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RESEARCH ARTICLE

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A Versatile Palladium Synthon: [Pd(NHC)(PhC≡CPh)] (NHC = N-Heterocyclic Carbene)

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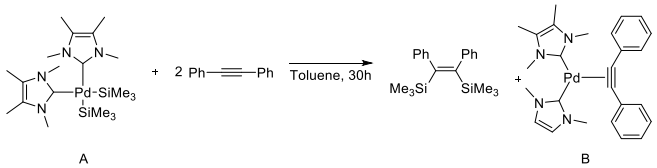
Abstract: The synthesis and isolation of [Pd(NHC)(PhC≡CPh)] complexes are reported. These new 14-electron Pd(0)-complexes are key synthons leading to known palladium(0) and palladium(II) species, as well as permitting access to unprecedented mixed NHC-phosphite palladium(0) complexes.This motif permits the facile catalytic hydrosilylation of allenes. DFT calculations have allowed to characterize the relatively weak interaction between the metal and the diphenylacetylene ligand, with a comparison with a series of ligands with more or less coordinating power, bearing varied structural and electronic effects.

Introduction

Palladium is a most versatile transition metal enabling the formation of carbon-carbon and carbon-nitrogen bonds.[1] Palladium complexes have proven their usefulness as mediators in a plethora of organic transformations ranging from bulk chemicals to the development of fine chemicals in the pharmaceutical industry.[2] These have also recently been used as therapeutic agents in the fight against cancer.[3] From the onset of palladium catalysed cross-coupling reactions,[4] a search for new, versatile, and highly reactive palladium complexes has been an important focus of the area.

Currently, N-heterocyclic carbenes (NHC) are a ubiquitously encountered family of ligands used in the development of such state-of-the-art catalysts due to their tuneable steric bulk, spatially shielding the metal centre, and their exceptionally strong σ-donating/π-accepting ability, leading to very strong metal-NHC bonds.[1,5]

In this quest for novel/highly reactive palladium complexes, two strategies have emerged. The first involves the development of fast-initiating Pd(II) pre-catalysts such as Pd-dimers,[6] PEPPSI-complexes,[7] or using other "throw-away" ligands, such as phosphites[8] and allyls,[9] allowing facile entry into the catalytic cycle. The other has focused on the direct use of a Pd(0) source often times coupled with ligand addition to generate the active species *in situ*.[10] The latter approach generates a species that can easily enter the catalytic cycle.[11] This ease of activation of Pd(0) complexes is in contrast to the need for an activation step involving the Pd(II) relative.[12] However, Pd(0) complexes are notoriously unstable in air. Therefore, the isolation and handling of Pd(0)-catalysts is often circumvented through the use of *in situ* generated species; $Pd_2(dba)_3$ as palladium source[13] and a ligand (L) to form the catalyst *in situ*, for example. The use of these ill-defined complexes results in much lower reactivity and selectivity, and difficulties of further design as the catalysis occurs essentially in a *black box*. These drawbacks have been



A B

the driving force behind the development of well-defined catalysts with controlled compositions.[14]

We hypothesized that a complex bearing one NHC ligand and a most easily displaceable ligand would suit our aim of creating an isolable/reactive 2-coordinate Pd(0) complex. Note here that no such stable/yet reactive species has thus far been reported.[15] The work of Navarro and co-workers[16] nearly achieved this goal (Scheme 1).

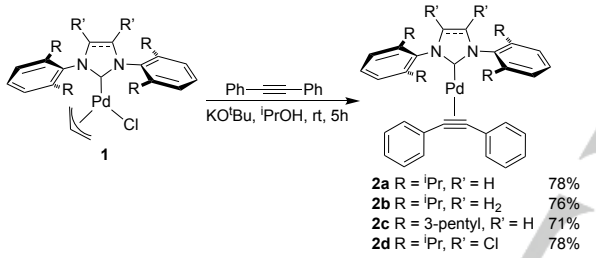
Scheme 1. [Pd(NHC)$_2$(η^2-alkyne)] complex (**B**) developed by Navarro.

In this instance, a Pd(II) species bearing two NHC ligands (**A**) is thermally degraded through alkyne disilylation, and the generated [Pd(NHC)$_2$] is trapped by an alkyne, leading to

[Pd(NHC)$_2$(η^2-alkyne)] (**B**). The mono NHC congener to **B** remains elusive. In 2018, Navarro expanded on the reactivity of this complex, achieving the displacement of the diphenylacetylene moiety with an azobenzene ligand.[17] The use of an alkyne as a stabilizing/potential leaving group is reminiscent of isolable [Au(I)(NHC)(η^2-alkyne)]$^+$ complexes that have played a key role in gold-mediated alkyne functionalisation.[18] The Periodic Table diagonal relationship between the isoelectronic Pd(0) and Au(I) also encouraged our efforts in targeting a [Pd(NHC)(η^2-alkyne)] complex.

Results and Discussion

Herein we report the straightforward synthetic access to well-defined Pd(0) complexes bearing a single NHC ligand and diphenylacetylene as the weakly coordinating ligand. This was achieved by reaction of [Pd(NHC)(η^3-allyl)(Cl)] (**1a-d**) with 1 equivalent of diphenylacetylene, in the presence of KO^{t}Bu in ^{i}PrOH. These 14-electron complexes, [Pd(NHC)(PhC≡CPh)] (**2a-d**), are illustrated in Scheme 2 and obtained in high isolated yields (71 to 78%).



Scheme 2. Synthesis of the [Pd(NHC)(PhC≡CPh)] complexes **2a-d**.

