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A General Synthetic Route to Mixed NHC–Phosphane Palladium(0) Complexes (NHC = N-Heterocyclic Carbene)

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Abstract: Mixed NHC–phosphane palladium(0) complexes [(NHC)Pd(PR_3)] (NHC: N-heterocyclic carbene) are synthesized directly from commercially available reagents, with the possibility to tune the nature of both the NHC and the phosphane. Reaction of [(NHC)Pd(allyl)Cl] (palladium source) and PR_3, in the presence of a base afforded, in isopropanol, [(NHC)Pd(PR_3)] in good yields. We found that the nature of the solvent played a key role in the efficient reduction of the Pd^{II} precursor to Pd^0. Supported by experimental evidence we propose that the reduction step is driven by the isopropoxide anion formed in situ from isopropanol and a base. Detection of acetone in the reaction mixture confirms that the isopropoxide anion acts as the reducing agent. Moreover, different bases proved efficient for the reaction. The structures of the complexes were unambiguously confirmed by X-ray analysis. Exposure of these complexes to air does not lead to decomposition, but to the oxo-complex [(NHC)Pd(PR_3)(O_2)], which is stable both in the solid state and in solution.

Keywords: N-heterocyclic carbenes · organometallic synthesis · oxygen · palladium · phosphanes

Introduction

N-Heterocyclic carbenes (NHCs) are nowadays widely employed as supporting ligands in transition metal-catalyzed reactions[1] including in ubiquitous palladium-catalyzed cross-coupling reactions,[2] in which their introduction has allowed for a dramatic increase in catalytic performance. Much attention has been devoted to Pd^{II} complexes pre-catalysts, but fewer reports on well-defined [Pd^0(NHC)] catalysts have appeared.[3] The interesting feature of a well-defined Pd^0 catalyst lies in the possibility of avoiding the in situ reduction of a Pd^{II} precursor, a procedure that may generate inactive palladium species, especially palladium black. In the course of our studies, we became interested in dicoordinated Pd^0 compounds. Studies by other groups showed that [$Pd(NHC)_2$] complexes generally displayed moderate activity in cross-coupling reactions.[3b–d,h,j,4] As monoligated Pd^0 moieties are believed to be the active catalytic species in cross-coupling reactions,[5] we thought that replacing one NHC by a less σ-donating ligand, could lead to improved catalytic activity. The new ligand has to stabilize the highly unsaturated Pd^0 complex, but also be able to be released from the metal center, to allow for the initiation of the catalytic cycle. Tertiary phosphanes appear as ideal candidates to this end. To the best of our knowledge only two reports on mixed NHC–phosphane Pd^0 complexes have appeared in the literature, with no crystal structure reported.[3d,4] These reports disclose complexes synthesized by ligand exchange from [Pd{P(*o*-tol)$_3$}$_2$] with NHCs {P(*o*-tol)$_3$} = tri-*ortho*-tolylphosphane). Besides the unappealing synthesis of the [Pd{P(*o*-tol)$_3$}$_2$] precursor,[6] only careful control of the reaction stoichiometry or the use of the highly sterically hindered IAd (1,3-bis(1-adamantyl)imidazol-2-ylidene) lead to [(NHC)Pd{P(*o*-tol)$_3$}] in good yields. Owing to the scope limitation of this synthetic procedure we decided to explore alternative routes with the aim to develop a general synthetic route to mixed NHC/PR_3 palladium(0) complexes.

Results and Discussion

Recently our group synthesized, in a very straightforward manner,[7] a family of Pd^{II} complexes, [(NHC)Pd(R-allyl)(Cl)] (R = H, Me, Ph, *gem*-Me_2), that showed excellent activity in the Suzuki–Miyaura, α-ketone arylation and the Buchwald–Hartwig reactions.[8] We suggested the initial for-

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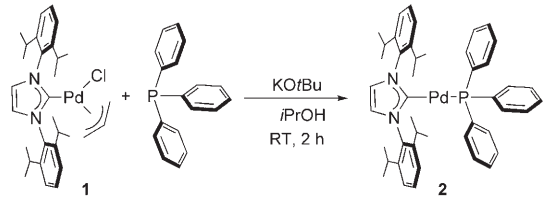
mation of a [Pd^0(NHC)] species generated by reduction of the Pd^{II} pre-catalyst by KO*t*Bu. In an in situ experiment, the [Pd^0(NHC)] species was trapped by addition of tricyclohexylphosphane (PCy_3) and the resulting complex, [(NHC)Pd(PCy_3)], was observed by ^{31}P NMR spectroscopy.[8a] Guided by this trapping experiment, we reasoned that reacting [(IPr)Pd(allyl)(Cl)] (**1**: IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) with one equivalent of KO*t*Bu in *i*PrOH in the presence of PPh_3 could lead to the formation of a mixed dicoordinate species. Indeed, carrying out this reaction in this manner leads, after two hours, to the formation of a yellow precipitate and a simple filtration allowed for the isolation of [(IPr)Pd(PPh_3)] (**2**) in 92% yield (Scheme 1).



Scheme 1. Synthesis of [(IPr)Pd(PPh_3)] (**2**).

The identity of **2** was determined by NMR characterization by using ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies (samples in C_6D_6). The coordination of the PPh_3 was confirmed by the ^{31}P NMR spectra as only one singlet appeared at $\delta =$ 33.6 ppm (δ(free PPh_3) = −2.1 ppm). In the ^{13}C NMR spectrum, the carbenic carbon signal is shown at $\delta = 198.0$ ppm (δ(free IPr) = 220.6 ppm) and appears as a doublet due to the coupling with phosphorus ($^2J = 93$ Hz). Notably, the imidazole backbone carbons ($\delta = 120.9$ ppm) appear as a doublet with a small coupling constant of 3 Hz.

Unequivocal confirmation of the structure of **2** is provided by X-ray analysis on a single crystal grown from a saturated diethyl ether solution at −35 °C. A ball-and-stick representation of **2** is presented in Figure 1. To the best of our knowledge, this is the first reported structure of a mixed NHC–phosphane Pd^0 complex.

