

## Palladium diazo adduct

# The elusive palladium-diazo adduct captured: synthesis, isolation and structural characterization of $[(\text{ArNHC-PPh}_2)\text{Pd}(\eta^2\text{-N}_2\text{C(Ph)CO}_2\text{Et})]$

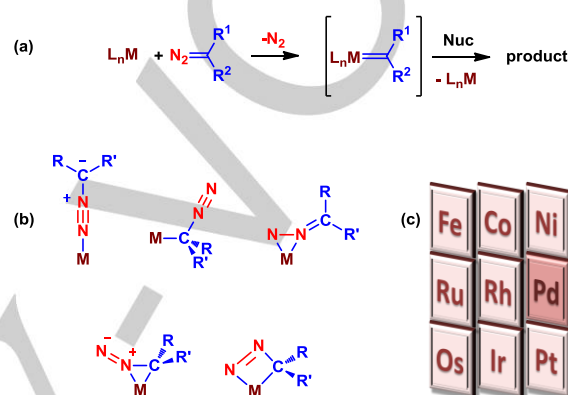
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**Abstract:** The first example of a diazo compound adduct of palladium is reported. The complexes  $[(\text{ArNHC-PPh}_2)\text{M}(\eta^2\text{-N}_2\text{C(Ph)CO}_2\text{Et})]$  ( $\text{M} = \text{Ni}$ , **3**;  $\text{M} = \text{Pd}$ , **4**;  $\text{ArNHC-PPh}_2 = 3$ -(2,6-diisopropylphenyl)-1-[(diphenylphosphino)ethyl]imidazol-2-ylidene) have been prepared by ligand exchange with the styrene precursors  $[(\text{ArNHC-PPh}_2)\text{M}(\text{styrene})]$  ( $\text{M} = \text{Ni}$ , **1**;  $\text{M} = \text{Pd}$ , **2**). Complex **4** has been fully characterized, including X-ray analyses, in what constitutes the first example of a diazo compound adduct with this metal, closing the gap within groups 8 to 10 regarding this type of compounds.

## Introduction

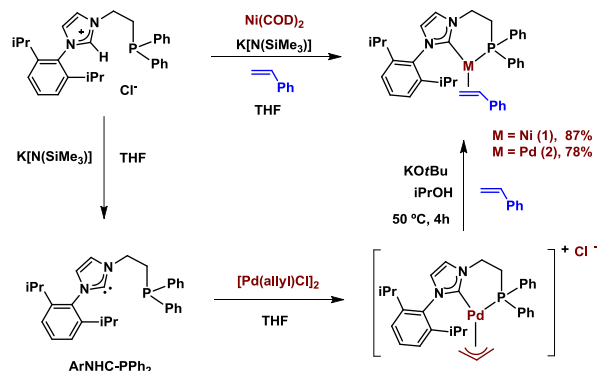
The well-known capabilities of late transition metals to decompose diazo compounds and transfer the carbene unit from their coordination sphere constitutes a powerful tool in organic synthesis (Scheme 1a).<sup>[1]</sup> It is assumed that the first step for such transformation consists of the interaction of the diazo molecule with the metal center, which might occur in different manners (Scheme 1b). Adducts with diazo compounds have been detected and/or isolated for all metals in Groups 8 to 10 with the exception of palladium, for which diazo compound adducts remain undescribed (Scheme 1c).<sup>[2]</sup> We have recently reported<sup>[3]</sup> the catalytic activity of the Pd(0) complex bearing an N-heterocyclic carbene ligand of type  $[(\text{IPr})\text{Pd}(\text{styrene})_2]$  (IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene) in the olefin cyclopropanation reaction using ethyl diazoacetate (EDA). In view of the lack of well-characterized palladium complexes bearing

diazo ligands,<sup>[4]</sup> we have concentrated our efforts on the preparation and isolation of such complexes and to ascertain their



**Scheme 1.** (a) The metal-catalyzed carbene transfer from diazo compounds. (b) Different coordination modes of diazoalkanes in monometallic complexes. (c) The palladium gap for diazo-metal adducts.

involvement in cyclopropanation. It is well established that this carbene transfer process from metal centers requires a certain electrophilic nature at the carbene ligand,<sup>[1]</sup> the higher the latter, the more active the catalyst. The search of isolable intermediates must therefore stand on less active catalysts, e. g., those in which the electron density at metal is enhanced. On these basis, we planned the synthesis of Pd(0) complexes bearing two strong donors such as NHC and phosphine groups, in a chelating bidentate ligand. With such precursor, and the appropriate diazo compound, we have prepared, isolated and structurally



**Scheme 2.** Synthesis of complexes  $[(\text{ArNHC-PPh}_2)\text{M}(\text{sty})]$  ( $\text{M} = \text{Ni}$ , **1**;  $\text{M} = \text{Pd}$ , **2**).

