# Oxidative Addition of the Imidazolium Cation to Zerovalent Ni, Pd, and Pt: A Combined Density Functional and Experimental Study

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**Abstract:** Oxidative addition of different imidazolium cations to zerovalent group 10 metals, to afford heterocyclic carbene complexes, has been investigated by both density functional theory (DFT) and experimental studies. The theoretical analysis shows that addition of imidazoliums to $Pt^0$ and $Ni^0$ is more exothermic than to $Pd^0$, and $Ni^0$ is predicted to react with a much lower barrier than either $Pt^0$ or $Pd^0$. Strongly basic supporting ligands on the metal, as well as cis-chelating ligands, increase the exothermicity of the reaction and also lower the activation barrier. The addition of 2-H imidazoliums is easier and more exothermic than addition of 2-alkylimidazoliums, and a halo-imidazolium is expected to further lower the barrier to oxidative addition and increase the exothermicity. The DFT results show that all three of the metals should be able to oxidatively add imidazolium cations under appropriate conditions. Experimental studies confirmed that oxidative addition is possible, and a number of Pt− and Pd−carbene complexes were prepared via oxidative addition of imidazolium salts to $M^0$ precursors. Most significantly, oxidative addition of 2-H azolium salts was found to readily occur, and the reaction of 1,3-dimethylimidazolium tetrafluoroborate with $Pt(PPh_3)_2$ and $Pt(PCy_3)_2$ affords $[PtH(dmiy)(PPh_3)_2]BF_4$ (**10**) and $[PtH(dmiy)(PCy_3)_2]BF_4$ (**11**), while reaction between 3,4-dimethylthiazolium tetrafluoroborate and $Pt(PCy_3)_2$ yields $[PtH(dmty)(PCy_3)_2]BF_4$ (**12**) (dmiy = 1,3-dimethylimidazolin-2-ylidene, dmty = 3,4-dimethylthiazolin-2-ylidene). Addition of 2-iodo-1,3,4,5-tetramethylimidazolium tetrafluoroborate to $Pt(PPh_3)_4$ or Pd(dcype)(dba) yields $[PtI(tmiy)(PPh_3)_2]BF_4$ (**9**) and $[PdI(tmiy)(dcype)]BF_4$ (**14**), respectively (tmiy = 1,3,4,5-tetramethylimidazolin-2-ylidene, dcype = 1,3-bis(dicyclohexylphosphino)ethane)). X-ray crystal structures are reported for complexes **9** and **11** (cis and trans). These studies clearly show for the first time that oxidative addition of imidazolium and thiazolium cations is possible, and the results are discussed in terms of the ramifications for catalysis in imidazolium-based ionic liquids with both carbene-based and non-carbene-based complexes.

## 1. Introduction

In the 10 years since the discovery of free N-heterocyclic carbenes by Arduengo and co-workers,[1] there has been an increasing number of reports of transition metal complexes of these ligands being used in homogeneous catalysis.[2] Reactions in which carbene complexes have found application include furan synthesis (Ru),[3] olefin metathesis (Ru),[4−9] hydrosilylation and hydroformylation (Rh),[10−15] copolymerization (Pd),[16] and C−C coupling reactions (Pd, Ni).[17−28] Consequently, the fundamental reaction chemistry of these species is of consider-

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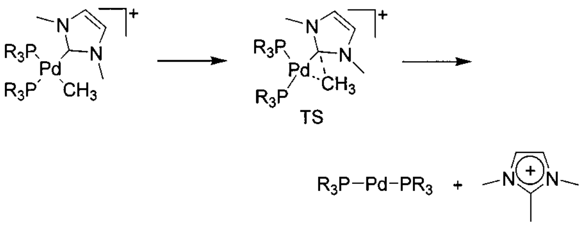
able interest. While the high activity of heterocyclic carbene complexes in various reactions is often attributed to strong M−carbene bonding, we have shown in several recent reports that heterocyclic carbene complexes of $\mathrm{Pd^{II}}$ and $\mathrm{Ni^{II}}$ which contain alkyl, aryl, and acyl groups may decompose via elimination of 2-organyl imidazolium salts.[21,22,24,29] A combined kinetic and density functional study of the reaction (M = Pd) has confirmed that this process can occur with a low activation barrier, proceeding via a concerted reductive elimination of the hydrocarbyl and carbene moieties (reaction 1).[30] Inasmuch as hydrocarbyl-metal species are considered to be intermediates in many catalytic reactions, this reaction represents a significant pathway for catalyst deactivation. Once a problem has been identified, the development of strategies by which it can be impeded becomes of major importance. Of the methods that can be envisaged as hindering reductive elimination of the imidazolium cation,[30] shifting the energetics of the reaction such that the oxidative addition of imidazolium to $M^0$ is favored over reductive elimination provides a possible approach. Thus, an understanding of which factors favor oxidative addition of the imidazolium cation will lead to the development of more stable catalysts. Furthermore, if it were found that oxidative addition of imidazolium cations was possible, this would suggest that operating in an imidazolium-based ionic liquid[31,32] should prevent catalyst decomposition by reductive elimination. The large excess of imidazolium salt, as present when it is used as the solvent, would be expected to favor reoxidation of the metal to give a carbene complex.



