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ARTICLE

Palladium Hydrazonato Complexes and their role in the Pd-Catalyzed Cross-Coupling Reactions of Hydrazones as Carbene Precursors

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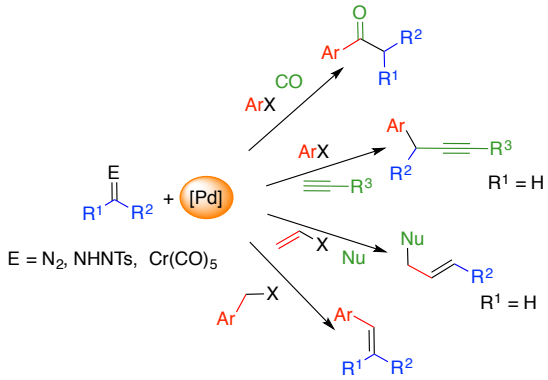
Hydrazones are common carbene precursors in many palladium-catalyzed cross coupling reactions of carbenes as a coupling partner, but their interaction with palladium has been overlooked. We have found that hydrazonato ligands readily coordinate to Pd aryl complexes leading to [Pd(Ar)(L-L){(TolSO$_2$)N-N=CHR}] (Ar = Ph, C_6F_5; L-L = dppe, dppf; R = CH=CHPh, Ph). Ligand substitution reactions on [Pd(Ar)(dppe)X] (X = Br, TolSO$_2$) show that the hydrazonato ligand coordinates preferently so the hydrazonato complexes are likely resting states in catalytic carbene coupling reactions using hydrazones as reactants. The decomposition of the hydrazonato moiety to a diazoalkane is needed during the catalysis and the analysis of the evolution of the hydrazonato complexes shows that it is not promoted by coordination to the metal and it does not occur in the coordination sphere of palladium. The substitution of diazoalkane for the metal-bound hydrazonato is possible and the steps that follow to form a new C-C bond, including the carbene migratory insertion, are fast.

Introduction

Palladium-catalyzed cross coupling reactions that involve a carbene fragment as reactant are widespread. The possibility of forming two new bonds on the carbene carbon has led to the discovery of interesting multicomponent cascade processes that allow the introduction of several functionalities in one synthetic step (Scheme 1).[1-3] The non-stabilized carbene fragments used in these reactions, usually CRR' (R, R' = H, hydrocarbyl), are generally transferred from a diazoalkane to palladium. Scheme 2 shows a general mechanism for these transformations that involves the formation of a Pd-R moiety, the carbene transfer to the metal, and a carbene migratory insertion step leading to a new C-C bond. Intermediates **A**-**C** are common to all the processes, although the formation of **A** and the evolution of **C** can occur by different routes depending on the specific reaction.

The synthesis of diazoalkanes is not always easy and these compounds are often unstable and hazardous.[4] In 2007 Barluenga and Valdés introduced the use of hydrazones as diazoalkane surrogates in the catalytic coupling reactions that involve carbenes.[5] Hydrazones and in particular *N*-tosylhydrazones slowly decompose in basic medium via the Bamford–Stevens reaction to the corresponding diazo compound (Scheme 2).[6] In contrast to the diazoderivatives, hydrazones are stable and easy to synthesize from a large variety of precursors.[7] For this reason, the use of hydrazones as carbene sources is a very attractive alternative and they have become the reactant of choice in many Pd-catalyzed coupling reactions.[2b,5b,8,9]



Scheme 1. Some examples of Pd-catalyzed coupling reactions with carbene precursors.

In the mechanistic proposals collected in the literature, the role of the reactant hydrazone is exclusively the generation of a diazoalkane by its decomposition outside the catalytic cycle, and no interaction with the metal has been considered (Scheme 2). However, hydrazones and the corresponding hydrazonatos formed upon deprotonation in basic medium are potential ligands used in large excess during the catalysis and

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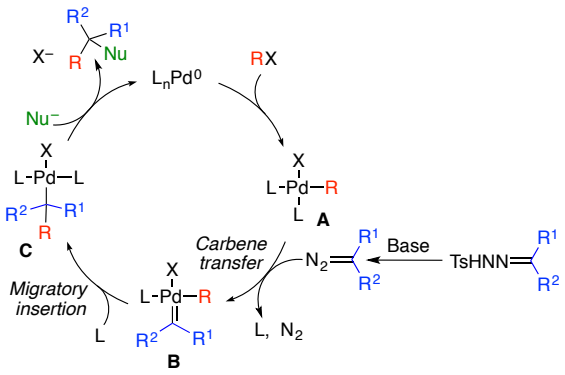


Scheme 2. A general catalytic cycle for Pd-catalyzed coupling reactions with hydrazones or diazo compounds as carbene precursors (the formation of Pd-R is shown here as the results of oxidative addition on Pd(0)).

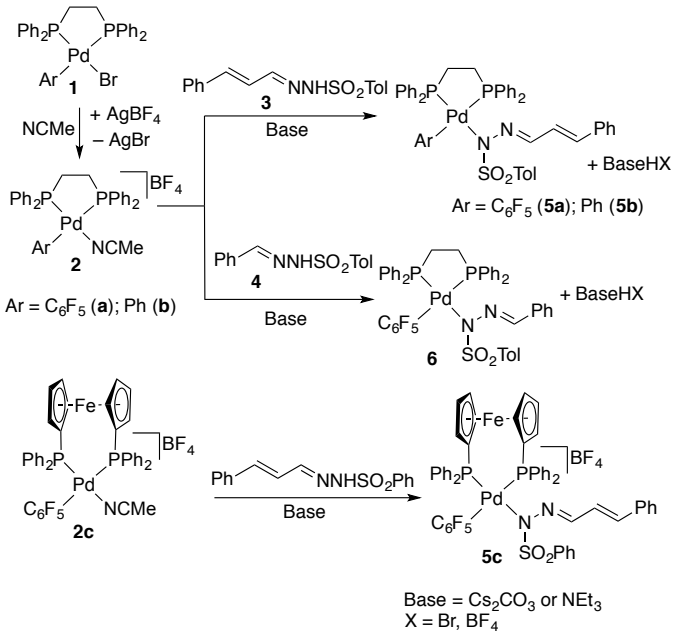
likely to coordinate to the metal. We have explored the reactions of palladium aryl complexes with hydrazones in basic media as well as their subsequent reactivity in conditions related to the catalytic process in which they are used. The results reported here give a more accurate picture of the catalytic scenario.

Results and discussion

[PdArBr(L-L)] (**1**) and [PdAr(L-L)(NCMe)]BF_4 (**2**) (Ar = C_6F_5, Ph; L-L = bis(diphenylphosphino)ethane, dppe; bis(diphenylphosphino)ferrocene, dppf) were used as well-defined aryl complexes which model intermediate **A** in Scheme 2. *N*-Tosylhydrazone derivatives R'SO_2NHNCHR (R = CH=CHPh (**3**), Ph (**4**); R' = Tol, Ph) were tested, since they are common reactants in many Pd-catalyzed processes.[2d,10,11] Additionally, the reactivity of complexes **2** with the analogous diazocompounds N_2CHR, which can be formed in basic media from the hydrazones, has been previously studied and therefore any product resulting from the in situ formed diazoalkanes can be detected.[12]

Hydrazonates are good ligands and, indeed, in the presence of a mixture of a *N*-tosylhydrazone and a base, complexes **1** or the solvento complexes **2** form the hydrazonato derivatives **5** and **6** (Scheme 3). This means that, under catalytic conditions (excess of hydrazonate), intermediate **A** in Scheme 2 is likely to be transformed into a derivative analogous to **5** or **6**. Complex **5c**, with a different set of ligands, was synthesized in order to perform a crossover experiment, as described below.

Palladium derivatives with monodentate hydrazonato ligands are rare and, to our knowledge, only one structurally characterized complex of this type has been reported before.[13] Complexes **5** and **6** were isolated in good yields and characterized. Figure 1 shows the molecular structure of complex **6** and **5c**. The hydrazonato ligand is quite bulky and, in solution, restricted rotation about the Pd-N bond leads to broad signals in the ^{1}H and ^{19}F NMR for most derivatives at room temperature. The slow rotation limit is observed at 233 K for **5a** (Figures S17-S18 and S20 in the ESI) but the process is already slow at 298 K for the more constrained derivative **5c** (Figures S30, S32 in the ESI).



