styrene the reaction does not reach completion (1 mmol of EDA should provide 1 mmol of N_2), in contrast with the experiment carried out in the presence of styrene, for which all of the initial EDA is consumed. The use of a phosphine-containing precatalyst, such as [(IPr)Pd(PPh_3)] (**3**) provided additional information. In this case, an initiation period of approximately 50 min was observed prior to nitrogen evolution (Figure 5, line A). A series of experiments in which different amounts of PPh_3 were added led to the observation of an increase in the initiation period (Figure 5, lines B and C) with eventual inhibition of the re-

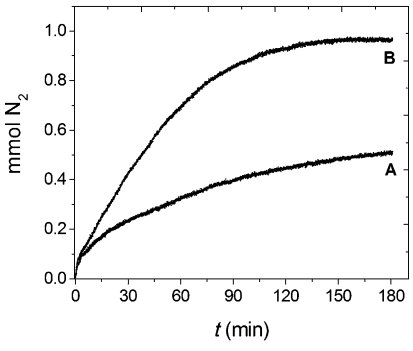


Figure 4. Plot of nitrogen evolution in the reaction of EDA in the absence (A) and in the presence of styrene (B), catalysed by **1**. Reaction conditions: A) [catalyst]/[EDA] = 1:48; [**1**] = 0.02 mmol; [EDA] = 0.95 mmol, solvent = CH_2Cl_2 (10 mL). B) [**1**]/[EDA]/[styrene] = 1:48:250; [**1**] = 0.02 mmol; [EDA] = 0.95 mmol; [styrene] = 5 mmol, solvent = CH_2Cl_2 (10 mL).

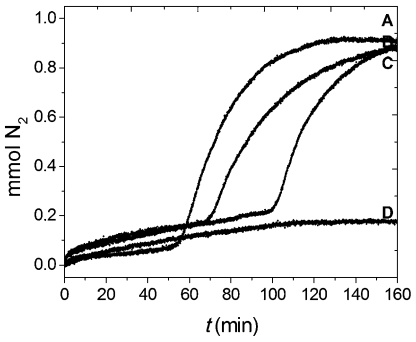


Figure 5. Plots of nitrogen evolution in the reaction of EDA in the presence of styrene and different amounts of added PPh_3 catalysed by **3**. Reaction conditions: [**3**]/[EDA]/[styrene] = 1:48:250; [catalyst] = 0.02 mmol; [EDA] = 0.96 mmol; [styrene] = 5 mmol; solvent = CH_2Cl_2 (10 mL). Amount of PPh_3 added: A) none, B) 0.01 mmol, C) 0.02 mmol, D) 0.03 mmol.

action (Figure 5, line D). From the data in Figures 4 and 5, we extracted the following conclusions: with the PPh_3-containing precatalyst, the first step must consist of PPh_3 dissociation to generate the [(IPr)Pd] species, the equilibrium of which is greatly affected by the addition of free phosphine. The generation of the [(IPr)Pd] species, the common species for **1** and **3** as precatalysts, initiates the catalytic cycle. In the absence of styrene, this species catalyses the diazo coupling reaction, which produces diethyl fumarate (DEF) and diethyl maleate (DEM). These olefins would bind to the [(IPr)Pd) unit to give [(IPr)Pd$(DEF)_2$] or [(IPr)Pd$(DEM)_2$], blocking the active catalytic site. It is worth mentioning that Cavell and co-workers have reported the complex [(IMes)Pd$(DMF)_2$].[16d] The formation of [(IPr)Pd$(DEF)_2$] or [(IPr)Pd$(DEM)_2$] in the presence of a large excess of styrene would be precluded, explaining the observation of complete EDA consumption and subsequent cyclopropane formation. To be sure that this proposal is correct, we ran two identical cyclopropanation experiments and added, after 1 h graph suggests approximately 50 min, a certain amount of diethyl fumarate to one of the reactions (Figure 6). The two experiments showed nearly identical nitrogen evolution

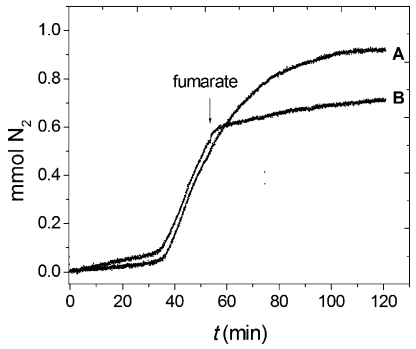


Figure 6. Plot of nitrogen evolution in the reaction of EDA and styrene catalysed by **3**. Reaction conditions: [**3**]/[EDA]/[styrene] = 1:48:250; [**3**] = 0.02 mmol; [EDA] = 0.95 mmol; [styrene] = 5 mmol; solvent = CH_2Cl_2 (10 mL). Diethyl fumarate (5 mmol) was added to experiment B after 50 min.

curves until the addition of DEF, at which time the reaction rate of the one containing added DEF dramatically decreased, providing evidence for the aforementioned inhibition pathway.