(1)

Concomitantly, the possible interaction of the imidazolium cation with low-valent transition metals during catalysis in ionic liquids using non-carbene-based complexes is of interest. Imidazolium-based ionic liquids[33−35] have found increasing application in catalysis as nonaqueous alternatives for biphasic catalysis.[31,32] These salts are highly polar and readily dissolve/immobilize metal-based catalysts while being nonvolatile. These properties make them suited to the development of cleaner technologies, and the term “green solvents” has been used to describe them.[36−38] As such, the reaction chemistry of these salts is presently of much interest. Among the reactions that have been performed in ionic liquids are olefin dimerization (Ni),[39,40] Heck-type reactions (Pd),[41,42] and hydroformylation (Pt, Rh).[43,44] It is generally believed that the anion in such systems usually determines their chemical properties. However, while the imidazolium cation is usually considered inert when used as an ionic liquid, there has been some recent speculation as to the possible involvement of carbene complexes in catalysis.[45] Consequently, the nature of the catalytically active species in these solvents is of critical importance.[42,46] Very recently, Xiao et al. isolated Pd−carbene complexes from an ionic liquid solvent in which $Pd(OAc)_2$ was used as a precatalyst for the Heck reaction.[46] The formation of carbene complexes in this case most likely resulted from deprotonation of the imidazolium C2 proton by $Pd(OAc)_2$, which is known to react with various imidazoliums to give carbene complexes.[17,20] However, the possibility that the imidazolium cation may oxidatively add to low-valent metals raises the question as to whether carbene metal complexes may form without the aid of a basic ligand to deprotonate the imidazolium. In many cases, the catalytic system used in ionic liquids consists of a group 10 metal in combination with phosphine ligands,[39,42,43,45] giving an opportunity for $M^0L_n$ species to form that would be amenable to oxidative addition.

A number of studies have been performed on conventional oxidative addition−reductive elimination of alkanes to low-valent metals, leading to an understanding of factors which affect this reaction. While the imidazolium system is considerably different from those previously studied, it seems possible that similar factors will influence the reaction. It is known that chelating ligands on zerovalent Pd and Pt favor oxidative addition, in terms of both activation barrier and exothermicity of the reaction.[47−52] This is a consequence of a bent geometry for the $M^0(L\wedge L)$ fragment, which has a high d-orbital energy relative to linear $ML_2$. Thus, the reverse reaction (in this case, reductive elimination from a carbene complex containing a chelating ligand) is expected to be disfavored.

It has been established that oxidative addition to $Pt^0$ is favored both kinetically and thermodynamically over oxidative addition

