Zerovalent Palladium and Nickel Complexes of Heterocyclic Carbenes: Oxidative Addition of Organic Halides, Carbon−Carbon Coupling Processes, and the Heck Reaction

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Zerovalent carbene complexes of Pd containing the 1,3,4,5-tetramethylimidazol-2-ylidene ligand (tmiy) have been synthesized. Pd(COD)(alkene) (COD = cyclooctadiene) reacts with the nucleophilic carbene tmiy to produce the complexes Pd(tmiy)$_2$(alkene) (alkene = maleic anhydride (MAH) (**2**), tetracyanoethylene (TCNE) (**3**)). Spectroscopic studies on the complexes provide strong evidence of the almost purely donor nature of the carbene ligand. Oxidative addition of hydrocarbyl halide and dihalide substrates to **2** and **3** yield the Pd^{II} derivatives Pd(tmiy)$_2$(Ph)I (**4**), Pd(tmiy)$_2$I$_2$ (**5**), Pd(tmiy)$_2$(4-nitrophenyl)I (**6**), and Pd(tmiy)$_2$Br$_2$ (**7**). The zerovalent Ni complex Ni(tmiy)$_2$ was produced in situ from the reaction of Ni(COD)$_2$ with tmiy, and the oxidative addition of organic halides yields Ni(tmiy)$_2$(o-tolyl)Br (**8**), Ni(tmiy)$_2$(Me)I (**9**), and Ni(tmiy)$_2$I$_2$ (**10**). X-ray crystal structures of complexes **8** and **10** are reported which reveal square-planar coordination with the carbene ligands inclined at significant angles to the coordination planes of the complexes. Metal to ligand bond distances are all indicative of the electron density induced on the metal center by the donor carbene ligands. Halide abstraction from **6** in the presence of *n*-butyl acrylate leads to migratory insertion of the olefin and elimination of the Heck coupling product. Under stoichiometric reaction conditions hydrocarbyl−imidazolium ions are also produced as byproducts. Selected complexes were tested as catalysts for the Heck reaction (Pd) and Suzuki coupling (Pd, Ni) and were found to be highly active. The observed reaction behavior is interpreted, and a mechanism for the Heck coupling is provided.

Introduction

Many transition-metal-catalyzed processes have been shown to proceed via an initial oxidative addition to the metal, often to a d^{10} (Ni^0, Pd^0) center stabilized by ancillary ligands. Examples of this include the Heck reaction, hydrocyanation, telomerization, Suzuki coupling, and hydrosilylation.[1,2] Two major roles of the ancillary ligand are (i) to stabilize reactive intermediates or transition states and (ii) to influence the activity and selectivity through electronic and steric effects. Thus, tertiary phosphine ligands have found widespread use in homogeneous catalysis due to their ability to stabilize different oxidation states and to effect the electronic and steric properties of the metal. Heterocyclic carbene complexes have been shown to have considerable potential as efficient catalysts for Heck (Pd) and Suzuki coupling (Pd, Ni)[3−6] and hydrosilylation (Rh),[7] apparently owing to the stability imparted on the active species by the strong donor heterocyclic carbene ligands. The carbene ligand appears to play a role similar to that for tertiary phosphine ligands, although it probably does not undergo dissociation equilibria typical of the phosphines. It is generally accepted that reactions such as Heck and Suzuki coupling proceed via a Pd^0 → Pd^{II} cycle when they are catalyzed by simple bis(phosphine) complexes, the active species being Pd(phosphine)$_2$, although there has been some speculation on the involvement of Pd^{IV} intermediates when ligands such

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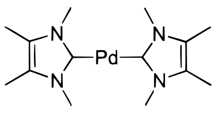
as phosphapalladacycles are employed.[8-11] Similar involvement of a Pd^0 active species in the Heck reaction catalyzed by Pd carbene complexes was indicated by the results of Herrmann.[12] Herrmann found noticeable induction periods for Pd^{II} complexes. The complexes, however, were rapidly activated on addition of a reducing agent, and when Pd^0 complexes were used as starting materials, no induction period was observed at all. Our recent mechanistic studies suggest that the active species in the Heck reaction, catalyzed by carbene complexes, is a 14-electron $Pd^0(carbene)_2$ complex such as **1**, which contains the tetramethylimidazol-2-ylidene ligand (tmiy).[13] The catalytic cycle is initiated by oxidative addition of an organic halide to **1** to yield a (hydrocarbyl)Pd^{II} intermediate. A theoretical study on the Heck reaction with a Pd carbene catalyst also shows oxidative addition to $Pd^0(carbene)_2$ to be a favorable reaction.[14]



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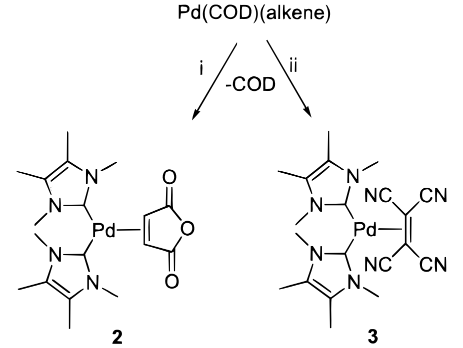
Although oxidative addition of halogens to Ni^0 carbene complexes has previously been carried out,[15] the addition of organic halides (RX) has not been reported, and Ni diaminocarbene complexes containing a simple aryl group are not known. Likewise, oxidative addition of RX to a Pd^0 carbene complex is limited to our initial report on the formation of $[Pd(tmiy)_2(4\text{-acetophenonyl})Br]$ from $Pd(tmiy)_2$ (produced in situ) and 4-bromoacetophenone.[13] It was thus of interest to us to prepare zerovalent carbene complexes of palladium and nickel and to investigate the addition of organic halides to such species. We have previously reported new routes to methylpalladium complexes through ligand displacement reactions.[13,16] Oxidative addition was expected to provide yet another route to hydrocarbyl carbene complexes applicable to a broader range of hydrocarbyl groups and metals. Furthermore, we have shown that introduction of a methyl group into Pd^{II} carbene complexes has a remarkable activating affect in the Heck reaction, presumably by providing a facile route to the Pd^0 active species.[13,17] Introduction of hydrocarbyl groups into Ni carbene complexes was expected to have a similar effect.

Scheme 1. Synthesis of Pd^0 Complexes[a]



[a] Legend: (i) tmiy, THF, −75 to +20 °C, alkene = MAH; (ii) tmiy, THF, −70 to +20 °C, alkene = TCNE.

We report here the synthesis and characterization of novel zerovalent carbene complexes of Pd and their subsequent reactions with a number of substrates to afford divalent complexes through oxidative addition. Furthermore, we present the synthesis of Ni^{II} carbene complexes via oxidative addition to $Ni(tmiy)_2$. Crystal structures of two Ni carbene complexes are reported. The variable-temperature reaction behavior of an aryl-Pd^{II} complex in the stoichiometric Heck coupling is reported, and the mechanism of the Heck reaction, catalyzed by Pd carbene complexes, is proposed. Additionally, the new complexes are evaluated as catalysts for Heck and Suzuki coupling reactions.

Results and Discussion

Zerovalent Palladium Complexes. Initial attempts to prepare bis(carbene) Pd^0 alkene complexes focused on displacement of the dba ligand (dba = dibenzylideneacetone) from $Pd(dba)_2$ by addition of free carbene (tmiy), followed by addition of an electron-deficient alkene such as tetracyanoethylene (TCNE), maleic anhydride (MAH), or diethyl fumarate (DEF). The expected complexes $Pd(tmiy)_2(alkene)$ formed, but the synthesis was complicated by a side reaction between the free carbene and displaced dba.[17] The addition of carbenes across activated double bonds such as occur in dba is a facile reaction[18,19] and appears to take place before all the carbene can coordinate to the metal center.