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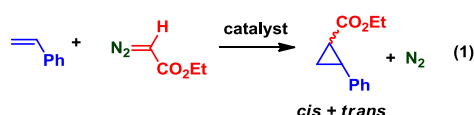
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characterized the first example of a diazo-palladium(0) complex, in which the coordination mode has been found as dihapto-N<sub>2</sub>.

We first targeted the preparation of Ni(0) and Pd(0) complexes bearing the mixed NHC-phosphine ligand (ArNHC-PPh<sub>2</sub> = 3-(2,6-diisopropylphenyl)-1-[(diphenylphosphino)ethyl]imidazol-2-ylidene).<sup>[5]</sup> The synthetic procedure is shown in Scheme 2, from which the novel compounds [(ArNHC-PPh<sub>2</sub>)M(sty)] (M = Ni, **1**; M = Pd, **2**; sty = styrene) were isolated in good yields. The characterization of these compounds on the basis of their spectroscopic and analytic data is fully described in the Supporting Information.

Once those materials were available, we tested their catalytic properties toward the carbene transfer reaction from ethyl diazoacetate, using the well-known probe of styrene cyclopropanation [Eq. (1)].<sup>[6]</sup> As shown in Table 1, the nickel-based catalyst required long times and relatively high temperatures to promote this transformation. The complex IPrNi(sty)<sub>2</sub>,<sup>[7]</sup> (IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene; sty = styrene) with a monodentate NHC ligand,



performed similarly to **1** (entries 2 and 3). In contrast, the palladium analogue **2** operated quite well at room temperature (entry 4), albeit the time needed for complete consumption of the EDA was much larger (18 h) than that observed for the IPrPd(sty)<sub>2</sub> catalyst (entry 5), previously described in our laboratory.<sup>[3]</sup> The observance of a similar diastereoselectivity in all cases is due to a somewhat large catalytic pocket around the metal center. It is well known<sup>[6]</sup> that the observation of *cis:trans*

**Table 1.** Catalytic activity of complexes **1** and **2** and IPrM(sty)<sub>2</sub> (M = Ni, Pd) toward the styrene cyclopropanation reaction with ethyl diazoacetate.<sup>[a]</sup>

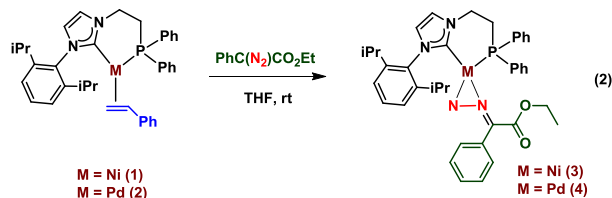
| Entry | Catalyst                | Temp (°C) | Time (h) | Yield(%) | <i>cis:trans</i> |
|-------|-------------------------|-----------|----------|----------|------------------|
| 1     | <b>1</b>                | 75        | 48       | 87       | 36:64            |
| 2     | <b>1</b>                | 110       | 18       | >99      | 36:64            |
| 3     | IPrNi(sty) <sub>2</sub> | 110       | 18       | >99      | 35:65            |
| 4     | <b>2</b>                | r t       | 18       | 90       | 38:62            |
| 5     | IPrPd(sty) <sub>2</sub> | r t       | 4        | >99      | 35:65            |

[a] [M]/[EDA]/[olefin] 1:100:500. [b] Yields of the cyclopropanes were determined by <sup>1</sup>H NMR using benzaldehyde as internal standard.