The mechanism of the reduction of a Pd(II) species to a Pd^0(NHC) intermediate, using KO^{t}Bu as a base with the key role of isopropanol as solvent, followed by the association of an incoming ligand to stabilize the highly unsaturated Pd(0) complex, has been described by Fantasia and Nolan.[19]

The molecular structure and atom connectivity of the acetylene complex **2a** was unambiguously established through diffraction study on a single crystal. A suitable crystal was grown by slow diffusion of pentane into a saturated solution of toluene of **2a** (Figure 1).[20]

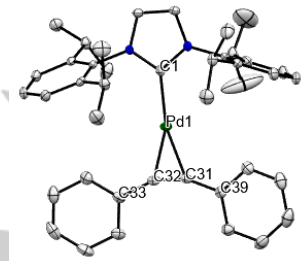


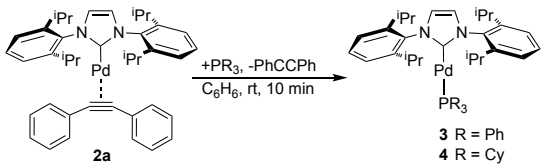
Figure 1. Molecular structure of **2a.** Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) Pd-C1 2.056(3), Pd-C31 2.062(3), Pd-C32 2.053(3), C$_1$-Pd-C31 163.56(13), C31-Pd-C31 35.35(12).

Interestingly, the geometry of the alkyne PhC≡CPh deviates substancially from linearity when bound to the Pd centre, as shown with the 157° C-C≡C bond angle values (C31-C32-C33 and C32-C31-C39 to 157.7(3)° and 157.1(3)°, respectively). This can be explained by the acetylene fragment donating electron density to the metal centre from its π-bonding orbital and accepting π-back-donation from the metal into an antibonding π* orbital. Both interactions reduce the bond order of the acetylene ligand, leading to a longer C-C distance (1.250(4) Å) and cause the phenyl ring to be bend away from the metal centre.[20] The C33 and C39 lie respectively +0.09(1) and +0.08(1) Å from the Pd-C2-C3 mean plane with the aryl rings inclined by 18.4(1)° and 3.8(1)° respective to this plane. The second independent molecule is flatter; C33 and C39 lie -.05(1) and -.03(1)Å from the Pd-C2-C2 mean plane with the aryl rings being inclined by 4.9(1)° and 2.5(1)° respectively, but the aryl rings are closer to each other; the bond angles of C2-C3-C33 and C3-C2-C39 are distorted to 157.5(3)° and 156.6(3)°, respectively. The Pd-C$_{alkyne}$ bond distances found are 2.062 (3) and 2.053 (3)Å, which are longer than the value found for bis-NHC-Pd-alkyne complex **B**.

The structure of these highly unsaturated 14-e$^-$ Pd complexes **2a-d**, bearing a weakly coordinated alkyne ligand, is very close to the monoligated 12-e$^-$ Pd(NHC) species that are widely accepted as the active catalytic species in numerous Pd catalysed reactions.[22]

We initially examined the ability of **2a** to release the diphenylacetylene moiety by simple ligand exchange with 1 equivalent of an incoming ligand. As shown in Scheme 3, phosphine ligands easily displace the alkyne fragment at room temperature, leading to the formation of mixed NHC/PR$_3$ Pd complexes [Pd(IPr)(PPh$_3$)] (**3**) and [Pd(IPr)(PCy$_3$)] (**4**),[19] and allows a rapid validation of our hypothesis that views **2a** as a powerful/versatile synthon.

Scheme 3. Ligand exchange reaction of **2a.**.



While complexes of the type [Pd(NHC)(PR$_3$)] such as **3** and **4** are known, their phosphite analogues remain unreported, as known synthetic methodologies are not compatible with the use of such ligands that are prone to transesterification.[23] On the other hand, such low valent mixed ligand complexes are of interest as mixing strong σ-donor ligands, such as NHCs, with strong π-acidic phosphites has been shown to lead to synergistic effects.[24] We thus further validated the stated role of **2a** as a synthon, and synthesised in a straightforward manner the first examples of complexes of the type [Pd(NHC){P(OR)$_3$}], complexes **5**, **6** and **7**, with R = 2,4-di-*tert*-butylphenyl, isopropyl and phenyl, respectively (Scheme 4). Interestingly, with the smallest ligand P(OMe)$_3$, the alkyne ligand remains coordinated, leading to the formation of the tri-coordinate complex **8**. These new complexes were fully characterized, and the geometry of **6**, **7** and **8** was confirmed by X-ray diffraction on single crystals obtained by slow

diffusion of pentane into a saturated toluene solution of the complex (Figures 2 and 3).[20] The experimentally determined metrical parameters for these are similar to previously reported Pd(0) and Pd(II) complexes.[8,12,16,19]

Interestingly, complex **8** represents a "freeze-frame" of a possible intermediate along the exchange reaction pathway. We found that, due to a considerably lower Tolman cone angle of the ligand (107°), compared to that of the other P-ligands, ranging from 128° to 192°,[25] the association of $P(OMe)_3$ to the unsaturated Pd centre does not cause the immediate release of PhC≡CPh. This might suggest that the phosphorus ligands first find their way to the unsaturated Pd centre, prior to release of PhC≡CPh , the final driving force leading to product would be steric pressure release. The binding of the smallest phosphite results in the three-coordinate complex Pd(IPr)(PhC≡CPh)(P(OMe_3)] (**8**), with bond angles of 104.59(15)°, 110.6(2)° and 108.61(15)° between the ligands. Complex **8** shows similar but more marked distortions from planarity compared to **2a**. Thus, the phenyl rings of diphenylacetylene are 0.07(1)° and -0.15(1)° from the Pd-C_2-C_3 mean plane whilst in the second independent molecule they lie 0.03(1)° and -0.16(1)° from the Pd-C_2-C_3 mean plane and the aryl rings are inclined by 18.7(1)° and 23.6(1)° in the first molecule and 6.4(1)° and 45.5(1)° in the second independent molecule. This intermediate appears disfavoured or unstable as the sterics of the incoming ligand increase. A tabular comparison of metrical parameters for **2a**, **6**, **7** and **8** can be found in the ESI.