To overcome the problem with dba, 2 equiv of tmiy was added to the Pd(0) complexes Pd(COD)(MAH) and Pd(COD)(TCNE)[20] in THF. The reaction proceeded smoothly to afford the bis(carbene) complexes $Pd(tmiy)_2(MAH)$ (**2**) and $Pd(tmiy)_2(TCNE)$ (**3**) through displacement of the COD ligand (Scheme 1). Complex **2** slowly decomposes in solution and after several days in the solid state when exposed to air. In contrast, **3** resists prolonged refluxing in DCM solution and the solid appears indefinitely stable in air. Complex **3** is extremely insoluble in all common solvents, and as a result only the ^1H NMR spectrum, which shows resonances at 2.11 and 3.72 ppm due to the tmiy ligand, could be obtained in solution. The ^{13}C CP/MAS spectrum shows peaks at 8.6, 35.2, and 126.3 ppm due to the carbene $C{-}CH_3$, $N{-}CH_3$ and $C{=}C$ carbons, respectively. The

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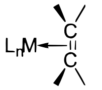
possibility exists that **3** is dimeric or oligomeric and is more complex than the simple structure shown in Scheme 1. There is evidence for this in the LSI mass spectrum, which shows a cluster at *m*/*z* 965 corresponding to the $[2M - H]^+$ ion along with the $[M - H]^+$ cluster at *m*/*z* 481. As well as η^2-olefin coordination, the TCNE ligand could also coordinate through the nitrile groups. An oligomeric structure has also been suggested for the precursor complex Pd(COD)(TCNE).[20]

Bonding in Complexes 2 and 3. An important aspect of these imidazole–carbene complexes is the nature of the carbene to metal bonding. It has been stated that the carbenes are strong donor ligands with little back-bonding from metal to carbene occurring.[6,12,21] Direct comparisons have been made between these carbenes and phosphine ligands.[22,23] To provide insight into the carbene–metal bonding in the (carbene)$_2$Pd^0(alkene) complexes we have monitored the effect of coordination on the alkene. In general, the bonding of alkenes to transition metals can be represented by two extremes, described as pure donor bonding (**I**) and pure acceptor bonding (**II**). The true nature of the bonding for most complexes lies somewhere between **I** and **II**, and the relative importance of each structure is influenced by the olefin, the metal, and the other ligands associated with the metal. It has been shown that "soft", electron-rich metal centers in combination with strongly electron withdrawing substituents on the olefin greatly increase the importance of **II**.[24] In view of the electron density induced on the metal center by heterocyclic carbene ligands,[6,21,25] it is expected that strong Pd to alkene back-bonding would be present in **2** and **3**, and consequently structure **II** would play an important role. In particular, this will be the case if little or no back-bonding occurs from the metal to the carbene ligands themselves. Therefore, very large differences in the IR and NMR spectra of the free and coordinated olefin ligands in **2** and **3** would be indicative of marked donor properties of heterocyclic carbene ligands and demonstrate an absence of Pd to carbene back-bonding.



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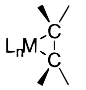

II

The ^{1}H NMR spectrum of **2** consists of resonances at 2.03 and 3.60 ppm for the C–CH$_3$ and N–CH$_3$ protons of the tmiy ligand, respectively, along with a peak at 3.34 ppm that represents the MAH protons. Comparison with the proton positions in free MAH (7.05 ppm) indicates a large upfield shift upon coordination to Pd. This may be attributed to the strong shielding afforded by π-back-bonding from the Pd center which somewhat lessens the double-bond character in MAH. This effect is just as pronounced in the ^{13}C NMR spectrum, where the C=C resonances of MAH, 136.6 ppm in the free ligand, are shifted upfield to 38.2 ppm in **2**, and the C=O groups of the coordinated MAH resonate at 175.5 ppm in **2** compared to 164.3 ppm in free MAH. These changes are consistent with a significant decrease in double-bond character of the olefin. The effect of back-bonding is also visible in the IR spectrum of **2**, which shows ν(CO) at 1749 and 1706 cm^{-1}, compared to 1850 and 1770 cm^{-1} for the free ligand. Significant back-bonding from the Pd center to TCNE is also evident and is manifest in the IR spectrum of **3**, which shows ν(C≡N) peaks at 2208 and 2122 cm^{-1} compared to 2261 and 2227 cm^{-1} in the free ligand.

Table 1. Spectroscopic Data for Selected (donor)$_2$Pd(alkene) Complexes

Pd complex	IR (cm^{-1})	^{1}H NMR (ppm)[a]	^{13}C NMR (ppm)[b]
(tmiy)$_2$Pd(TCNE)	2208, 2122 (ν(C≡N))		
(tmiy)$_2$Pd(MAH)	1749, 1706 (ν(C=O))	3.34	38.2
(PPh$_3$)$_2$Pd(TCNE)[c]	2230 (ν(C≡N))		
(PPh$_3$)$_2$Pd(MAH)[c]	1794, 1730 (ν(C=O))	4.00	56.3
(^{t}BuNC)$_2$Pd(TCNE)[d]	2226 (ν(C≡N))		
(^{t}BuNC)$_2$Pd(MAH)[d]	1805, 1732	4.07	
(COD)Pd(TCNE)[e]	2265, 2225 (ν(C≡N))		
(COD)Pd(MAH)[e]	1802, 1731 (ν(C=O))	4.40[f]	

[a] Olefinic protons (in CDCl$_3$). [b] Olefinic carbons (in CDCl$_3$). [c] Reference 26. [d] Reference 27. [e] Reference 20. [f] NMR run in acetone-d_6.

A comparison of spectroscopic data for **2** and **3** with those for a selection of (donor)$_2$Pd(MAH) and (donor)$_2$Pd(TCNE) complexes (Table 1)[20,26,27] provides further evidence of the Pd to olefin back-bonding and hence strong donor characteristics of these carbenes. Thus **2** and particularly **3** could be envisaged as approaching Pd^{II} derivatives, although both complexes undergo reactions typical of Pd^0 (vide infra).

Oxidative Addition Reactions of 2 and 3. Oxidative addition to **2** was initially attempted using phenyl iodide as the substrate. At ambient temperature no reaction is observed and **2** is recovered unchanged. Upon heating to ca. 60 °C oxidative addition does occur, but the product undergoes further reaction at this temperature and a complex mixture of products is obtained. The mixture was characterized by NMR and mass spectroscopy, which show the presence of the expected complex Pd(tmiy)$_2$(Ph)I (**4**) plus the diiodide Pd(tmiy)$_2$I$_2$ (**5**) and the 2-phenyl-1,3,4,5-tetramethylimidazolium iodide salt. Additionally, analysis of the crude reaction mixture by GC-MS reveals the formation of biphenyl.

To explain these products, the reaction sequence shown in Scheme 2 is proposed. Oxidative addition of phenyl iodide would afford complex **4**, which could then decompose via elimination of the phenylimidazolium ion, yielding Pd^0 and other unidentified product(s) from the second carbene moiety. We have previously shown that this is a facile mode of decomposition for cationic methylpalladium carbene complexes,[13] and we have shown here that it may also occur from neutral species. It is possible that the diiodide complex **5** and biphenyl may be formed via a Pd^{IV} intermediate, but it is most likely that they result from an intermolecular exchange reaction of **4** in which phenyl/halide exchange occurs, resulting in complex **5** and a bis(phenyl) complex, from

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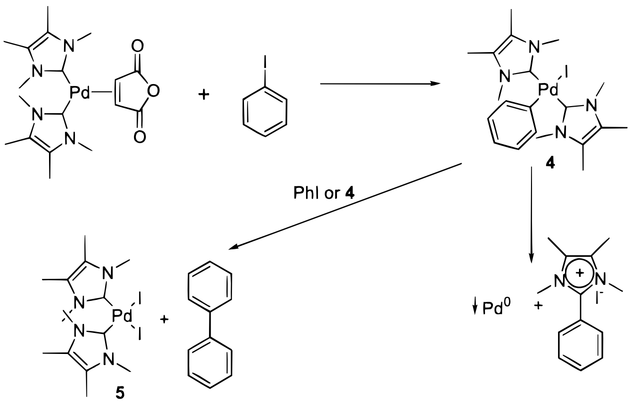
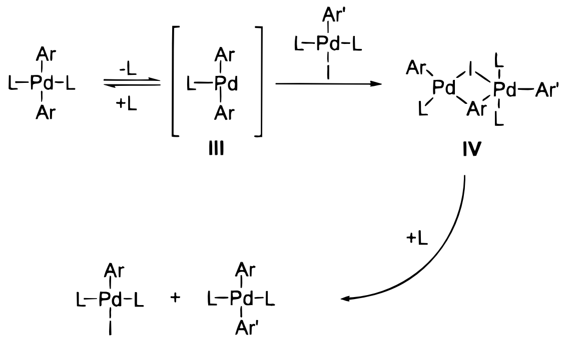
Scheme 2

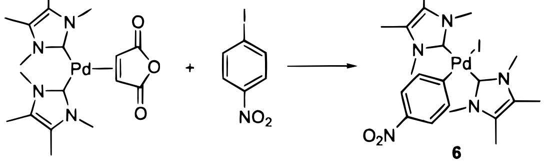


which biphenyl could reductively eliminate. A spectroscopic investigation of the reaction mixture failed to detect any evidence of Pd^{IV} species. Furthermore, it has been shown for related phosphine systems that formation of biaryls results not from a Pd^{IV} intermediate but via an intermolecular exchange reaction similar to that postulated above.[28,29] It was shown that the intermolecular exchange reaction requires dissociation of a ligand to give the three-coordinate complex **III**, which then forms the aryl-bridged dimer **IV**, from which ligand exchange can occur (Scheme 3). It seems unlikely that dissociation of a carbene ligand would occur in the present system. It is possible, however, that the iodide ion could reversibly dissociate to give a cationic three-coordinate species, which could then react in a manner similar to **III**.

