A Stable Crystalline Imino-*N*-Heterocyclic Carbene Ligand and Its Corresponding Palladium(II) and Rhodium(I) Complexes

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The crystalline heteroditopic, acyclic, and nonenolizable imino-*N*-heterocyclic carbene chelating ligand 1-*tert*-butyl-3-(1-phenyliminophenylmethylene)imidazol-2-ylidene (designated as C∧imine) has been isolated and structurally characterized. The metal complexes [Pd(C∧imine)Cl_2], [Pd(allyl)(C∧imine)]-PF_6, [Rh(COD)(C∧imine)]PF_6, and [Rh(CO)(C∧imine)$_2$]Cl have been prepared either by Ag transfer or by reaction with the free carbene. The palladium(II) complexes have been tested for catalytic application in Suzuki type C−C cross-coupling reactions of aryl bromides and the rhodium(I) complexes for the catalytic hydroformylation of 1-octene. The metal complexes [Pd(C∧imine)Cl_2], [Pd(allyl)(C∧imine)]-PF_6, and [Rh(CO)(C∧imine$_2$]Cl have been structurally characterized by single-crystal X-ray diffraction.

Introduction

Since their isolation, *N*-heterocyclic carbenes (NHCs)[1] have attracted much interest as a new class of ligand in organo-transition metal chemistry[2−13] especially for their application in homogeneous catalysis.[3,4,13−17] Metal complexes containing NHC ligands have demonstrated catalytic activity for hydrosilylation,[18−21] ring-opening and -closing metathesis,[16,22−27] cross-coupling,[28−34] Kumada,[35] Sonogashira,[36] atom transfer radical polymerization,[37,38] Wacker oxidation,[39] and carbon monoxide/ethylene copolymerization reactions.[40,41]

Our interests lie in the synthesis and reactivity of heteroditopic ligands that incorporate nitrogen or oxygen donor atoms along with strong donors such as tertiary phosphines[42,43] and carbenes.[44,45] Such hybrid ligands exhibit hemilabile behavior, which can be tuned for applications in small molecule activation

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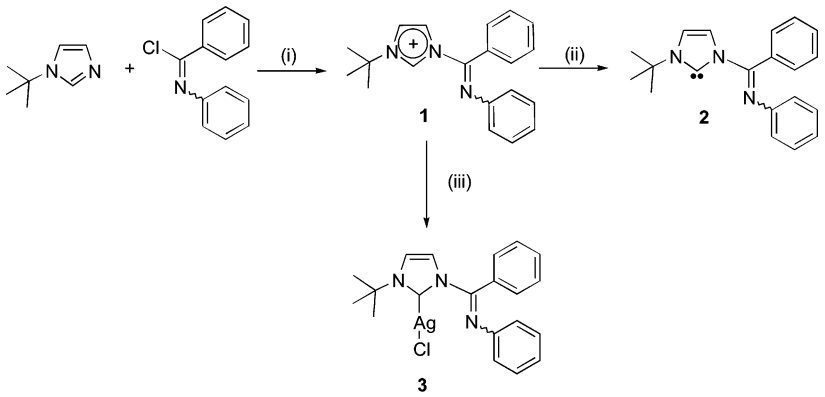
Scheme 1 [a]



[a] (i) THF, 60 °C, 2 h; (ii) $KN[Si(CH_3)_3]_2$, THF, -78 °C, 10 min; (iii) Ag_2O, 4 Å molecular sieves, CH_2Cl_2, RT, 12 h.[45]

and homogeneous catalysis. Recently we have shown that the imino-*N*-heterocyclic carbene ligand [1-(2,4,6-$Me_3C_6H_2$)imidazol-2-ylidene-3-{CH_2C(*t*-Bu)═N(*i*-Pr)}] undergoes tautomerization of the imine moiety to an enamine upon ligand transfer from the silver(I) complex [Ag{[1-(2,4,6-$Me_3C_6H_2$)imidazol-2-ylidene-3-{CH_2C(*t*-Bu)═N(*i*-Pr)}]}$_2$]$AgBr_2$ to palladium(II) and rhodium(I), affording [$PdCl_2$(C∧enamine)] and [Rh(COD)(C∧enamine)], where (C∧enamine) = [1-(2,4,6-$Me_3C_6H_2$)-imidazol-2-ylidene-3-{CH═C(*t*-Bu)═NH(*i*-Pr)}].[44] Herein we report a new ligand system where we have removed the methylene spacer to eliminate the possibility of such tautomerization. The acyclic imino-*N*-heterocyclic carbene ligand has been structurally characterized and subsequently coordinated to palladium(II) and rhodium(I).

Results and Discussion

Synthesis of 1-*tert*-Butyl-3-(1-phenyliminophenylmethylene)imidazol-2-ylidene (2). The imine-functionalized imidazolium salt **1**, prepared by reaction of *tert*-butyl imidazole with the chloro imine ClC(Ph)═NPh,[45] was readily deprotonated with $KN[Si(CH_3)_3]_2$ to afford the stable free carbene [1-(*t*-Bu)-imidazol-2-ylidene-3-{C(Ph)═N(Ph)}] **2**, denoted C∧imine, in good yield (75%), Scheme 1. The choice of base for the synthesis of **2** was found to be crucial; attempts to synthesize the free carbene using KO^{t}Bu, NaH, ^{n}BuLi, and LDA, as the base, led only to decomposition and the formation of intractable products. The free carbene **2** was characterized by elemental analysis, high-resolution mass spectrometry (ES^+), single-crystal X-ray diffraction, and ^{1}H and $^{13}C\{^1H\}$ NMR studies using gCOSY, gHMBC, gHMQC, ROESY, and TOCSY experiments.

The ^{1}H NMR spectrum of **2** shows the presence of two isomers in a ratio of approximately 10:1 and are attributed to the *E* and *Z* isomers, respectively. Although no exchange broadening was observed at room temperature in the ^{1}H NMR spectrum, exchange peaks in the NOE spectrum showed that the isomers are in slow equilibrium. In the $^{13}C\{^1H\}$ NMR spectrum the imine carbon resonance was found at δ 157.4 with the carbene carbon at δ 223.6, which, as expected, is shifted to higher frequency when compared to the −N*C*HN− carbon resonance (δ 134.2) observed for the imidazolium salt **1**, confirming the weaker π-delocalization of electrons in **1**.[45] Full ^{1}H and ^{13}C assignments are given in the Experimental Section.