We have also carried out experiments to study the effect that variation of the total concentration of Pd ($[Pd]_{tot}$) would have on the reaction rate of the cyclopropanation of styrene by using **1** as the precatalyst. As shown in Figure 7, k_{obs} is linearly dependent on $[Pd]_{tot}$.

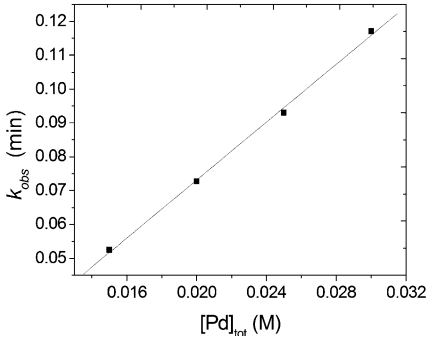


Figure 7. Graph of k_{obs} versus $[Pd]_{tot}$ by using **1** as the catalyst precursor at room temperature.

The role of the olefin: a Hammett plot: Noels and co-workers proposed that, in Pd-catalysed olefin cyclopropanation, coordination of the olefin is crucial for the reaction to occur in an intramolecular fashion (both the carbene and olefin units are bound to the metal). This contrasts with copper- or rhodium-based systems in which the reaction between the metallocarbene and the olefin takes place intermolecularly, that is, with the non-coordinated olefin attacking the metallocarbene carbon atom. Aiming to collect data to support one route over the other, we performed competition experiments with a series of *para*-substituted styrenes by using complex **3** as the catalyst [Eq. (5)] and plotted the relative rates against the Hammett constant σ. As shown in Figure 8, the data adequately fit a Hammett plot, although it has a positive slope. This is in contrast with most of the catalytic systems previously described that provide correlations with negative slopes. The fact that the reactivity of an olefin towards cyclopropanation increases if an electron-withdrawing

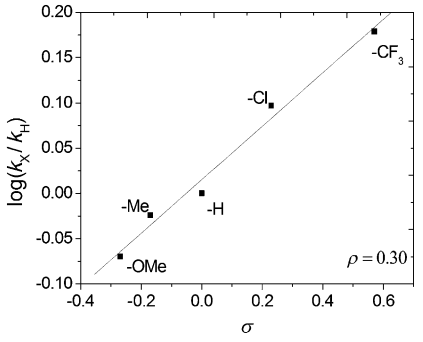
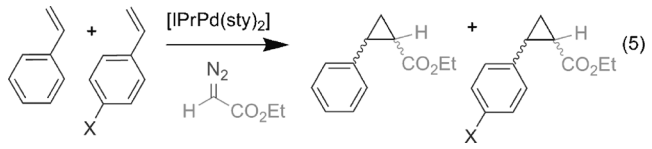
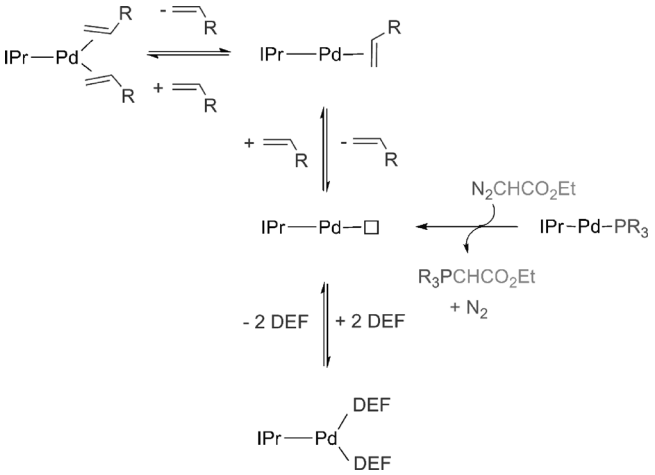


Figure 8. Hammett plot reflecting the electronic effect of the olefin in the cyclopropanation reactions by using complex **3** as the catalyst.

group is present must be considered to be the result of previous coordination of the olefin to an electron rich metal centre, that is, to the {(IPr)Pd} fragment.