Scheme 3. Reactions of Pd-aryl complexes with hydrazonates

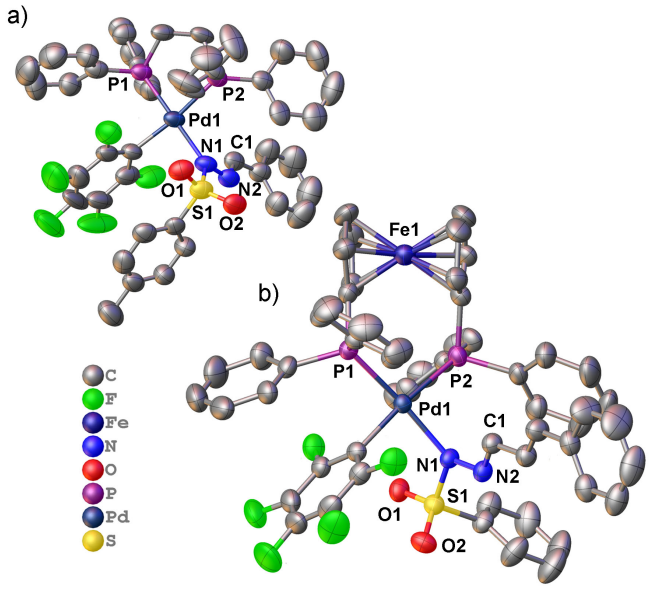
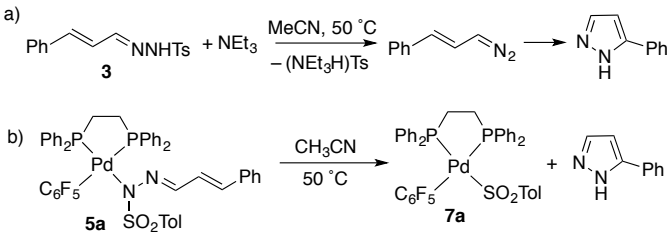


Figure 1. Molecular structures of complexes **6** (a) and **5c** (b) (ORTEP plots 40 % probability ellipsoids). Hydrogens have been omitted for clarity. Selected distances (Å) **6**: Pd1–N1, 2.105(5); N1–N2, 1.382(6); N2–C1 1.270(7); **5c**: Pd1–N1, 2.109(4); N1–N2, 1.380(5); N2–C1 1.282(5).

Since the coordination of the hydrazonate derivatives to palladium is so facile, we wondered if the metal played any role in the decomposition of this moiety to the diazoalkane, a necessary step in the catalysis. The decomposition of the free hydrazone **3** in the presence of triethylamine as base in acetonitrile at 50 ˚C leads to 5-phenyl-1*H*-pyrazole, via the *in situ* generation and subsequent cyclization of the diazo compound (Scheme 4, a).[14] NEt_3 was used as a base in this experiment to ensure the formation of the soluble ammonium hydrazonate. In contrast, the use of an alkali carbonate leads to very insoluble hydrazonate salts and therefore the

decomposition is controlled by the small concentration of the reactant hydrazonate. This is the reason why the use of ammonium halides as phase transfer agents is common in many catalytic processes that use hydrazones. Complex **5a** decomposes under the same conditions used for the free hydrazone to give the tosylate complex **7a** as well as 5-phenyl-1*H*-pyrazole (Scheme 4, b). Figure 2 shows the molecular structure of **7a** determined by X-ray diffraction. As expected,



Scheme 4. Decomposition of free (a) and coordinated (b) hydrazonates.

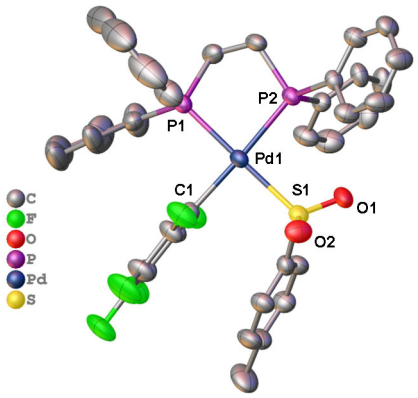


Figure 2. Molecular structures of complex **7a** (ORTEP plots 40 % probability ellipsoids). Hydrogens have been omitted for clarity. Selected distances (Å): Pd1–S1, 2.337(2); Pd-C1, 2.058(7); Pd-P1, 2.278(2); Pd-P2, 2.3203(19).

the tosyl fragment is coordinated to the metal via the S atom, according to the soft nature of the Pd(II) center.[15] Interestingly, the monitorization of the decomposition of **5a** at 50 ˚C shows a very slow decomposition at the beginning of the reaction that undergoes a strong acceleration when about 10 % conversion is reached (Figure 3, a). The observed profile conforms to a situation where, in the course of the decomposition, a species is formed that catalyzes the reaction. When the same monitorization was carried out in the presence of 10 mol % of $NaSO_2Tol$ the reaction is faster and reproduces the concentration-time evolution in the later stage of the decomposition of **5a** (Figure 3, b).[‡] This is consistent with the tosylate increasing the rate of substitution of the coordinated hydrazonate. The same experiment was carried out adding 10 mol % of 5-phenyl-1*H*-pyrazole, also a product formed in the decomposition of **5a**, instead of sodium tosylate. However, a small increase of the rate was observed (half-life of **5a**, $t_{1/2}$ = 7.8 h) consistent with the lower coordination ability of pyrazole (Figure 3, c).[§]

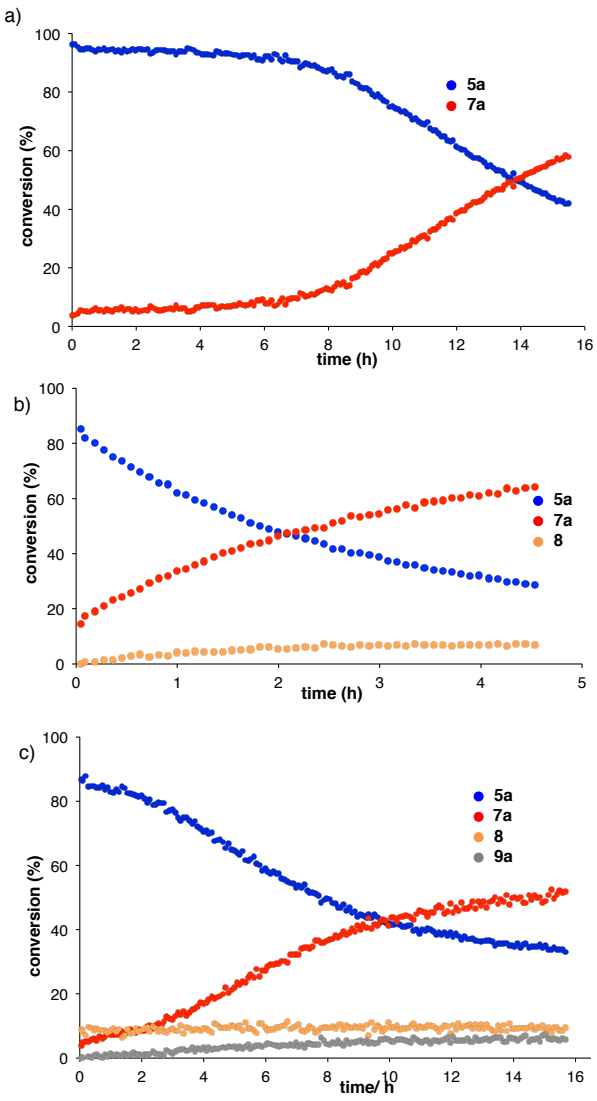
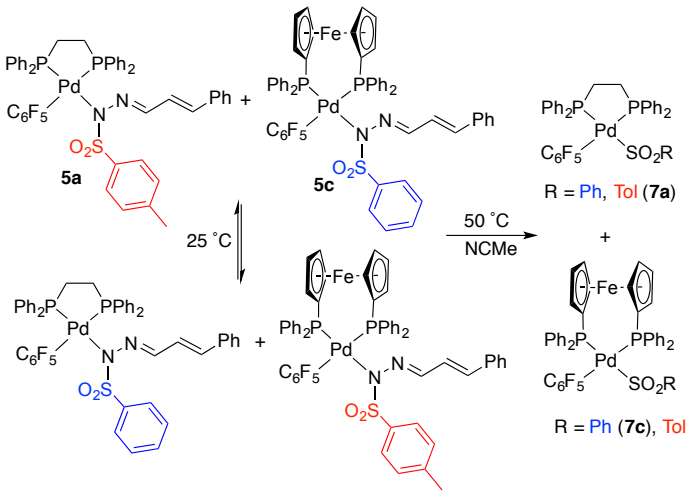