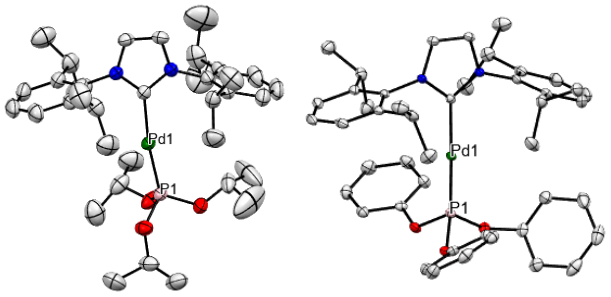


Figure 2. Molecular structure of **6** (left) and **7** (right). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **6** Pd-$C_{carbene}$ 2.0609(15), Pd-P 2.1727(5), $C_{carbene}$-Pd-P 171.10(5) and for **7** Pd-$C_{carbene}$ 2.0981(15), Pd-P 2.1383(5), $C_{carbene}$-Pd-P 176.68(5).

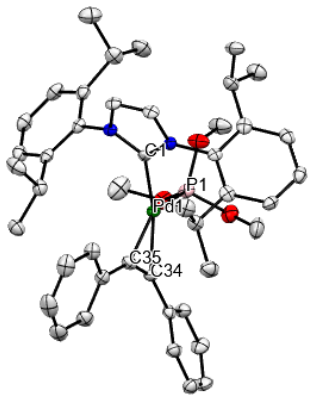


Figure 3. Molecular structure of **8**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) Pd-C1 2.089(5), Pd-P 2.2293(16), Pd-C34 2.040(5), Pd-C35 2.085(5), P-Pd-C1 104.59(15), C1-Pd-C35 110.6(2), P-Pd-C34 108.61(15).

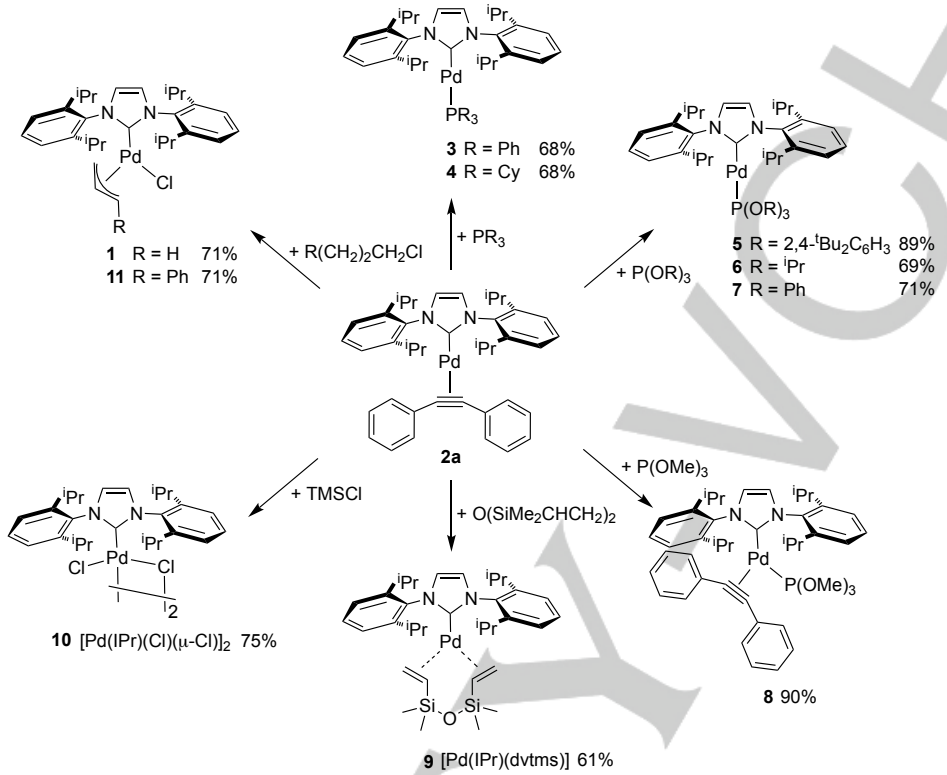
We next examined the ability of our synthon **2a** to lead to the commercially available [Pd(IPr)(dvtms)] (dvtms = 1,3-divinyl-1,1,3,3-dimethyl siloxane) (**9**), by simple addition of dvtms to **2a** (Scheme 4). Finally, we explored the ability of **2a** to act as a synthon for the generation of Pd(II) complexes, also important pre-catalysts that have the advantage of long-term stability. Reaction of **2a** with trimethylsilyl chloride (TMSCl) leads to the formation of the dimeric species of the type $[Pd(NHC)(Cl)(\mu\text{-}Cl)]_2$ (**10**),[6b] while reaction with allyl and cinnamyl chlorides lead to monomeric species of the type [Pd(NHC)(η^3-R-allyl)Cl] (**1** and **11**) (Scheme 4). This last reaction is of particular importance as it allows access to libraries of allyl derivatives, that are state-of-the-art catalysts, and whose activity partially rely on the propensity of the allyl moiety to be released. The rate of this process has been shown to increase with increasing steric properties of the R group on the allyl fragment.[26] However, this has only been shown using a limited number of R groups (H, Me, Ph), presumably due to the lack, so far, of synthetic strategies allowing rapid generation of libraries. The use of **2a** as synthon provides a solution to this issue, and provides access to catalyst libraries. This is presently being further investigated in our laboratories.