Coordination to palladium deviates from ideal linear geometry with the C(1)–Pd(1)–P(1) bond angle measuring $\theta =$ 169.49(2)°. Compared with reported structures of biscarbene complexes [Pd(NHC)$_2$] (NHC = IPr: $\theta = 175.98°$,[3i] IMes: $\theta =$ 178.80(13)°,[9] IAd: $\theta = 180.00°$[4]), **2** shows the highest deviation from linearity. Comparison of C(1)–Pd bond lengths between **2** ($d = 2.0547(8)$ Å) and [Pd(NHC)$_2$] complexes gives further insights into the steric environment around palladium. For example, the C(1)–Pd bond in **2** is longer than in [Pd(IMes)$_2$] and [Pd(IPr)$_2$] ($d = 1.990(3)$ Å and $d =$ 2.022(4) Å respectively), but shorter than in [Pd(IAd)$_2$] ($d =$ 2.076(5) Å). These data reflect the relative steric hindrance of the different NHCs (IMes < IPr < IAd). More interestingly, direct comparison with [Pd(IPr)$_2$] shows that substitution of one IPr for PPh_3 in the palladium coordination sphere lengthens the C(IPr)–Pd bond by 0.03 Å. On the other hand, the P(1)–Pd bond length in **2** (d = 2.100(2) Å) is considerably shorter than in [Pd(PPh_3)$_3$] (d = 2.307–2.322 Å).[10] Undoubtedly, steric hindrance, arising from the presence of a third ligand in [Pd(PPh_3)$_3$], plays a key role in defining the P–Pd bond length.

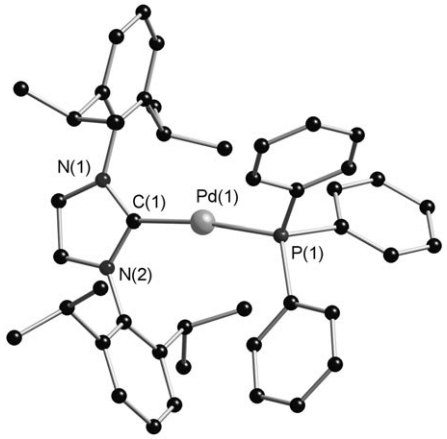
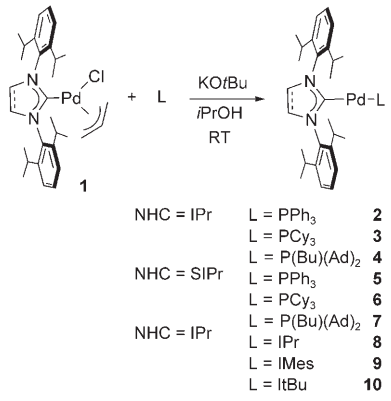


Figure 1. Ball-and-stick representation of **2**. Selected bond lengths [Å] and angles [°]: C(1)–Pd(1) 2.0547(8), P(1)–Pd(1) 2.2100(2), C(1)–Pd(1)–P(1) 169.49(2), N(1)–C(1)–N(2) 102.98(7).

To prove the generality of this synthetic route, we varied the nature of both the phosphane and the NHC. Reaction of **1** with PCy_3 and P(*n*Bu)(Ad)$_2$ (Ad: 1-adamantyl) afforded complexes **3** and **4** in good and moderate yields respectively (Scheme 2). SIPr analogues **5**, **6**, and **7** were synthesized



Scheme 2. Synthesis of [(NHC)Pd(L)] complexes.

starting from [(SIPr)Pd(allyl)Cl]. To further generalize this synthetic procedure we attempted the synthesis of bis-NHC complexes [(NHC)Pd(L)], employing as ligand L different free NHCs. We observed the formation of [Pd(IPr)$_2$] (**8**), [(IPr)Pd(IMes)] (**9**), and [(IPr)Pd(I*t*Bu)] (**10**) in good yields.

Relevant NMR data and yields of the different Pd^0 complexes are summarized in Table 1.

The complex [(IPr)Pd(PCy_3)] (**3**) was also characterized by single-crystal X-ray diffraction studies. Ball-and-stick representation of its structure is depicted in Figure 2. The complex shows a distorted linear geometry, the C(1)–Pd(1)–

Table 1. Relevant NMR spectroscopy data[a] and yields for [(NHC)Pd(L)].

Complex		Yield [%]	δ^{31}P [ppm][b]	$\delta^{13}C_{carb}$ [ppm][c]	$^2J_{C-P}$ [Hz]
[(IPr)Pd(PPh_3)]	**2**	92	33.6	198.0	94
[(IPr)Pd(PCy_3)]	**3**	85	49.4	199.2	90
[(IPr)Pd{$P(Ad)_2(n$Bu)}]	**4**	61	63.2	199.3	86
[(SIPr)Pd(PPh_3)]	**5**	80	33.0	218.1	86
[(SIPr)Pd(PCy_3)]	**6**	80	48.1	218.6	83
[(SIPr)Pd{$P(Ad)_2(n$Bu)}]	**7**	74	61.0	218.5	83
[(IPr)Pd(IPr)]	**8**	87	–	199.0	–
[(IPr)Pd(IMes)]	**9**	72	–	200.6 197.7	–
[(IPr)Pd(I*t*Bu)]	**10**	59	–	200.7 194.5	–

[a] Solution in C_6D_6. [b] δ(free phosphane) = −2.1 (PPh_3), 13.1 (PCy_3), 27.5 ppm {$P(Ad)_2(n$Bu)}. [c] δ(free carbene) = 220.6 (IPr), 244.0 (SIPr), 219.7 (IMes), 213.2 ppm (I*t*Bu).