Crystals of the free carbene **2**, suitable for single-crystal X-ray diffraction, were grown from a saturated pentane solution at −78 °C. An ORTEP view of **2** is shown in Figure 1; crystal data and refinement data are given in the Supporting Information, Table S1. In the solid state the free carbene **2** adopts the *E*-isomer configuration (also the major isomer in solution) presumably due to steric reasons. The C(1)−N(1) and C(1)−N(2) bond lengths are 1.356(3) and 1.389(3) Å, respectively, which are comparable to bond lengths of 1.37 Å reported for a free NHC[1] and are longer than those found in the imidazolium salt **1** (1.328(2) and 1.338(2) Å, respectively).[45] The longer C(1)−N(2) bond length when compared with the C(1)−N(1) bond is mainly due to the electron-withdrawing effect of functional groups attached to N(2). Similarly, the N(2)−C(4) bond (1.417(3) Å) is shorter than the corresponding bond length (1.4611(19) Å) observed for the imidazolium salt[45] **1**. The C(4)−N(3) bond length is 1.280(3) Å and consistent with significant double-bond character.[42,43,46] The N(1)−C(1)−N(2) bond angle of 101.89(17)° is comparable with the bond angle expected for free NHCs[1] and less than the angle typically found for imidazolium salts (ca. 108°).[44,45]

Interestingly, during our studies Bildstein and co-workers reported the attempted synthesis of imino-*N*-heterocyclic carbenes.[46,47] In this work compounds of the type [1-(Me)-imidazolium-3-{C(Ph)═N(2,6-$R_2C_6H_3$)}] chloride, prepared by a different route, where R = Me, ^{i}Pr, H, were reported to undergo a [1,2]-rearrangement upon attempted synthesis of the free carbene by the addition of base (KH). All attempts to trap any carbene species failed, leading the authors to suggest that these 1,2-rearrangements are unavoidable under normal experimental conditions, thereby ruling out the existence of imino-*N*-heterocyclic carbene species.[46,47] This is in stark contrast to our work described here. It is reasonably well established that [1,2]-migrations are fundamental reactions for singlet carbenes, typically proceeding via an intramolecular pathway.[48,49] However NHCs, being aromatic, cannot follow this in-plane pathway due to orbital constraints. Similarly, an out-of-plane intramolecular pathway, involving deformation of the ring to remove the electronic delocalization of the nitrogen lone pairs, has almost entirely been ruled out since the activation energy of this rearrangement is high (ca. 40 kcal/mol for the simplest imidazol-2-ylidene).[48] Elegant work by Bertrand and co-workers has demonstrated that for aromatic carbenes, generated from triazolium salts, [1,2]-migrations proceed via intermolecular processes involving the nucleophilic carbene and the electrophilic triazolium salt.[49] Presumably Bildstein's compounds,

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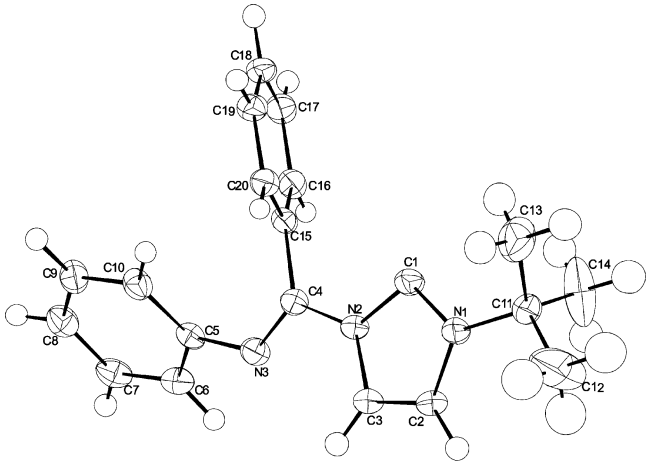


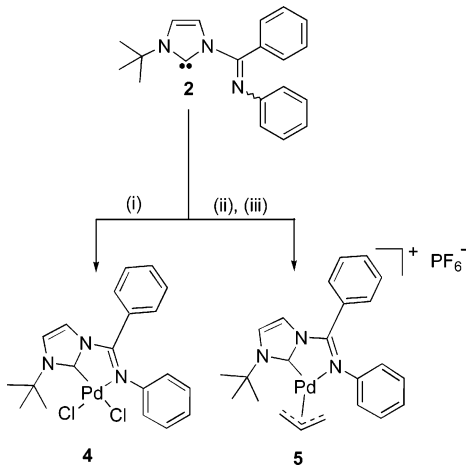
Figure 1. ORTEP diagram of the molecular structure of the free carbene **2** at 40% probability. Selected bond lengths (Å) and bond angles (deg): C(1)−N(1) 1.356(3), C(1)−N(2) 1.389(3), N(1)−C(11) 1.489(3), N(2)−C(4) 1.417(3), C(4)−N(3) 1.280(3), C(2)−C(3) 1.334(3); N(2)−C(4)−C(15) 115.96(17), C(1)−N(1)−C(11) 122.47(17), C(1)−N(2)−C(4) 123.98(17), N(2)−C(4)−N(3) 116.01-(18), N(1)−C(1)−N(2) 101.89(17). Space group $P2_1/c$, a = 14.1279(15) Å, b = 5.8199(6) Å, c = 20.954(2) Å, α = 90°, β = 104.181(14)°, γ = 90°, V = 1670.4 (3) Å^3, Z = 4, D_c = 1.206 Mg/m^3, μ = 0.072 mm^{-1}.

[1-(Me)imidazolium-3-{C(Ph)═N(2,6-$R_2C_6H_3$)}] chloride, where R = Me, ^{i}Pr, H, undergo a similar intermolecular [1,2]-rearrangement. Assuming no major electronic differences between a methyl and *tert*-butyl group, the fact that we observe no such rearrangement in the free carbene **2** could be due to steric effects, as the intermolecular mechanism proposed by Bertrand would result in the formation of a sterically crowded and presumably unfavorable intermediate with bulky substituents on the 1, 2, and 3 positions of the heterocyclic ring.

Synthesis and Characterization of [$PdCl_2$(C∧imine)] (4) and [Pd(allyl)(C∧imine)]PF_6 (5). The palladium complex [$PdCl_2$(C∧imine)], **4**, was synthesized in good yield (70%) either by the transfer of the carbene ligand from the silver complex[45] [AgCl(C∧imine)], **3**, to [$PdCl_2(MeCN)_2$] in dichloromethane or by direct coordination of the free carbene **2** to (COD)$PdCl_2$ in THF. Similarly, the palladium complex [Pd(allyl)(C∧imine)]-PF_6, **5**, was synthesized in good yield (78%) by the reaction of **2** with the dimer [(Pd(η-C_3H_5)(μ-Cl)]$_2$ and $AgPF_6$ in THF (Scheme 2), where C∧imine = [1-(*t*-Bu)imidazol-2-ylidene-3-{C(Ph)═N(Ph)}]. The palladium complexes **4** and **5** were characterized by elemental analysis, high-resolution mass spectrometry (ES$^+$), X-ray crystallography, and ^{1}H and ^{13}C-{^{1}H} NMR studies using gCOSY, gHMBC, gHMQC, ROESY, and TOCSY experiments.