Scheme 3. Postulated Mechanism for Aryl Exchange Leading to Biaryl Formation for the System $Pd(PR_3)_2(Ar)_2/Ar'-I$[28,29]



To limit side reactions, an activated aryl halide was used, allowing milder conditions to be employed. Thus, the oxidative addition of 4-iodonitrobenzene to **2** was carried out at room temperature to produce Pd(tmiy)$_2$-(4-nitrophenyl)I **6** in 51% yield (reaction 1). The expected trans coordination of the carbene ligands is suggested by the ^{1}H NMR spectrum, which shows only two sharp singlets for the tmiy methyl groups (2.04 and 3.87 ppm), indicating that both carbenes are in equivalent environments. Likewise, only one peak for each chemically different carbon of tmiy is observed in the ^{13}C NMR spectrum. Complex **6** slowly decomposes in CD_2Cl_2 solution ($t_{1/2} \approx 3$ days) to yield the 2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium ion as the major product along with metallic Pd.



6 [1]

Oxidative addition of dihalides to the Pd^0 complexes is a facile reaction. Thus, treatment of **2** with iodine yields Pd(tmiy)$_2$I$_2$ (**5**) in 96% yield. Only one isomer is present according to NMR data. The tendency of the plane of the carbene ligand to sit at an angle to the Pd coordination plane means that the tmiy ligand is not particularly sterically demanding and a cis arrangement of the carbene ligands is expected, as previously found for the 1,3-dimethylimadazol-2-ylidene (dmiy) analogue.[3] Consistent with our previous suggestion that the iodide ligand in these complexes exhibits lability, in $CDCl_3$ solution **5** undergoes halide exchange, yielding Pd(tmiy)$_2$ICl and Pd(tmiy)$_2$Cl$_2$. As a result, three closely spaced peaks are observed for the N(CH$_3$) and C(CH$_3$) methyl groups in the ^{1}H NMR spectrum—corresponding to **5** and the two chloro complexes.

The TCNE complex **3** is less reactive than the MAH analogue **2**, as might be expected from the greater Pd to olefin back-bonding and consequent stronger binding of the olefin ligand. With hydrocarbyl halides no reaction was observed under conditions in which the product would be stable. However, **3** reacted with bromine at ambient temperature to yield Pd(tmiy)$_2$Br$_2$ (**7**) in ca. 50% yield. The ^{1}H NMR spectrum shows only two peaks for the methyl groups (2.09 and 3.85 ppm), indicating only one isomer is present, probably the cis isomer. The ^{13}C NMR spectrum likewise shows only one resonance for each chemically different carbon of tmiy. The carbene carbon appears at 157.8 ppm, which is similar to that in **5** (158.9 ppm). This is somewhat upfield from those in the aryl complexes **4** (167.1 ppm) and **6** (175.6 ppm) and probably reflects the greater electron donation from the carbene to the metal in **5** and **7**.

Oxidative Addition to Ni(tmiy)$_2$. Displacement of the COD ligand from Ni(COD)$_2$ and Pt(COD)$_2$ has been reported by Arduengo and co-workers as a route to 14-electron bis(carbene) M^0 complexes.[30] This method was regarded as a suitable starting point to study oxidative addition reactions of Ni^0. Thus, Ni(COD)$_2$ was treated with 2 equiv of tmiy in THF to afford Ni(tmiy)$_2$, which was not isolated but rather was reacted in situ.

When the THF solution of Ni(tmiy)$_2$ was treated with *o*-tolyl bromide, the complex Ni(tmiy)$_2$(*o*-tolyl)Br (**8**) was isolated as an air-stable orange powder in 71% yield (reaction 2). Complex **8** represents one of only two examples of a hydrocarbyl Ni complex containing a diaminocarbene ligand such as tmiy.[31] Importantly, this result shows that Ni^0 carbene complexes readily undergo oxidative addition to give a stable hydrocarbyl Ni^{II} fragment, the first step in many established catalytic reactions. A trans arrangement of the ligands is sug-

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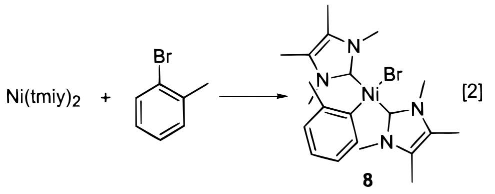
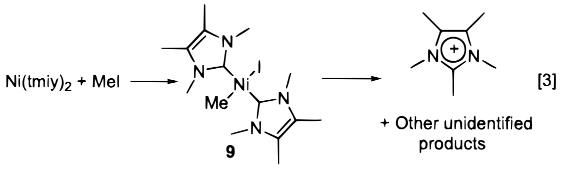


gested for **8** by the NMR spectra. The tmiy methyl groups give rise to only two peaks in the ^{1}H NMR spectrum at 2.00 and 4.05 ppm, and only single peaks are observed for the tmiy carbons in the ^{13}C NMR spectrum.

A crystal structure determination was undertaken for complex **8**, which exhibits a trans arrangement of the carbene ligands and a distorted-square-planar core geometry (Figure 1, Table 2). The Ni−C$_{tmiy}$ distance in **8** is longer than in other Ni^{II} diaminocarbene complexes,[6,32−34] probably reflecting the high electron density induced on the Ni by two tmiy ligands and the tolyl group. The insignificance of π-back-bonding in the Ni−C$_{tmiy}$ bond is confirmed by the Ni−C$_{tmiy}$ distance, which is within the range for normal Ni−C(alkyl/aryl) bonds. The Ni−C$_{tolyl}$ distance (1.947(3) Å) is typical of those in the more electron rich NiL$_2$RAr type complexes (1.933(16)−1.950(12) Å).[35−41] Considering the relatively low trans influence of the bromide ligand, this feature is probably also related to the high electron density induced on the Ni center by the carbene ligands, reducing σ-donation from the tolyl group. We have previously observed a rather long M−C bond in the methylpalladium complex Pd(dmiy)$_2$(Me)Cl for the same reason.[13,17] Steric congestion around the Ni center is relieved by rotation of the carbene ligand planes from the plane of coordination. Dihedral angles of the carbene ligands relative to the coordination plane are 70.71(9) and 74.87(9)°, respectively. Here, this correlates with relief of intermethyl substituent clashes, although such twists are a characteristic feature of heterocyclic carbene complexes.[5,6,12,42,43] The planar tolyl group is likewise rotated by 63.7(1)° from the plane of coordination.