Figure 3. Plot of conversion vs time for the decomposition of a) **5a** in MeCN at 50 ˚C; b) **5a** and $NaSO_2Tol$ (10 mol %) in MeCN at 50 ˚C (the formation of a small amount of [Pd(C_6F_5)(dppe)(κ^1-5-phenyl-pyrazolate)] (**8**) was also observed); c) **5a** and 5-phenyl-pyrazole (10 mol %) in MeCN at 50 ˚C (the formation of a small amount of **8** and the allylic complex **9a** was also observed (see below))

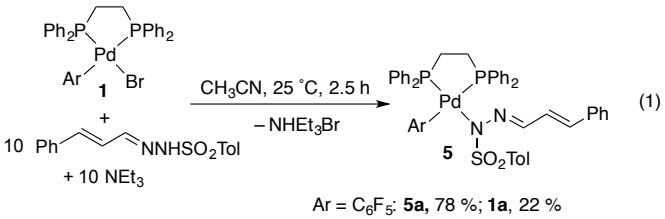
The half-life of the hydrazone **3** in the reaction shown in Scheme 4a is $t_{1/2}$ = 2.6 h (Figure S3 in the ESI), similar to that of **5a** in the presence of sodium tosylate ($t_{1/2}$ = 2 h, Figure 3, b). Therefore, the most plausible scenario is the latter case is the decoordination of the hydrazonate and its decomposition outside the coordination sphere of palladium. The decoordination of the hydrazonato ligand is easier in the more constrained dppf palladium complex **5c**. The crossover experiment depicted in Scheme 5 shows that the scrambling of the hydrazonato ligands in the mixture **5a**/**5c** occurs at room temperature as clearly seen by ^{19}F NMR (Figure S4 in the ESI). When the mixture **5a**/**5c** was heated at 50 ˚C in acetonitrile both complexes decompose to a mixture of tosylate derivatives with a half-life ($t_{1/2}$ = 2.9 h) similar to that observed for the decomposition of the free hydrazone (Scheme 5 and Figures S5 and S6 in the ESI).



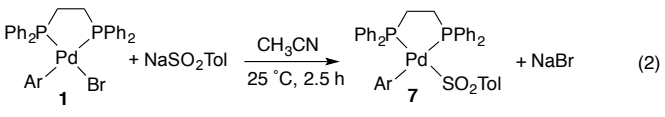
Scheme 5. Crossover experiment showing the facile exchange of hydrazonato ligands (25 °C).

All these experiments show that the metal does not promote the hydrazonate decomposition and the latter process occurs after decoordination of the hydrazonato ligand, outside the catalytic cycle.

The experiments shown above indicate that, in the course of a reaction with *N*-tosylhydrazones as carbene precursors, there are several competing ligands that influence the speciation of palladium, i.e. [PdArL$_2$Y] Y = halide, hydrazonate, TolSO$_2$. Eqs. 1 and 2 show substitution reactions using the ligands in mol ratios close to those under catalytic conditions. In the presence of an excess of hydrazonate, the substitution of hydrazonate for bromide is favored and complexes **5** are the predominant species (Eq. 1). The substitution of tosylate for bromide can also occur (Eq. 2) but it is less facile at least at the beginning of the reaction when the amount free tosylate is low. Nonetheless the actual ratio of species will be dependent on the concentration of free X ligands, which will be in turn controlled by the relative solubility of the formed byproduct salts MX (M$^+$ = alkali cation, NR$_4^+$), according to the base chosen to deprotonate the hydrazone. Since the reactions are usually carried out using a large excess of hydrazone, the complex [PdArL$_2$(hydrazonato)] is a plausible resting state.

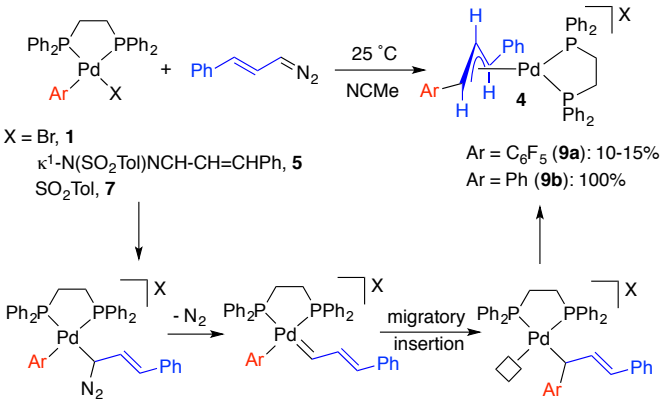


Ar = C_6F_5: **5a,** 78 %; **1a**, 22 %
Ar = Ph: **5b**: 87 %; **9b,** 13 %



Ar = C_6F_5: **1a**, 95 %; **7a**, 5 %
Ar = Ph: **1b**, 83 %; **7b**, 17 %

For the catalytic reaction to proceed as shown in Scheme 2, the *in situ* generated diazoalkane by decomposition of the free hydrazonate has to enter the metal coordination sphere, and we have evaluated the feasibility of the substitution of diazoalkane for X. Scheme 6 shows the reactions tested at room temperature (see also Table S2 in the ESI). The diazoalkane substitutes all X ligands with similar ability. This is followed by a fast Pd-carbene formation and migratory insertion, so only the allylic products **9** resulting from the aryl-carbene coupling can be detected, as has been reported before.[12] The most important difference is introduced by the aryl group, the phenyl group leading to a more efficient formation of the migratory insertion product **9**. The better donor phenyl group can reduce the electrophilicity of the metal making the substitution of the anionic X ligand by the entering neutral diazocompound more favored. The subsequent formation of the carbene (by N_2 extrusion) and migratory insertion will also be affected by the nature of the aryl, but these steps have low energy barriers and it is unlikely that they control the reactivity observed.[12]



Scheme 6. Ligand substitution reactions of complexes of complexes **1**, **5**,and **7** with a diazoalkane leading to the aryl-carbene coupling product **9**.

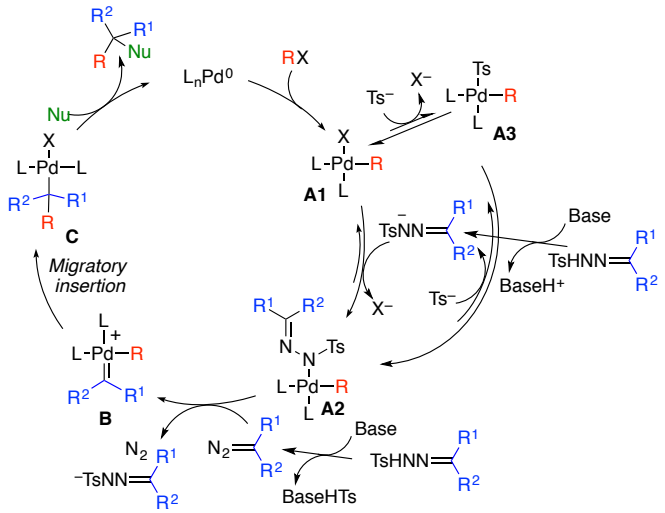
Conclusions

Using well-defined model aryl palladium complexes it is possible to gather information about the interaction of *N*-tosylhydrazones with these complexes and their evolution, both relevant to the catalytic C-C coupling processes that involve the abovementioned carbene precursors. A more detailed catalytic cycle could be derived from this information that completes the general one shown above (Scheme 2) and it is depicted in Scheme 7.