We then probed the stability of the [Pd(IPr)(PhC≡CPh)] complex **2a**. In the solid state, the complex shows no signs of degradation when kept under inert conditions (for at least 4 months) or when exposed to water (for at least 3 hours). However, when exposed to CO_2 or O_2, the diphenylacetylene ligand dissociates from the Pd-centre. However, this degradation happens rather slowly; after 1 hour of exposure to air 15% of the synthon had decomposed as monitored by ^{1}H-NMR spectroscopy. After 14 hours, the complex decomposes completely, resulting in the formation of palladium black.

Lastly, we hypothesised that **2a** can be a fast-initiating catalyst. We selected the hydrosilylation reaction to test our hypothesis. A first example using [Pd(IPr)(PhC≡CPh)] (**2a**) as catalyst for the hydrosilylation of cyclohexylallene is presented. Most reactions involving the hydrosilylation of allenes generate vinylsilanes or linear allylsilanes.[27] DFT calculations on the mechanism of this reaction determined that Pd-NHC catalysis could give great stereoselective control towards the desired branched allylsilanes.[28] The first and only showcase of the reaction of allenes and tertiary silanes towards branched allylsilanes was published in 2013 by Montgomery and co-workers.[29a] However, they relied on a high loading of 5 mol% $Pd_2(dba)_3$ (that is 10 mol% Pd) with 10 mol% IMes·HCl and 10 mol% of the strong base KO^{t}Bu (Scheme 5). Tafazolian and Schmidt later used the well-defined [Pd(3IP)(allyl)]OTf species in 1 mol% loading and without the use of a base to access allylsilanes (Scheme 5).[29b] This strategy has worked exceedingly well for primary and secondary silanes, however when it comes to tertiary silanes, the major product remained the vinylsilanes or very poor selectivities were observed.[29c-e]

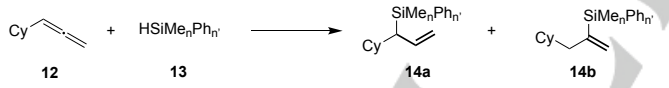
The reaction between cyclohexylallene (**12**) and tertiary silane methyldiphenylsilane (n = 1, n' = 2, **13**) in THF with a loading of 1 mol% of **2a** resulted in quantitative conversion

with outstanding regioselectivity (99%) of the desired branched allylsilane regio-isomer cyclohexylallyl(methyl) diphenylsilane (**14a**) (Table 1). After a short work-up, the desired product is isolated in excellent 97% yield. This protocol shows an improved, shorter reaction time, isolated yield, and a never attained stereoselectivity of tertiary silanes to the branched allylsilane compared to previously reported hydrosilylation protocols.[27,29] Further catalytic uses of this family of catalysts is presently being examined in our laboratories.



Scheme 4. Overview of complexes synthesized using the [Pd(IPr)(PhC≡CPh)] (**2a**) synthon.

Table 1. State-of-the-art hydrosilylation of cyclohexylallene and comparison to our hydrosilylation of cyclohexylallene (0.3 mmol) (**12**) with methyldiphenylsilane (0.3 mmol) (**13**).



12 13 14a 14b

Catalyst (Loading [mol%])	n,n'	Regiosel. a:b	Isolated Yield [%]	Ref
$Pd_2(dba)_3$ (5) IMesHCl (10) KOtBu (10)	2,1	98:2	91	28a
[(3IP)Pd(allyl)]OTf (1)	2,1	0:100	91	28b
[(3IP)Pd(allyl)]OTf (1)	1,2	0:100	94	28b
[Pd(IPr)(PhCCPh)] **2a** (1)	1,2	99:1	97	**This work**

[a] Reaction conditions: **2a** (1 mol%), THF (3 mL), rt, 2 hours. Conversion and ratio determined by ^{1}H-NMR spectroscopy.

To further analyse the nature of the interaction between the Pd and the diphenylacetylene ligand, we performed Density Functional Theory (DFT) calculations at the B3LYP-D3/Def2TZVPP~sdd(smd-benzene)//B3LYP-D3/Def2SVP~sdd level of theory. Table 2 includes the binding energy of several ligands to the NHC-Pd moiety. The binding energies (BE) ranging up to 29.5 kcal/mol for $P(OPh)_3$, and for homologous phosphine, 29.2 kcal/mol; and for the sterically less demanding PMe_3, a value 29.3 kcal/mol is obtained. Diphenylacetylene has a value in the lower range, at 21.4 kcal/mol. It should be mentioned that the DFT calculations made it possible to explain entry 8 of Scheme 4, where both $P(OMe)_3$ and diphenylacetylene ligands are bound to Pd, with an overall BE of 26.9 kcal/mol, hence the energy of dissociation of the diphenylacetylene would only represent 0.8 kcal/mol since the BE for $P(OMe)_3$ is 27.6 kcal/mol. On the other hand, and in line with what has been mentioned, the combination of $P(OPh)_3$ and diphenylacetylene is not feasible, releasing the latter from the ligands. In addition, the BE of the NHC onto the Pd-diphenylacetylene moiety increases to 42.7 kcal/mol. Therefore, the weakly binding nature of the diphenylacetylene ligand is clear and its formal 2-electron donor status is also clear from the analysis.

Following this initial analysis, an effort to find a structural/electronic relationship of the bond energies led to a predictive model through multilinear regression,[30,31] where with two structural variables (the Mayer Bond Order (MBO) of the Pd with the atom coordinates of the *trans* ligand in the

NHC and the $\%V_{Bur}$ of the NHC ligand[32]) and comparing these parameters with the Natural Bond Orbital (NBO) charge on the palladium, a good correlation is achieved with a $R^2 = 0.847$ (BE = 161.29 -21.71 MBO + 8.72 NBO -3.53 $\%V_{Bur}$). Thus, in general terms, a higher BE is defined by a higher $\%V_{Bur}$, which means less pressure from the *trans* ligand to the NHC ligand; and also a greater binding energy to the metal, as well as a greater amount of electron donation residing at the palladium center.