The ^{1}H NMR spectra of the palladium complexes **4** and **5** are well resolved and show the presence of only one geometric isomer. The backbone protons (−NC*H*C*H*N−) resonate at δ 6.85 and 7.21 for complex **4** and δ 6.97 and 7.37 for complex **5** compared with δ 6.32 and 7.91 for the free carbene **2** and are shifted to lower frequency when compared with the imidazolium salt **1** (δ 7.56 and 8.35).[45] In the ^{13}C{^{1}H} NMR the imine carbon resonance is found at δ 161.7 and 163.4 for complex **4** and **5**, respectively, and is shifted to higher frequency when compared with the free carbene **2** (δ 157.4). This shift is indicative of coordination (chelation), with the transfer of electron density from the imine to the metal center. The complexed carbene resonance is observed as a singlet at δ 163.3 and 180.7 for complex **4** and **5**, respectively. These values are comparable with the carbene resonances for previously reported[8,50−52] NHC palladium complexes.

Scheme 2 [a]



[a] (i) Pd(COD)Cl_2, THF, −78 °C, 30 min and then RT, 5 h; (ii) [(allyl)PdCl]$_2$, THF, 5 h, RT; (iii) $AgPF_6$, THF, 30 min, RT.

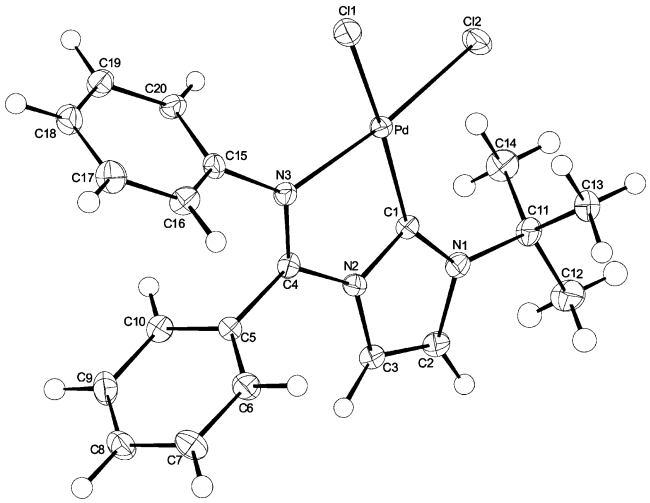


Figure 2. ORTEP diagram of the molecular structure of **4** at 40% probability. Selected bond lengths (Å) and bond angles (deg): Pd−C(1) 2.035(3), Pd−N(3), 2.051(2), C(4)−N(3) 1.279(4), Pd−Cl-(1) 2.3255(7), Pd−Cl(2) 2.2984(7); Pd−N(3)−C(4) 115.12(18), C(1)−N(2)−C(4) 120.3(2), C(1)−Pd−N(3) 80.2(1), Pd−C(1)−N(1) 147.7(2), Pd−C(1)−N(2) 108.35(18), N(1)−C(1)−N(2) 103.6-(2). Space group $P2_1/n$, a = 10.2281(2) Å, b = 16.4845(4) Å, c = 11.6363(3) Å, α = 90°, β = 98.8095(9)°, γ = 90°, V = 1938.79-(8) Å^3, Z = 4, D_c = 1.647 Mg/m^3, μ = 1.242 mm^{-1}.

Crystals of complex **4** suitable for X-ray crystallography were grown by the layering of diethyl ether onto a saturated dichloromethane solution. An ORTEP view of **4** is shown in Figure 2, and crystal data are summarized in the Supporting Information, Table S1.

The palladium complex **4** has a distorted square-planar geometry in which the coordinated carbene carbon, nitrogen atom, and one of the chloride ligands are all approximately coplanar, with the remaining chloride ligand distorted away from this plane by approximately 0.58 Å. Interestingly, the C(4)−N(3) bond measures 1.279(4) Å and is the same as that observed

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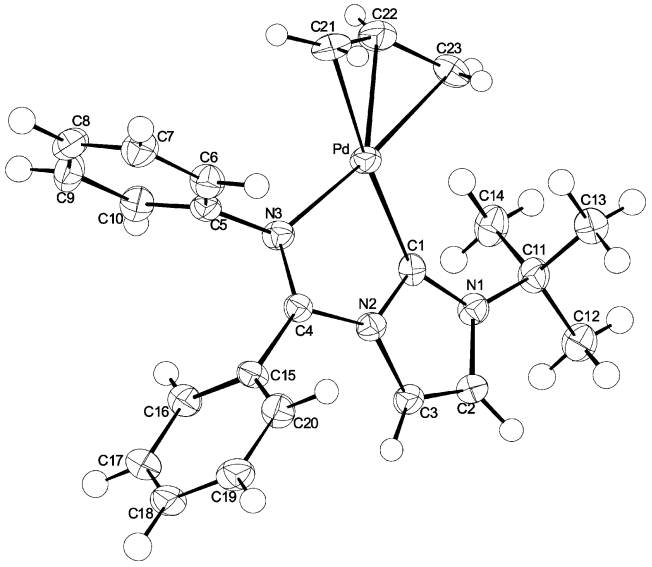


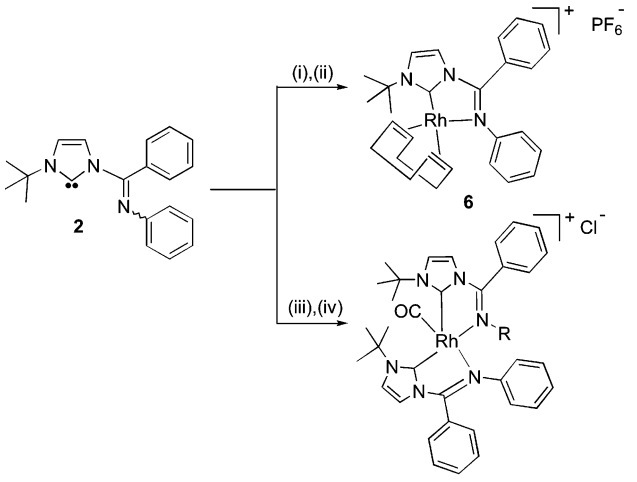
Figure 3. ORTEP diagram of the molecular structure of **5** at 40% probability. Selected bond lengths (Å) and bond angles (deg): C(4)−N(3) 1.278(6), Pd−C(1) 2.058(5), Pd−N(3) 2.109(4), Pd−C(21) 2.173(6), Pd−C(22) 2.127(6), Pd−C(23) 2.123(6); C(1)−Pd−N(3) 78.79(17), C(1)−Pd−C(22) 145.9(2), C(1)−Pd−C(23) 110.0(2), Pd−C(1)−N(2) 109.2(3), C(1)−N(2)−C(4) 120.0(4), N(2)−C(4)−N(3), 115.1(4), Pd−N(3)−C(4) 114.4(3). Space group *Fdd*2, $a = 30.3999(10)$ Å, $b = 31.8427(9)$ Å, $c = 10.0134(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 9693.1(5)$ Å^3, $Z = 16$, $D_c = 1.633$ Mg/m^3, $\mu = 0.894$ mm^{-1}.