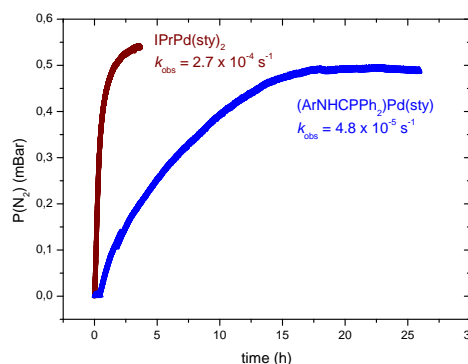
ratios within the 1:1 to 1:2 intervals is due to this feature.

We have further investigated the difference in activity upon kinetic studies based on the measurement of the nitrogen evolved in the reaction mixture. Figure 1 displays the plots of the variation of [N<sub>2</sub>] with time for **2** or IPrPd(sty)<sub>2</sub> as catalyst, assessing the lower catalytic properties of the former, the feature that, as mentioned above, we are now pursuing in order to trap intermediates.

With such goal in mind, we investigated the stoichiometric reactions of complexes **1** and **2** with ethyl diazoacetate. Attempts



to isolate materials from these reactions proved unsuccessful. In situ NMR studies with such mixture showed the decoordination of styrene and the shift of some resonances of the EDA. However, we could not ascertain the nature of the species formed. On the other hand, the use of ethyl 2-phenyl-2-diazoacetate (PhEDA) as the diazo reagent was satisfactory at the preparative scale. Solutions of **1** or **2** in THF were reacted at the room temperature with 1.5 equiv of PhEDA for ca. 10 min [Eq. (2)]. After removal of volatiles, yellow-brownish crystalline materials of complexes **3** and **4** were obtained from THF-hexane mixtures upon cooling at -30 °C. Their <sup>1</sup>H NMR spectra showed the resonances expected for the ArNHC-PPh<sub>2</sub> ligand and a set of signals accounting for one equiv of the Ph and CO<sub>2</sub>Et groups of PhEDA, although

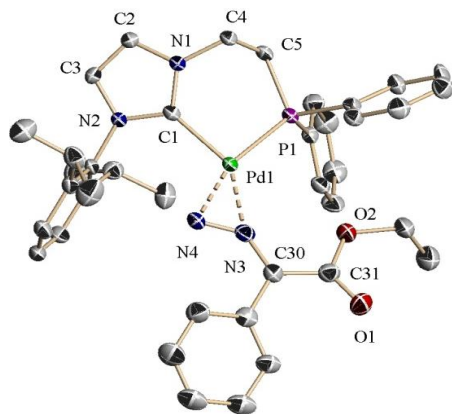


**Figure 1** Nitrogen evolution in the reaction of EDA and styrene ([Pd]/[EDA]/[styrene] 1:50:100) using [(IPr)Pd(sty)<sub>2</sub>] and complex **2** as catalysts.

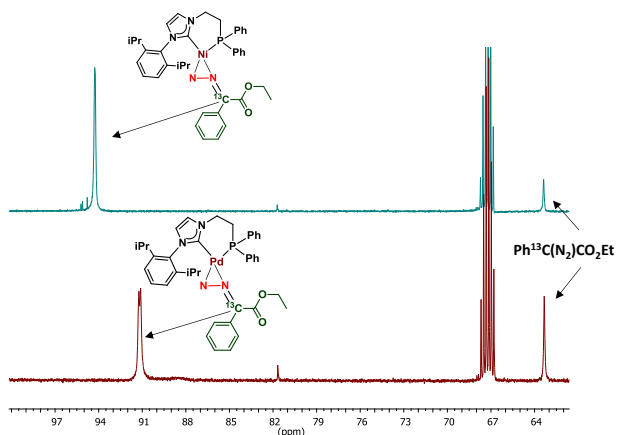
shifted from those of the free diazo reagent. The FTIR spectra showed weak absorptions centered at 2087 and 2085 cm<sup>-1</sup>, for **3** and **4** respectively, assigned to the ν(N=N) band of a coordinated diazo compound molecule.<sup>[8]</sup> Since free PhEDA shows this absorption at 2084 cm<sup>-1</sup>, this information provides no useful information about the coordination mode. Fortunately, single crystals of the palladium complex **4** were grown and the solid state structure was determined by X-ray studies.<sup>[9]</sup> As shown in Scheme 3, the molecules of **4** consists of a Pd(0) center bonded to the ArNHC-PPh<sub>2</sub> ligand in a bidentate fashion and the diazo compound, the latter linked to the metal in a side-on fashion. To the best of our knowledge, this is the first example of a structurally characterized diazo-adduct of this metal.