Hydrazonates are excellent ligands that coordinate to palladium and, in the presence of an excess of hydrazone and a base, a common mixture in catalytic reactions, these species are easily formed by halide substitution. When the hydrazonato decomposes via the Bamford-Stevens reaction to a diazoalkane, free tosylate is generated that can also coordinate to palladium. Therefore, a mixture of aryl species [PdArL$_2$Y], Y = halide, hydrazonate, TolSO$_2$, coexist in equilibrium, the hydrazonato complexes being the more abundant (**A1**-**A3** in Scheme 7, analogous to the isolated complexes **1**, **5** and **7**). The decomposition of the hydrazonato

moiety to a diazoalkane is not promoted by coordination to the metal and it does not occur in the coordination sphere of palladium. A previous decoordination is needed, so the conventional evolution of the free hydrazonato to the corresponding diazo compound takes place. The coordination of the diazoalkane to palladium occurs by substitution of the hydrazonato ligand, as it has been tested independently. The substitution of halide or tosylate by the diazoalkane is also possible.

The hydrazonato species **A2** is a likely resting state of these reactions. Once the diazoalkane is formed from the non-coordinated hydrazonato in solution, the substitution of the metal-bound hydrazonato is possible and the steps that follow are fast. Therefore, the substitution equilibria with the diazoalkane, formed in lower concentration, is key for turnover.



Scheme 7. A more detailed catalytic cycle for Pd-catalyzed coupling reactions with hydrazones

Experimental

General considerations.

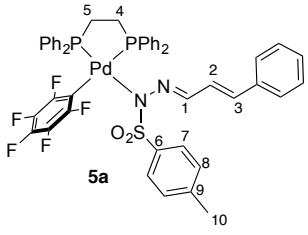
^{1}H, $^{13}C\{^{1}H\}$ ^{31}P and ^{19}F NMR spectra were recorded on Bruker AV-400 or Agilent MR-500 and MR-400 spectrometers equipped with variable-temperature probes at the LTI (UVa). Chemical shifts (δ units, ppm) were referenced to $SiMe_4$ (^{1}H and ^{13}C), $CFCl_3$ (^{19}F) and H_3PO_4 (85%, ^{31}P). For the NMR spectra registered in non-deuterated solvents, a coaxial tube containing DMSO-d_6 was used to maintain the lock to the ^{2}H signal. The temperature for the NMR probe was calibrated with a methanol standard (low temperature).[16] Homonuclear (^{1}H-COSY and ^{1}H-ROESY) and heteronuclear (^{1}H-^{13}C HSQC and HMBC) experiments were used to help with the signal assignments. NMR data are given at 298 K unless otherwise noted. Elemental analyses were carried out in a Carlo Erba 1108 microanalyser (at Vigo University, Spain). Infrared spectra were recorded (in the range 4000-200 cm^{-1}) on a Perkin-Elmer FT-IR Spectrum Frontier with an ATR diamond accessory. All reactions were conducted under a N_2 atmosphere. Solvents were dried using a solvent purification system SPS PS-MD-5 (ether, hexane, THF and CH_2Cl_2) or distilled from appropriate drying agents under nitrogen prior to use and stored over 3 Å or 4 Å molecular sieves (acetonitrile). Sodium *p*-toluenesulfinate and sodium benzenesulfinate, are commercially available. The syntheses of the hydrazone derivatives (**3**, **4** and $(PhSO_2)$NH-N=CH-CH=CHPh),[17] N_2=CH-CH=CHPh,[18] and 5-phenyl-1*H*-pyrazole,[19] were carried out according to the literature methods. [Pd(Br)(C_6F_5)(dppe)],[20] [Pd(Br)(C_6F_5)(dppf)],[21] [PdBr(dppe)Ph],[22] [PdAr(dppe)($NCCH_3$)]-(BF_4) (Ar = Ph, C_6F_5),[12] and the allylic complexes **9** were prepared as reported before.[12] The preparation and characterization of [Pd(C_6F_5)(dppf)-($NCCH_3$)](BF_4) is included in the ESI.

Syntheses of complexes.

[Pd(C_6F_5)(dppe){(*p*-TolSO$_2$)N-N=CH-CH=CHPh}] (5a). [PdBr(C_6F_5)(dppe)] (102.2 mg, 0.135 mmol) and $AgBF_4$ (26.5 mg, 0.135 mmol) were mixed in dry MeCN (3 mL) and stirred for 15 min at room temperature under nitrogen. The suspension was filtered through Kieselghur to remove the AgBr. The resulting solution was added to a mixture of the *N*-tosylhydrazone **3** (40.8 mg, 0.135 mmol) and Cs_2CO_3 (265.7 mg, 0.815 mmol) in MeCN (5 mL) and then stirred for 2 h at room temperature. The reaction mixture was filtered and the filtrate was evaporated to dryness. Addition of Et_2O (5 mL) afforded complex **5a** as a yellow solid, which was collected by filtration, washed with cold Et_2O (2 x 5 mL), and air-dried. Yield: 0.11 mg, (83 %).

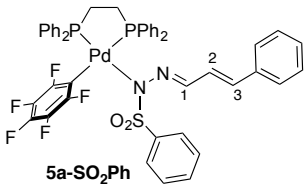
^{1}H NMR (399.86 MHz, δ, $CDCl_3$, 298 K): 7.95 (d, J = 9.1 Hz, 1H, H^{1}), 7.86-7.27 (m, 24H, H^{arom}), 7.33 (d, J = 8.2 Hz, 2H, H^{7}), 7.20 (m, 1H, H^{arom}), 6.87 (d, J = 8.2 Hz, 2H, H^{8}), 6.61 (dd, J = 15.9, 9.1, Hz, 1H, H^{2}), 6.10 (d, J = 15.9 Hz, 1H, H^{3}), 2.51 (br, 2H, H^{5}), 2.27 (m, 2H, H^{4}), 2.20 (s, 3H, H^{10}). $^{13}C\{^{1}H\}$ NMR (100.56 MHz, δ, $CDCl_3$, 298 K): 146.1 (m, $^{1}J_{C\text{-}F}$ = 229.6 Hz, CF_{ortho}), 137.8 (m, $^{1}J_{C\text{-}F}$ = 247.1 Hz, CF_{para}), 141.6 (C^{1}), 140.6 (C^{9}), 140.2 (C^{6}), 137.5 ($C^{ipso\text{-}Ph}$), 134.0 (d, $J_{C\text{-}P}$ = 11.6 Hz, C^{arom}), 132.9 (br, C^{arom}), 132.1 (C^{3}), 131.9 (s br, C^{arom}), 129.5 (d, $^{1}J_{C\text{-}P}$ = 42.0 Hz, C^{arom}), 129.2 (d, $J_{C\text{-}P}$ = 10.5 Hz, C^{arom}), 128.9 (d, $J_{C\text{-}P}$ = 10.5 Hz, C^{arom}), 128.5 (C^{arom}), 128.3 (C^{arom}), 127.8 (C^{8}), 127.4 (C^{2}), 127.1 ($C^{para\text{-}Ph}$), 126.1 (C^{7}), 126.1 (d, $J_{C\text{-}P}$ = 10.0 Hz, C^{arom}), 27.7 (dd, J = 31.8, 17.4 Hz, C^{5}), 24.1 (dd, J = 29.5, 11.5 Hz, C^{4}), 21.0 (C^{10}).* ^{19}F NMR (376.19 MHz, δ, $CDCl_3$, 298 K): -114.05 (br, 2F, F_{ortho}), -160.89 (t, J = 21 Hz, 1F, F_{para}), -163.10 (br, 2F, F_{meta}).† $^{31}P\{^{1}H\}$ NMR (161.87, MHz, δ, $CDCl_3$, 298 K): 52.78 (dt, J = 17.5, 4.4 Hz, 1P), 42.74 (m, 1P). IR (neat, cm^{-1}): C_6F_5, 1453, 1048, 952, 747, 685; SO_2, 1137. Anal. Calcd. for $C_{48}H_{39}F_5N_2O_2P_2PdS$: C, 59.36 %; H, 4.05 %; N, 2.88 %. Found: C, 59.36 %; H, 4.12 % N, 2.88 %.

*The ^{13}C signals for the C_{meta} and C_{ipso} of the C_6F_5 group, heavily coupled to ^{19}F, could not be observed. †Restricted rotation about the Pd-C_6F_5 or Pd-N bonds leads to broad F_{ortho} and F_{meta} signals at 298 K.