for the free carbene **2** and is consistent with significant double-bond character. The Pd−N(3) bond distance of 2.051(2) Å is within the expected range for palladium imine complexes, while the Pd−C(1) bond distance of 2.035(3) Å and the bite angle C(1)−Pd−N(3) of 80.2(1)° are similar to those of other palladium(II) NHC complexes.[42−44,53−55] The Pd−Cl(1) distance of 2.3255(7) Å and the Pd−Cl(2) distance of 2.2984(7) Å are as expected, with the longer metal−chloride bond *trans* to the carbene, a consequence of the greater *trans* influence. The remaining bond lengths and angles are unexceptional and lie within the range expected.

Crystals of complex **5** suitable for single-crystal X-ray diffraction were grown by slow diffusion of pentane into a saturated dichloromethane solution. An ORTEP view of the molecular structure of **5** is shown in Figure 3, and a summary of crystal data is given in the Supporting Information, Table S1. The palladium complex **5** has a slightly distorted square-planar geometry, as expected for bidentate palladium allyl complexes. As in complex **4**, the C(4)−N(3) bond distance of 1.278(6) Å is similar to that observed for the free carbene **2**. The Pd−N(3) and Pd−C(1) bond distances of 2.109(4) and 2.058(5) Å are similar to those found in the palladium complex **4** and are within the expected range, and the remaining bond lengths and angles are unexceptional.

Synthesis and Characterization of [Rh(COD)(C∧imine)] (6) and [Rh(CO)(C∧imine)$_2$]Cl (7). The rhodium complex [Rh(COD)(C∧imine)], **6**, where COD = 1,5-cyclooctadiene, was synthesized in good yield (82%) by the reaction of C∧imine **2** with $[Rh(COD)Cl]_2$ and $AgPF_6$ in THF, Scheme 3. The rhodium

Scheme 3 [a]



[a] (i) $[Rh(COD)Cl]_2$, $AgPF_6$, THF, −78 °C, 10 min; (ii) RT, 2 h; (iii) $[Rh(CO)(PPh_3)_2Cl]$, THF, −78 °C, 10 min; (iv) RT, 12 h.

complex **6** was characterized by elemental analysis, high-resolution mass spectrometry (ES^+), and ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy using gCOSY, gHMBC, gHMQC, ROESY, and TOCSY experiments.

In the ^{1}H NMR spectrum the backbone (−NC*HCH*N−) resonances at δ 6.71 and 7.94 were shifted to slightly higher frequency with respect to the free carbene **2** (δ 6.32 and 7.91), indicative of coordination of the carbene to the rhodium center. The carbene carbon in the $^{13}C\{^1H\}$ NMR spectrum was observed as a doublet, due to coupling to the rhodium center, at δ 180.7 ($J_{(Rh-C)} = 55.2$ Hz), and is consistent with data reported for an oxazoline-NHC system.[54] Full ^{1}H and ^{13}C assignments are given in the Experimental Section.

The rhodium complex $[Rh(CO)(C\wedge imine)_2]Cl$, **7**, was obtained as an unexpected product from the reaction of C∧imine **2** with $[Rh(CO)(PPh_3)_2Cl]$ in THF in 45% yield, Scheme 3. Interestingly, there was no evidence for the formation of [Rh(CO)(C∧imine)Cl]. Complex **7** was isolated as a reddish brown solid, which was characterized by elemental analysis, infrared spectroscopy (ν(CO) = 1924 cm^{-1}), high-resolution mass spectrometry (ES^+), single-crystal X-ray diffraction, and ^{1}H and $^{13}C\{^1H\}$ NMR studies using gCOSY, gHMBC, gHMQC, ROESY, and TOCSY experiments.

The ^{1}H NMR spectrum of **7** confirms the presence of one geometric isomer, with the two coordinated ligands chemically and magnetically equivalent, with the backbone (−NC*HCH*N−) protons at δ 7.05 and 7.29. The $^{13}C\{^1H\}$ NMR spectrum shows the presence of two sets of doublets at δ 187.1 ($J_{(Rh-C)} = 39.7$ Hz) and 195.1 ($J_{(Rh-C)} = 94.5$ Hz), which are assigned to the *trans* carbene and the coordinated CO, respectively. The carbene carbon resonance and $^1J_{Rh-C}$ coupling constant are in good agreement with the values obtained for the complex *trans*-[Rh(CO)Cl(1,3-dimethylimidazol-2-ylidene)$_2$] (δ 183.6, $J_{Rh-C} = 39.1$ Hz).[56] Full ^{1}H and ^{13}C assignments are given in the Experimental Section.

Crystals of the rhodium complex **7** suitable for X-ray diffraction were grown by slow diffusion of pentane into a saturated dichloromethane solution. An ORTEP view of the molecular structure of **7** is shown in Figure 4, and a summary of crystal data is given in the Supporting Information, Table S1. X-ray diffraction studies reveal that the rhodium complex

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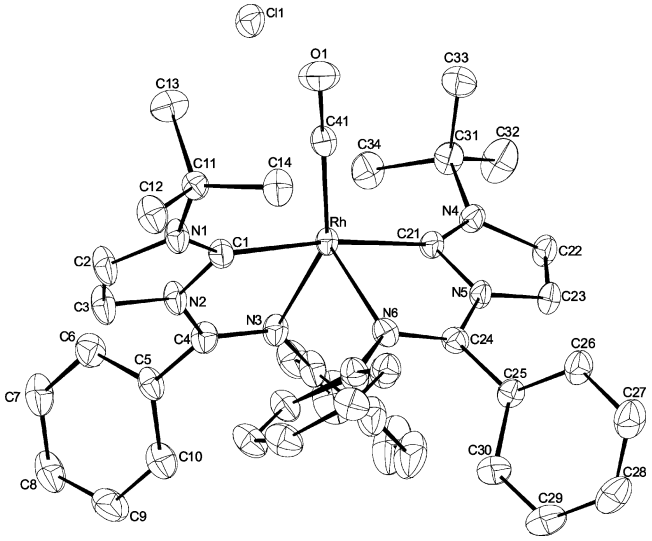