We have already mentioned that the observation of similar activities and diastereoselectivities induced by complexes **1**–**4** in the styrene cyclopropanantion reaction with EDA supports the proposal of a common intermediate. On the basis of the data obtained from the previously discussed competition experiments, this species should be the 14e$^-$, unsaturated [(IPr)Pd(olefin)] complex that could be formed from **1** by olefin dissociation or from **2**–**4** by simultaneous phosphine dissociation and olefin addition (Scheme 1).



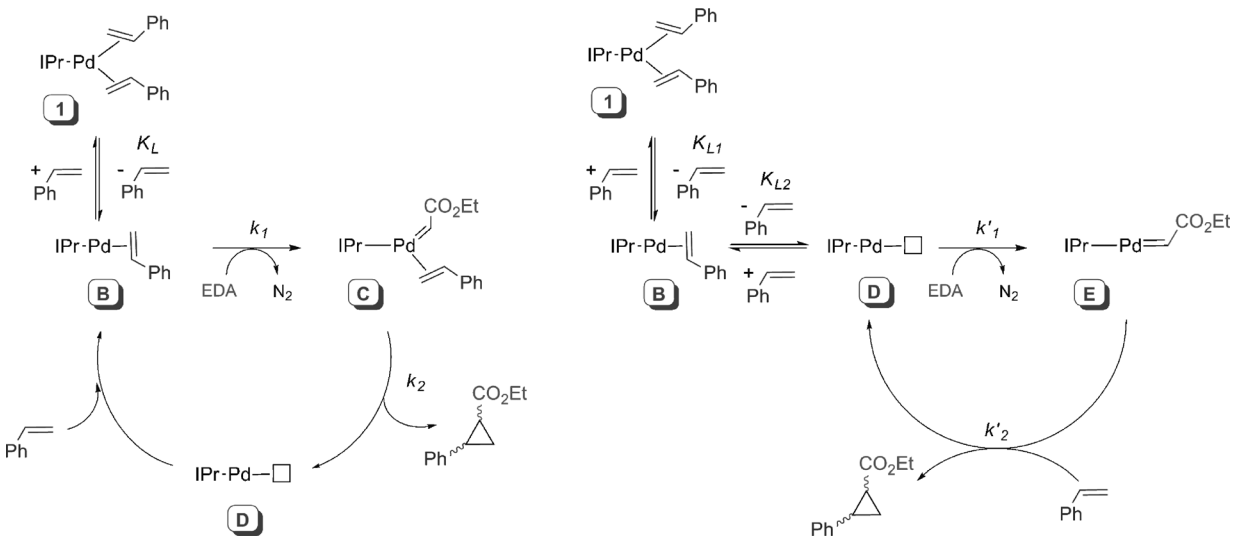
Scheme 1. Equilibria leading to the generation of the catalytic species

These equilibria would control the relative amount of [(IPr)Pd(olefin)] available to react with EDA in the first step of the catalytic cycle. Whereas dissociation of styrene from **1** would occur readily at room temperature, loss of the PR_3 ligand from [(IPr)Pd(PR_3)] seems to be much slower, as inferred from the observation of an initiation period (Figure 6). On the basis of the already described formation of a phosphine ylide from the reaction of [Pd(PPh_3)$_4$] with the diazo ketone $N_2CHCOtBu$,[25] we searched for this type of compound in the reaction mixture when using **3** as the catalyst precursor. We have observed that when three equivalents of EDA were added to a solution of **3** in C_6D_6 (0.6 mL), the intensity of the resonance corresponding to **3** decreased in the ^{31}P NMR spectrum and two new peaks appeared at $\delta = 19.3$ and 17.5 ppm (ratio 4:1) that correspond to the two geometric isomers of the ylide (see the Supporting information), the ratio of which depends on the solvent and temperature.[26] Accordingly, in the ^{1}H NMR spectrum, the resonance of the Ph_3PCH proton for the major isomer (*cis*) could be observed at $\delta = 3.32$ ppm (d, $J_{HP} = 24$ Hz). The induction time observed with [(IPr)Pd(PR_3)] would then correspond to the time required to consume the PR_3 in the reaction mixture, and from that point the catalytic reaction would be indistinguishable from that carried out with **1** as the catalyst.