^{1}H NMR (499.73 MHz, δ, $CDCl_3$, 233 K): 8.15 (m, 2H, H^{arom}), 8.03 (m, 1H, H^1), 7.84 (m, 2H, H^{arom}), 7.62 (m, 4H, H^{arom}), 7.52 (m, 5H, H^{arom}), 7.33 (m, 11H, H^{arom}), 7.22 (m, 3H, H^{arom}), 6.88 (d, J = 8.2 Hz, 2H, H^8), 6.67 (dd, J = 15.9, 9.4, Hz, 1H, H^2), 6.13 (d, J = 15.9 Hz, 1H, H^3), 2.62 (m, 1H, H^5), 2.37 (m, 2H, $H^{5'}$, H^4), 2.36 (m, 1H, H^4), 2.25 (m, 1H, $H^{4'}$), 2.20 (s, 3H, H^8). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$, 233 K): -114.61 (m, 1F, F_{ortho}), -114.86 (m, 1F, F_{ortho}), -160.34 (t, J = 21 Hz, 1F, F_{para}), -162.66 (m, 1F, F_{meta}), -163.40 (m, 1F, F_{meta}). ^{31}P{^{1}H} NMR (202.31, MHz, δ, $CDCl_3$, 233 K): 53.06 (m, 1P), 44.06 (m, 1P).

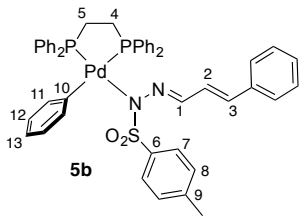
[Pd(C_6F_5)(dppe){($PhSO_2$)N-N=CH-CH=CHPh}] (5a-SO_2Ph). [PdBr(C_6F_5)dppe] (34.0 mg, 0.045 mmol) and $AgBF_4$ (9.0 mg, 0.045 mmol) were mixed in dry MeCN (0.6 mL) and stirred for 15 min at room temperature under nitrogen. The suspension was filtered through Kieselghur to remove the AgBr. The resulting colorless solution was added to a mixture of the N-phenylsulfonyl hydrazone ($PhSO_2$)NH-N=CH-CH=CH-Ph (13.2 mg, 0.045 mmol) and Cs_2CO_3 (29.3 mg, 0.09 mmol) and then stirred for 2 h at room temperature. The reaction mixture was filtered and the resulting yellow solution was characterized by NMR.



5a-SO_2Ph

^{1}H NMR (499.73 MHz, δ, CH_3CN/$(CD_3)_2SO$ capillary): 8.20 (d, J = 9.0 Hz, 1H, H^1), 8.14-7.42 (m, 28H, H^{arom}), 7.39 (t, J = 7.5 Hz, 2H, H^{arom}), 6.64 (m, J = 15.9, 9.0 Hz, 1H, H^2), 6.53 (d, J = 15.9 Hz, 1H, H^3), 2.60 (m, 2H, CH_2), 2.47 (m, 2H, C'H_2). ^{19}F NMR (470.17 MHz, δ, CH_3CN,$(CD_3)_2SO$ capillary): -113.96 (br, 2F, F_{ortho}), -162.40 (t, J = 19.4 Hz, 1F, F_{para}), -164.57 (br, 2F, F_{meta}). ^{31}P{^{1}H} NMR (202.31, MHz, δ, CH_3CN,$(CD_3)_2SO$ capillary): 54.49 (dt, J = 16.2, 4.1 Hz, 1P), 44.50 (m, 1P).

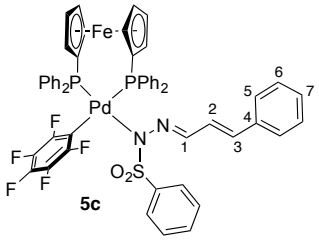
[PdPh(dppe){(*p*-TolSO_2)N-N=CH-CH=CHPh}] (5b). [PdBr(dppe)Ph] (290.0 mg, 0.438 mmol) and $AgBF_4$ (85.3 mg, 0.438 mmol) were mixed in dry MeCN (5 mL) and stirred for 15 min at room temperature under nitrogen. The suspension was filtered through Kieselghur to remove the AgBr. The resulting solution was added to a mixture of the *N*-tosylhydrazone **3** (200.0 mg, 0.665 mmol) and Cs_2CO_3 (420.0 mg, 1.3 mmol) in MeCN (5 mL) and then stirred for 2 h at room temperature. The reaction mixture was filtered and the filtrate was evaporated to dryness. Addition of Et_2O (5 mL) afforded complex **5b** as a yellow solid, which was collected by filtration, washed with Et_2O (2 x 5 mL), MeOH (3 x 5 mL) and air-dried. Yield: 0.243 g (63 %).



5b

^{1}H NMR (399.86 MHz, δ, $CDCl_3$): 8.14 (d, J = 9.1 Hz, 1H, H^1), 8.27-7.21 (m, 24H, H^{arom}), 7.16 (tt, J = 6.7, 1.9 Hz, 1H, H^{arom}), 7.05 (t, J = 7.5 Hz, 2H, H^{11}), 6.97 (d, J = 8.5 Hz, 2H, H^7), 6.78 (d, J = 8.5 Hz, 2H, H^8), 6.72 (m, 1H, H^{13}), 6.67 (m, 2H, H^{12}), 6.64 (dd, J = 15.9, 9.1 Hz, 1H, H^2), 6.05 (d, J = 15.9 Hz, 1H, H^3), 2.48 (m, 2H, H^5), 2.24 (m, 2H, H^4), 2.18 (s, 3H, Me). ^{13}C{^{1}H} NMR (100.56 MHz, δ, $CDCl_3$): 156.9 (d, J_{C-P} = 123.9 Hz, C^{10}), 140.3 (C^1, C^9), 139.9 (C^6), 137.7 (C^{arom}), 137.2 (C^{11}), 133.3 (d, $^1J_{C-P}$ = 10.0 Hz, C^{arom}), 131.2 (C^{arom}), 130.9 (C^3), 129.7 (C^{arom}), 129.0 (d, J_{C-P} = 8.8 Hz, C^{arom}), 128.8 (d, J_{C-P} = 10.1 Hz, C^{arom}), 128.5 (C^{arom}), 128.1 (C^8), 127.7 (C^2), 127.5 (C^7), 127.2 (C^{12}), 127.2 (C^{arom}), 126.9 (C^{arom}), 126.8 (C^{arom}), 125.9 (C^{arom}), 122.9 (C^{13}), 29.1 (dd, J_{C-P} = 30.8, 20.9 Hz, C^5), 24.2 (dd, J_{C-P} = 25.6, 11.5 Hz, C^4), 21.22 (Me). ^{31}P{^{1}H} NMR (161.87, MHz, δ, $CDCl_3$): 47.72 (d, J = 24.5 Hz, 1P), 32.65 (d, J = 24.5 Hz, 1P). IR (neat, cm^{-1}): SO_2, 1136. Anal. Calcd. for $C_{48}H_{44}N_2O_2P_2PdS$: C, 65.42 %; H, 5.03 %; N, 3.18 %. Found: C, 65.39 %; H, 5.22 % N, 3.21 %.

[Pd(C_6F_5)(dppf){($PhSO_2$)N-N=CH-CH=CHPh}] (5c). Equimolar amounts of [PdBr(C_6F_5)dppf] (110.0 mg, 0.12 mmol) and $AgBF_4$ (23.6 mg, 0.12 mmol) were mixed in dried MeCN (3 mL) and stirred for 15 min at room temperature under nitrogen. The suspension was filtered through Kieselghur to remove the AgBr. The resulting solution was added to a mixture of ($PhSO_2$)NH-N=CH-CH=CH-Ph (34.7 mg, 0.12 mmol) and Cs_2CO_3 (78.9 mg, 0.24 mmol) and then stirred for 2 h at room temperature. The reaction mixture was filtered and the filtrate was evaporated to dryness. Addition of n-hexane (5 mL) afforded the complex as an orange solid, which was collected by filtration, washed with n-hexane (2 x 5 mL), and air-dried. Yield: 94 mg (70 %). It can be crystallized from slow diffusion of hexane into a dichloromethane solution (orange crystals).