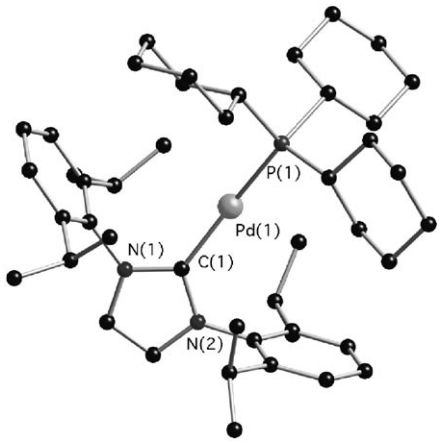
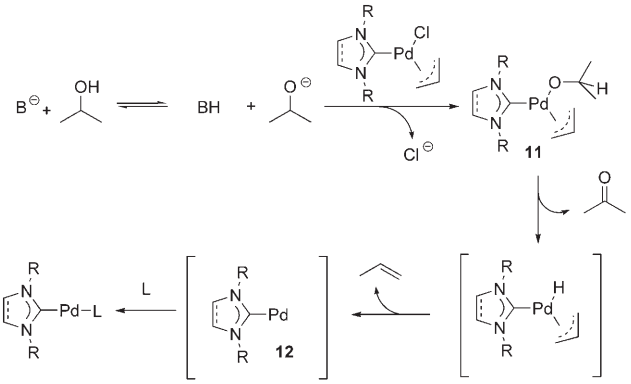


Figure 2. Ball-and-stick representation of **3**. Selected bond lengths [Å] and angles [°]: C(1)–Pd(1) 2.0292(9), P(1)–Pd(1) 2.2212(3), C(1)–Pd(1)–P(1) 170.88(2), N(1)–C(1)–N(2) 103.27(7).

P(1) angle measuring 170.88°. Pd–C and Pd–P distances does not significantly differ from that found in **2**.

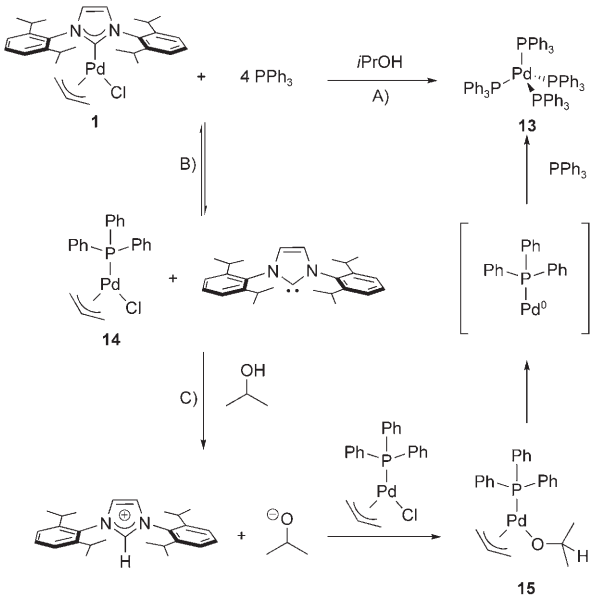
Examining reaction parameters, we found that the nature of the solvent dramatically affected the outcome of the reaction, notably the Pd^{II}/Pd^0 reduction step. Indeed, the reaction of **1** and KO*t*Bu in THF at room temperature did not lead to the reduction of Pd^{II}. On the other hand, **1** is stable in isopropanol, with only slight decomposition observed over several days. Hence, it seems that both isopropanol and KO*t*Bu are necessary for the formation of the Pd^0 complex. At this point we wondered if the use of a base such as KO*t*Bu was absolutely necessary. We decided to perform the reaction with an alternative, less expensive base. Employing NaOH in lieu of KO*t*Bu, afforded complex **2** in 87% yield. This evidence suggested that KO*t*Bu might not be directly involved in the reduction of Pd^{II} to Pd^0, and that the base might only have the role of generating the reducing agent, in this case very likely being the isopropoxide anion. Previous studies conducted by our group on the activation mechanism of [(NHC)Pd(allyl)Cl] complexes in aprotic solvents (such as benzene or THF), strongly supported a direct involvement of KO*t*Bu in the reduction of the Pd^{II} precursor. Based on the detection of allyl *tert*-butyl ether in the reaction mixture, we hypothesized either a direct nucleophilic attack of *tert*-butoxide anion on the coordinated allyl moiety or a chloride/*tert*-butoxide metathesis on the Pd center followed by reductive elimination (in both cases allyl *tert*-buthyl ether is formed).[11] However, this mechanism does not seem at play when isopropanol is used as solvent, as the reaction proceeds also with NaOH as the base. To gain more insights into this activation step, we performed a GC-MS analysis on the isopropanol solution at the end of the reaction. Allyl *tert*-butyl ether was not identified in the reaction mixture, whereas detection of acetone strongly supported the involvement of isopropanol in the Pd^{II}/Pd^0 reduction step. A possible mechanism illustrating this reduction/trapping is depicted in Scheme 3. We propose that the isoprop-



Scheme 3. Proposed mechanism for the formation of [(NHC)Pd(L)].

oxide anion, generated from deprotonation of isopropanol, substitutes the chloride in [(NHC)Pd(allyl)Cl], giving rise to **11**. Then a mechanism involving β-hydride elimination of the coordinated isopropoxide and reductive-elimination of 1-propene, leads to reduction of Pd^{II} to Pd^0.[12] Coordination of L (L = phosphane or NHC) to **12** would finally produce [(NHC)Pd(L)].

Wanting to shed more light on this reaction mechanism, and notably on the role of the base, we performed a test reaction between [(IPr)Pd(allyl)Cl] and PPh_3 in the *absence* of base. Unexpectedly, we observed the formation of a mixture of **1** and another product that, after characterization, was revealed to be [$Pd(PPh_3)_4$] (**13**). The yield of **13** is quantitative if the reaction is carried out with four equivalent of PPh_3 (Scheme 4, reaction A). Acetone was detected by GC-MS from aliquots of the reaction, suggesting that isopropoxide is, even in this case, the reducing agent. We were then intrigued by the nature of the base, since this reaction did not contain any added base. Careful analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed the presence of imidazolium salts. We therefore believe that, in this case, free IPr acts as the base. We propose the mechanism depicted in Scheme 4 for this process. In the absence of



Scheme 4. Proposed mechanism for the formation of $[Pd(PPh_3)_4]$.

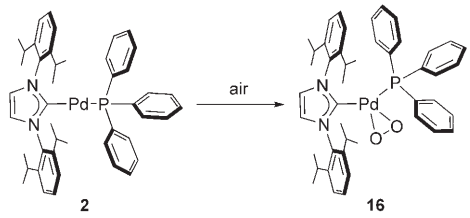
base, triphenylphosphane could displace IPr from the coordination sphere of the palladium, giving rise to **14** $[(PPh_3)Pd(allyl)Cl]$. The newly generated free IPr, could then act as the base, deprotonating isopropanol. Isopropoxide anion, through formation of **15**, subsequently drives the reduction of Pd^{II} to Pd^0.