Figure 4. ORTEP diagram of the molecular structure of **7** at 40% probability (hydrogen atoms and two molecules of solvent CH_2Cl_2 have been omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Rh(1)−C(1) 2.038(4), Rh(1)−N(3) 2.259(3), Rh(1)−C(21) 2.041(4), Rh(1)−N(6) 2.251(3), Rh(1)−C(41) 1.796(4), C(1)−N(1) 1.339(5), C(1)−N(2) 1.397(5), N(2)−C(4) 1.400(5), C(4)−N(3) 1.288(5), C(21)−N(4) 1.349(5), C(21)−N(5) 1.386(5), N(5)−C(24) 1.415(5), C(24)−N(6) 1.288(5); C(1)−Rh(1)−C(21) 172.02(15), N(3)−Rh(1)−N(6) 89.70(11), C(1)−Rh(1)−C(41) 92.70(17), C(21)−Rh(1)−C(41) 95.06(16), C(1)−N(2)−C(4) 121.2-(3), N(5)−C(24)−N(6) 115.1(3), C(21)−N(5)−C(24) 120.5(3). Space group $P2_1/c$, $a = 15.5620(2)$ Å, $b = 15.6420(3)$ Å, $c = 19.9844(4)$ Å, $\alpha = 90°$, $\beta = 110.6700(7)°$, $\gamma = 90°$, $V = 4551.48-(14)$ Å^3, $Z = 4$, $D_c = 1.376$ Mg/m^3, $\mu = 0.708$ mm^{-1}.

7 has no crystallographic symmetry, but if the phenyl substituents are neglected, it can be closely approximated to the C_2 point group. The structure also discloses a disorder in one of the phenyl rings at two positions, which was approximated and refined with coordinates, anisotropic thermal parameters, and site occupancies of the solvent molecules and the chloride ion. The coordination geometry around rhodium atom is a distorted trigonal-bipyramid with carbene carbon atoms occupying the axial sites.

The C(4)−N(3) and C(24)−N(6) bond distances of 1.288(5) Å are similar to those observed for the free carbene **2**. The Rh−C(1) and Rh−C(21) bond lengths of 2.038(4) and 2.041(4) Å, respectively, are comparable with the Rh−carbene distances found in rhodium complexes containing *trans* NHCs.[56] The rhodium carbonyl bond length, Rh−C(41), of 1.796(4) Å is in the expected range.[57,58] The Rh−N(3) and Rh−N(6) bond lengths are 2.259(3) and 2.251(3) Å, respectively, and are comparable with the distances observed in rhodium complexes with an NHC-oxazoline ligand system.[59] The C(1)−Rh−C(21) bond angle measures 172.02(15)° and confirms that the two carbene rings are almost *trans* to each other and occupy the axial sites in a distorted trigonal-bipyramidal geometry around the rhodium metal center. The remaining bond lengths and angles are unexceptional and lie within the expected range.

Catalytic Studies. Suzuki Coupling. Palladium complexes **4** and **5** were found to be active catalyst precursors for the Suzuki cross-coupling reaction and proved to be thermally robust for the high-temperature coupling of activated and deactivated aryl bromides with a range of boronic acids, Table 1. In initial attempts KO^{t}Bu and K_2CO_3 failed to activate the catalyst and no coupling product using aryl bromide was obtained even after 36 h at 80 °C in dioxane. Addition of 1.5 M KOH activated the catalyst, but resulted in a reasonable amount of the undesired homocoupling of the aryl boronic acid (10%, entries 1 and 2; Table 1). The use of Cs_2CO_3 proved to be the best choice of base, as it activated the catalyst quickly, although some homocoupling still occurred (Table 1, entries 5 and 13, 5% and 30%, respectively). The palladium catalysts **4** and **5** showed very little or no activity for activated or deactivated aryl chlorides, and only 10% coupled product was obtained using 4-chloroanisole with phenyl boronic acid after 24 h at 80 °C (entries 6 and 7, Table 1). Representative catalytic results are summarized in Table 1. Although unexceptional, the results are in line with those of similar NHC complexes of Pd(II).[32,33]

Table 1. Coupling of Aryl Halides with Aryl Boronic Acids Using Complexes 4 and 5 as Catalyst Precursors

Entry	Substrate	Product	Time (hours)	% Yield GC (isolated)
Catalyst [$PdCl_2$(C^imine)] 4[a]				
1			24	87[b,c]
2			24	80[b,c]
3			2.0	90[d]
4			1.0	95
Catalyst [Pd(allyl)(C^imine)]PF_6 5[a]				
5			2.0	≥97[d]
6			24	10
7			24	10
8			1.0	92
9			1.5	≥90
10			1.5	≥98 (95)
11			1.5	≥96
12			1.5	≥98 (95)
13			1.5	50[e]

[a] Reaction condition: 0.5 mmol of ArX; 0.75 mmol of boronic acid; 4.0 mL of 1,4-dioxane; 1.0 mmol of Cs_2CO_3; 1.0 mol % catalyst. [b] 1.5 mL of 1.5 M KOH used as base. [c] 10% homocoupling product. [d] 5% homocoupling product. [e] 30% homocoupling product.

Hydroformylation. The rhodium complex [Rh(COD)-(C∧imine)][PF_6], **6**, was tested for the hydroformylation of 1-octene, and the data are summarized in Table 2. The greatest yields of aldehyde were obtained with higher pressures of H_2/CO, while the linear versus branched ratio varied from 0.8 to 2.5. These results are similar (TOF and TON) to those obtained for the hydroformylation of 1-hexene using [Rh(COD)L][PF_6], where L = 1,3-di-[3′-*t*-Bu-imidazole-2′-ylidene]propane, where 100% conversion to aldehyde with a linear-to-branch ratio of 1:1 was observed at 80 °C and 80 bar after 16 h.[60]

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Table 2. Hydroformylation of 1-Octene Using [Rh(COD)(C∧imine)][PF$_6$] (6) (0.1 mol %)

				aldehyde[b]		alcohol[b]			
entry	*T* (°C)	*p*[a] (bar)	*t* (h)	%	l/b	%	l/b	2-octene (%)	octane (%)
1	100	8	18	10	1.28			64	8
2	60	10	12	30	2.5			10	1
3	100	15	24	17	1.6	10	2.5	40	5
4	30	30	24	≥99	1.2				
5	60	55	24	≥77	1.9	18	2.0	5	
6	100	20	24	≥99	0.82				

[a] CO/H_2, 33:67. [b] Conversion to linear (l) and branched (b) aldehydes as determined by GC and reported as an average of two runs.