Table 2. Binding energies (BE) in Gibbs energies (kcal/mol) of the NHC-Pd-R complexes, Mayer Bond Orders (MBO) of the Pd···X (X = linking atom of the ligand *trans* to the NHC), $\%V_{Bur}$ of the NHC ligand, and Natural Bond Orbital (NBO) charge on Pd.

R	BE	MBO	$\%V_{Bur}$	NBO
Diphenylacetylene	-21.4	0.618	47.4	-0.059
dimethylacetylene	-14.7	0.602	46.8	-0.070
Acetylene	-21.4	0.726	46.0	-0.060
Ethylene	-17.6	0.696	46.7	-0.080
H_2	-9.6	0.442	46.1	-0.253
NH_3	-14.4	0.491	45.6	-0.296
PH_3	-23.4	0.801	46.7	-0.339
PMe_3	-29.3	0.740	47.5	-0.394
PPh_3	-29.2	0.699	48.2	-0.374
$P(OMe)_3$	-27.6	0.935	47.8	-0.381
$P(OPh)_3$	-29.5	0.981	47.4	-0.325

Conclusion

In summary, we have presented the synthesis of new versatile and well-defined NHC-Pd-alkyne complexes that can be used as synthons leading to existing and unprecedented palladium complexes and pre-catalysts. DFT calculations confirm the formation of a formally 14-electron Pd(0) η^2-alkyne species. Additionally, a first example of the use of one of these new complexes in the hydrosilylation of cyclohexylallene with a tertiary silane shows a one order of magnitude improve catalytic activity, compared to state-of-the-art, with outstanding regioselectivity under mild conditions. Further studies aimed at exploring the reactivity of this new family of complexes are ongoing in our laboratories.

Experimental

General Considerations: All reactions were performed in a glovebox under an argon atmosphere, unless otherwise stated. Solvents and liquid reagents were dried using distillation and/or molecular sieves and bubbled through with argon prior to using. Other reagents were used as received. ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker ADVANCE 400 MHz or 500 MHz spectrometer. Spectra were referenced using the residual solvent peak (C_6D_6 : δ_H = 7.16 ppm; δ_C = 128.06 ppm and $CDCl_3$: δ_H = 7.26 ppm; δ_C = 77.16 ppm) at 298 K.

Preparation of [Pd(NHC)(PhC≡CPh)] complexes: In a glovebox, a vial was charged with [Pd(NHC)(η^3-allyl)(Cl)], KOtBu (1 equiv.), diphenylacetylene (1equiv.) and iPrOH. This reaction mixture was stirred for 5 hours at room temperature. After the reaction, the orange precipitate is collected and washed with iPrOH. The orange solid is then dissolved in benzene and the solution is re-filtered to remove any insoluble material. The remaining solvent is evaporated in vacuo to afford the desired compound as an orange solid.

[Pd(IPr)(PhC≡CPh)] (2a): Following the general procedure using [Pd(IPr)(η^3-allyl)(Cl)] (1.72 g, 3.00 mmol), KOtBu (373 mg, 3.00 mmol), diphenylacetylene (535 mg, 3.00 mmol) and iPrOH (10 mL). Isolated yield: 1.542 g; 78%. ^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 1.17 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH-CH_3), 1.51 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH-C*H*$_3$), 2.95 (septet, $^3J_{H-H}$ = 6.9 Hz, 4H, C*H*-$(CH_3)_2$), 6.46 (s, 2H, *H*^{4} and *H*^{5}), 7.03-7.08 (m, 6H, m-C*H* and p-C*H* phenyl), 7.14-7.20 (m, 4H, overlap with solvent, o-C*H* phenyl), 7.23 (d, $^3J_{H-H}$ = 7.8 Hz, 4H, m-C*H* aryl), 7.43 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, p-C*H* aryl); ^{13}C-{^{1}H}-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 23.9 (s, CH*C*H$_3$), 25.3 (s, CH*C*H$_3$), 29.1 (s, *C*HCH$_3$), 101.4 (s, *C*≡*C*), 121.6 (s, *C*^{4} and *C*^{5}), 124.1 (s, C_{Ar}H), 126.6 (s, C_{Ar}H), 129.1 (s, C_{Ar}H), 129.6 (s, C_{Ar}H), 131.6 (s, C_{Ar}H), 137.1 (s, *C*^{IV}), 147.2 (s, *C*^{IV}), 197.2 (s, *C*^{2}).; Anal. Calcd for C41H46N2Pd: C, 73.15; H, 6.89; N, 4.16. Found: C, 73.12; H, 7.00; N, 4.21.

[Pd(SIPr)(PhC ≡ CPh)] (2b): Following the general procedure using [Pd(SIPr)(η^3-allyl)(Cl)] (100 mg, 0.17 mmol), KO^{t}Bu (19.6 mg, 0.17 mmol), diphenylacetylene (34.1 mg, 0.18 mmol) and ^{i}PrOH (1 mL). Isolated yield: 89 mg; 76%. ^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 1.27 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH-C*H*$_3$), 1.59 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH-C*H*$_3$), 3.31+3.34 (overlap of septet and singlet, $^3J_{H-H}$ = 6.9 Hz, 10H, C*H*-$(CH_3)_2$ and *H*$_2^4$ and *H*$_2^5$), 6.99-7.08 (m, 10H, C*H* phenyl), 7.22 (d, $^3J_{H-H}$ = 7.8 Hz, 4H, m-C*H* aryl), 7.41 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, p-C*H* aryl); ^{13}C-{^{1}H}-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 24.10 (s, CH*C*H$_3$), 25.85 (s, CH*C*H$_3$), 29.25 (s, *C*HCH$_3$), 53.53 (s, *C*^{4} and *C*^{5}), 101.6 (s, *C*≡*C*), 124.51 (s, C_{Ar}H), 126.61 (s, C_{Ar}H), 128.83 (s, C_{Ar}H), 128.92 (s, C_{Ar}H), 131.65 (s, C_{Ar}H), 137.32 (s, *C*^{IV}), 148.26 (s, *C*^{IV}), 218.08 (s, *C*^{2}).