To support the aforementioned mechanism, we followed the reaction by ^{31}P NMR. After 20 minutes a resonance corresponding to $[(PPh_3)Pd(allyl)(Cl)]$[13] appeared in the reaction mixture, confirming the exchange between IPr and PPh_3 (Scheme 4, reaction B). Moreover the presence of a broad peak at $\delta = 2.7$ ppm suggests a rapid exchange between the coordinated and the free phosphane. Substitution of NHC ligands by phosphanes on transition metals has been reported previously in the literature.[3d,14] Additionally, to support that free IPr, liberated by substitution with PPh_3 in **2**, can act as a base towards *i*PrOH we directly performed the reaction between $[(PPh_3)Pd(allyl)(Cl)]$ **14**, 3 equivalents of PPh_3 and free IPr in *i*PrOH (Scheme 4, reaction C). In this manner, we obtained $[Pd(PPh_3)_4]$ (**13**) in 85% yield. To further prove that free IPr could act as a base towards *i*PrOH, we performed the synthesis of $[(IPr)Pd(PPh_3)]$ (**2**) using, as the base, free IPr (Scheme 5).

We were pleased to obtained **2** in 72% yield. This experiment additionally confirms that isopropoxide is the reducing agent for Pd^{II}, and that any base able to deprotonate isopropanol (including free IPr) can drive the reaction to completion.

All $[(NHC)Pd(PR_3)]$ complexes synthesized are stable in the solid state and in solution under inert atmosphere. To test the stability of these new mixed NHC–phosphane complexes, we challenged their stability to air. Surprisingly, if exposed to air, they showed no sign of immediate decomposition to palladium black. However, their color changed from yellow to bright green in a few minutes. Analysis of the ^1H NMR spectra of **2** after exposure to air revealed a change in the chemical shift of all signals. Notably, the imidazole backbone protons signal ($\delta = 6.80$ ppm) is shifted downfield by 0.23 ppm. Phosphane protons also display a downfield shift, whereas the methyl signals of the IPr isopropyl moiety are shifted upfield by some 0.2 ppm. In the ^{13}C NMR spectra changes in the chemical shift are even more evident. The IPr carbenic carbon falls at $\delta = 191.1$ ppm with an upfield shift of 8 ppm, whereas the carbon backbone is shifted downfield by 4 ppm when compared with **2**. The ^{31}P signal of PPh_3 is shifted to $\delta = 36.5$ ppm.

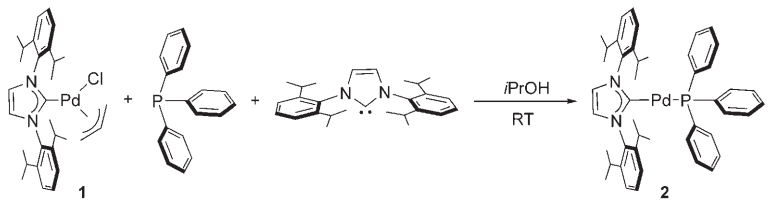
X-Ray analysis on a single crystal of **2** grown in air revealed that, under these conditions, coordination of molecular oxygen to Pd^0 took place very effectively, giving rise to complex **16** $[(IPr)Pd(PPh_3)(O_2)]$ (Scheme 6).



Scheme 6. Formation of oxygenated complex **16**.

Ball-and-stick representation of **16** is given in Figure 3. Pd–C and Pd–P distances only slightly change from **2** (0.02) Å. The coordinated dioxygen displays a bond length of 1.430(2) Å, very close to the known value of 1.48 Å for a single O–O bond.[15] Hence, it appears that oxidative addition of molecular oxygen takes place on $[(IPr)Pd(PPh_3)]$ affording the Pd^{II} peroxo complex **16**, that is stable in the solid state and in solution under air, showing signs of decomposition only after days.[16]

Coordination of dioxygen to highly unsaturated complexes has already some precedents.[17] More surprisingly, in this case, an unsaturated Pd^0 complex, which could be thought to decompose rapidly when exposed to air, reacts with molecular oxygen to afford the well-defined and stable $[(IPr)Pd(PPh_3)(O_2)]$ (**16**).



Scheme 5. Synthesis of **2** employing IPr as the base.

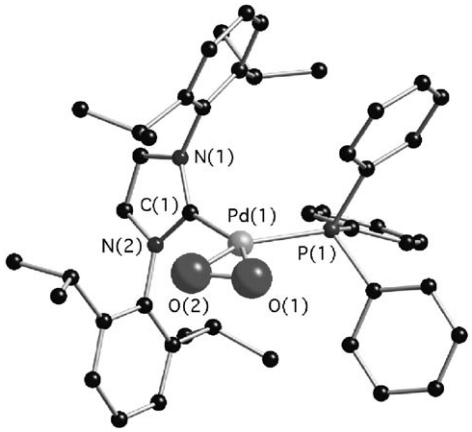


Figure 3. Ball-and-stick representation of **16**. Selected bond lengths [Å] and angles [°]: C(1)–Pd(1) 2.0360(18), P(1)–Pd(1) 2.2646(5), Pd(1)–O(1) 1.9912(16), Pd(1)–O(2) 2.0138(15), O(1)–O(2) 1.430(2), C(1)–Pd(1)–P(1) 104.74(5) , N(1)–C(1)–N(2) 103.53(15). O(1)–Pd-O(2) 41.83(6).