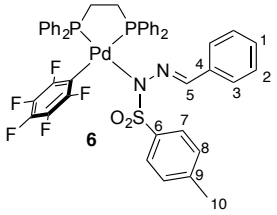


5c

^{1}H NMR (399.86 MHz, δ, $CDCl_3$): 8.35 (m, 3H, H^{arom}, H^1), 8.12 (m, 2H, H^{arom}), 7.64 (m, 4H, H^{arom}), 7.56 (m, 2H, H^{arom}), 7.48 (m, 2H, H^{arom}), 7.41-7.25 (m, 7H, H^{arom}), 7.22 (m, 2H, H^{arom}), 7.14 (m, 3H, H^{arom}), 7.10-7.00 (m, 6H, H^{arom}), 6.55 (dd, J = 16.0, 8.8 Hz, 1H, H^2), 6.41 (d, J = 15.7 Hz, 1H, H^3), 4.82 (s, 1H, H^{Cp1}), 4.56 (s, 1H, H^{Cp2}), 4.43 (s, 1H, H^{Cp1}), 4.38 (s, 1H, H^{Cp2}), 4.35 (s, 1H, H^{Cp1}), 4.26 (s, 1H, H^{Cp2}), 4.20 (s, 1H, H^{Cp1}), 3.91 (s, 1H, H^{Cp2}). ^{13}C{^{1}H} NMR (100.56 MHz, δ, $CDCl_3$): 143.7 ($C^{ipso-(SO2-Ph)}$), 141.2 (C^1), 137.5 (C^4), 137.3 (d, J_{C-P} = 13.1 Hz, C^{arom}), 135.5 (d, J_{C-P} = 12.4 Hz, C^{arom}), 133.0 (d, J_{C-P} = 10.6 Hz, C^{arom}), 132.3 (d, J_{C-P} = 11.6 Hz, C^{arom}), 132.2 (C^3), 132.1 (d, J_{C-P} = 12.1 Hz, C^{arom}), 132.0 (C^{arom}), 131.0 (d, $^1J_{C-P}$ = 54.3 Hz, C^{arom}), 130.1 (C^{arom}), 130.0 (d, $^1J_{C-P}$ = 46.1 Hz, C^{arom}), 129.6 (C^{arom}), 128.6 (C^{arom}), 128.3 (d, J_{C-P} = 10.9 Hz, C^{arom}), 128.0 (d, J_{C-P} = 9.8 Hz, C^{arom}), 127.3 (d, J_{C-P} = 12 Hz, C^{arom}), 127.2 (C^{arom}), 127.6 (C^2), 127.0 (C^7), 126.1 (C^5), 126.0 (C^6), 76.6 (C^{Cp1}), 75.6 (d, J = 5.6 Hz, C^{Cp2}) 74.8 (br, 2C^{Cp1}, 1C^{Cp1}),

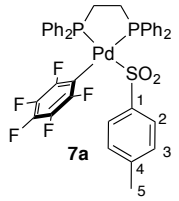
74.3 (d, J = 4.2 Hz, C^{Cp1}), 72.7 (d, J = 5.5 Hz, C^{Cp1}), 72.5 (d, J = 5.2 Hz, C^{Cp2}).* ^{19}F NMR (376.19 MHz, δ, $CDCl_3$): -113.23 (m, 1F, F_{ortho}), -116.72 (m, 1F, F_{ortho}), -160.88 (t, J = 20.5 Hz, 1F, F_{para}), -161.44 (m, 1F, F_{meta}), -163.30 (m, 1F, F_{meta}). $^{31}P\{^1H\}$ NMR (161.87, MHz, δ, $CDCl_3$): 20.57 (t, J = 11.8 Hz, 1P), 12.84 (m, 1P). IR (neat, cm^{-1}): C_6F_5, 1499, 1029, 953, 692, 616; SO_2, 1150. Anal. Calcd. for $C_{55}H_{41}F_5FeN_2O_2P_2PdS$. CH_2Cl_2: C, 56.14 %; H, 3.62 %; N, 2.34 %. Found: C, 56.15 %; H, 3.88 % N, 2.48 %.
*The signals for the Cp carbons bound to P could not be observed.

[Pd(C_6F_5)(dppe){(*p*-TolSO$_2$)N-N=CHPh}] (6). [PdBr(C_6F_5)dppe] (111.0 mg, 0.14 mmol) and $AgBF_4$ (28.7 mg, 0.14 mmol) were mixed in dry MeCN (3 mL) and stirred for 15 min at room temperature under nitrogen. The suspension was filtered through Kieselghur to remove the AgBr. The resulting solution was added to a mixture of the *N*-tosylhydrazone **4** (60.77 mg, 0.22 mmol) and Na_2CO_3 (46.74 mg, 0.44 mmol) in MeCN (5 mL) and then stirred for 2 h at room temperature. The reaction mixture was filtered and the filtrate was evaporated to dryness. Addition of Et_2O (5 mL) to the residue afforded complex **6** as a yellow solid, which was collected by filtration, washed with cold Et_2O (2 x 5 mL), and air-dried. Yield: 0.12 g, (87%). It can be crystallized from slow diffusion of hexane into a dichloromethane solution.



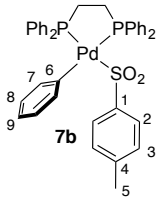
^1H NMR (499.73 MHz, δ, $CDCl_3$): 8.02 (s, 1H, H^5), 7.99-7.49 (m, 9H, H^{arom}), 7.54 (t, J = 7.4 Hz, H^{arom}), 7.42 (m, 5H, H^{arom}), 7.37 (d, J = 8.3 Hz, 2H, H^7), 7.21-7.0 (m, 6H, H^{arom}), 6.89 (d, J = 8.3 Hz, 2H, H^8), 2.52 (m, 2H, CH_2), 2.24 (m, 2H, C'H_2), 2.21 (s, 3H, H^{10}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 140.6 (C^6), 140.0 (C^9), 138.5 (C^5), 136.4 (C^4), 132.9 (br, $2C^{arom}$), 132.0 (C^{arom}), 131.5 (C^{arom}), 129.6 (d, $^1J_{C-P}$ = 41.8 Hz, C^{arom}), 129.0 (d, J_{C-P} = 10.6 Hz, C^{arom}), 128.9 (d, J_{C-P} = 10.9 Hz, C^{arom}), 128.7 (d, $^1J_{C-P}$ = 42.3 Hz, C^{arom}), 127.8 (C^8), 127.6 (C^2), 126.8 (C^1), 126.4 (C^7), 126.0 (C^3), 27.7 (dd, J_{C-P} = 31.5, 17.4 Hz, CH_2), 24.1 (dd, J_{C-P} = 28.8, 12.2 Hz, C'H_2), 21.1 (C^{10}). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -113.83 (br, 2F, F_{ortho}), -161.04 (t, J = 19.9 Hz, 1F, F_{para}), -163.18 (br, 2F, F_{meta}). $^{31}P\{^1H\}$ NMR (202.31, MHz, δ, $CDCl_3$): 52.74 (dt, J = 17.4, 4.5, Hz, 1P), 42.45 (m, 1P). IR (neat, cm^{-1}): C_6F_5, 1454, 1046, 952, 689, 746; (SO_2, st), 1145. Anal. Calcd. for $C_{46}H_{37}F_5N_2O_2P_2PdS$. CH_2Cl_2: C, 54.80 %; H, 3.82 %; N, 2.72 %. Found: C, 54.59 %; H, 3.80 % N, 2.60 %.

[Pd(C_6F_5)(dppe)(SO_2-*p*-Tol)] (7a). Equimolar amounts of [PdBr(C_6F_5)dppe] (76.42 mg, 0.101 mmol) and $AgBF_4$ (19.79 mg, 0.101 mmol) were mixed in dry MeCN (10 mL) and stirred for 15 min at room temperature under nitrogen. The solution was filtered through Kieselghur and the filtrate was added to a solution of sodium *p*-toluenesulfinate (18.10 mg, 0.101 mmol) in CH_3CN (5 mL). The mixture was stirred for 3 h at room temperature and an almost colorless solution was formed. The reaction mixture was filtered and the filtrate was evaporated to dryness. A mixture of MeOH/H_2O (1:5, 6 mL) was added to the residue and the resulting white solid was filtered, washed with water (3 x 5 mL) and air-dried. Yield: 49.63 mg (60 %).