Oxidative addition of methyl iodide to Ni(tmiy)$_2$ was attempted at a variety of temperatures in THF solution. Although a Ni^{II} complex formed, it rapidly decomposed via elimination of the 1,2,3,4,5-pentamethylimidazolium ion (reaction 3). Even when the reaction and workup



were conducted at less than −50 °C, the imidazolium salt was the major product; thus, the oxidative addition product was not obtained pure. However, formation of the Ni^{II} complex **9** was verified by a peak at −0.77 ppm in the ^{1}H NMR spectrum, corresponding to the Ni-coordinated methyl group. The high-field position of this methyl group reflects the high electron density on Ni coordinated to two tmiy ligands. Similar Ni−Me chemical shifts were observed in electron-rich complexes containing the strongly basic PEt$_3$ ligand.[44,45] The LSI mass spectrum of the product mixture is dominated by the imidazolium ion at m/z 139, but a small cluster at m/z 321 corresponding to $[M - I]^+$ appears along with

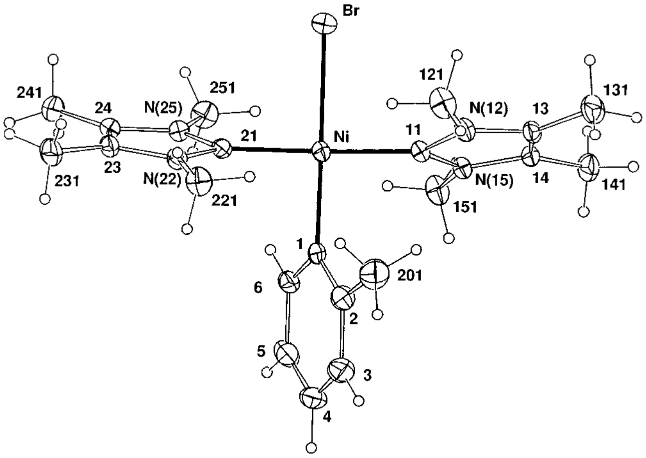


Figure 1. Projection of **8**, normal to the coordination plane. Thermal ellipsoids with 20% probability are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Interplanar Angles (deg) in Ni(tmiy)$_2$(*o*-tolyl)Br[a]

	Bond Lengths		
Ni−C(1)	1.947(3)	Ni−Br	2.4317(6)
Ni−C(11)	1.919(3)	C(21)−N(22)	1.346(4)
N−C(21)	1.911(3)	C(21)−N(25)	1.356(4)
	Bond Angles		
Br−Ni−C(1)	175.20(9)	C(1)−Ni-C(11)	92.4(1)
Br−Ni−C(11)	88.56(8)	C(1)−Ni-C(21)	89.3(1)
Br−Ni−C(21)	89.72(9)	C(11)−Ni-C(21)	178.2(1)
	Planes		
I: C(n1),N(n2),C(n3),C(n4),N(n5)		$\chi^2 = 4, 18$	
II: C(1),C(11),Br,C(21)		$\chi^2 = 596$	
III: C(1),C(2),C(3),C(4),C(5),C(6)		$\chi^2 = 13$	
	Interplanar Angles		
I/II	70.71(9) 74.87(9)	III/II	63.7(1)

[a] Esd's are given in parentheses; see Figure 1 for atomic numbering.

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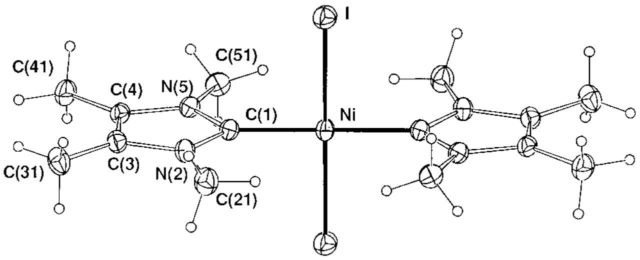


Figure 2. Projection of **10** (centrosymmetric), normal to the coordination plane.

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Interplanar Angles (deg) in Ni(tmiy)$_2$I$_2$[a]

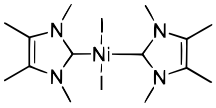
	Bond Lengths		
Ni−C(1)	1.897(3)	C(1)−N(2)	1.349(4)
Ni−I	2.5180(3)	C(1)−N(5)	1.347(3)
	Bond Angles		
I−Ni−C(1)	90.79(8)	Ni−C(1)−N(5)	127.3(2)
Ni−C(1)−N(2)	127.7(2)	N(2)−C(1)−N(5)	104.9(2)
	Planes		
I: C(1),N(2),C(3),C(4),N(5)		$\chi^2 = 2.0$	
II: C(1)$_2$I$_2$			
	Interplanar Angle		
I/II		86.97(8)	

[a] Esd's are given in parentheses; see Figure 2 for atomic numbering.

others at *m/z* 306 ([M − MeI]$^+$) and *m/z* 182 ([Ni(tmiy)]$^+$). No molecular ion could be observed for **9**.

The mode of decomposition of **9** is a notable result, as it shows that hydrocarbyl Ni^{II} complexes are also susceptible to the carbene elimination reaction we have observed for hydrocarbyl Pd complexes.[13,17] Nickel is a commonly used metal in catalysis, and hydrocarbylmetal complexes are considered to be intermediates in a number of catalytic cycles, so that this observation has important implications with respect to possible catalyst deactivation.

The zerovalent Ni complex reacts with halogens in a manner similar to that for the Pd^0 complexes. Thus, when Ni(tmiy)$_2$ is treated with iodine in THF, the Ni^{II} complex Ni(tmiy)$_2$I$_2$ (**10**) is obtained as violet crystals after recrystallization from DCM/ether. Only one isomer is indicated by NMR spectroscopy. A trans arrangement is the most likely structure.[6]



10

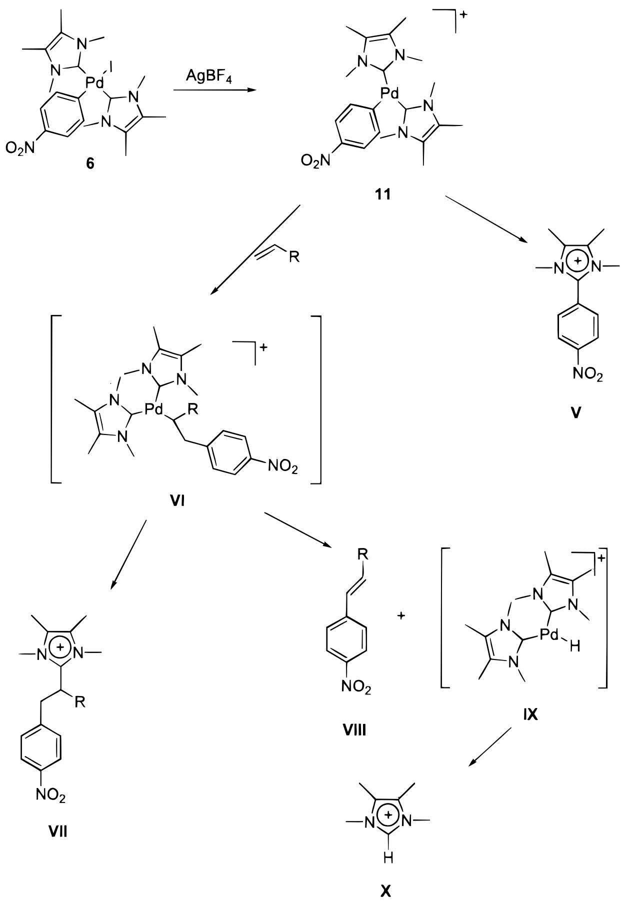
The results of a room-temperature, single-crystal X-ray structure determination of **10** show the solid-state Ni environment to be a centrosymmetric square-planar trans array, with half of the molecule comprising the asymmetric unit of the structure (Figure 2, Table 3). The tmiy ligand plane lies quasi-normal (interplanar dihedral angle 86.97(8)°) to the (Ni)C$_2$I$_2$ coordination plane. The Ni−C$_{\text{tmiy}}$ distance is rather shorter (ca. 0.02 Å) than in **8** but is still within the range for normal Ni−C(alkyl/aryl) bonds, confirming that there is no significant Ni−C π-bonding in **10**.