[Pd(IPent)(PhC ≡ CPh)] (2c): Following the general procedure using [Pd(IPent)(η^3-allyl)(Cl)] (100 mg, 0.15 mmol), KO^{t}Bu (16.6 mg,0.15 mmol), diphenylacetylene (28.7 mg, 0.16 mmol) and ^{i}PrOH (2 mL). Isolated yield: 85.4 mg; 71%. ^{1}H-NMR (400 MHz, C_6D6, 298 K): δ (ppm) = 0.81 (t, $^3J_{H-H}$ = 7.2 Hz, 12H, CH_2-C*H*$_3$), 0.99 (t, $^3J_{H-H}$ = 7.2 Hz, 12H, CH_2-C*H*$_3$), 1.41-1.65 (m, 8H, CH-C*H*$_2$-CH_3), 1.78 (m, 4H, CH-C*H*$_2$-CH_3), 2.05 (m, 4H, CH-C*H*$_2$-CH_3), 2.64 (quintet, $^3J_{H-H}$ = 6.9 Hz, 4H, C*H*-$(CH_2)_2$), 6.60 (s, 2H, *H*^{4} and *H*^{5}), 7.01-7.07 (m, 6H, m-C*H* and p-C*H* phenyl), 7.13-7.16 (m, 4H, overlap with solvent, o-C*H* phenyl), 7.18 (d, $^3J_{H-H}$ =7.8 Hz, 4H, m-C*H* aryl), 7.43 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, p-C*H* aryl); ^{13}C-{^{1}H} NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 12.6 (s, CH_2*C*H$_3$), 12.7 (s, CH_2*C*H$_3$), 28.2 (s, CH*C*H$_2$CH$_3$), 29.3 (s, CH*C*H$_2$CH$_3$), 42.74 (s, *C*HCH$_2$), 101.6 (s, *C*≡*C*), 122.4 (s, *C*^{4} and *C*^{5}), 124.8 (s, C_{Ar}H), 126.5 (s, C_{Ar}H), 128.9 (s, C_{Ar}), 129.0 (s, C_{Ar}H), 129.6 (s, C_{Ar}H), 139.6 (s, *C*^{IV}), 144.8 (s, *C*^{IV}), 196.8 (s, *C*^{2}).

[Pd(IPr^{Cl})(PhC ≡ CPh)] (2d): Following the general procedure using [Pd(IPr^{Cl})(η^3-allyl)(Cl)] (100 mg, 0.15 mmol), KO^{t}Bu (17.5 mg, 0.15 mmol), diphenylacetylene (30.6 mg, 0.16 mmol) and ^{i}PrOH (2 mL). Isolated yield: 113 mg; 79%. ^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 1.19 (d, $^3J_{H-H}$ = 6.9 Hz, 12H,

CH-C*H*$_3$), 1.50 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH-C*H*$_3$), 2.94 (septet, ^3J*H-H* = 6.9 Hz, 4H, C*H*-(CH$_3$)$_2$), 6.98-7.08 (m, 6H, m-C*H* and p-C*H* phenyl), 7.08-7.14 (m, 4H, o-C*H* phenyl), 7.20 (d, $^3J_{H-H}$ = 7.8 Hz, 4H, m-C*H* aryl), 7.41 (t, 3JH-H = 7.8 Hz, 2H, p-CH aryl); ^{13}C-{^{1}H}-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 23.43 (s, CH*C*H$_3$), 25.24 (s, CH*C*H$_3$), 29.52 (s, *C*HCH$_3$), 90.19 (s, *C*^{4} and *C*^{5}), 100.78 (s, *C*≡*C*), 124.45 (s, *C*$_{Ar}$H), 126.81 (s, *C*$_{Ar}$H), 128.46 (s, *C*$_{Ar}$H), 128.66 (s, *C*$_{Ar}$H), 130.53 (s, *C*$_{Ar}$H), 131.62 (s, *C*$_{Ar}$H), 131.98 (s, *C*$_{Ar}$H) 134.07 (s, *C*^{IV}), 147.7 (s, *C*^{IV}), 197.2 (s, *C*^{2}).

General Procedure for Ligand Exchange Reactions: In a glovebox, a vial was charged with [Pd(IPr)(PhC ≡ CPh)] (1 equiv.), ligand (1 equiv.) (except for compound **10**, which was made by adding 5 equivalents of TMSCl) and benzene. The reaction mixture is stirred for 10 minutes at room temperature. The solution is then concentrated in vacuo and the remaining solid is washed with methanol and filtered, to remove impurities, affording the desired compound.