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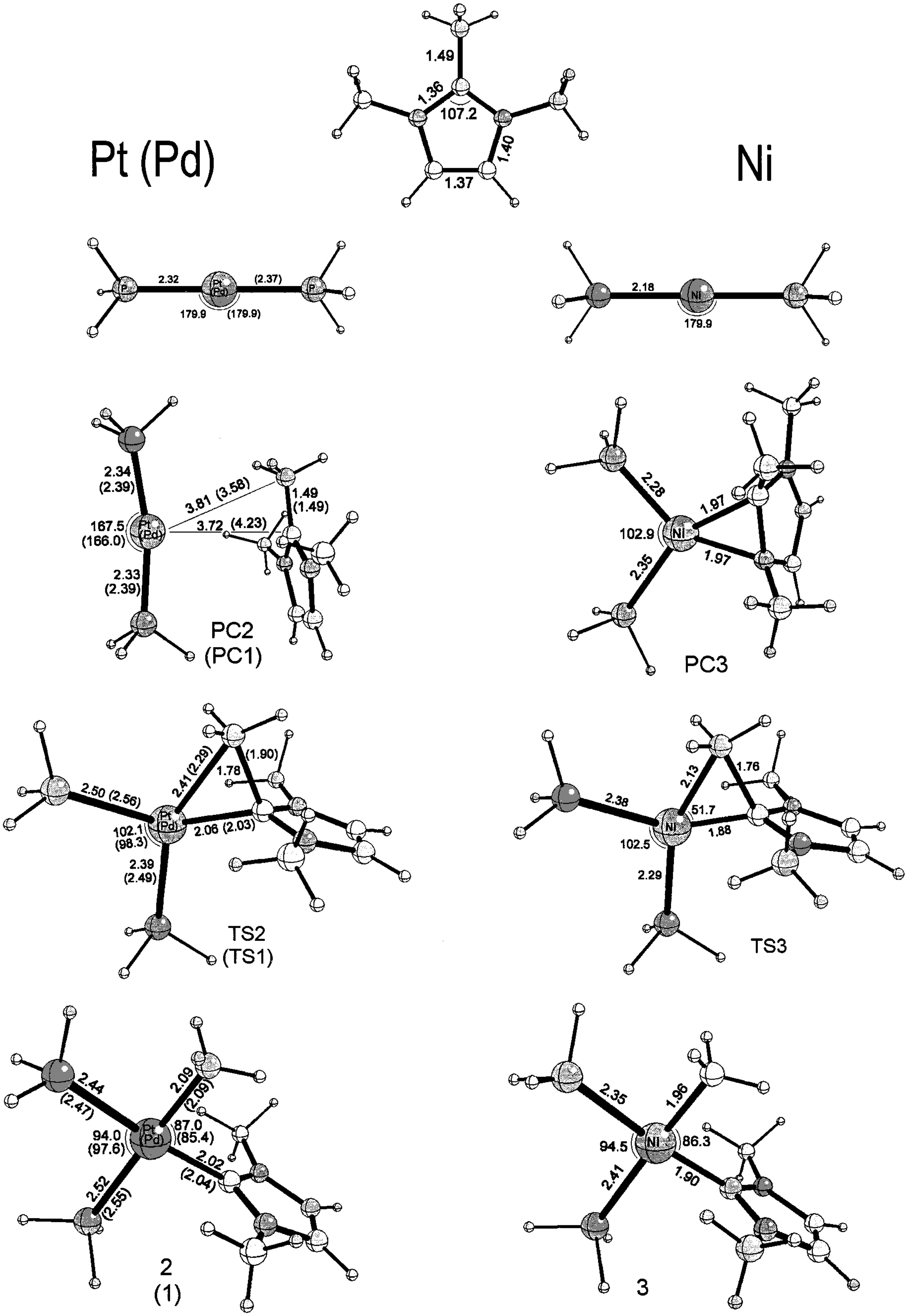

**Figure 1.** Optimized geometries corresponding to oxidative addition to give complex **2** (**1**) (left) and complex **3** (right).

to an equivalent $Pd^0$ system.[48,53,54] This has been attributed to Pt having a more accessible $d^9s^1$ state, as required for M−H and M−C bond formation. Experimental observations support this idea.[49−51] The behavior of $Ni^0$ is less predictable.

In a previous investigation, the reaction of a 2-methylimidazolium cation with Pd was studied.[30] However, ionic liquids

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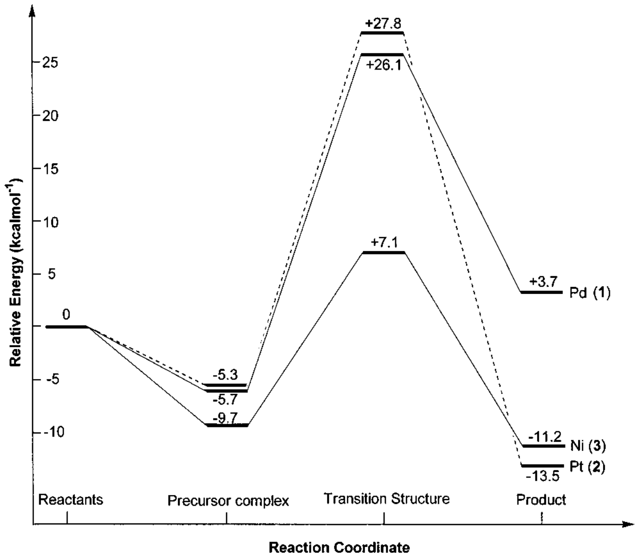