Mechanistic Aspects of the Heck Reaction. Oxidative addition of 4-iodonitrobenzene to Pd^0(tmiy)$_2$ may be regarded as the first step in the Heck reaction if a Pd^0 → Pd^{II} cycle is active. Following this first step, coordination and migratory insertion of an olefin into the Pd−aryl bond is required before β-hydride elimination can release the product. Recent theoretical results of Albert et al. with the system Pd(carbene)$_2$(Ph)Br suggest insertion occurs via halide abstraction and subsequent olefin coordination.[14] In an attempt to identify intermediates in such an insertion mechanism, Pd(tmiy)$_2$(4-nitrophenyl)I **6** was treated with AgBF$_4$ and 1 equiv of *n*-butyl acrylate in CD$_2$Cl$_2$ at −50 °C. Abstraction of iodide is verified by a downfield shift in the NCH$_3$ resonance of tmiy and an upfield shift in the aromatic protons, although coordination of the *n*-butyl acrylate was not observed. Even when the halide abstraction is carried out at −80 °C, using Ag[(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B] to increase the solubility of the cationic complex, only signals due to free *n*-butyl acrylate are observed. When the solution is warmed to −30 °C, signals due to the 2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium ion **V** begin to appear with minor amounts of the ion **VII**. At −20 °C signals due to *n*-butyl (*E*)-4-nitrocinnamate (**VIII**) emerge together with those from the 1,3,4,5-tetramethylimidazolium ion **X**. It is apparent that under the conditions of this stoichiometric experiment the migratory insertion and elimination steps are fast and that the concentration of the intermediate with coordinated alkene very low. We propose the reactions shown in Scheme 4 to explain the formation of these products.

Initial halide abstraction from **6** would yield the cationic complex **11**. This complex then partially decomposes via the arylimidazolium elimination reaction to give 2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium (**V**) and Pd^0. We have noted previously that the hydrocarbyl−carbene elimination reaction is most facile for cationic complexes.[13] This is consistent with the much lower temperature at which it occurs for the cationic complex **11** compared to its neutral parent **6**. Formation of compound **VII** is explained by coordination and rapid migratory insertion of the olefin to afford the alkyl intermediate **VI**, from which product elimination would give **VII**. At −20 °C it seems β-hydride elimination becomes competitive, resulting in formation of *n*-butyl (*E*)-4-nitrocinnamate (**VIII**) and the unstable intermediate hydride complex **IX**. Decomposition of **IX** would then produce 1,3,4,5-tetramethylimidazolium (**X**) and Pd^0. The species **X** can be considered as a proton trap, and its appearance, clearly identified by ^{1}H NMR, provides evidence for the intermediate **IX**. The intermediates **VI** and **IX** are not observed. However, each product in Scheme 4 has been identified by ^{1}H NMR and MS of the NMR solution (full spectroscopic data are provided in the Experimental Section).

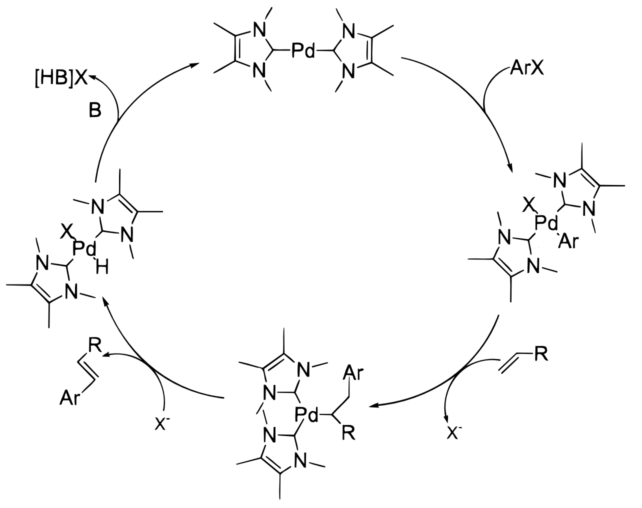
The relative proportions of each product depend on the reaction conditions. When the experiment is conducted at room temperature, the main products are the migratory insertion/β-hydride elimination Heck product **VIII** along with the 1,3,4,5-tetramethylimidazolium ion. Only a small amount of 2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium product is formed, and signals due to **VII** are not observed. It appears that β-hydride elimination is greatly accelerated at higher temperatures and can compete with the carbene elimination

Scheme 4[a]



[a] R = COOBu. The counterion BF_4^- is excluded from the scheme. Formation of **V**, **VII**, and **X** is accompanied by the formation of other unidentified product(s) from the second carbene moiety.

Scheme 5



reactions, suggesting that under catalytic Heck conditions (120 °C, appropriate base, excess substrate) **6** should give rise to an effective Heck catalyst. Importantly, this was found to be the case. Under Heck conditions complex **6** forms an efficient catalyst for the coupling of 4-iodonitrobenzene with butyl acrylate to yield *n*-butyl (*E*)-4-nitrocinnamate, the same product that was obtained from the stoichiometric modeling experiments. The *E* geometry of **VII** is verified by the 16 Hz coupling of the olefinic protons in the ^{1}H NMR spectrum. Turnover numbers were high, and there was little evidence of decomposition to Pd^0. Complex **6** (amount of catalyst 1.7×10^{-3} mol %) and the Pd^0 complex **3** (2.1×10^{-3} mol %) also catalyzed the coupling of *n*-butyl acrylate with 4-bromoacetophenone to produce *n*-butyl (*E*)-4-formylcinnamate with TONs of ca. 50 000.

These results provide experimental evidence that the mechanism of olefin insertion into the Pd−aryl bond during the Heck reaction is one in which halide abstraction from the Pd^{II} complex, formed from the oxidative addition of an aryl halide to a Pd^0 complex, allows coordination and insertion of the olefin. In the absence of silver salts no insertion is observed at lower temperatures. The elevated temperatures (120 °C)[13] required for the insertion step in the absence of a halide scavenger may be necessary for bromide dissociation before alkene coordination and insertion can proceed, although insertion via a five-coordinate species cannot be ruled out. On the basis of this new experimental information we propose that the mechanism for the Heck reaction catalyzed by Pd−carbene complexes is that shown in Scheme 5 and is essentially identical with that predicted by the theoretical work of Albert et al.[14] The likely active species is the 14-electron Pd^0 complex Pd(tmiy)$_2$, to which oxidative addition of an aryl halide occurs to yield the Pd^{II} aryl complex. Dissociation of the halide ligand is accompanied by olefin coordination, insertion, and β-hydride elimination to release the product and give (after recoordination of the halide) Pd(tmiy)$_2$HX. Reductive elimination of HX in the presence of base then regenerates the active Pd^0 species.

Suzuki Coupling. The Suzuki coupling of 4-bromoacetophenone with phenylboronic acid was investigated with selected examples of the new complexes. The application of Pd complexes with chelating heterocyclic dicarbene ligands in Suzuki coupling has been reported by Herrmann et al,[6] but 1 mol % catalyst was used such that turnover numbers of only ca. 100 were obtained. In contrast, the (aryl)Pd^{II} complex **6** and the Pd^0 complex **3** catalyze the coupling with high turnover numbers. For example, using 2×10^{-3} mol % of **6** a turnover number of 28 000 is obtained after 24 h. We believe the high activity of **6** is a further example of the activating influence that the hydrocarbyl group has in Pd carbene complexes of this type, by providing a facile route to the Pd^0 active species.[13,17] Whereas in the Heck reaction the Pd^0 species is generated by olefin insertion into the Pd−C bond followed by β-hydride elimination and reductive elimination of HX, in Suzuki coupling the arylboronic acid could react with the (aryl)Pd complex, giving a bis(aryl) complex from which the biaryl coupling product and a Pd^0 active species are formed. In contrast, dihalide complexes are not so readily reduced, requiring a significant induction period before they become active and leading to a loss of catalyst activity. The Pd^0 complex **3** is even more active, giving a turnover number of 55 700 with 1×10^{-3} mol % catalyst. In the case of **3** it is likely that the high activity results from its ability to undergo oxidative addition (under the forcing conditions of the Heck reaction, 120 °C) and hence undergo the first and possibly rate-determining step in the catalytic cycle.

The Suzuki coupling reaction is also catalyzed by Ni–carbene complexes, although not as efficiently as observed with Pd. The use of $Ni(tmiy)_2I_2$ (3×10^{-2} mol %) as a catalyst precursor resulted in a 19% conversion of aryl halide after 24 h, corresponding to a turnover number of 630. When $Ni(tmiy)_2$(*o*-tolyl)Br is used under the same conditions, a 58% conversion is obtained (TON = 1930). Thus, introduction of an aryl group into the catalyst precursor leads to a large increase in activity, although not as pronounced as in the Pd case. The lower activity of the Ni complex relative to its Pd analogue does not appear to result from decomposition of the catalyst, as there was no observation of Ni^0 deposits even after reaction times of 24 h.