Conclusion

In summary, we have reported a general and straightforward synthetic route to mixed NHC–phosphane palladium(0) complexes, for the first time conclusively characterized by X-ray diffraction analysis. The possibility to tune both the NHC and the tertiary phosphane allows for the preparation of complexes with varied stereoelectronic properties. Homoleptic and heteroleptic bis-carbene complexes can also be synthesized in this fashion. The combination of isopropanol and basic conditions revealed to be a key factor to achieve the Pd^{II}/Pd^{0} reduction. We showed that under these conditions the isopropoxide anion is very likely the reducing agent. Experimental evidence supports a mechanism involving a direct attack of $iPrO^{-}$ on [(IPr)Pd(allyl)Cl], followed by a β-hydride elimination that finally affords the [Pd^{0}(IPr)] species. Moreover, we found that exposure of [(IPr)Pd-(PPh_3)] to air leads to the formation of a palladium dioxygen adduct, stable in the solid state and in solution. The availability of a library of Pd^{0} complexes, will allow for the systematic study of the structure/catalytic activity relationship of this family of complexes. Moreover, the formation of a stable Pd peroxo complex, paves the way for the systematic study of aerobic catalytic reactions. Exploration of the catalytic behavior of such species is ongoing in our laboratories.

Experimental Section

General: All reactions were carried out in a MBraun glovebox containing dry argon and less than 1 ppm of oxygen. Anhydrous solvent were either distilled from appropriate drying agents or purchased from Aldrich and degassed prior to use by purging with dry argon and kept over molecular sieves. Solvents for NMR spectroscopy were degassed with argon and dried over molecular sieves. NMR spectra were recorded by using a 400 MHz Bruker spectrometer. Exact mass measurements were performed on a ESI-TOF waters LCT Premier instrument. [(IPr)Pd-(allyl)Cl], [(SIPr)Pd(allyl)(Cl)] and $[Pd(allyl)Cl]_2$ were synthesized according to literature procedures.[18]

[(IPr)Pd(PPh_3)] (2): In a 50 mL Schlenk flask, [(IPr)Pd(allyl)Cl] (1 g, 1.75 mmol) and KO*t*Bu (213 mg, 1.75 mmol) were dissolved in *i*PrOH (25 mL). Triphenylphosphane was added (459 mg, 1.75 mmol) and after a few minutes a yellow precipitate started to form. After 2 h of stirring at room temperature, the precipitate was filtered and washed with *i*PrOH (5 mL). Recrystalization from pentane affords 1.212 g of product (92% yield). ^{1}H NMR (C_6D_6): δ = 7.59 (m, 6H; CH-o PPh_3), 7.38 (t, J = 8 Hz, 2H; CH-p IPr), 7.26 (d, J = 8 Hz, 4H; CH-m IPr), 7.11 (m, 9H; CH-(m+p) PPh_3), 6.57 (s, 2H; CH imid), 3.09 (sept, J = 8 Hz, 4H; $CH(CH_3)_2$), 1.70 (d, J = 8 Hz, 12H; $CH(CH_3)_2$), 1.31 ppm (d, J = 8 Hz, 12H; CH-$(CH_3)_2$); ^{13}C NMR (C_6D_6): δ = 198.0 (d, $J_{C\text{-}P}$ = 94 Hz, C carbene), 146.2 (s, C arom IPr), 139.4 (d, $J_{C\text{-}P}$ = 28 Hz, C arom PPh_3), 137.4 (s, C arom IPr), 134.7 (d, $J_{C\text{-}P}$ = 17 Hz, CH-o PPh_3), 129.2 (s, CH-p IPr), 128.0 (s, CH-p PPh_3), 127.5 (d, $J_{C\text{-}P}$ = 10 Hz, CH-m PPh_3), 123.45 (s, CH-m IPr), 120.9 (d, $J_{C\text{-}P}$ = 2 Hz, CH imid), 28.9 (s, $CH(CH_3)_2$), 25.2 (s, $CH(CH_3)_2$), 23.5 ppm (s, $CH(CH_3)_2$); ^{31}P NMR (C_6D_6): δ = 33.6 ppm; MS (ESI-TOF): calcd for $C_{45}H_{51}N_2PPd$ (M^+): 756.2825; found 756.2855.

[(IPr)Pd(PCy_3)] (3): In a 25 mL Schlenk flask, [(IPr)Pd(allyl)Cl] (100 mg, 0.175 mmol) and KO*t*Bu (24.3 mg, 0.199 mmol) was dissolved in *i*PrOH (15 mL). Tricyclohexylphosphane was then added (52.1 mg, 0.186 mmol). After 4 h stirring at room temperature, the yellow solution was filtered. Evaporation of the solvent affords 115 mg of the yellow product (85% yield) ^{1}H NMR (C_6D_6): δ = 7.38 (t, J = 8 Hz, 2H; C*H-p*), 7.29 (d, J = 8 Hz, 4H; C*H-m*), 6.59 (s, 2H; C*H* imid), 3.11 (sept, J = 7 Hz, 4H; C*H*$(CH_3)_2$), 1.93 (d broad, 6H; CH_2 Cy), 1.81 (d, J = 7 Hz, 12H; CH(CH_3)$_2$), 1.83–1.78 (m broad, 9H; CH_2 Cy), 1.55 (m, 3H; C*H* Cy), 1.39–1.27 (m, 12H; CH_2 Cy), 1.34 ppm (d, J = 7 Hz, CH(CH_3)$_2$); ^{13}C NMR (C_6D_6): δ = 199.2 (d, J = 90 Hz, *C* carbene), 146.2 (s, *C* arom), 137.8 (s, *C* arom), 128.8 (s, *CH-p*), 123.1 (s, *CH-m*), 120.4 (d, J = 3 Hz, *C*H imid), 34.5 (d, J = 12 Hz, *C*H Cy), 31.7 (d, J = 7 Hz, *C*H_2 Cy), 28.8 (s, *C*H$(CH_3)_2$), 27.9 (d, J = 11 Hz, *C*H_2 Cy), 26. 9 (d, J = 3 Hz, *C*H_2 Cy), 25.21 (s, CH(*C*H_3)$_2$), 23.7 ppm (s, CH(*C*H_3)$_2$); ^{31}P NMR (C_6D_6): δ = 49.4 ppm; MS (ESI-TOF) calcd for $C_{45}H_{69}N_2PPd$ (M^+): 774.4233; found 774.4231.