The palladium center is located within a three-coordinated geometry of the ligands, the diazo function being coordinated through both N-donors in an η<sup>2</sup>-fashion. The Pd-C1 bond distance to the carbene ligand, 2.036(6) Å in **4** is similar to the value reported by Danopoulos and co-workers for [(ArNHC-PPh<sub>2</sub>)(Pd(methallyl))(BPh<sub>4</sub>)]<sup>[10]</sup> which contained the same ancillary ligand. The angle N4-Pd-N3, 35.8(2)°, is similar to those reported for η<sup>2</sup>-coordinated in the case of nickel complexes: for example, 39.63(9)° for the nickel-diphenyldiazomethane adduct described by Radius,<sup>[11]</sup> or 39.1(1)° for the nickel-diazo fluorene complex reported by Ibers.<sup>4b</sup> The N3-N4 distance of 1.266(7) Å compares well with that described<sup>[12]</sup> by Hillhouse and co-worker for a (dtbpe)Ni(η<sup>2</sup>-N<sub>2</sub>C(H)(dmp)) (1.257(2) Å, dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane, dmp = 2,6-dimesitylphenyl) The value of the N-N bond length and the bond angle N3-N4-C30 of 133.5(5)° point out a significant π-back bond donation to the diazoester in **4**.<sup>[11]</sup>

The NMR data collected for complex **4** was in agreement with the solid-state structure, albeit the resonance of the carbon atom supporting the diazo functionality was not observed, probably due to its low intensity and broadening. In order to detect such resonance, we prepared  $^{13}\text{C}$ -enriched  $\text{N}_2^{13}\text{C}(\text{Ph})\text{CO}_2\text{Et}$  and monitored its reaction with **1** or **2** by  $^{13}\text{C}\{^1\text{H}\}$  NMR.



**Figure 2** ORTEP diagram of the molecular structure **4** (ellipsoids are set at 30% probability level). H atoms have been omitted for clarity. Selected bond lengths/Å and angles/°: Pd-C1 2.036(6), Pd-P1 2.2814(14), Pd-N3 2.084(5), Pd-N4 2.026(5), N3-N4 1.266(7), N3-C30 1.344(8), C1-Pd-P1 91.72(15), N4-Pd-N3 35.8(2), N3-N4-C30 133.5(5), N3-Pd-C1 141.7(2), N4-Pd-C1 105.9(2), N3-Pd-P1 126.57(15), N4-Pd-P1 162.40(15).

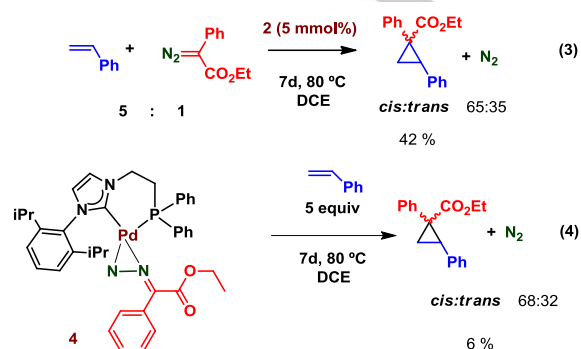


**Figure 3**  $^{13}\text{C}\{^1\text{H}\}$  NMR of the in situ reaction of complexes **1** or **2** with  $\text{N}_2^{13}\text{C}(\text{Ph})\text{CO}_2\text{Et}$ .

Figure 3 shows the portion of such spectra containing the resonances of the  $\text{C}=\text{N}_2$  moiety. For free  $\text{N}_2^{13}\text{C}(\text{Ph})\text{CO}_2\text{Et}$ , that nucleus resonates at 63.4 ppm. The palladium diazo adduct showed a resonance at 91.1 ppm assigned to that carbon, whereas for the nickel analogue the coordination of the diazo molecule is assessed by the observation of a resonance at 94.3 ppm. Coupling with the phosphorus nuclei is found in both cases ( $^3J_{\text{C-P}} = 6$  Hz for **3**,  $^3J_{\text{C-P}} = 15$  Hz for **4**).