Summary

Zerovalent bis(carbene)Pd(olefin) complexes have been prepared and fully characterized. Although these complexes may be considered as having Pd^{II} character, they undergo oxidative addition reactions typical of Pd^0. In this regard there are similarities to related phosphine complexes such as $Pd(PR_3)_2$ and $Pd(PR_3)$(olefin) as previously highlighted.[16,23,25] This similarity is in part supported by the present work, which shows carbenes may play a role similar to that of phosphine ligands in stabilizing and activating the metal toward oxidative addition. The oxidative addition of organic halides was carried out to yield Pd^{II} carbene complexes, providing a new route to Pd hydrocarbyl carbene complexes. Likewise, a stable Ni^{II} hydrocarbyl diaminocarbene complex was prepared via oxidative addition to a Ni^0 center stabilized by the tmiy ligand. These results give valuable mechanistic insights into reactions catalyzed by Pd/Ni carbene complexes. The subsequent steps in the Heck reaction—insertion of an olefin into the Pd–aryl bond and *β*-hydride elimination of the product—have been demonstrated using complex **6**. Other catalytic reactions, for instance, Suzuki coupling and telomerization,[17,46] may likewise be formulated as proceeding through a $M^0 \rightarrow M^{II}$ cycle when catalyzed by carbene-stabilized Pd/Ni complexes.

Although comparisons have been made between phosphine and carbene ligands, there are, however, clear differences between the ligands. One is a distinction in degree—carbenes appear to be stronger donors than even the most basic phosphines, thus greatly reducing the possibility of ligand (carbene) dissociation, a common process for many phosphine complexes. The second major distinction is the reactivity of the coordinated carbene, possibly caused by the lack of back-donation from the metal to the carbene. We have demonstrated that hydrocarbyl (and hydride) complexes decompose via attack of the hydrocarbyl group on the carbene with elimination of imidazolium salts and subsequent reduction of the metal. This appears to be a common mode of carbene loss for Pd^{II} and Ni^{II} hydrocarbyl complexes and indicates a significant pathway for catalyst deactivation, as hydrocarbyl species are expected to be intermediates in many catalytic cycles. We are currently conducting combined theoretical and kinetic investigations in an attempt to elucidate the detailed mechanism of this decomposition reaction.

Experimental Section

General Comments. Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox. All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use.[47] Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature unless otherwise stated, and peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). Elemental analysis, MS, and GC-MS were carried out by the Central Science Laboratory, University of Tasmania. Pd(COD)(MAH), Pd(COD)(TCNE),[20] $Ni(COD)_2$[48] and tmiy[49] were prepared as described in the literature.

Structure Determinations. Room-temperature spheres of data were measured using a Bruker AXS CCD instrument, with proprietary SMART, SAINT, and SADADS data processing ($2\theta_{max} = 58°$, ω-scans; monochromatic Mo Kα radiation, $\lambda = 0.710\,7_3$ Å, T ca. 298 K). N_t total reflections were reduced to N_r unique reflections (R_{int} cited) and N_o reflections with $|F_o| > 4\sigma|F_o|$ being considered "observed" and used in the full-matrix least-squares refinement. An "empirical" absorption correction was applied. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$ being refined for **10** and constrained at estimated values for **8**. Conventional residuals R and R_w (statistical weights) at convergence are cited. Neutral atom complex scattering factors were employed; computation used the XTAL 3.4 program system.[50]

Crystal/Refinement Data. **8**: $C_{21}H_{31}BrN_4Ni$, $M_r = 478.1$, orthorhombic, space group *Pbca* (D_{2h}^{15}, No. 61), $a = 15.553(3)$ Å, $b = 16.941(3)$ Å, $c = 16.941(3)$ Å, $V = 4464(2)$ Å^3. $D_c(Z = 8) = 1.42_3$ g cm^{-3}, $F(000) = 1984$, $\mu_{Mo} = 26.7$ cm^{-1}, specimen $0.23 \times 0.20 \times 0.12$ mm, $T_{min,max} = 0.59, 0.86$, $N_t = 28\,825$, $N_r = 5659$ ($R_{int} = 0.062$), $N_o = 3794$, $R = 0.035$, $R_w = 0.043$, $n_v = 244$; $|\Delta\rho_{max}| = 0.6$ e Å^{-3}.

10: $C_{14}H_{24}I_2N_4Ni$, $M_r = 280.4$, monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 10.026(2)$ Å, $b = 10.204(2)$ Å, $c = 8.208(1)$ Å, $\beta = 102.902(2)°$, $V = 979._0$ Å^3, $D_c(Z = 2) = 1.90_2$ g cm^{-3}, $F(000) = 540$, $\mu_{Mo} = 41$ cm^{-1}, specimen $0.39 \times 0.28 \times 0.26$ mm, $T_{min,max} = 0.48, 0.80$, $N_t = 10\,969$, $N_r = 2463$ ($R_{int} = 0.023$), $N_o = 2128$, $R = 0.027$, $R_w = 0.039$, $n_v = 98$, $|\Delta\rho_{max}| = 0.7$ e Å^{-3}.

Preparation of Compounds. $Pd(tmiy)_2$(MAH) (2). To a stirred (−75 °C) suspension of Pd(COD)(MAH) (200 mg, 0.64 mmol) in 20 mL of THF was added dropwise over 10 min a solution of tmiy (160 mg, 1.29 mmol) in 20 mL of THF. The resulting deep red solution was stirred for 30 min at ca. −50 °C before being warmed to room temperature. The solution was filtered through Celite, the THF removed in vacuo, and the solid washed with THF/ether (3 mL/10 mL) and twice with ether (10 mL) to afford a red-pink powder. Yield: 250 mg (86%). Anal. Calcd for $C_{18}H_{26}N_4O_3Pd\cdot 0.25THF$ (indicated by NMR): C, 48.47; H, 5.99; N, 11.90. Found: C, 48.17; H, 6.37; N, 11.66. MS (LSIMS; *m*/*z*): 354, [M − (MAH)]$^+$ (62%); 125, [tmiyH]$^+$ (100%). ^1H NMR (200 MHz, $CDCl_3$): δ 3.60 (s, 12H, NCH_3), 3.34 (s, 2H, $HC{=}CH$), 2.03 (s, 12H, CCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 185.5 (NCN), 175.5 ($C{=}O$), 125.3 ($C{=}C_{tmiy}$), 38.3 ($C{=}C_{MAH}$), 35.7 (NCH_3), 9.7 (CCH_3). IR (KBr): 1749, 1706 cm^{-1} (ν(CO)).

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[46] McGuinness, D. S.; Cavell, K. J., Unpublished results. Methylpalladium carbene complexes have been found to be effective catalysts for the telomerization of butadiene with methanol to selectively yield 1-methoxy-2,7-octadiene.

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$Pd(tmiy)_2(TCNE)$ (3). This compound was prepared in the same manner as for **2** (from 228 mg, 0.665 mmol of Pd(COD)(TCNE) and 166 mg, 1.34 mmol of tmiy) except for a modified workup: approximately half of the THF was removed in vacuo and 10 mL of ether added to complete precipitation. The solid was collected by filtration, washed with ether (3 × 10 mL), and dried in vacuo to yield an orange powder. Yield: 273 mg (85%). Anal. Calcd for $C_{20}H_{24}N_8Pd$: C, 49.75; H, 5.01; N, 23.20. Found: C, 49.53; H, 4.81; N, 23.08. MS (LSIMS; *m/z*): 965, $[2M - H]^+$ (3%); 605, $[M - H + (tmiy)]^+$ (8%); 481, $[M - H]^+$ (40%); 354, $[M - (TCNE)]^+$ (100%). ^1H NMR (400 MHz, CD_2Cl_2): δ 3.72 (s, 12H, NCH_3), 2.11 (s, 12H, CCH_3). ^{13}C CP/MAS NMR: δ 126.3 ($C{=}C_{tmiy}$), 35.2 (NCH_3), 8.6 (CCH_3). IR (KBr): 2208, 2122 cm^{-1} (ν(CN)).