*The rate law for the styrene cyclopropanation with **1***: Experimental data collected to this point seem to imply that [(IPr)Pd(olefin)] is the catalytic system in this reaction. However, we have not yet distinguished between the two posible synthetic routes that may explain the formation of the cyclopropanes. The first pathway would involve attack of the diazocompound onto [(IPr)Pd(olefin)] **B** (Scheme 2, left) to give a transient olefin–palladacarbene that would collapse into the products. However, it could also be possible that the unsaturated, olefin-free [(IPr)Pd] species (**D**) could react with EDA to give the corresponding palladacarbene [(IPr)Pd=C(H)CO_2Et] (**E**) that would then interact with the olefin (Scheme 2, right). A detailed kinetic analysis for both possible pathways has been carried out, leading to the reaction rate laws given by Equations (6) and (9) (see the Supporting Information for the derivation of both equations). The experimentally observed (Figure 7) linear dependence of k_{obs} on $[Pd]_{tot}$ (i.e., the initial amount of **1**) cannot be employed to distinguish between the two mechanisms because, as shown in Equations (7) and (10), both routes would show this behaviour. However, there is a significant distinction regarding the dependence of the inverse of k_{obs} on [sty]. In one case, this dependence should be linear [Eq. (8)], whereas, for the mechanism involving species **E** as an intermediate, that is, with no olefin coordinated to palladium, second-order behavior would be expected [Eq. (11)]. Consiquently, a series of kinetic experiments was performed in which only the amount of styrene added to the reaction was modified. Figure 9 shows a plot of $1/k_{obs}$ versus [sty]. The linear correlation between the magnitude of these leaves no doubt about the pathway responsible for this transformation; it is the 14e$^-$ unsaturated species **B**, [(IPr)Pd(sty)], that reacts with EDA to generate **C** prior to cyclopropane formation. The intercept at the y-axis provides the value of $1/(k_1[Pd]_{tot})$ and hence the value for k_1 is determined to be 1.77×10^2 min^{-1}. The slope corresponds to the value of $1/k_1K_L[Pd]_{tot}$, from which the value of K_L was found to be 5×10^{-2}. This result explains the decrease in the reaction rate with added olefin, since most of the palladium in solution remains in the form of **1**.

$$\frac{d[N_2]}{dt} = -\frac{d[EDA]}{dt} = k_1\frac{[Pd]_{tot}}{1+\frac{[Sty]}{K_L}}[EDA] \quad (6)$$

$$k_{obs} = \frac{[Pd]_{tot}}{1+\frac{[Sty]}{K_L}} \quad (7)$$



Scheme 2. Possible catalytic cycles for the styrene cyclopropanation reaction with ethyl diazoacetate and [(IPr)Pd(sty)$_2$] as the catalyst: Left: [(IPr)Pd(sty)] as the species that reacts with EDA; Right: [(IPr)Pd] as the species that reacts with EDA.

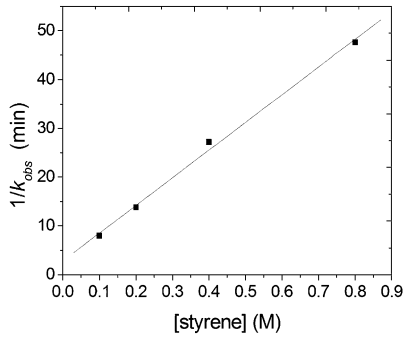


Figure 9. Dependence of $1/k_{obs}$ on the concentration of styrene. The value of k_1 is obtained from the intercept and K_L from the slope of the line.

$$\frac{1}{k_{obs}} = \frac{1}{k_1[Pd]_{tot}} + \frac{[Sty]}{k_1 K_L [Pd]_{tot}} \quad (8)$$

$$\frac{d[N_2]}{dt} = -\frac{d[EDA]}{dt} = k'_1 \frac{[Pd]_{tot}}{1 + \frac{[Sty]}{K_{L1}} + \frac{[Sty]^2}{K_{L2}}}[EDA] \quad (9)$$