[(IPr)Pd{P(Ad)$_2$(*n*Bu)}] (4): In a 25 mL Schlenk flask, [(IPr)Pd(allyl)Cl] (100 mg, 0.175 mmol) and KO*t*Bu (26.5 mg, 0.217 mmol) was dissolved in *i*PrOH (10 mL). Then bis(adamanthyl)(*n*butyl)phosphane was added (62.7 mg, 0.175 mmol). After stirring for 48 h at room temperature, the yellow solution is filtered, and the solvent evaporated. Acetonitrile (2 mL) is added. Filtration of the yellow precipitate affords 90 mg of product (61% yield). ^{1}H NMR (C_6D_6): δ = 7.41 (dd, J = 8 Hz, J = 7 Hz, 2H; C*H-p*), 7.31 (d, J = 8 Hz, 4H; C*H-m*), 6.62 (s, 2H; C*H* imid), 3.18 (sept, J = 7 Hz, 4H; C*H*$(CH_3)_2$), 2.04(s broad, 12H; CH_2 Ad), 2.00 (s broad, 6H; C*H* Ad), 1.82 (s broad, 12H; CH_2 Ad), 1.81 (d, J = 7 Hz, 12H; CH(CH_3)$_2$), 1.76 (m, 2H; CH_2 *n*Bu), 1.56 (m, 2H; CH_2 *n*Bu), 1.37 (m, 2H; CH_2 *n*Bu), 1.33 (d, J = 7 Hz, 12H; CH(CH_3)$_2$), 1.15 ppm (t, J = 7 Hz, 3H; CH_3 *n*Bu); ^{13}C NMR (C_6D_6): δ = 199.3 (d, J = 86 Hz, *C* carbene), 146.1 (s, *C* arom), 138.1 (s, *C* arom), 128.8 (s, *CH-p*), 123.1 (s, *CH-m*), 120.4 (d, J = 2 Hz, *C*H imid), 41.3 (d, J = 7 Hz, *C*H_2 Ad), 38.2 (d, J = 8 Hz, *C* Ad), 37.36 (s, *C*H_2 Ad), 34.5 (d, J = 16 Hz, *C*H_2 *n*Bu), 29.1 (d, J = 8 Hz, *C*H Ad), 28.8 (s, *C*H$(CH_3)_2$), 25.4 (d, J = 14 Hz, *C*H_2 *n*Bu), 25.0 (s, CH(*C*H_3)$_2$), 23.8 (s, CH(*C*H_3)$_2$), 18.9 (d, J = 8 Hz, *C*H_2 *n*Bu), 14.3 ppm (s, *C*H_3 *n*Bu); ^{31}P NMR (C_6D_6): δ = 63.2 ppm; MS (ESI-TOF) calcd for $C_{51}H_{75}N_2PPd$ (M^+): 852.4703; found 852.4738.

[(SIPr)Pd(PPh_3)] (5): In a 25 mL Schlenk flask, [(SIPr)Pd(allyl)Cl] (100 mg, 0.174 mmol) and KO*t*Bu (21.3 mg, 0.175 mmol) were dissolved in *i*PrOH (15 mL). Triphenylphosphane was then added (45.9 mg, 0.175 mmol) and after a few minutes a pale green precipitate started to appear. After 4 h stirring at room temperature the solvent volume was reduced to 5 mL. Filtration of the solid, followed by washings with pentane (2×5 mL), affords 105 mg of product (80% yield). ^{1}H NMR (C_6D_6): δ = 7.50 (m, 6H; C*H-o* PPh_3), 7.36 (dd, J = 8 Hz, J = 7 Hz, 2H; C*H-p* SIPr), 7.26 (d, J = 8 Hz, 4H; C*H-m* SIPr), 7.10 (m, 9H; C*H-*(*m*+*p*) PPh_3), 3.47 (s, 4H; CH_2 imid), 3.44 (sept, J = 7 Hz, 4H; C*H*$(CH_3)_2$), 1.79 (d, J = 7 Hz, 12H; CH(CH_3)$_2$), 1.42 ppm (d, J = 7 Hz, CH(CH_3)$_2$); ^{13}C NMR (C_6D_6): δ = 218.1 (d, J = 86 Hz, *C* carbene), 147.3 (s, *C* arom

SIPr), 139.2 (d, $J=29$ Hz, *C* arom PPh_3), 137.6 (s, *C* arom SIPr), 134.6 (d, $J=17$ Hz, *CH-o* PPh_3), 128.4 (s, *CH-p* SIPr), 128.0 (s, *C*H arom PPh_3), 127.5 (s, *C*H arom PPh_3), 123.8 (s, *CH-m*, SIPr), 52.9 (d, $J=2$ Hz, CH_2 imid), 29.0 (s, $CH(CH_3)_2$), 25.9 (s, $CH(CH_3)_2$), 23.7 ppm (s, $CH(CH_3)_2$); ^{31}P NMR (C_6D_6): $\delta=33.0$ ppm; MS (ESI-TOF) calcd for $C_{45}H_{53}N_2PPd$ (M^+): 758.2981; found 758.3017.

[(SIPr)Pd(PCy$_3$)] (6): In a 25 mL Schlenk flask, [(SIPr)Pd(allyl)Cl] (100 mg, 0.174 mmol) and KO*t*Bu (21.3 mg, 0.175 mmol) were dissolved in *i*PrOH (15 mL). Tricyclohexylphosphane was then added (48.9 mg, 0.175 mmol). After 5 h stirring at room temperature, the yellow solution was filtered. Evaporation of the solvent affords 108 mg of yellow product (80% yield). ^{1}H NMR (C_6D_6): $\delta=7.36$ (dd, $J=7$ Hz, $J=8$ Hz, 2H; C*H*-*p*), 7.28 (d, $J=8$ Hz, 4H; C*H*-*m*), 3.48 (s, 4H; CH_2 imid), 3.43 (sept, $J=7$ Hz, 4H; $CH(CH_3)_2$), 1.91 (d, $J=7$ Hz, 12H; $CH(CH_3)_2$), 1.86–1.77 (m broad, 15H; CH_2 Cy), 1.52 (m, 3H; C*H* Cy), 1.45 (d, $J=7$ Hz, 12H; $CH(CH_3)_2$), 1.30 ppm (m broad, 15H; CH_2 Cy); ^{13}C NMR (C_6D_6): $\delta=218.6$ (d, $J=83$ Hz, *C* carbene), 147.3 (s, *C* arom), 138.1 (s, *C* arom), 128.2 (s, *C*H-*p*), 123.5 (s, *C*H-*m*), 52.7 (d, $J=3$ Hz, CH_2 imid), 34.4 (d, $J=12$ Hz, *C*H Cy), 31.5 (d, $J=7$ Hz, CH_2 Cy), 29.0 (s, $CH(CH_3)_2$), 27.9 (d, $J=11$ Hz, CH_2 Cy), 26.8 (s, CH_2 Cy), 25.9 (s, $CH(CH_3)_2$), 23.9 ppm (s, $CH(CH_3)_2$); ^{31}P NMR (C_6D_6): $\delta=48.1$; MS (ESI-TOF) calcd for $C_{45}H_{71}N_2PPd$ (M^+): 776.4390; found 776.4410.