^1H NMR (499.73 MHz, δ, $CDCl_3$): 8.00 (m, 4H, H^{arom}), 7.61-7.52 (m, 6H, H^{arom}), 7.49 (m, 2H, H^{arom}), 7.43-7.32 (m, 9H, H^{arom}), 7.20 (d, J = 8.0 Hz, 2H, H^2), 6.84 (d, J = 8.0 Hz, 2H, H^3), 2.37-2.22 (m, 4H, CH_2), 2.20 (s, 3H, H^5). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 150.8 (d, J_{C-P} = 19.4 Hz, C^1), 145.4 (d, $^1J_{C-F}$ = 226.2 Hz, CF_{ortho}), 139.7 (C^4), 137.7 (d, $^1J_{C-F}$ = 230.3 Hz, CF_{para}), 135.7 (d, $^1J_{C-F}$ = 246.1 Hz, CF_{meta}), 134.0 (d, J_{C-P} = 11.7 Hz, C^{arom}), 132.9 (d, J_{C-P} = 11.4 Hz, C^{arom}), 132.0 (d, J_{C-P} = 2.6 Hz, C^{arom}), 131.7 (d, J_{C-P} = 2.5 Hz, C^{arom}), 129.1 (d, J_{C-P} = 11.0 Hz, C^{arom}), 128.9 (d, J_{C-P} = 11.0 Hz, C^{arom}), 128.6 (d, $^1J_{C-P}$ = 45.2 Hz, C^{arom}), 128.1 (d, $^1J_{C-P}$ = 47.8 Hz, C^{arom}), 127.7 (C^3), 125.27 (C^2), 26.8 (dd, J_{C-P} = 28.4, 15.1 Hz, CH_2), 26.3 (dd, J_{C-P} = 30.0, 14.6 Hz, C'H_2), 21.0 (C^5). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -116.08 (m, 2F, F_{ortho}), -161.18 (t, J = 21 Hz, 1F, F_{para}), -162.79 (m, 2F, F_{meta}). $^{31}P\{^1H\}$ NMR (202.31, MHz, δ, $CDCl_3$): 49.31 (d, J = 25.7 Hz, 1P), 44.61 (m, 1P). IR (neat, cm^{-1}): C_6F_5, 1460, 1089, 959, 829, 699; SO_2, 1186. Anal. Calcd. for $C_{39}H_{31}F_5O_2P_2PdS$: C, 56.64 %; H, 3.78 %. Found: C, 56.48 %; H, 3.47 %.

[PdPh(dppe)(SO_2-*p*-Tol)] (7b). [PdBr(dppe)Ph] (130.8 mg, 0.197 mmol) and $AgBF_4$ (38.5 mg, 0.197 mmol) were mixed in dry MeCN (10 mL) and stirred for 15 min at room temperature under nitrogen. The suspension was filtered through Kieselghur and the filtrate was added to a solution of sodium *p*-toluenesulfinate (42.3 mg, 0.237 mmol) in dry CH_3CN (5 mL). The mixture was stirred for 3 h at room temperature to give an almost colorless solution, which was filtered. The filtrate was evaporated to c.a. 2 mL and Et_2O (5 mL) was added to the suspension. The white solid was filtered, washed with diethylether (3 x 5 mL), MeOH (3 x 5 mL) and air-dried. Yield: 78 mg (54 %).



^1H NMR (399.86 MHz, δ, $CDCl_3$): 8.02 (m, 4H, H^{arom}), 7.53 (m, 6H, H^{arom}), 7.40 (td, J = 7.3, 1.8 Hz, 2H, H^{arom}), 7.30-7.22 (m, 10H, H^{arom}), 7.01 (d, J = 8.1 Hz, 2H, H^2), 6.75 (d, J = 8.1 Hz, 2H, H^3), 6.73 (m, 2H, H^7), 6.57 (t, J = 7.0 Hz, 1H, H^9), 6.46 (td, J = 7.5, 2.1 Hz, 2H, H^8), 2.35 (m, 2H, CH_2), 2.22 (m, 2H, CH_2), 2.18 (s, 3H, H^5). $^{13}C\{^1H\}$ NMR (100.56 MHz, δ, $CDCl_3$): 158.5 (C^6), 150.6 (C^1), 138.3 (C^4), 136.4 (C^3), 133.6 (C^{arom}), 133.8 (C^{arom}), 133.2 (C^{arom}), 131.1 (C^{arom}), 130.9 (C^{arom}), 128.9 (C^{arom}), 128.8 (C^{arom}), 128.2 (C^{arom}), 127.6 (C^7), 126.8 (C^8), 126.0 (C^2), 122.5

(C^9), 28.4 (dd, J_{C-P} = 27.5, 18.5 Hz, CH_2), 25.6 (dd, J_{C-P} = 26.6, 12.9 Hz, C'H_2), 21.1 (C^5).* $^{31}P\{^1H\}$ NMR (161.87, MHz, δ, $CDCl_3$): 43.50 (d, J = 22.1 Hz, 1P), 35.83 (d, J = 22.1 Hz, 1P). IR (neat, cm^{-1}): SO_2, 1102. Anal. Calcd. for $C_{39}H_{36}O_2P_2PdS$: C, 63.55 %; H, 4.92 %. Found: C, 63.59 %; H, 5.20 %.

*The complex is not very stable in solution and most chemical shifts were determined using ^1H-^{13}C HSQC and HMBC NMR experiments.

[Pd(C_6F_5)(dppf)(SO_2Ph)] (7c). Equimolar amounts of [PdBr(C_6F_5)dppf) (111.9 mg, 0.123 mmol) and $AgBF_4$ (24.0 mg, 0.123 mmol) were mixed in dry MeCN (10 mL) and stirred for 15 min at room temperature under nitrogen. The solution was filtered through Kieselghur to remove the AgBr. The filtrate was added to a solution of sodium benzenesulfinate (30.4 mg, 0.18 mmol) in CH_3CN (5 mL). The mixture was stirred for 3 h at room temperature and then, it was filtered. The resulting solution was evaporated to dryness and a 1:5 v/v ratio of MeOH/H_2O (6 mL) was added to the residue. A white solid appeared which was filtered, washed with water (3 x 5 mL) and air-dried. Yield: 93 mg (78 %).

^1H NMR (499.73 MHz, δ, $CDCl_3$): 8.13 (m, 4H, H^{arom}), 7.60 (m, 6H, H^{arom}), 7.38 (m, 4H, H^{arom}), 7.30 (t, J = 7.4 Hz, 2H, H^{arom}), 7.15 (m, 3H, H^{arom}), 7.10 (m, 4H, H^{arom}), 7.04 (t, J = 7.4 Hz, 2H, H^{arom}), 4.88 (s, 2H, H^{Cp}), 4.60 (s, 2H, H^{Cp}), 4.16 (s, 2H, H^{Cp}), 3.49 (s, 2H, H^{Cp}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 153.3 (d, J_{C-P} = 18.5 Hz, $C^{ipso-(SO2-Ph)}$), 134.9 (d, J_{C-P} = 12.7 Hz, C^{arom}), 133.4 (d, J_{C-P} = 11.8 Hz, C^{arom}), 132.5 (d, $^1J_{C-P}$ = 50.7 Hz, C^{arom}), 131.3 (d, $^1J_{C-P}$ = 44.4 Hz, C^{arom}), 131.0 (2C^{arom}), 129.4 (C^{arom}), 128.5 (d, J_{C-P} = 10.8 Hz, C^{arom}), 128.0 (d, J_{C-P} = 10.8 Hz, C^{arom}), 127.1 (C^{arom}), 125.3 (C^{arom}), 77.2 (C^{Cp}), 76.4 (m, P-C^{Cp}), 74.9 (d, J_{C-P} = 8.4 Hz, C^{Cp}), 74.1 (d, J_{C-P} = 7.6 Hz, C^{Cp}), 72.7 (m, P-C^{Cp}), 72.4 (d, J_{C-P} = 5.8 Hz, C^{Cp}).* ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -117.26 (m, 2F, F_{ortho}), -160.99 (t, J = 21 Hz, 1F, F_{para}), -162.02 (m, 2F, F_{meta}). $^{31}P\{^1H\}$ NMR (202.31, MHz, δ, $CDCl_3$): 25.64 (d, J = 27.6 Hz, 1P), 17.73 (m, 1P). IR (neat, cm^{-1}): C_6F_5, 1461, 1046, 953, 743, 687; ν(S=O): 1199. Anal. Calcd. for $C_{46}H_{33}F_5O_2P_2SPd$: C, 57.02 %; H, 3.43 %. Found: C, 57.38 %; H, 3.49 %.

*The ^{13}C signals for the C_6F_5 group, heavily coupled to ^{19}F, could not be observed.