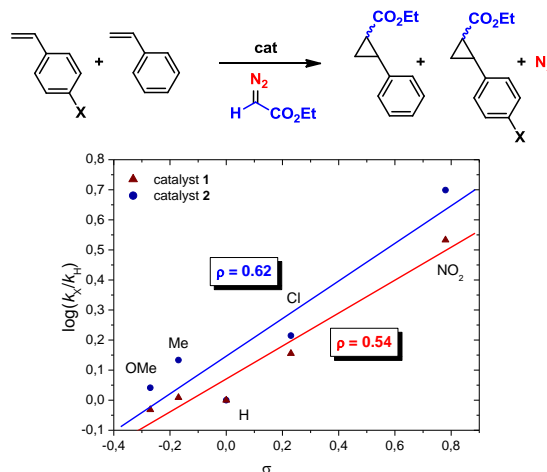
After isolating and characterizing the complexes **3** and **4**, we wondered about their role during the catalytic reaction, focusing in the latter, due to the already mentioned low reactivity of the nickel system with EDA. Monitoring of the reaction of PhEDA with

styrene in the presence of **2** at 80 °C showed that after 7 days some diazo reagent was yet unreacted, leading to the formation of a modest 42% of cyclopropanes [Eq. (3)]. This is a poor degree of conversion compared with that observed with EDA (Table 1). Moreover, when isolated complex **4** was submitted to those reaction conditions, only 6% of cyclopropanes were formed along



with massive complex decomposition [Eq. (4)]. We believe that this is in disagreement with the role of **4** as an active intermediate in the catalytic cycle of olefin cyclopropanation.

We have also performed competition experiments between *p*-substituted styrenes with EDA and **1** and **2** as catalysts. An interesting feature was observed: the more reactive substrates were those olefins bearing electron-withdrawing groups attached to the arene ring. This is at variance with most of the olefin cyclopropanation catalytic systems, where usually electron-rich olefins are more prone to react.<sup>[6]</sup> Data from Hammett plots (Figure 4) provided the values of  $\rho = 0.54(0.07)$  for **1** and  $\rho = 0.62(0.14)$  for **2**. This unusual feature was also observed in a previous contribution from our laboratory using complex  $\text{IPrPd}(\text{sty})_2$  as the catalyst,<sup>[3]</sup> in that case with a  $\rho$  value of 0.30. The increase of  $\rho$  to more positive values evidences a higher electron density at the metal center as expected from both a NHC and phosphine ligands in the coordination sphere. Stahl and co-workers have also observed<sup>[13]</sup> this behavior with electron-rich palladium complexes. The overall mechanistic picture is shown in Scheme 3. Complex **2** reacts with the diazo compound providing an equilibrium mixture containing the different species that might arise from the distinct coordination



**Figure 4** Competition experiments with substituted styrenes and Hammett plots obtained using complexes **1** or **2** as catalysts with EDA as the carbene source.

sites,<sup>[1]</sup> e. g., the N- (complex **4**, for R = Ph), O- (species **A**) or C-donor atoms (species **B**), the latter being the only productive species toward further reactivity involving carbene transfer. For R = H, we did not isolate any diazo adduct, probably due to the fast equilibrium between all those species. Though, for R = Ph, the Pd- $\eta^2$ -N<sub>2</sub>C(Ph)CO<sub>2</sub>Et adduct seems the most stable compound (**4**) from that equilibrium mixture, as inferred from its isolation and low reactivity as well. Thus, the main difference with both diazo reagents is that in the case of R = Ph, the formation of **4** is a nearly dead end. On the other hand, with R = H, the system seems to be driven toward formation of the metalcarbene intermediate **C**. From here, two possible routes can be proposed. On one hand, the external sphere mechanism would suppose the attack of free styrene onto the carbene carbon atom of **C**. On the other, styrene could coordinate the palladium atom to generate intermediate **D** favoring an internal sphere interaction with the carbene ligand. We believe that the aforementioned higher reactivity of styrenes bearing electron-withdrawing groups supports the latter option, since the electron-rich metal center favors coordination of electron poor olefins, and it would also agree with the previous observation by Stahl and co-workers. Actually, we have learnt that such 18 e<sup>-</sup> intermediates are involved in the olefin exchange reaction of complex **2** with 4-chlorostyrene, where an increasing concentration of this olefin induces a growth in the reaction rate (see SI). From **D**, direct coupling of olefin and carbene ligands, as previously proposed, would release the cyclopropane molecule and, upon coordination