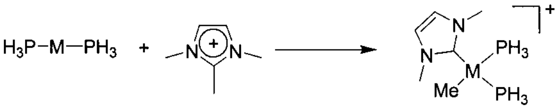
**Figure 2.** Potential energy profile for the oxidative addition of 1,2,3-trimethylimidazolium to Pd, Pt, and Ni, giving complexes **1**, **2**, and **3**, respectively.

are usually composed of an imidazolium cation with hydrogen in the 2-position, and it is known that C−H oxidative addition is more facile than C−C activation. Hence, we present here theoretical and experimental studies aimed at elucidating the factors that favor oxidative addition of imidazolium and thiazolium cations to M$^0$. The effects of different metals (Ni, Pd, Pt), ligands, and imidazolium salts have been evaluated computationally, and the first isolated examples of C−H oxidative addition of an imidazolium cation are reported. Crystal structures of several products are provided. A preliminary communication concerning oxidative addition of the imidazolium cation to Pt$^0$ has recently been published.[55]

## 2. Theoretical Studies

**2.1. Theoretical Methods.** Full geometry optimizations were carried out with the B3LYP[56,57] density functional level of theory combined with the LANL2DZ basis set.[58,59] Sets of five d-functions were used in the basis sets throughout these calculations. For the optimized geometries, harmonic vibrational frequencies were calculated at the B3LYP level, and zero-point vibrational energy corrections were obtained using unscaled frequencies. The vibrational frequencies were also used to obtain thermodynamic corrections and entropies. All transition structures possessed one and only one imaginary frequency, and they were further characterized by following the corresponding normal mode toward each product and reactant. All structures were treated as singlets, and electronic wave function stability optimizations reveal no singlet−triplet instability. Single-point energies on B3LYP/LANL2DZ optimized geometries were calculated at the B3LYP level with the 6-311+G(2d,p) basis set[60−62] on all atoms for the Ni system, a LANL2DZaugmented: 6-311+G(2d,p) basis set for Pd, which incorporates the LANL2 effective core potential and the large f-polarized valence basis set of Bauschlicher and co-workers[63] on Pd together with the 6-311+G(2d,p) basis set on all other atoms, and a LANL2DZaugmented: 6-311+G(2d,p) basis set for Pt, which incorporates the LANL2TZ+(3f) basis set on Pt[64] and 6-311+G-(2d,p) on all other atoms. The energy values in the text refer to these final levels of theory together with thermodynamic corrections from B3LYP/LANL2DZ frequency calculations.

**2.2. Effect of Metal.** First calculations were aimed at evaluating the effect of different group 10 metals on the reaction. As this work was undertaken to see whether oxidative addition of imidazolium cations to M$^0$ is possible, the reactions modeled are depicted throughout as proceeding as an oxidative addition as opposed to reductive elimination.[30] Previous theoretical results predict that oxidative addition of 1,2,3-trimethylimidazolium to Pd(PH$_3$)$_2$ to yield complex **1** is endothermic, with the product lying 3.7 kcal mol$^{-1}$ above the reactants (reaction 2, M = Pd).[30]



(2)

M = Pd (**1**), Pt (**2**), Ni (**3**)

Calculations on the analogous Pt and Ni systems, to yield complexes **2** and **3**, respectively (reaction 2), were performed. The optimized geometries of the stationary points along the potential energy surface are shown in Figure 1. The geometry of the Pd system is also given in parentheses on the Pt stationary point structures for comparison. In each case, a precursor complex was found to precede the transition structure. In the case of Pd and Pt, the geometry of M(PH$_3$)$_2$ is distorted only to a small extent in the precursor complexes (**PC1** and **PC2**), and the imidazolium cation remains unperturbed and distant to the metal. This indicates a weak interaction between Pt and the imidazolium, as indicated for Pd with previous NBO results. In contrast, both reactant fragments are distorted to a large extent in the Ni case, **PC3**. The angle between the phosphines is reduced to 102.9°, and bonds are formed with Ni between C$_{\text{carbenoid}}$ and a nitrogen of the imidazolium ring, both bond lengths being 1.97 Å (Figure 1). This interaction causes the methyl groups attached to C$_{\text{carbenoid}}$ and the bonding nitrogen to be bent out of the imidazolium plane.