[(SIPr)Pd{P(Ad)$_2$(*n*Bu)}] (7): In a 25 mL Schlenk flask, [(SIPr)Pd(allyl)Cl] (100 mg, 0.174 mmol) and KO*t*Bu (26.5 mg, 0.217 mmol) were dissolved in *i*PrOH (15 mL). Bis(adamanthyl)(*n*butyl)phosphane was then added (62.8 mg, 0.175 mmol). After 48 h stirring at room temperature, the yellow solution was filtrated, and the solvent evaporated. Addition of acetonitrile (2 mL) followed by filtration of the yellow precipitate affords 110 mg of product (74% yield). ^{1}H NMR (C_6D_6): $\delta=7.37$ (dd, $J=8$ Hz, $J=7$ Hz, 2H; C*H*-*p*), 7.28 (d, $J=8$ Hz, 4H; C*H*-*m*), 3.53 (s, 4H; CH_2 imid), 3.46 (sept, $J=7$ Hz, 4H; $CH(CH_3)_2$), 1.98 (s broad, 18H; $CH+CH_2$ Ad), 1.91 (d, $J=7$ Hz, 12H; $CH(CH_3)_2$), 1.77 (s broad, 12H; CH_2 Ad), 1.73 (m, 2H; CH_2 *n*Bu), 1.54 (m, 2H; CH_2 *n*Bu), 1.43 (d, $J=7$ Hz, 12H; $CH(CH_3)_2$), 1.38 (m, 2H; CH_2 *n*Bu), 1.16 ppm (t, $J=7$ Hz, 3H; CH_3 *n*Bu); ^{13}C NMR (C_6D_6): $\delta=218.5$ (d, $J=82.5$, *C* carbene), 147.2 (s, *C* arom), 138.3 (s, *C* arom), 128.0 (s, *C*H-*p*), 123.5 (C*H*-*m*), 52.5 (d, $J=3$ Hz, CH_2 imid), 41.1 (d, $J=7$ Hz, CH_2 Ad), 38.1 (d, $J=7$ Hz, *C* Ad), 37.3 (s, CH_2 Ad), 33.8 (d, $J=14$ Hz, CH_2 *n*Bu), 29. 0 (d, $J=17$ Hz, *C*H Ad), 29.04 (s, $CH(CH_3)_2$), 25.8 (s, $CH(CH_3)_2$), 25.6 (d, $J=15$ Hz, CH_2 *n*Bu), 24.1 (s, $CH(CH_3)_2$), 19.3 (d, $J=8$ Hz, CH_2 *n*Bu), 14.3 ppm (s, CH_3 *n*Bu); ^{31}P NMR (C_6D_6): $\delta=61.0$ ppm; MS (ESI-TOF) calcd for $C_{51}H_{77}N_2PPd$ (M^+): 854.4859; found 854.4825.

[Pd(IPr)$_2$] (8): In a 25 mL Schlenk flask, [(IPr)Pd(allyl)Cl] (100 mg, 0.175 mmol) and KO*t*Bu (21.4 mg, 0.175 mmol) are dissolved in *i*PrOH (15 mL). IPr was then added (75.0 mg, 0.193 mmol). The solution was stirred for 4 days. Filtration followed by washing with pentane (2×2 mL) affords 135 mg of orange complex (87% yield). ^{1}H NMR (C_6D_6): $\delta=7.40$ (t, $J=8$ Hz, 4H; C*H*-*p*), 7.20 (d, $J=8$ Hz, 8H; C*H*-*m*), 6.38 (s, 4H; *CH* imid), 2.99 (sept, $J=7$ Hz, 8H; $CH(CH_3)_2$), 1.32 (d, $J=7$ Hz, 24H; $CH(CH_3)_2$), 1.23 ppm (d, $J=7$ Hz, 24H; $CH(CH_3)_2$); ^{13}C NMR (C_6D_6): $\delta=199.0$ (s, *C* carbene), 145.8 (s, *C* arom), 138.9 (s, *C* arom), 128.3 (s, *C*H-*p*), 123.2 (s, *C*H-*m*), 121.0 (s, *C*H imid), 28.4 (s, $CH(CH_3)_2$), 24.9 (s, $CH(CH_3)_2$), 23.8 ppm (s, $CH(CH_3)_2$); MS (ESI-TOF) calcd for $C_{54}H_{72}N_4Pd$ (M^+): 882.4792; found 882.4814.

[(IPr)Pd(IMes)] (9): In a 25 mL Schlenk flask, [(IPr)Pd(allyl)Cl] (100 mg, 0.175 mmol) and KO*t*Bu (21.4 mg, 0.175 mmol) were dissolved in *i*PrOH (10 mL). IMes was then added (53.3 mg, 0.175 mmol). The solution was stirred for 24 h. Filtration of the precipitate followed by washing with PrOH (1 mL) affords 100 mg of orange complex (72% yield). ^{1}H NMR (C_6D_6): $\delta=7.43$ (t, $J=8$ Hz, 2H; C*H*-*p* IPr), 7.21 (d, $J=8$ Hz, 4H; C*H*-*m* IPr), 6.83 (s, 4H; C*H*-*m* IMes), 6.51 (s, 2H; C*H* imid IPr), 6.23 (s, 2H; C*H* imid IMes), 2.92 (sept, $J=7$ Hz, 4H; $CH(CH_3)_2$), 2.44 (s, 6H; CH_3), 2.13 (s, 12H; CH_3), 1.46 (d, $J=7$ Hz, 12H; $CH(CH_3)_2$), 1.30 ppm (d, $J=7$ Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (C_6D_6): $\delta=200.6$ (s, *C* carbene), 197.7 (s, *C* carbene), 145.9 (s, *C* arom), 138.4 (s, *C* arom), 138.3 (s, *C* arom), 135.8 (s, *C* arom), 134.2 (s, *C* arom), 128.7 (s, *C*H-*m* IMes), 128.2 (s, *C*H-*p* IPr), 122.8 (s, *C*H-*m* IPr), 119.8 (s, *C*H imid IPr), 118.7 (s, *C*H imid IMes), 28.5 (s, $CH(CH_3)_2$), 24.7 (s, $CH(CH_3)_2$), 23.6 (s, $CH(CH_3)_2$), 21.1 (s, CH_3), 18.2 ppm (s, CH_3); MS (ESI-TOF) calcd for $C_{48}H_{60}N_4Pd$ (M^+): 798.3853; found 798.3853.