Conclusion. In conclusion we describe, to the best of our knowledge, the first example of a stable crystalline noncyclic imino *N*-heterocyclic carbene, which has been structurally characterized, and the preparation of the corresponding palladium(II) and rhodium(I) metal complexes. Such carbenes and metal complexes were previously thought to be impossible to prepare due to a reported [1,2]-rearrangement of an early example of this type of NHC.[46,47] The palladium(II) complexes show moderate activity in Suzuki type C−C cross-coupling reactions, while the rhodium(I) complexes show activity in the hydroformylation of 1-octene.

Experimental Section

General Procedures. All manipulations were performed under dinitrogen using standard Schlenk techniques or in an inert atmosphere glovebox. All solvents were dried by passage through an alumina column under a positive pressure of dinitrogen and deoxygenated by bubbling dry dinitrogen through the dried solvents for 20 min before use. NMR spectra were recorded on either a Varian Unity Plus 500 (^{1}H at 500 MHz, ^{13}C at 125.7 MHz) or a Varian Mercury 300 (^{1}H at 300 MHz, ^{13}C at 75.5 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances, and chemical shifts were reported with respect to $\delta = 0$ for tetramethylsilane. Electrospray mass spectra were recorded in acetonitrile on a Micromass LC TOF spectrometer. Microanalyses were performed by the microanalytical department of the Inorganic Chemistry Laboratory, University of Oxford. Gas chromatographs were recorded using a Perkin-Elmer XL 1100 instrument with a Perkin-Elmer NCI 900 network chromatography interface using a fused silica, nonpolar SGE column, 25QC2/BP1 1.0.

Metal precursors were supplied by Johnson Matthey and all remaining reagents purchased from Aldrich and used as received unless otherwise stated. The reagents 1-*tert*-butylimidazole,[61] [Rh(COD)Cl]$_2$,[62] [(COD)PdCl$_2$],[63] η^3-allylpalladium(II) chloride dimer,[64] and [Rh(CO)(PPh$_3$)$_3$Cl][65] were prepared using published procedures. The imidoyl chloride (PhN=CPhCl) was prepared by heating benzanilide and phosphorus pentachloride under vacuum in the absence of solvent.[66,67]

Synthesis of [1-(*t*-Bu)imidazolium-3-{C(Ph)=N(Ph)}] Chloride (1) and [AgCl(1-(*t*-Bu)imidazol-2-ylidene-3-{C(Ph)=N(Ph)})], [AgCl(C∧imine)] (3). The nonenolizable imine-imidazolium salt **1** was prepared by the reaction of imidoyl chloride ClC(Ph)=N(Ph) with 1-*tert*-butylimidazole in THF (Scheme 1). The imidazolium salt **1** was isolated as an air-stable white solid. The corresponding mononuclear [AgCl(C∧imine)] complex **3** was prepared by treating **1** with Ag_2O in CH_2Cl_2 (Scheme 1). The complete synthetic protocol is reported elsewhere.[45]

Synthesis of 1-(*t*-Bu)imidazol-2-ylidene-3-{C(Ph)=N(Ph)}, C∧imine (2). The imidazolium salt **1** (1.00 g, 2.9 mmol) was suspended in THF (10 mL) and cooled to −78 °C. KN[Si(CH$_3$)$_3$]$_2$ (0.60 g, 3.0 mmol) was suspended in 10 mL of THF and cooled to −78 °C. The base solution was then added dropwise to **1** at −78 °C over a period of 10 min and stirred for 30 min. The resulting yellow reaction mixture was gradually warmed to room temperature, stirred for 2 h, and then evaporated under reduced pressure to give a yellow solid. The product was extracted with warm pentane (4 × 30 mL). The solvent was removed at reduced pressure to give **2** as an off-white solid. Yield: 0.65 g, 75%. Crystals of **2** suitable for X-ray diffraction studies were grown from a saturated solution of **2** in pentane at −78 °C.

***E* Isomer (major).** ^{1}H NMR (C_6D_6, 300 MHz): 1.03 (s, 9H, ^{t}Bu), 6.32 (d, 1H, $^3J_{HH}$ = 1.9 Hz, −NC*H*CHN−), 6.45 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, N-Phenyl H$_4$), 6.50−6.59 (m, 5H, Phenyl-CH), 6.68 (t, 2H, $^3J_{HH}$ = 7.6 Hz, C-Phenyl H$_{3,5}$), 7.01 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, C-Phenyl H$_{2,6}$), 7.91 (d, 1H, $^3J_{HH}$ = 1.9 Hz, −NCHC*H*N−). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): 30.9 (s, ^{t}Bu), 56.5 (s, ^{t}Bu-C), 116.8 (s, −N*C*HCHN−), 117.7 (s, −NCH*C*HN−), 121.9 (s, C-Phenyl-C$_{2,6}$), 123.3 (s, N-Phenyl-C$_4$), 123.9 (s, N-Phenyl-C$_{(ipso)}$), 127.4 (s, C-Phenyl-C$_4$), 128.9 (s + br, N-Phenyl-C$_{3,5}$), 131.9 (s, N-Phenyl-C$_{2,6}$), 149.2 (s, C-Phenyl-C$_{(ipso)}$), 157.44 (s, C=N), 223.6 (s, C$_{(carbene)}$).

***Z* Isomer (minor).** ^{1}H NMR (C_6D_6, 300 MHz): 1.07 (s, 9H, ^{t}Bu), 6.09 (s + br, 1H, −NC*H*CHN−), 6.62 (t + br, 4H, $^3J_{HH}$ = 2.07 Hz, C-Phenyl H$_{3,5}$), 6.78−6.87 (m, 4H, Phenyl-CH) 7.80−7.87 (m, 2H, Phenyl-CH) 7.91 (d, 1H, $^3J_{HH}$ = 1.9 Hz, −NCHC*H*N−). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): 31.1 [s, ^{t}Bu] 115.6 [s, −N*C*HNCH−], 119.8 [s, −NCHN*C*H−], 121.4 [s, Phenyl-C], 128.2 [s, Phenyl-C], 130.4 [s, Phenyl-C], 133.1[s, Phenyl-C]. MS (ES$^+$, C_6H_6): *m*/*z* 180.0598 [M − *tert*-butylimidazole]$^+$ (100%), 304.1810 [M + H]$^+$, (10%). Anal. (%) Found (calcd): C 79.12 (79.17); H 6.87 (6.98); N 13.72 (13.85).