[Pd(IPr)(P{OC$_6$H$_3$-2,4-^{t}Bu$_2$}$_2$)] (5): Following the general procedure using **2a** (50 mg, 0.074 mmol), tris(2,4-di-*tert*-butylphenyl)phosphite (48.04 mg; 0.074 mmol) and benzene (1 mL). Isolated yield: 75.4 mg; 89%. ^{1}H-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 1.13 (d, 12H, $^3J_{H-H}$ = 6.9 Hz, CHC*H*$_3$), 1.31 (s, 27H, CC*H*$_3$), 1.32 (d, 12H, $^3J_{H-H}$ = 6.9 Hz, CHC*H*$_3$), 1.55 (s, 27H, CC*H*$_3$), 2.68 (septet, 4H, $^3J_{H-H}$ = 6.9 Hz, C*H*CH3), 6.32 (s, 2H, *H*^{4} and *H*^{5}), 6.89 (dd, 3H, $^3J_{H-H}$ = 8.5 Hz, $^3J_{H-H}$ = 2.2 Hz, C$_{Ar}$*H*), 7.18 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, C$_{Ar}$*H*), 7.38 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, C$_{Ar}$*H*), 7.45 (d, 3H, $^3J_{H-H}$ = 2.2 Hz, C$_{Ar}$*H*), 8.03 (dd, 3H, $^3J_{H-H}$ = 8.5 Hz, 3JHH = 2.2 Hz, C$_{Ar}$H); ^{13}C-{^{1}H} NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 23.7 (s, CH*C*H$_3$), 25.4 (s, CH*C*H$_3$), 29.0 (s, *C*HCH$_3$), 121.9 (d, $^3J_{CP}$= 7.7 Hz, *C*^{IV}), 123.0 (s, *C*^{4} and *C*^{5}), 123.8 (s, *C*$_{Ar}$H), 129.3 (s, *C*$_{Ar}$H), 129.8 (s, *C*$_{Ar}$H), 137.6 (s, *C*$_{Ar}$H), 146.2 (s, *C*^{IV}), 153.2 (s, *C*^{IV}), 195.8 (d, $^2J_{CP}$= 129.0 Hz, *C*^{2}); ^{31}P-{^{1}H} NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 126.1.

[Pd(IPr){P(O^{i}Pr)$_3$)}] (6): Following the general procedure using **2a** (50 mg, 0.074 mmol), triisopropylphosphite (18.32 µL; 0.074 mmol) and benzene (1 mL). Isolated yield: 36.3 mg; 69%. ^{1}H-NMR (300 MHz, C_6D_6, 298K): δ (ppm) = 1.16 (d, 18H, $^3J_{H-H}$ = 6.3 Hz, CHC*H*$_3$), 1.18 (d, 12H, $^3J_{H-H}$ = 6.8 Hz, CHC*H*$_3$), 1.61 (d, 12H, $^3J_{H-H}$ = 6.8 Hz, CHC*H*$_3$), 2.86 (septet, 4H, $^3J_{H-H}$ = 6.8 Hz, C*H*CH$_3$), 4.68 (m, 3H, C*H*CH$_3$), 6.42 (s, *H*^{4} and *H*^{5}), 7.10 (d, 4H, $^3J_{H-H}$ = 7.6 Hz, C*H* aryl), 7.21 (t, 2H, $^3J_{H-H}$ = 7.6 Hz, C*H* aryl); ^{13}C-{^{1}H}-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 23.5 (s, CH*C*H$_3$), 24.4 (d, $^3J_{CP}$ = 4.5 Hz, CH*C*H$_3$), 25.1 (s, CH*C*H$_3$), 28.7 (s, *C*HCH$_3$), 66.4 (d, $^2J_{CP}$ = 15.7 Hz, *C*HCH$_3$), 121.1 (d, $^4J_{CP}$ = 2.4 Hz, *C*^{4} and *C*^{5}), 123.2 (s, *C*$_{Ar}$H), 129.1 (s, *C*$_{Ar}$H), 137.0 (s, *C*^{IV}), 145.9 (s, *C*^{IV}), 198.0 (d, $^2J_{CP}$ = 122.2 Hz, *C*^{2}); ^{31}P-{^{1}H}-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 155.9; Anal. Calcd for C36H57N2O3PPd: C, 61.48; H, 8.17; N, 3.98. Found: C, 61.69; H, 8.40; N, 4.15.

[Pd(IPr){P(OPh)$_3$}] (7): Following the general procedure using **2a** (50 mg, 0.074 mmol), triphenylphosphite (19.46 µL; 0.074 mmol) and benzene (1 mL). Isolated yield: 43.7 mg; 73%. ^{1}H-NMR (500 MHz, C_6D_6, 298 K): δ (ppm) = 1.11 (d, 12H, $^3J_{H-H}$ = 6.8 Hz, C*H*$_3$-CH), 1.33 (d, 12H, $^3J_{H-H}$ = 6.8 Hz, C*H*$_3$-CH), 2.67 (septet, 4H, $^3J_{H-H}$ = 6.8 Hz, C*H*-(CH$_3$)$_2$), 6.30 (s, 2H, *H*^{4} and *H*^{5}), 6.85-6.91 (m, 3H, p-C*H* phenyl), 6.95-7.00 (m, 6H, m-C*H* phenyl), 7.10 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, C*H* aryl), 7.21 (d, $^3J_{H-H}$ = 7.2 Hz, 6H, o-C*H* phenyl), 7.26 (t, 2H, $^3J_{H-H}$ = 7.8 Hz, C*H* aryl); ^{13}C-{^{1}H} NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 23.7 (s, CH*C*H$_3$), 25.4 (s, CH*C*H$_3$), 29.0 (s, *C*HCH$_3$), 121.9 (d, $^3J_{CP}$= 7.7 Hz, *C*^{IV}), 123.0 (s, *C*^{4} and *C*^{5}), 123.8 (s, *C*$_{Ar}$H), 129.3 (s, *C*$_{Ar}$H), 129.8 (s, *C*$_{Ar}$H), 137.6 (s, *C*$_{Ar}$H), 146.2 (s, *C*^{IV}), 153.2 (s, *C*^{IV}), 195.8 (d, $^2J_{CP}$= 129.0 Hz, *C*^{2}); ^{31}P-{^{1}H}-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 144.2; Anal. Calcd for C45H51N2O3PPd: C, 67.12; H, 6.38; N, 3.48. Found: C, 67.28; H, 6.45; N, 3.64