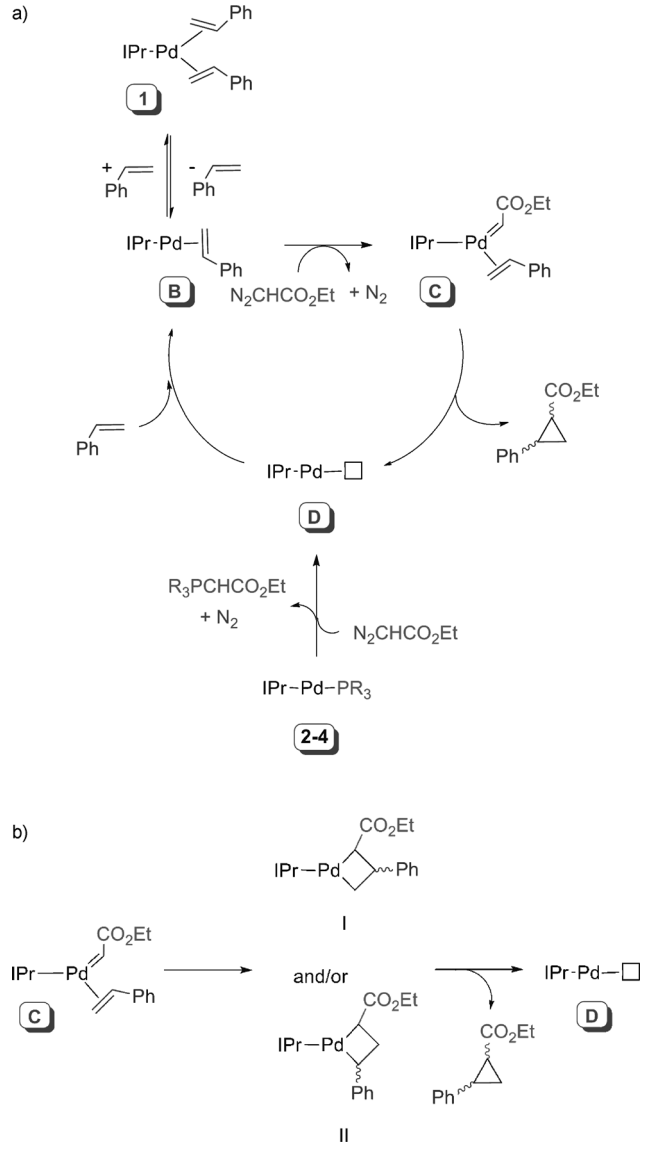
$$k_{obs} = k'_1 \frac{[Pd]_{tot}}{1 + \frac{[Sty]}{K_{L1}} + \frac{[Sty]^2}{K_{L2}}} \quad (10)$$

$$\frac{1}{k_{obs}} = \frac{1}{k'_1[Pd]_{tot}}\left[1 + \frac{[Sty]}{K_{L1}} + \frac{[Sty]^2}{K_{L2}}\right] \quad (11)$$

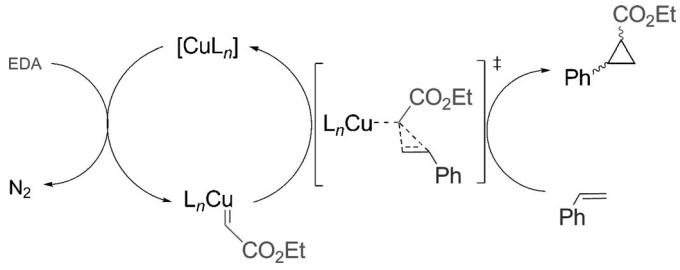
Overall mechanism: On the basis of the collected experimental data, an overall mechanistic proposal has been developed (Scheme 3) for the catalytic styrene cyclopropanation by using complexes **1**–**4** as the catalyst precursors. First, the catalyst precurors undergo either ligand dissociation (for precursor **1**) or transformation of a ligand into an ylide (for precursors **2**–**4**). In the latter case, the unsaturated species [(IPr)Pd] (**D**) would then be trapped by styrene to give the real catalytic species in this system, the 14e$^-$ complex [(IPr)Pd(sty)] (**B**). This complex reacts with EDA to afford the transient metallocarbene [(IPr)Pd(=CHCO$_2$Et)(Sty)] species (**C**), which collapses into the cyclopropanes (*cis* and *trans*) and produces complex **D** on the way to forming **B** and restarting the catalytic cycle.

At this stage, only the exact nature of the coupling of styrene to the carbene unit CHCO$_2$Et remains somewhat undiscovered. However, this has been proposed to occur by facile and irreversible intramolecular [2+2] cycloaddition to form a palladacyclobutane molecule[27] (Scheme 3). It is worth mentioning that this would be the sole species in the overall catalytic cycle in which the metal center would be in a formal oxidation state of +2. The subsequent reductive elimination would afford the cyclopropane and complex **C**.

Finally, although the mechanism proposed herein is clearly different from those reported for other transition metals, such as copper (Scheme 4),[2f,28] the diastereroselectivity is similar to those observed for other complexes containing NHC ligands. For instance, the N-heterocyclic carbene complex [(IPr)CuCl] afforded a diastereoselectivity (*cis*/*trans*) of 32:68 in the cyclopropanation of styrene with EDA,[4q] which is almost indentical to those found for the NHC–Pd^0 complexes. Theoretical calculations for copper C_2-symmetric complexes[28b] have revealed that the alkene substituent does not interact significantly with the ligand in any *exo* pathway (structure I in Scheme 3), meaning that the *cis*/*trans* selectivity is only a consequence of the relatively weak steric repulsion between the carboxylate and alkene substituents in the transition state or intermediate, independent of the mechanism (through metallacyclobutane or direct carbene transfer to the olefin). However, other transition-metal systems are highly diastereroselective. For example, the [Tp^{Ms}Cu] complex affords a 98:2 *cis*/*trans* mixture of the cyclopropanes from styrene.[4s] In this case, the combination of C_{3v} symmetry and the steric bulk of the ligand makes [Tp^{Ms}Cu] a highly diastereoselective catalyst.