Synthesis of [PdCl$_2$(C∧imine)] (4). Method A: Synthesis via Carbene Transfer from [AgCl(C∧imine)] (3). The silver compound [AgCl(C∧imine)], **3** (0.90 g, 2.02 mmol), was dissolved in CH_2Cl_2 (10 mL), and a solution of Pd(MeCN)$_2$Cl$_2$ (0.50 g, 1.9 mmol) in CH_2Cl_2 (10 mL) was added dropwise in the absence of light. The reaction mixture was stirred for 12 h in the dark and filtered through a plug of Celite, and the filtrate was evaporated to dryness. The crude product was purified by flash chromatography using CH_2Cl_2/pentane (40:60). Yield: 0.66 g, 70%.

Method B: Synthesis by the Reaction of C∧imine (2) with (COD)PdCl$_2$. The compound (COD)PdCl$_2$ (0.30 g, 1.1 mmol) was dissolved in THF (5 mL), and a solution of C∧imine **2** (0.37 g, 1.2 mmol) in THF (5 mL) was added dropwise at −78 °C with constant stirring over a period of 5 min. The reaction mixture was stirred for 15 min at −78 °C and then gradually warmed to room temperature and stirred for a further 5 h. The solvent volume was reduced to 3 mL and pentane (10 mL) added to afford an orange-yellow precipitate, which was filtered and washed with pentane (3 × 5 mL). The product was purified by slow crystallization using CH_2Cl_2/pentane. Yield: 0.42 g, 72%. Crystals suitable for X-ray diffraction studies were grown from a saturated solution of **4** in CH_2Cl_2, which was layered with pentane, at room temperature.

^{1}H NMR (CD_2Cl_2, 500 MHz): 1.96 (s, 9H, ^{t}Bu CH$_3$), 6.85 (d, 1H, $^3J_{HH}$ = 2.5 Hz, −NC*H*CHN−), 7.01 (dd, 2H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.2 Hz, N-Phenyl-H$_{2,6}$), 7.13 (tt, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, N-Phenyl-H$_4$), 7.19 (dd, 2H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.6 Hz, C-Phenyl-H$_{2,6}$), 7.21 (d, 1H, $^3J_{HH}$ = 2.4 Hz, −NCHC*H*N−), 7.23 (td, 2H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, N-Phenyl-H$_{3,5}$), 7.39

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(td, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, C-Phenyl-$H_{3,5}$), 7.47 (tt, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, C-Phenyl-H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 30.9 (s, ^{t}Bu), 62.5 (s, ^{t}Bu-C), 117.9 (s, −N*C*HCHN−), 120.9 (s, −NCH*C*HN−) 125.4 (s, C-Phenyl-$C_{2,6}$), 125.9 (s, N-Phenyl-$C_{(ipso)}$), 126.9 (s, N-Phenyl-C_4), 127.9 (s, C-Phenyl-C_4), 128.7 (s, C-Phenyl $C_{3,5}$), 129.2 (s, N-Phenyl-$C_{3,5}$), 132.0 (s, N-Phenyl-$C_{2,6}$), 143.8 (s, C-Phenyl-$C_{(ipso)}$), 161.7 (s, C═N), 163.3 (s, $C_{(carbene)}$). MS (ES+, CH_3CN): *m*/*z* 485.3 [M − Cl + CH_3CN)]$^+$ (90%). Anal. (%) Found (calcd): C 48.91 (49.97); H 4.41 (4.40); N 8.57 (8.74).

Synthesis of [(η^3-allyl)Pd(C∧imine)][PF_6] (5). The compound [(allyl)PdCl]$_2$ (0.20 g, 0.55 mmol) was dissolved in THF (5 mL), and a solution of C∧imine **2** (0.35 g, 1.2 mmol) in THF (5 mL) was added dropwise at room temperature with constant stirring over a period of 5 min. The reaction mixture was stirred for a further 5 h and then added dropwise in the absence of light to a stirred solution of $AgPF_6$ (0.28 g, 1.1 mmol) in THF (3 mL). The reaction mixture was stirred for a further 30 min at room temperature. The solvent was evaporated and the residual solid dissolved in CH_2Cl_2 (10 mL) and filtered through Celite. The pale yellow filtrate was reduced to a volume of 2 mL, and pentane (15 mL) was added to precipitate the product as an off-white solid. The solid was filtered and washed with pentane (3 × 5 mL) and dried under vacuum. Yield: 0.51 g, 76%. Crystals of **5** suitable for X-ray crystallography were grown from CH_2Cl_2/pentane.

^1H NMR (CD_2Cl_2, 500 MHz): 1.79 (s, 9H, ^{t}Bu-CH_3), 3.16 (d, 1H, J_{HH} = 12.6 Hz, allyl-H), 3.51 (d, 1H, J_{HH} = 13.7 Hz, allyl-H), 3.55 (dd, 1H , $^2J_{HH}$ = 2.3 Hz, $^3J_{HH}$ = 7.6 Hz, allyl-H), 4.10 (td/ddd, 1H, $^2J_{HH}$/$^4J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 6.9 Hz, allyl-H), 5.77 (m, 1H, allyl-H), 6.97 (d, 1H, $^3J_{HH}$ = 2.3 Hz, −(^{t}Bu)NCHC*H*N−), 7.03 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, N-Phenyl-$H_{2,6}$), 7.16 (tt, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, N-Phenyl-H_4), 7.23 (dt, 2H, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.7 Hz, N-Phenyl-$H_{3,5}$), 7.35 (dd + br, 2H, C-Phenyl-$H_{2,6}$) 7.37 (d, 1H, $^3J_{HH}$ = 2.3 Hz, −(^{t}Bu)N*C*HCHN−), 7.46 (s + br, 2H, C-Phenyl-$H_{3,5}$), 7.54 (tt, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, C-Phenyl-H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2,75.5 MHz): 30.8 (s, ^{t}Bu), 59.1 (s, allyl-CH_2), 76.4 (s, allyl-CH_2), 60.5 (s, ^{t}Bu-C), 119.2 (s, allyl-CH), 120.7 (s, −N*C*HCHN−), 121.1 (s, −NCH*C*HN−), 122.6 (s, N-Phenyl-$C_{3,5}$), 126.9 (s, C-Phenyl-$C_{(ipso)}$), 127.1 (s, C-Phenyl-$C_{3,5}$), 129.3 (s, N-Phenyl-C_4), 129.5 (s, C-Phenyl-C_4), 129.6 (s, N-Phenyl-$C_{2,6}$), 132.5 (s, C-Phenyl-$C_{2,6}$), 148.5 (s, N-Phenyl-$C_{(ipso)}$), 163.4 (s, C═N), 180.7 (s, $C_{(carbene)}$). MS (ES+, CH_3CN): *m*/*z* 450.1162 [M$^+$] (100%). Anal. (%) Found (calcd): C 46.29 (46.36); H 4.35 (4.40); N 6.95 (7.05).