The stronger interaction of imidazolium with Ni in **PC3** is reflected in the potential energy profile of the reaction, which is shown in Figure 2. The Pt and Pd precursor complexes have stabilization energies of −5.3 and −5.7 kcal mol$^{-1}$, respectively, compared to a stabilization of −9.7 kcal mol$^{-1}$ in the Ni case. The geometry about the transition structure is very similar in **TS1**, **TS2**, and **TS3**, the main differences being shorter bond lengths to the metal in the Ni structure. The geometries are likewise related in the products **1**, **2**, and **3**. The major differences between the metals comes in the relative energies of the stationary points on the potential energy surface. For the Pt system, the activation barrier ($\Delta H^{\ddagger}$) is predicted to be +27.8 kcal mol$^{-1}$, which is similar to that predicted for the Pd system, +26.1 kcal mol$^{-1}$. However, the product of oxidative addition to Pt lies 13.5 kcal mol$^{-1}$ below the reactants. Thus, in contrast to the reaction with Pd, addition of the imidazolium cation to Pt(PH)$_3$ is predicted to be exothermic. Oxidative addition to Ni is likewise predicted to be exothermic by 11.2 kcal mol$^{-1}$.

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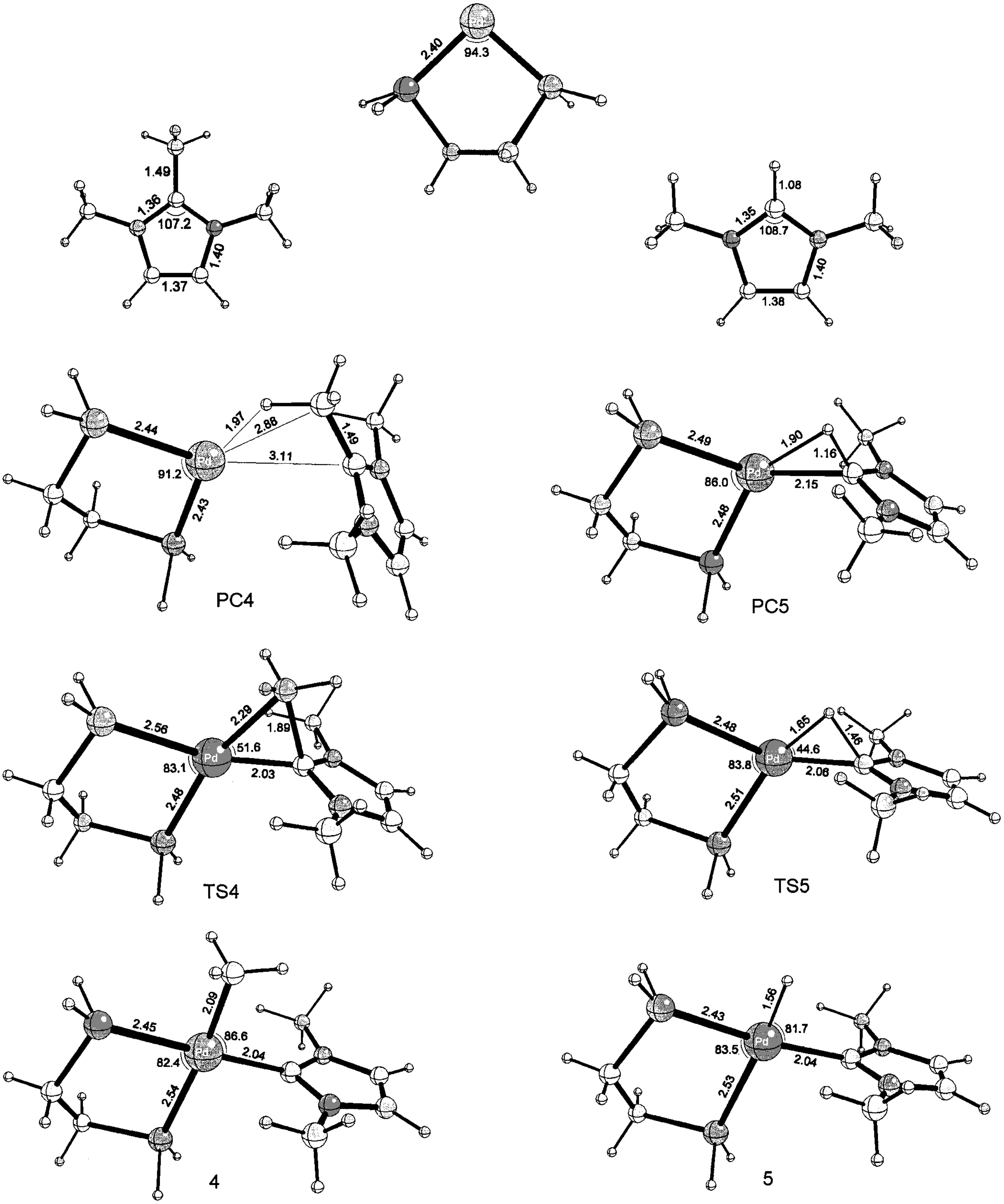