Reaction of 2 with Phenyl Iodide. In a typical experiment $Pd(tmiy)_2(MAH)$ (91 mg, 0.20 mmol) was dissolved in 15 mL of THF and phenyl iodide (23 μL, 0.21 mmol) syringed in. The solution was heated to near reflux for 30 min, during which time Pd^0 deposits form; these were cooled and filtered through Celite to yield a homogeneous yellow solution. Removal of the solvent in vacuo led to a mixture of yellow and white solids. The product was washed with 3 mL of THF to leave a white solid that was composed mainly of $Pd(tmiy)_2(Ph)I$ (**4**) with some 2-phenyl-1,3,4,5-tetramethylimidazolium iodide. MS (LSIMS; *m/z*): 605, $[M - Ph + tmiy]^+$ (5%); 555, $[M - I + tmiy]^+$ (2.6%); 481, $[M - Ph]^+$ (2.2%); 431, $[M - I]^+$ (1.8%); 354, $[M - PhI]^+$ (4%); 201, [2-phenyl-1,3,4,5-tetramethylimidazolium]$^+$ (100%); 125, $[tmiyH]^+$ (68%). ^1H NMR of **4** (200 MHz, DMSO-d_6): δ 7.21–6.60 (m, br, 5H, Ph *H*), 3.86 (s, br, 12H, NCH_3), 2.07 (s, br, 12H, CCH_3). ^{13}C NMR of **4** (100 MHz, DMSO-d_6): δ 167.1 (NCN), 136.2, 134.8, 130.6, 129.5 (PhC), 125.8 ($C{=}C$), 34.6 (NCH_3), 8.5 (CCH_3). The THF washings were found to contain a mixture of the starting complex, $Pd(tmiy)_2I_2$ (**5**), the imidazolium salt, and some oxidative addition product **4**. The ratio of products obtained depended on the conditions employed. Thus, when the system was heated for a prolonged time (ca. 2 h), the major product was **5** along with the imidazolium salt. Complex **5** was identified by comparison to the spectra (MS, $^1H/^{13}C$ NMR) of an authentic sample prepared by oxidative addition of I_2 to **2** (vide infra). MS (LSIMS of imidazolium salt; *m/z*): 201 $[M]^+$ (100%). ^1H NMR (400 MHz, DMSO-d_6): δ 7.67 (t, $J = 7$ Hz, 2H, Ph *H*), 7.47 (t, $J = 7$ Hz, 2H, Ph *H*), 7.03 (d, $J = 7$ Hz, 1H, Ph *H*), 3.68 (s, 6H, NCH_3), 2.04 (s, 6H, CCH_3). GC-MS of the reaction solution showed peaks due to biphenyl (*m/z* 154) and 2-phenyl-1,4,5-trimethylimidazole (*m/z* 185) resulting from pyrolysis of the imidazolium salt on the heated injector/column.

$Pd(tmiy)_2I_2$ (5). To a solution (0 °C) of $Pd(tmiy)_2(MAH)$ (54 mg, 0.12 mmol) in 5 mL of DCM was added dropwise over 1 h a DCM solution (10 mL) of iodine (35 mg, 0.14 mmol). The orange solution was filtered through Celite and washed through with 5 mL of DCM. The solvent was removed in vacuo and the residue washed with DCM/ether (2 mL/6 mL) and further with ether (2 × 10 mL) before drying in vacuo to afford an orange powder. Yield: 70 mg (96%). Anal. Calcd for $C_{14}H_{24}N_4I_2Pd{\cdot}0.5DCM$ (indicated by NMR): C, 26.75; H, 3.87; N, 8.61. Found: C, 26.88; H, 3.58; N, 8.14. MS (LSIMS; *m/z*): 607, mixed cluster $[M]^+$ and $[M - I + tmiy]^+$ (17%); 481, $[M - I]^+$ (100%); 354, $[M - 2I]^+$ (50%). ^1H NMR (200 MHz, DMSO-d_6): δ 3.75 (s, 12H, NCH_3), 2.07 (s, 12H, CCH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 158.9 (NCN), 126.1 ($C{=}C$), 35.9 (NCH_3), 8.8 (CCH_3).

$Pd(tmiy)_2$(4-nitrophenyl)I (6). A DCM solution (10 mL) of $Pd(tmiy)_2(MAH)$ (68 mg, 0.15 mmol) and 4-iodonitrobenzene (43 mg, 0.17 mmol) was stirred at ambient temperature for 3 h, during which time the solution changes from dark red to a lighter orange-red. The solution was filtered through Celite and washed through with 5 mL of DCM and the solvent removed in vacuo until ca. 2 mL remained. Acetone (5 mL) was added and the solvent removed in vacuo until a precipitate began to form, at which point 5 mL of ether was added to complete precipitation. The solvent was decanted off and the powder washed twice with acetone/ether (1 mL/6 mL) and again with 15 mL of ether. Drying in vacuo gave an off-white powder. Yield: 46 mg (51%). Anal. Calcd for $C_{20}H_{28}N_5O_2IPd{\cdot}0.1(acetone)$ (indicated by NMR): C, 40.00; H, 4.73; N, 11.49. Found: C, 40.01; H, 4.48; N, 11.05. MS (LSIMS; *m/z*): 604, mixed cluster $[MH]^+$ and $[M - I + tmiy]^+$ (14%); 480, mixed cluster $[M - I]^+$ and $[Pd(tmiy)_3]^+$ (6%); 354, $[Pd(tmiy)_2]^+$ (11%); 246, [2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium]$^+$ (100%). ^1H NMR (200 MHz, CD_2Cl_2): δ 7.62 (d, $J = 9$ Hz, 2H, Ph *H*), 7.42 (d, $J = 9$ Hz, 2H, Ph *H*), 3.87 (s, 12H, NCH_3), 2.04 (s, 12H, CCH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 175.6 (NCN), 163.9 (CNO_2), 136.6 (PhC), 132.5 (PhC), 124.4 ($C{=}C_{tmiy}$), 119.4 (PhC), 34.6 (NCH_3), 8.4 (CCH_3). IR (KBr): 1652, 1335 cm^{-1} ($\nu(NO_2)$). In DCM solution **6** was allowed to fully decompose and found to consist of the 2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium ion and other unidentified product(s) from the second carbene moiety. MS (LSIMS; *m/z*): 246, $[M]^+$ (100%); 125, $[tmiyH]^+$ (41%). ^1H NMR (200 MHz, CD_2Cl_2): δ 8.47 (d, $J = 9$ Hz, 2H, Ph *H*), 8.14 (d, $J = 9$ Hz, 2H, Ph *H*), 3.62 (s, 6H, NCH_3), 2.36 (s, 6H, CCH_3).

$Pd(tmiy)_2Br_2$ (7). To a DCM (20 mL) suspension of $Pd(tmiy)_2(TCNE)$ (108 mg, 0.22 mmol) was added bromine (12 μL, 0.23 mmol) dropwise and the solution stirred for 40 min. The solution was filtered through Celite, the DCM removed in vacuo, and the dark residue extracted with THF (4 × 5 mL). The combined extracts were put under vacuum until ca. 5 mL remained, and the product was precipitated by the addition of 10 mL of ether. The solvent was decanted off and the solid washed twice with 10 mL of ether. The crude product was then taken up in 3 mL of DCM and precipitated by vapor diffusion of ether to yield deep red analytically pure crystals. Yield (crude): 61 mg (53%). Anal. Calcd for $C_{14}H_{24}N_4Br_2Pd$: C, 32.68; H, 4.70; N, 10.89. Found: C, 32.60; H, 4.48; N, 10.70. MS (LSIMS; *m/z*): 513, $[MH]^+$ (1.4%); 433, $[M - Br]^+$ (17%); 354, $[Pd(tmiy)_2]^+$ (4%); 125, $[tmiyH]^+$ (100%). ^1H NMR (400 MHz, CD_2Cl_2): δ 3.85 (s, 12H, NCH_3), 2.09 (s, 12H, CCH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 157.4 (NCN), 125.7 ($C{=}C$), 35.4 (NCH_3), 8.6 (CCH_3).