Scheme 3. Top: Overall mechanism for the styrene cyclopropanation reaction by using complexes **1**–**4** as the catalyst precursors and ethyl diazoacetate as the carbene source. Bottom: A plausible explanation for the intramolecular formation of cyclopropane.



Scheme 4. Proposed mechanism for the styrene cyclopropanation reaction catalysed by copper systems.

Conclusion

We have shown that several [(NHC)Pd^0] complexes can act as very active catalysts in the olefin cyclopropanation reaction with ethyl diazoacetate as the carbene source, improving on the previously described catalytic systems based on the use of this metal. On the basis of the kinetic data, as well as other experimental data, we have proposed a mechanism for this transformation in which, independent of the catalyst precursor employed ([(IPr)Pd(sty)$_2$] or [(IPr)Pd(PR$_3$)]), the same catalytic species is responsible of the decomposition of EDA and subsequent carbene addition, that is, the intermediate [(IPr)Pd(sty)] complex, which leads to the formation of [(IPr)Pd(=CHCO$_2$Et)(sty)] after interaction with EDA and nitrogen extrusion. The cyclopropane should then be formed by a [2+2] cycloaddition reaction, involving a palladacyclobutane intermediate. The development of this catalytic system for diazo compound decomposition and carbene transfer, along with knowledge of the intramolecular nature of the reaction (regarding the carbene–olefin coupling), appears promising for the future design of new catalysts to induce high levels of diastereo- or enantioselectivity by conveniently modifying the NHC ligand. Work aimed at such catalyst improvement is currently underway in our laboratory.

Experimental Section

General Methods: All reactions and manipulations were carried out under an oxygen-free nitrogen atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. All substrates were purchased from Aldrich. Solvents were dried and degassed before use. The Pd complexes **2**–**5**[18] and the NHC carbene ligands[29] were prepared according to literature methods. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. GC data were recorded in a Varian CP-3800 instrument. X-ray crystal structure analysis was performed in the Unidad de Analyses Elemental of the Instituto de Investigaciones de Química, CSIC-Universidad de Sevilla and elemental analyses in the Centro de Investigación en Química Sostenible, CIQSO-Universidad de Huelva.

[(IPr)Pd(sty)$_2$] (1): Styrene (0.8 mL, 6.98 mmol) was added to a solution of [(IPr)Pd(allyl)Cl][18] (1.05 g, 1.50 mmol) and KO*t*Bu (0.185 g, 1.65 mmol) in *i*PrOH (20 mL). Almost immediately, a white precipitate was formed. After 15 min of stirring at room temperature, the solid was filtered of and washed with water and *i*PrOH. Complex [(IPr)Pd(sty)$_2$], **1**, was isolated as a white solid (90%, 0.94 g). By recrystallisation in toluene at −30°C, a crystalline solid was isolated (80%, 0.84 g). IR (KBr): $\tilde{\nu}$ = 1505 cm^{-1} (C=C); ^{1}H NMR (400 MHz, −40°C, [D$_8$]toluene): δ = 6.67 (s, 2H), 3.75 (dd, J = 9.3, J = 12.0 Hz, 2H), 3.35–3.51 (m, 2H), 3.07 (d, J = 12.4 Hz, 2H), 2.94, (d, J = 8.9 Hz, 2H), 2.76–2.89 (m, 2H), 1.40 (d, J = 6.6 Hz, 6H), 1.16 (d, J = 6.5 Hz, 6H), 1.07 (d, J = 7.1 Hz, 6H), 1.05 ppm (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, 40°C, CD$_2$Cl$_2$): δ = 146.8 (s; *C* arom), 145.8 (s; *C* arom), 144.9 (s; *C* arom), 137.5 (s; *C* arom), 129.5 (s; *C* arom), 127.5 (s; *C* arom), 124.2 (s; *C* arom), 124.1, (s; *C* arom), 124.0 (br s; *C*H imid), 123.28 (s; *C*H arom), 74.66 (s; *C*H olefin), 53.01 (s; *C*H$_2$ olefin), 28.93 (s; *C*H(CH$_3$)$_2$), 28.32 (s; *C*H(CH$_3$)$_2$), 27.21 (s; CH(*C*H$_3$)$_2$), 25.28 (s; CH(*C*H$_3$)$_2$), 22.84 (s; CH(*C*H$_3$)$_2$), 22.31 ppm (s; CH(*C*H$_3$)$_2$); elemental analysis calcd (%) for C$_{43}$H$_{53}$N$_2$Pd: C 73.37, H 7.53, N 3.98; found: C 72.75, H 7.52, N 3.97.