**Figure 3.** Optimized geometries corresponding to oxidative addition to give complexes **4** (left) and **5** (right).

However, in this case the activation barrier ($\Delta H^{\ddagger} = +7.1$ kcal mol$^{-1}$) is predicted to be much lower than that for Pd and Pt. These results show that oxidative addition of imidazoliums to Pt and Ni should be much more favorable than to Pd, and in the case of Ni the activation barrier will be much smaller.

**2.3. Effect of Chelation.** The model phosphine 1,2-diphosphinoethane (dpe) was used in initial calculations to mimic the effect of a bidentate, chelating phosphine. The optimized geometries corresponding to oxidative addition of 1,2,3-trimethylimidazolium are shown in Figure 3 (left column). In the precursor complex, **PC4**, the imidazolium cation is somewhat nearer the Pd center than is the case when unidentate phosphines are coordinated (**PC1**). This is understandable, as the P−Pd−P angle in Pd(dpe) is constrained at 94.3° by chelation of the

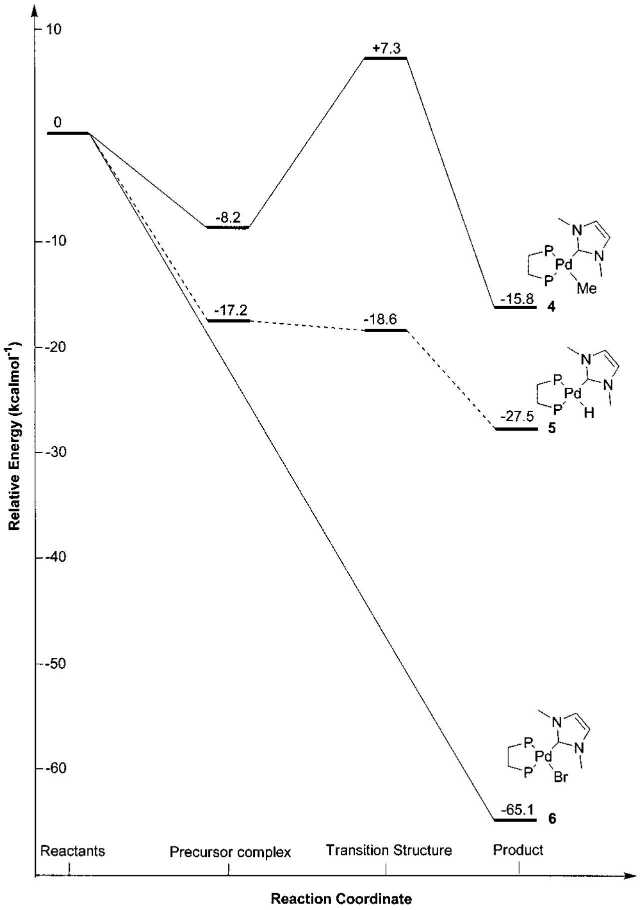

**Figure 4.** Potential energy profile for the oxidative addition of different imidazolium cations to Pd(dpe).

phosphine, such that in **PC4** the phosphine has to undergo little distortion for the imidazolium to interact. Similar trends were observed in theoretical studies on $CH_4$ oxidative addition.[48,65] In the transition structure **TS4**, the Pd−Me, Pd−$C_{carbenoid}$, and Me−$C_{carbenoid}$ bonds are virtually the same as in the nonchelated model **TS1**. The only difference observed is in the P−Pd−P angle, which is 83.1° in **TS4** compared to 98.3° in **TS1**. In the product **4**, the bond distances to Pd are also very similar to those in **1**, and again the only real difference between geometries is in the P−Pd−P angle. The potential energy changes for the reaction (Figure 4) reveal a stabilization energy of −8.2 kcal $mol^{-1}$ for **PC4** (cf. −5.3 kcal $mol^{-1}$ for **PC1**), which is consistent with the closer approach of the imidazolium cation relative to **PC1**. The major difference, however, is in $\Delta H^{\ddagger}$, which is reduced to +7.3 kcal $mol^{-1}$ for **TS4**, compared to +26.1 kcal $mol^{-1}$ for **TS1**. Furthermore, the reaction is predicted to be exothermic by 15.8 kcal $mol^{-1}$, compared to an endothermic reaction when monodentate phosphines are coordinated. The results thus show that oxidative addition of imidazolium to chelated $Pd^0$ is strongly favored over that to linear $Pd(PR_3)_2$ species, and that the barrier to this reaction is also much lower when a chelating phosphine is present.