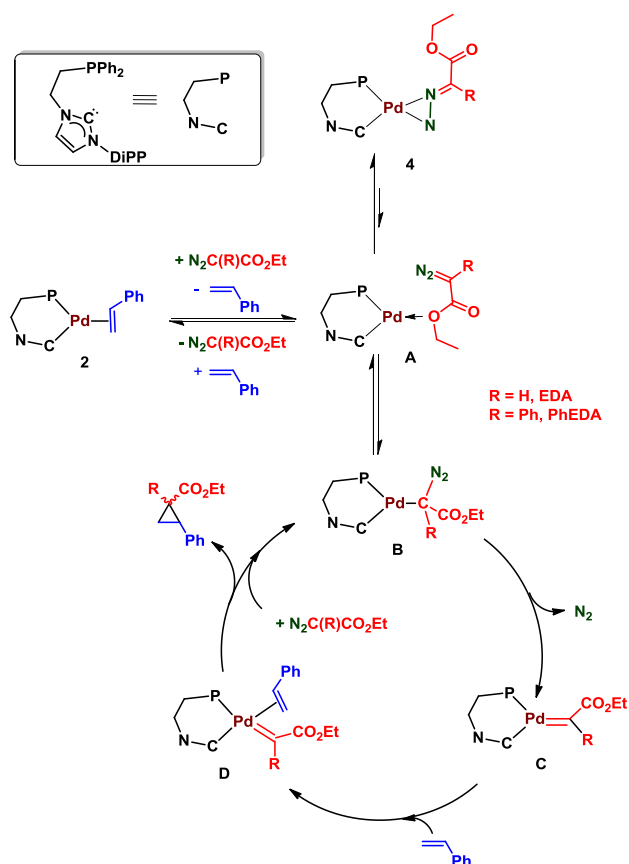
of the diazo reagent, the cycle would start again.

In conclusion, we have prepared, isolated and structurally characterized the first palladium complex bearing a diazo-compound as a ligand, [(ArNHC-PPh<sub>2</sub>)Pd( $\eta^2$ -N<sub>2</sub>C(Ph)CO<sub>2</sub>Et)] (**4**) that is coordinated to the metal center in a dihapto (side-on) fashion through both nitrogen donors. The nickel analogue **3** has also been isolated and spectroscopically characterized. Kinetic and spectroscopic studies evidenced that this complex is not relevant in the catalytic cycle involving carbene transfer and subsequent olefin cyclopropanation, unless the more reactive ethyl diazoacetate reagent is employed.

## Acknowledgements

The authors wish to thank MINECO for financial support (CTQ2014-52769-C03-01 and CTQ2011-24502). S. G. R. thanks MINECO for a FPI fellowship.

**Keywords:** palladium diazo adduct • NHC-phosphine ligand • diazo ligands • carbene transfer • palladium (0) complexes



**Scheme 3** Plausible reaction pathway for the Pd(0) catalyzed olefin cyclopropanation with complex **2**.

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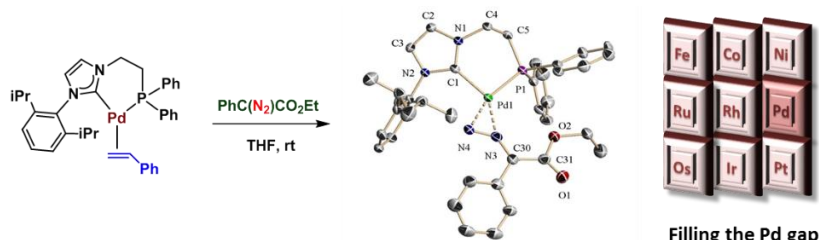
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Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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## COMMUNICATION



Filling the Pd gap

All metals from Groups 8 to 10 are known to form adducts with diazo compounds but palladium. We report the first example of such type of Pd-N<sub>2</sub>CR<sup>1</sup>R<sup>2</sup> complexes, isolated and fully characterized, as well as its role in carbene transfer reactions.

### ■ Palladium diazo adduct

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■ ■ - ■ ■

**The elusive palladium-diazo adduct captured: synthesis, isolation and structural characterization of [(ArNHC-PPh<sub>2</sub>)Pd(η<sup>2</sup>-N<sub>2</sub>C(Ph)CO<sub>2</sub>Et)]**