In situ preparation of [(IMes)Pd(PCy$_3$)] (6): Compound **6** was generated in situ by the following procedure: IMes[28] (30 mg, 0.01 mmol) was

added to a solution of $[Pd(PCy_3)_2]$[30] (66 mg, 0.01 mmol) in CH_2Cl_2 (10 mL). After 10 min of stirring, the solution was used directly in the cyclopropanation experiments. To characterise **6** by NMR spectroscopy this complex was also prepared in situ by dissolving a stoichiometric amount of IMes and $[Pd(PCy_3)_2]$ in C_6D_6 (0.7 mL). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 6.79$ (s, 4H), 6.21 (s, 2H), 2.30 (s, 12H), 2.16 (s, 6H), 2.0–1.0 ppm (m, 30H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 198.2$ (d, $^2J_{CP} = 90.79$ Hz; *C* carbene), 138.4 (s; *C* arom), 137.1 (s; *C* arom), 135.3 (s; *C*H arom), 128.7 (s; *C*H arom), 121.2 (d, $^4J_{CP} = 4.3$ Hz; *C* imid), 34.5 (d, $^2J_{CP} = 12.1$ Hz; *C*H Cy), 31.9 (d, $^4J_{CP} = 7.3$ Hz; CH_2 Cy), 27.8 (s; CH_3), 26.8 (s; CH_3), 21.1 (d, $^2J_{CP} = 16.1$ Hz; CH_2 Cy), 18.7 ppm (d, $^3J_{CP} = 9.0$ Hz; CH_2 Cy); ^{31}P (100 MHz, C_6D_6): $\delta = 46.6$ ppm.

Genaral catalytic cyclopropanation reaction: EDA (0.12 mL, 1 mmol) was added to a solution of the palladium complex (0.01 mmol, **6** generated in situ) in CH_2Cl_2 (10 mL) and the corresponding olefin (5 mmol). The consumption of EDA was monitored by GC. When the reaction was finished, the volatiles were removed under vacuum and the crude product mixture was analysed by ^{1}H NMR spectroscopy. All of the products have previously been described and thus were identified by straightforward comparison with reported data.[31] Conversions were determined by ^{1}H NMR spectroscopy by using 1,4-dimethoxybenzene as an internal standard.

Reaction of 3 with EDA: **ylide formation, $Ph_3P{=}CHCO_2Et$**: EDA (7 μL, 3 equiv) was added to a solution of $[(IPr)PdPPh_3]$ (**3** 0.02 mmol) in C_6D_6 (0.6 mL). After 24 h, the reaction was analysed by NMR spectroscopy at room temperature and the ylide formation was observed. The ^{31}P NMR spectrum of the reaction mixture contained two peaks corresponding to the geometric isomers of the ylide ($\delta = 19.3$ and 17.4 ppm) and, accordingly, a doublet corresponding to the coupling of the C*H* in $Ph_3P{=}CHCO_2Et$ can be observed at $\delta = 3.61$ ppm ($^2J_{HP} = 24.0$ Hz) in the ^{1}H NMR spectrum.

Reaction of 1 with DEF: detection of $[(IPr)Pd(DEF)_2]$: Diethyl fumarate (10 μL, 3 equiv) was added to a solution of **1** (0.02 mmol) in CD_2Cl_2 (0.6 mL). The reaction was monitored by ^{1}H NMR spectroscopy. At room temperature, fluxional behaviour was observed. At low temperature (−40 °C), selected resonances of the adduct $[(IPr)Pd(DEF)_2]$ can be assigned; two doublets at $\delta = 4.51$ and 3.73 ppm (d, 2H, $^3J_{HH} = 10.4$ Hz) were observed corresponding to the C*H* in the coordinated DEF, assigned by comparison with the related complex $[(IMes)Pd(DMF)_2]$.[16d]

Competition reactions: EDA (60 μL, 0.5 mmol) was added in one portion to a solution of $[(IPr)Pd(PPh_3)]$ (**3**, 7.5 mg, 0.01 mmol), styrene (0.28 mL, 2.5 mmol) and 1-hexene or cyclooctene (2.5 mmol) in dichloromethane (10 mL). The reaction mixture was monitored by CG until all of the EDA was consumed. The volatiles were removed under vacuum and the crude reaction mixture was analysed by ^{1}H NMR spectroscopy. The resonances of the corresponding cyclopropanes were assigned in the ^{1}H NMR spectra by comparison with the values reported in the literature.[30] The ratio of the cyclopropanes was obtained by integration (average of at least two runs).