[Pd(C_6F_5)(dppe)($N_2C_3H_2$Ph)] (8). Equimolar amounts of [PdBr(C_6F_5)dppe] (39.8 mg, 0.053 mmol) and $AgBF_4$ (10.3 mg, 0.053 mmol) were mixed in dry MeCN (5 mL) and stirred for 15 min at room temperature under nitrogen. The solution was filtered through Kieselghur to remove the AgBr. The filtrate was added to a mixture of 5-phenyl-1*H*-pyrazole (7.6 mg, 0.053 mmol) and Cs_2CO_3 (34.5 mg, 0.10 mmol) in dry CH_3CN (5 mL) and then stirred for 3 h at room temperature to give a colorless suspension. The reaction mixture was filtered and the filtrate was evaporated to c.a. 2 mL. Diethylether (5 mL) was added to the residue to give a white solid, which was filtered, washed with diethylether (3 x 5 mL), MeOH (3 x 5 mL) and air-dried. Yield: 21 mg (48 %).

^1H NMR (499.73 MHz, δ, $CDCl_3$): 7.81 (m, 4H, H^{arom}), 7.58 (m, 4H, H^{arom}), 7.51 (m, 3H, H^{arom}), 7.47 (m, 2H, H^{arom}), 7.39 (m, 8H, H^{arom}), 7.14 (d, J = 7.9 Hz, 2H, $H^{ortho-Ph-pz}$), 7.05 (t, J = 7.1 Hz, 2H, $H^{meta-Ph-pz}$), 6.99 (t, J = 7.1 Hz, 1H, $H^{para-Ph-pz}$), 6.95 (d, J = 1.7 Hz, 1H, H^3, pz), 6.25 (t, J = 1.7 Hz, 1H, H^4, pz), 2.50 (m, 2H, CH_2), 2.19 (m, 2H, C'H_2). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 151.0 (m, C^5, pz), 140.2 (C^3, pz), 136.2 ($C^{ipso-Ph-pz}$), 133.7 (d, J_{C-P} = 11.6 Hz, C^{arom}), 133.0 (d, J_{C-P} = 11.4 Hz, C^{arom}), 131.8 (d, J_{C-P} = 2.7 Hz, C^{arom}), 130.9 (d, J_{C-P} = 2.4 Hz, C^{arom}), 130.0 (d, $^1J_{C-P}$ = 44.6 Hz, C^{arom}), 128.9 (d, $^1J_{C-P}$ = 35.6 Hz, C^{arom}), 128.8 (d, J_{C-P} = 11.0 Hz, C^{arom}), 128.7 (d, J_{C-P} = 10.6 Hz, C^{arom}), 127.6 ($C^{meta-Ph-pz}$), 125.1 ($C^{ortho-Ph-pz}$), 124.9 ($C^{para-Ph-pz}$), 99.7 (C^4, pz), 28.8 (dd, J_{C-P} = 31.7, 17.5 Hz, CH_2), 25.5 (dd, J_{C-P} = 29.8, 12.9 Hz, C'H_2).* ^{19}F NMR (MHz, δ, $CDCl_3$): -115.39 (br, 2F, F_{ortho}), -160.24 (t, J = 20.8 Hz, 1F, F_{para}), -162.31 (br, 2F, F_{meta}). $^{31}P\{^1H\}$ NMR (202.31 MHz, δ, $CDCl_3$): 53.63 (m, 1P), 44.71 (m, 1P). IR (neat, cm^{-1}): C_6F_5, 1451, 1057, 949, 740, 688. Anal. Calcd. for $C_{41}H_{31}F_5N_2P_2Pd$: C, 60.42 %; H, 3.83 %; N, 3.44 %. Found: C, 60.67 %; H, 3.87; N, 3.41 %.

*The ^{13}C signals for the C_6F_5 group, heavily coupled to ^{19}F, could not be observed.

Decomposition of N-tosylhydrazonato palladium complexes.

Monitorization at 50 ˚C. Complex **5a** (13.6 mg, 0.014 mmol) and dry CH_3CN (0.6 mL) were added to a 5 mm NMR tube along with a sealed glass capillary filled with $(CD_3)_2SO$ as NMR lock signal. The formation of the palladium tosylato complex **7a** was monitored by ^{19}F NMR at 50 ˚C for 15 h (Figure 3, a). Analogous experiments were carried out adding 10 mol % of $NaSO_2$Tol (Figure 3, b) and 10 mol % of 5-phenyl-1*H*-pyrazole (Figure 3, c).

Crossover experiment: Reaction of 5a and 5c. Complex **5c** (3.0 mg, 0.0027 mmol), complex **5a** (2.6 mg, 0.0027 mmol) and dry CH_3CN (0.6 mL) were added to a 5 mm NMR tube along with a sealed glass capillary filled with $(CD_3)_2SO$ as NMR lock signal. The species formed in solution at room temperature were examined by ^{31}P and ^{19}F NMR (Figure S4, ESI). The resulting mixture was heated at 80 ˚C and checked after 2 h (Figures S5, S6, ESI). The same experiment was carried out and monitored by ^{19}F NMR at 50 ˚C for 4 h (Figure S7). The species formed were identified by comparison with samples of the complexes prepared independently and are shown in Scheme 5.

General procedure for the ligand substitution reactions.

Ligand substitution reactions by diazoalkanes. The corresponding palladium complex (0.01 mmol) was placed into an NMR tube along with CH_3CN (0.6 mL) and a sealed glass capillary filled with $(CD_3)_2SO$ as NMR lock signal. After that, a solution of the diazoalkane (0.01 mmol) in dichloromethane was added to the NMR tube under a nitrogen atmosphere. The tube was introduced into the NMR probe and the species formed in solution at room temperature were examined by ^1H ^{19}F and ^{31}P NMR nuclei depending on the complexes.

Bromide substitution reactions in [PdArBr(dppe)]. The corresponding palladium complex (0.01 mmol) was placed into an NMR tube along with CH_3CN (0.6 mL) and a sealed glass capillary filled with $(CD_3)_2SO$ as NMR lock signal. *N*-tosylhydrazone **3** (0.1 mmol) and NEt_3 (0.1 mmol) in one experiment set or $NaSO_2$(*p*-Tol) (0.01 mmol) in the second experiment set were added. The mixture was allowed to stand

for 1-2.5 h and then checked by ^{19}F and ^{31}P NMR. The products formed are shown in Eq. 1 and Eq. 2.

Data for X-Ray molecular structure determinations.

Crystals suitable for X-ray analyses for were obtained by: a) slow diffusion of Et_2O layered onto a solution of the complex in CH_2Cl_2 at -28 ˚C (**5c** and **6**); b) slow evaporation a solution of the complex in CH_2Cl_2 (**7a** and **7c**). In each case, the crystal was attached to the tip of a glass fiber and transferred to an Agilent Supernova diffractometer with an Atlas CCD area detector. Data collection was performed with Mo Kα radiation (0.71073 Å) at 298 K. Data integration and empirical absorption correction was carried out using the CrysAlisPro program package.[23] The structures were solved by direct methods and refined by full-matrix least squares against F^2 with SHELX,[24] in OLEX2.[25] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Complex **7a** crystallized with a CH_2Cl_2 solvent molecule that was modeled. Two independent molecules were found in the asymmetric unit for **5c** and a solvent mask was used for the CH_2Cl_2 co-crystallized solvent. Refinement proceeded smoothly to give the residuals shown in Table S3 (ESI). The crystal structures have been deposited in the CCDC database: CCDC-2184726 (**5c**), CCDC-2184727 (**6**), CCDC-2184731 (**7a**) and CCDC-2184733 (**7c**).

Author Contributions

F.V. conducted the investigation under A. C. A. supervision. A. C. A. wrote the manuscript and F.V. prepared the ESI. All authors contributed to the conceptualization of the project and the review and editing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ As can be seen in Figure 3b, a small amount of [Pd(C_6F_5)(dppe)(κ^1-5-phenyl-pyrazolate)] (**8**) is also formed. The origin of this product is the coordination of the deprotonated 5-phenyl-pyrazole formed by decomposition of the free hydrazonato as shown in Scheme 4. Complex **8** was synthesized independently.

§ In addition to a small amount of complex **8**, the allylic derivative **9a** was also observed. This is the result of the carbene-aryl coupling from reaction with the small concentration of diazoalkane formed (see Schemes 4 (a) and 6).

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