$Ni(tmiy)_2$(*o*-tolyl)Br (8). To a THF (20 mL, −70 °C) solution of $Ni(COD)_2$ (342 mg, 1.24 mmol) was added a solution of tmiy (315 mg, 2.54 mmol) in 20 mL of THF. After the mixture was warmed to ambient temperature, *o*-tolyl bromide (0.15 mL, 1.25 mmol) was syringed in and the solution stirred for 1 h. The solution was filtered through Celite to yield a homogeneous orange solution, from which the THF was removed in vacuo until ca. 10 mL remained. The product was precipitated by the addition of 15 mL of hexane, the solvent decanted off, and the solid washed with hexane (25 mL) to yield an orange powder after drying in vacuo. Crystals suitable for X-ray analysis were grown by vapor diffusion of hexane into a THF solution of the complex. Yield: 420 mg (71%). Anal. Calcd for $C_{21}H_{31}N_4BrNi$: C, 52.76; H, 6.54; N, 11.72. Found: C, 52.53; H, 6.54; N, 11.65. MS (LSIMS; *m/z*): 397, $[M - Br]^+$ (86%); 306, $[Ni(tmiy)_2]^+$ (93%); 215, $[tmiy + tolyl]^+$ (100%); 182, $[Ni(tmiy)]^+$ (45%); 125, $[tmiyH]^+$ (97%). ^1H NMR (400 MHz, DMSO-d_6, 60 °C): δ 7.50 (s, br, 1H, Ph *H*), 6.49 (d, $J = 7$ Hz, 2H, Ph *H*), 6.43 (d, $J = 7$ Hz, 1H, Ph *H*), 4.05 (s, 12H, NCH_3), 2.61 (s, 3H, $PhCH_3$), 2.00 (s, 12H, CCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 180.2 (NCN), 156.0, 143.3, 138.4, 126.8, 122.3, 121.0 (PhC), 124.6 ($C{=}C_{tmiy}$), 35.8 (NCH_3), 26.2 ($PhCH_3$), 9.4 (CCH_3).

Reaction of $Ni(tmiy)_2$ and Methyl Iodide. In a typical experiment tmiy (168 mg, 1.35 mmol) in 20 mL of THF was added to $Ni(COD)_2$ (182 mg, 0.662 mmol) dissolved in 20 mL of THF (−60 °C) and the solution warmed to ambient temperature. The solution was then cooled again (−60 °C) and methyl iodide (43 μL, 0.69 mmol) syringed in. After it was stirred for 20 min at −40 °C, the solution was filtered through Celite and the solvent removed in vacuo until ca. 10 mL remained. Hexane (20 mL) was added to precipitate the product, and the solvent was decanted off. The solid was washed with 10 mL of hexane and dried in vacuo to yield a light orange solid. The ^{1}H NMR and MS data indicated that the crude product consisted of Ni(tmiy)$_2$(Me)I (**9**) and the 1,2,3,4,5-pentamethylimidazolium ion as the major products (ca. 1:2) along with other unidentified decomposition products (the imidazolium assignments were made by comparison to an authentic sample). All attempts at purification resulted in further decomposition. MS (LSIMS; *m/z*): 321, [M − I]$^+$ (8%); 306, [Ni(tmiy)$_2$]$^+$ (34%); 182, [Ni(tmiy)]$^+$ (16%); 139, [1,2,3,4,5-pentamethylimidazolium]$^+$ (100%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.13 (s, 12H, NCH_3 (**9**)), 3.71 (s, 6H, NCH_3 (imid)), 2.76 (s, 3H, C_2CH_3 (imid)), 2.25 (s, 6H, CCH_3 (imid)), 2.06 (s, 12H, CCH_3 (**9**)), −0.77 (s, 3H, NiCH_3).

Ni(tmiy)$_2$I$_2$ (10). Ni(tmiy)$_2$ was produced in situ as for **8** (227 mg, 0.825 mmol of Ni(COD)$_2$ and 209 mg, 1.68 mmol of tmiy), and an iodine (210 mg, 0.827 mmol) solution in 20 mL of THF was slowly syringed in at 0 °C. The solution was stirred at ambient temperature for 30 min and filtered through Celite and the solvent removed in vacuo until ca. 5 mL remained. Ether (10 mL) was added and the precipitate collected by filtration and washed with DCM/ether (2 mL/10 mL) followed by ether (2 × 10 mL) and dried in vacuo to yield an orange-brown powder. The product was purified by vapor diffusion of ether into a DCM (2 mL) solution to afford analytically pure violet crystals suitable for X-ray analysis. Yield (crude): 324 mg (70%). Anal. Calcd for $C_{14}H_{24}N_4I_2Ni$: C, 29.98; H, 4.31; N, 9.99. Found: C, 30.04; H, 4.37; N, 10.01. MS (LSIMS; *m/z*): 557, mixed cluster [M]$^+$ and [M − I + (tmiy)]$^+$ (38%); 433, [M − I]$^+$ (13%); 306, [Ni(tmiy)$_2$]$^+$ (34%); 125, [tmiyH]$^+$ (100%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.02 (s, 12H, NCH_3), 1.94 (s, 12H, CCH_3). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 169.4 (*N*CN), 125.5 (*C*=*C*), 34.2 (N*C*H$_3$), 8.1 (C*C*H$_3$).

Olefin Insertion Experiments with Pd(tmiy)$_2$(4-nitrophenyl)I. In a typical experiment, an NMR sample of **6** in CD_2Cl_2 was treated with 1 equiv of *n*-butyl acrylate and a slight excess of $AgBF_4$ at −50 °C. A ^{1}H NMR spectrum of the product at −50 °C showed resonances due to complex **11** (400 MHz, CD_2Cl_2, −50 °C): δ 7.68 (d, J = 8 Hz, 2H, Ph *H*), 7.54 (d, J = 8 Hz, 2H, Ph *H*), 3.91 (s, 12H, NCH_3), 2.06 (s, 12H, CCH_3). At −30 °C peaks due to 2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium (**V**) begin to appear, which were identified by comparison to those resulting from decomposition of **6** (vide supra), along with peaks due to **VII** (400 MHz, CD_2Cl_2, −30 °C): δ 8.35 (d, J = 9 Hz, 2H, Ph *H*), 7.83 (d, J = 9 Hz, 2H, Ph *H*), 3.86 (s, 6H, NCH_3), 2.74 (t, J = 7 Hz, 1H, C_2CH). (The 7 Hz doublet expected for the benzylic protons of **VII** was not observed and is probably obscured by one of the several other peaks in the expected region. Likewise, in each of species **VII** and **VIII** the methylene signals of the butyl group overlap with those of remaining *n*-butyl acrylate, and hence a complex pattern is observed in which assignment of signals cannot be made. The signals due to the CH_3 protons of the butyl group in **VII** are obscured by the strong signals of **VIII** and butyl acrylate which are considerably more abundant.) At −20 °C the formation of *n*-butyl (*E*)-4-nitrocinnamate (**VIII**) is observed along with the 1,3,4,5-tetramethylimidazolium ion **X**, which were both indentified by comparison the spectral data of authentic samples. The NMR solution was analyzed by MS (ESI; *m/z*): 125 [tmiyH]$^+$ (9%); 246 [2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium]$^+$ (15%); 251 [$C_{13}H_{17}O_4N$]$^+$ (**VII**-imidazolium ring) (100%).

Heck Coupling. In a typical run, a 100 mL two-necked flask fitted with an air-cooled condenser and a septum was charged with 4-bromoacetophenone (4.98 g, 25 mmol) and anhydrous sodium acetate base (2.29 g, 28 mmol) and degassed by successive vacuum−nitrogen cycles. *N*,*N*-Dimethylacetamide (25 mL), *n*-butyl acrylate (5 mL, 27 mmol) and bis(ethylene glycol) butyl ether (1000 μL, internal standard) were then injected, and the mixture was heated to 120 °C by means of an oil bath. A solution of the catalyst dissolved in DCM was then injected. After the desired time, a sample of the solution (500 μL) was taken, washed with 5% HCl (5.00 mL). and extracted with 2.50 mL of DCM. The DCM extracts were analyzed by gas chromatography.

Suzuki Coupling. A two-necked 100 mL flask equipped with a reflux condenser and septum was charged with 4-bromoacetophenone (1.99 g, 10 mmol), phenylboronic acid (1.34 g, 11 mmol), and potassium carbonate (2.76 g, 20 mmol) before being put under an atmosphere of N_2. Toluene (20 mL) was injected and the solution brought to reflux in an oil bath with vigorous stirring. A solution of the catalyst (DCM or THF, 0.2 mL) was then injected and the solution left for 24 h, after which time bis(ethylene glycol) butyl ether was added (200 μL, internal standard) and the solution analyzed by GC-FID.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates with isotropic displacement parameters, bond lengths, bond angles, anistropic displacement parameters, and H-atom coordinates with isotropic displacement parameters for compounds **8** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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