[Pd(IPr)(PhC≡CPh)(P(OMe)$_3$)] (8): Following the general procedure using **2a** (50 mg, 0.074 mmol), trimethylphosphite (8.76 µL; 0.074 mmol) and benzene (1 mL). Isolated yield: 53.5 mg, yield = 90%. ^{1}H-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 1.27 (d, 12H, $^3J_{H-H}$ = 6.9 Hz, CH-C*H*$_3$), 1.73 (d, 12H, $^3J_{H-H}$ = 6.9 Hz, CH-C*H*$_3$), 2.95 (septet, 4H, $^3J_{H-H}$ = 6.9 Hz, C*H*-(CH$_3$)$_2$), 3.42 (d, 9H, $^3J_{H-P}$ = 13.0 Hz, CC*H*$_3$), 6.51 (s, 2H, *H*^{4} and *H*^{5}), 7.05-7.13 (m, 6H, C$_{Ar}$*H*), 7.19 (d, 4H, $^3J_{H-H}$ = 7.9 Hz, C$_{Ar}$*H* IPr), 7.29 (t, 2H, $^3J_{H-H}$ = 7.9 Hz, C$_{Ar}$*H* IPr), 7.58-7.65 (m, 4H, C$_{Ar}$*H*); ^{13}C-{^{1}H}-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 24.1 (s, CH*C*H$_3$), 25.9 (s, CH*C*H$_3$), 29.4 (s, *C*HCH$_3$), 50.4 (d, $^3J_{CP}$= 11.5 Hz, *C*H$_3$), 90.5 (s, *C*^{IV}), 121.9 (s, *C*^{4} and *C*^{5}), 124.0 (s, *CAr*H), 129.0 (s, *C*$_{Ar}$H), 129.1 (s, *C*$_{Ar}$H), 129.9 (s, *C*$_{Ar}$H), 132.3 (s, *C*$_{Ar}$H), 137.0 (s, *C*^{IV}), 146.1 (s, *C*^{IV}), 198.1 (d, $^2J_{CP}$= 125.2 Hz, *C*^{2}); ^{31}P-{^{1}H}-NMR (400 MHz, C_6D_6, 298K): δ (ppm) = 156.6; Anal. Calcd for C44H55N2O3PPd: C, 66.28; H, 6.95; N, 3.51. Found: C, 66.09; H, 7.04; N, 3.43.

Procedure for the Hydrosilylation: In a glovebox, a vial equipped with a stirring bar and sealed with a screw cap fitted with a septum was charged with [Pd(IPr)(PhC≡CPh)] (2.0 mg; 1 mol%) and dissolved in THF. MePh$_2$SiH(60µL; 0.3 mmol) was added and the reaction mixture stirred for 10 minutes. A solution of cyclohexylallene (44 µL; 0.3 mmol) in THF was added dropwise and the reaction mixture was stirred at room temperature for 2h. The solution was concentrated in vacuo and the crude was purified by flash chromatography using pentane as eluent.

(1-cyclohexylallyl)(methyl)diphenylsilane (14a): Isolated yield: 187mg; 97%. ^{1}H-NMR (500 MHz, $CDCl_3$, 298K): δ (ppm) = 0.74 (s, 3H, C*H*$_3$), 1.12-1.35 (m, 5H, C*H* and C*H*$_2$), 1.64-1.88 (m, 6H, C*H*$_2$), 2.28-2.35 (m, 1H, C*H*), 4.93-5.01 (s, 1H, C*H*$_2$), 5.05-5.11 (m, 1H, C*H*$_2$), 5.88-6.00 (s, 1H, C*H*), 7.45-7.53 (m, 6H, C*H* Ar), 7.69-7.75 (m, 4H, C*H* Ar); ^{13}C-{1H}-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = -3.9 (s, *C*H$_3$), 26.4 (s, *C*H$_2$), 26.9 (s, *C*H$_2$), 26.9 (s, *C*H$_2$), 31.5 (s, *C*H$_2$), 34.6 (s, *C*H$_2$), 38.6 (s, *C*H-CH-Si), 40.8 (s, *C*H-Si) ,115.0 (s, *C*H$_2$-CH), 127.8 (s, *C*H$_{Ar}$), 127.9 (s, *C*H$_{Ar}$), 129.1 (s, *C*H$_{Ar}$), 129.2 (s, *C*H$_{Ar}$), 135.0 (s, *C*H$_{Ar}$), 135.1 (s, *C*H$_{Ar}$), 136.9 (s, *C*^{IV}), 137.2 (s, *C*^{IV}), 137.4 (s, *C*H-CH$_2$).

Conflicts of interest

There are no conflicts of interest to declare.

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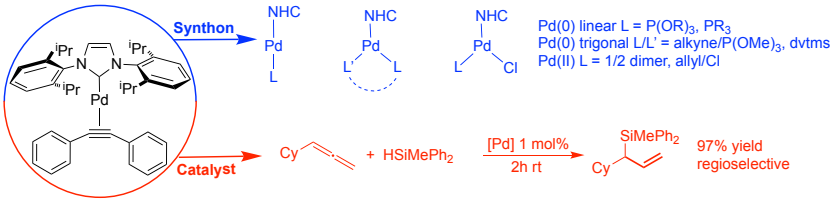

Low coordination number yet stable: The synthesis and characterisation of new low-valent palladium (0) complexes are reported, and provide simple access to known and novel complexes whose instrinsic reactivity prevented their isolation using existing methods. One complex performs exceptionally well as catalyst in hydrosilylation reaction.