Cyclopropanation competition experiments of *para*-substituted styrenes (Hammett plot): Ethyl diazoacetate (0.5 mmol) was added to a solution of **1** (0.01 mmol) and an equimolar mixture of styrene (2.5 mmol) and the corresponding *para*-substituted styrene (2.5 mmol) in dichloromethane (10 mL). The reaction was monitored by CG. The volatiles were removed under vacuum and the crude reaction mixture was analysed by ^{1}H NMR spectroscopy. The resonances of the corresponding cyclopropanes were assigned in the ^{1}H NMR spectra by comparison with the values reported in the literature.[32] The ratios of the cyclopropanes obtained by integration (average of at least two runs): *p*-OMe/H = 0.85; *p*-Me/H = 0.94; *p*-Cl/H = 1.25; *p*-CF_3/H = 1.50.

Olefin exchange reaction between $[(IPr)Pd(sty)_2]$ (1) and styrene (Eyring plot): A solution of olefin (84 mM, 6 equiv) and $[(IPr)Pd(sty)_2]$ (**1**; 14 mM) in [D$_8$]toluene (0.6 mL) was transferred into an NMR tube. The solution was monitored by NMR spectroscopy at different temperatures.

General kinetic experiments: Nitrogen evolution measurements were performed in a device consisting of a stainless-steel gas reservoir connected to a pressure transmitter and an electronic pressure meter/controller (EL-Press, Bronkhorst HI-TEC). The outlet of the pressure controller was connected to a reaction flask (100 mL) that was also connected to a Schlenk manifold to allow for manipulation of the reaction and degassing. The N_2 pressure increase was measured after addition of EDA (0.95 mmol) to a stirred solution of styrene and the palladium catalyst in dichloromethane at room temperature. The apparatus was tested by carrying out the cyclopropanation reaction of styrene with EDA by using $[Tp^{Br_3}Cu]$ as the catalyst. Styrene (5 mmol) and $[Tp^{Br_3}Cu]$ (0.0025 mmol) were dissolved in dichlomethane (10 mL) and EDA (0.95 mmol) was added. The $[Tp^{Br_3}Cu]$ complex catalysed the decomposition of 0.95 mmol of EDA (100 μL) and the N_2 pressure increased by 0.25 bar.

Crystal data for 1: A single crystal of suitable size, crystallised from toluene, coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream to the goniometer head. Reflections were collected from a Bruker-Nonius X8 Apex-II CCD diffractometer in the range $2.74 > 2\theta > 56.62°$. The data were reduced (SAINT) and corrected for Lorentz polarisation effects and absorption by the multiscan method applied by SADABS.[33,34] The asymmetric unit of **1** is formed of two independent half-complexes having twofold rotational symmetry and also two solvating toluene molecules; one of the toluene molecules was observed to be disordered and in two positions with an occupancy factor fixed at 0.6 and 0.4. The structure was solved by direct methods (SIR-2002)[35] and refined against all F^2 data by full-matrix least-squares techniques (SHELXL97).[35] $C_{57}H_{68}N_2Pd$ [$C_{43}H_{52}N_2Pd$, $2(C_7H_8)$]; $M_w = 887.53$; orthorhombic; space group *Pccn* (no. 56); crystal size $0.43 \times 0.42 \times 0.40$ mm^3; yellow prism; $a = 19.8389(14)$ Å; $b = 22.3293(14)$ Å; $c = 22.5270(16)$ Å; $V = 9979.2(12)$ Å^3; $\alpha = 90°$; $\beta = 90°$; $\gamma = 90°$; $Z = 8$; 173(2) K; $\rho_{calcd} = 1.181$ g cm^{-3}; λ(Mo $_{K\alpha1}$) = 0.71073 Å; $F(000) = 3760$; $\mu = 0.409$ mm^{-1}; 163375 reflns collected; 12363 independent reflns ($R_{int} = 0.0695$); 583 parameters; goodness of fit on F^2, $S = 1.072$; $R_1 = 0.0594$ [$I > 2\sigma(I)$]; $wR_2 = 0.2017$.

Acknowledgements

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