[(IPr)Pd(I*t*Bu)] (10): In a 25 mL Schlenk flask, [(IPr)Pd(allyl)Cl] (200 mg, 0.350 mmol) and KO*t*Bu (42.8 mg, 0.35 mmol) were dissolved in of *i*PrOH (15 mL). I*t*Bu is then added (63.2 mg, 0.35 mmol). The red solution was stirred for 3 d. The volume of the solvent was thenreduced to 2 mL and filtration affords 140 mg of red complex (59% yield). ^{1}H NMR (C_6D_6): $\delta=7.42$ (t, $J=7$ Hz, 2H; C*H*-*p*), 7.32 (d, $J=7$ Hz, 4H; C*H*-*m*), 6.75 (s, 2H; C*H* imid IPr), 6.64 (s, 2H; C*H* imid I*t*Bu), 3.43 (sept, $J=7$ Hz, 4H; $CH(CH_3)_2$), 1.72 (s, 18H; $C(CH_3)_3$), 1.71 (d, $J=7$ Hz, 12H; $CH(CH_3)_2$), 1.34 ppm (d, $J=7$ Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (C_6D_6): $\delta=200.7$ (s, *C* carbene), 194.5 (s, *C* carbene), 145.9 (s, *C* arom), 139.3 (s, *C* arom), 128.2 (s, *C*H-*p*), 123.5 (*C*H-*m*), 120.4 (s, *C*H imid IPr), 113.3 (s, *C*H imid I*t*Bu), 56.7 (s, $C(CH_3)_3$), 32.0 (s, $C(CH_3)_3$), 28.7 (s, $CH(CH_3)_2$), 24.4 (s, $CH(CH_3)_2$), 23.9 ppm (s, $CH(CH_3)_2$); MS (ESI-TOF) calcd for $C_{38}H_{56}N_4Pd$ (M^+): 674.3540; found 674.3512.

[(PPh$_3$)Pd(allyl)Cl] (14): In a 25 mL flask $[Pd(allyl)Cl]_2$ (106.0 mg, 0.29 mmol) was dissolved in THF (15 mL). After addition of PPh_3 (155.0 mg, 0.59 mmol), the solution was stirred at room temperature for 3 h. The solvent was then evaporated and recrystallization from DCM (3 mL), *t*butylether (2 mL) and pentane (5 mL) affords 190 mg of product (74% yield). ^{1}H NMR ($CDCl_3$): $\delta=7.60$ (m, 6H; C*H*-*o*), 7.44 (m, 9H; C*H*-(*m*+*p*)), 5.62 (m, 1H; C*H*), 4.78 (m, 1H; CH_2), 3.79 (dd, $J=14$ Hz, $J=10$ Hz, 1H; CH_2), 3.13 (d, $J=7$ Hz, 1H; CH_2), 2.85 ppm (d, $J=12$ Hz, 1H; CH_2); ^{13}C NMR ($CDCl_3$): $\delta=134.0$ (d, $J=12$ Hz, *C*H-*o*), 132.3 (d, $J=41$ Hz, *C*), 130.5 (d, $J=2$ Hz, *C*H-*p*), 128.6 (d, $J=12$ Hz, *C*H-*m*), 118.1 (d, $J=5$ Hz, *C*H), 80.0 (d, $J=30$ Hz, CH_2), 61.1 ppm (s, CH_2); ^{31}P NMR ($CDCl_3$): $\delta=25.7$ ppm; elemental analysis calcd (%) for $C_{21}H_{20}ClPPd$ (444.82): C 56.65, H 4.53; found: C 56.43, H 4.42.

[(IPr)Pd(PPh$_3$)(O$_2$)] (16): ^{1}H NMR (C_6D_6): $\delta=7.40$ (m, 6H; C*H*-*o*), 7.20 (t, $J=8$ Hz, 2H; C*H*-*p* IPr), 7.15 (d, $J=8$ Hz, 4H; C*H*-*m* IPr), 7.02 (m, 3H; C*H*-*o*), 6.97 (m, 6H; C*H*-*m*), 6.80 (s, 2H; C*H* imid), 3.27 (sept, $J=8$ Hz, 4H; $CH(CH_3)_2$), 1.38 (broad, 12H; $CH(CH_3)_2$), 1.15 ppm (d, $J=8$ Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (C_6D_6): $\delta=191.1$ (s, *C* carbene), 146.1 (s, *C* arom IPr), 136.0 (s, *C* arom IPr), 134.2 (d, $J=14$ Hz, *C*H-*o* PPh_3), 134.0 (d, $J=36$ Hz, *C* PPh_3), 130.1 (s, *C*H IPr), 129.4 (d, $J=2$ Hz, *C*H-*p* PPh_3), 128.0 (d, $J=10$ Hz, *C*H-*m* PPh_3), 124.9 (s, *C*H-*m* IPr), 124.1 (s, *C*H imid), 29.0 (s, $CH(CH_3)_2$), 26.1 (s, $CH(CH_3)_2$), 22.9 ppm (s, $CH(CH_3)_2$); ^{31}P NMR (C_6D_6): $\delta=36.45$ ppm.

CCDC 682046 (**2**), 682047 (**3**) and 682048 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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