Synthesis of [(cod)Rh(C∧imine)][PF_6] (6). The compound [Rh(cod)Cl]$_2$ (0.30 g, 0.6 mmol) was dissolved in THF (5 mL) and added to a solution of $AgPF_6$ (0.31 g, 1.21 mmol) in THF (3 mL) at room temperature and stirred for 10 min. The solution was then filtered and the filtrate added to a solution of C∧imine **2** (0.39 g, 1.28 mmol) in THF (5 mL) at −78 °C, stirred for 5 min, and then gradually warmed to room temperature. The reaction mixture was stirred for 2 h, during which time the color changed from orange-yellow to a reddish-brown. The reaction mixture was filtered, and the solvent was reduced in volume to 3 mL. A solid was precipitated by addition of pentane (10 mL). The crude product was recrystallized from CH_2Cl_2/pentane and dried in a vacuum. Yield: 0.65 g, 82%.

^1H NMR (CD_2Cl_2, 500 MHz): 1.75 (s, 9H, ^{t}Bu-CH_3), 1.97(m, 2H, cod-CH_2), 2.14 (m, 2H, cod-CH_2), 2.29 (m, 2H, cod-CH_2), 2.38 (m, 2H, cod-CH_2), 4.14 (m + br, 1H, cod-CH), 4.63 (m, 1H, cod-CH), 6.71 (d, 1H, $^3J_{HH}$ = 1.3 Hz, −(^{t}Bu)NCHC*H*N−) 6.95 (dd, 2H, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.2 Hz, N-Phenyl-$H_{2,6}$), 7.14 (tt, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, N-Phenyl-H_4), 7.27 (dt, 2H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, N-Phenyl-$H_{3,5}$) 7.36 (d, 2H, $^3J_{H-H}$ = 7.9 Hz, C-Phenyl-$H_{2,6}$), 7.45 (t, 2H,$^3J_{HH}$ = 7.6 Hz, C-Phenyl-$H_{3,5}$), 7.53 (tt, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, C-Phenyl-H_4), 7.94 (d, 1H, $^3J_{HH}$ = 1.3 Hz, −(^{t}Bu)NC*H*CHN−). $^{13}C\{^1H\}$ NMR (CD_2Cl_2,75.5 MHz): 29.3 (s, cod-CH_2), 29.4 (s, cod-CH_2), 31.2 (s, cod-CH_2), 31.8 (s, ^{t}Bu), 32.4 (s, cod-CH_2), 60.9 (s, ^{t}Bu-C), 80.9 (d, $J_{(Rh-C)}$ = 12.6 Hz, cod-CH), 98.2 (d, $J_{(Rh-C)}$ = 8.7 Hz, cod-CH), 119.6 (s, −N*C*HNCH−), 121.5 (s, −NCHN*C*H−), 124.4 (s, N-Phenyl-$C_{3,5}$), 127.0 (s, C-Phenyl-$C_{(ipso)}$), 127.5 (s, C-Phenyl-$C_{3,5}$), 129.0 (s, N-Phenyl-C_4), 129.3 (s, C-Phenyl-C_4), 129.4 (s, N-Phenyl-$C_{2,6}$), 132.3 (s, C-Phenyl-$C_{2,6}$) 143.5 (s, N-Phenyl-$C_{(ipso)}$), 143.5 (s, C═N), 180.7 (d, J_{Rh-C} = 55.2 Hz, $C_{(carbene)}$). MS (ES+, CH_3CN): *m*/*z* 406.0834 [M$^+$ − (cod)] (100%), 438.0787 [M$^+$ − Ph] (40%). Anal. (%) Found (calcd): C 50.89 (51.00); H 4.98 (5.04); N 6.27 (6.37).

Synthesis of [Rh(CO)(C∧imine)$_2$][PF_6] (7). The compound Rh(PPh$_3$)$_2$(CO)Cl (0.40 g, 0.58 mmol) was dissolved in THF (5 mL) and cooled to −78 °C, a solution of C∧imine **2** (0.20 g, 0.66 mmol) in THF (5 mL) was then added dropwise, and the reaction mixture was stirred for 10 min at −78 °C, after which time it was gradually warmed to room temperature and stirred for a further 12 h. The color of the reaction mixture changed from yellow to a reddish-brown. The mixture was filtered and evaporated to dryness. Diethyl ether (10 mL) was added to precipitate the product. The solid was filtered and washed with diethyl ether (3 × 10 mL). The resulting orange-brown solid was dried in a vacuum and kept under dinitrogen. The product was crystallized from CH_2Cl_2/pentane. Yield: 0.21 g, 45%.

^1H NMR (CD_2Cl_2, 500 MHz): 1.49 (s, 9H, ^{t}Bu-CH_3), 6.42 (dd, 2H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.5 Hz, C-Phenyl-$H_{2,6}$), 6.89 (tt, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.7 Hz, C-Phenyl-H_4), 6.94 (dt, 2H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, C-Phenyl-$H_{3,5}$), 7.05 (d, 1H, $^3J_{HH}$ = 2.4 Hz, −NC*H*CHN−), 7.29 (s + br, 1H, −NCHC*H*N−), 7.36 (dd, 2H, $^3J_{H-H}$ = 6.9 Hz, $^4J_{HH}$ = 1.8 Hz, N-Phenyl-$H_{2,6}$), 7.44 (dt, 2H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.5 Hz, N-Phenyl-$H_{3,5}$), 7.48 (tt, 1H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, N-Phenyl-H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2,-75.5 MHz): 30.7 (s, ^{t}Bu), 59.8 (s, ^{t}Bu-C), 119.2(s, −N*C*HNCH−), 121.5 (s, −NCHN*C*H−), 122.0 (s, C-Phenyl-$C_{2,6}$), 125.7 (s, C-Phenyl-C_4), 127.7 (s, C-Phenyl-$C_{(ipso)}$, 127.5 (s, C-Phenyl-$C_{3,5}$), 128.9 (s, N-Phenyl-$C_{2,6}$), 129.4 (s, N-Phenyl-$C_{3,5}$), 131.5 (s, N-Phenyl-C_4), 146.9 (s, N-Phenyl-$C_{(ipso)}$), 156.3 (s, C═N), 187.1 (d, J_{Rh-C} = 39.7 Hz, $C_{(carbene)}$), 195.1 (d, J_{Rh-CO} = 94.5 Hz, C_{CO}). IR (Nujol): $\nu_{C=O}$ 1922 cm^{-1}. Anal. (%) Found (calcd): C 63.60 (63.69); H 5.42 (5.48); N 10.75 (10.87).

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Supporting Information Available: Catalysis protocol for Suzuki coupling and hydroformylation reactions and crystallographic data (CIF and a table containing a summary of crystal data) are available free of charge via the Internet at http://pubs.acs.org.

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