**2.4. Effect of Imidazolium Substituent.** The effect of different substituents at C2 on the oxidative addition of imidazoliums was studied initially by calculation of the reaction between Pd(dpe) and 1,3-dimethylimidazolium. Oxidative addition of the C−H bond to yield complex **5** is shown in Figure 3 (right column). In the precursor complex, **PC5**, the imidazolium cation closely interacts with the Pd center, resulting in distortion of the proton on $C_{carbenoid}$ out of the imidazolium plane and elongation of the $C_{carbenoid}$−H bond. This is reflected in the potential energy profile (Figure 4), which shows a large stabilization energy of 17.2 kcal $mol^{-1}$ for **PC5**. The transition structure is similar to the precursor complex, the main difference being a further elongation of the $C_{carbenoid}$−H bond and shortening of the Pd−$C_{carbenoid}$ and Pd−H distances. This geometrical similarity is consistent with the similar relative energies of **TS5** (−18.6 kcal $mol^{-1}$) and **PC5**.[66] Importantly, the results therefore predict that oxidative addition of 2-H imidazolium to Pd(dpe) occurs without an energy barrier. The energy of the product of oxidative addition **5** lies 27.5 kcal $mol^{-1}$ below that of the reactants, showing that addition of 2-H imidazolium is thermodynamically favored over addition of 2-alkylimidazolium.

The apparent oxidative addition of 2-halogenated thiazoliums to $Pd^0$ was reported some time ago by Stone and co-workers.[67] As oxidative addition of alkyl and aryl halides is facile compared to C−C or C−H activation, it was of interest to study this reaction using halo-imidazolium species for comparison with the oxidative addition using 2-H imidazolium. Thus, oxidative addition of the 2-bromo-1,3-dimethylimidazolium cation to Pd(dpe) was studied. The optimized geometries of the imidazolium cation and the product **6** are shown in Figure 5. No precursor complex or transition structure was found for the reaction. Optimization of the reactants when the imidazolium cation was positioned in the vicinity of Pd(dpe) (within 5 Å) always led to complex **6**. It is therefore concluded that the reaction occurs without barrier, as shown on the potential energy surface (Figure 4). This also shows that oxidative addition is strongly exothermic, with the product lying 65.1 kcal $mol^{-1}$ below the reactants. This result demonstrates that oxidative addition of 2-haloimidazoliums (halo = bromo, iodo, chloro) should occur and, in the case of bromo and iodo at least, should be very facile and easier than C−H or C−C oxidative addition.

**2.5. Effect of Ligand Substituent.** It was shown in a previous study[30] that placing hydrogens on the phosphine as in $PH_3$ is adequate for modeling the oxidative addition reaction, and that replacing $PH_3$ with a more realistic phosphine $[P(OPh)_3]$ leads to the same mechanism, but with different energetics. It is known that a less basic phosphine favors reductive elimination, as does increased steric bulk. It was therefore of interest to study the effect of a compact and highly basic phosphine on oxidative addition. The addition of the 1,3-dimethylimidazolium species to Pd[1,3-bis(dimethylphosphino)ethane] [Pd(dmpe)] to yield complex **7** was thus studied, as shown in Figure 6 (left column). Comparison of the geometry of **PC7** with **PC5** (which contains hydrogens in place of methyl groups on the phosphine) shows that the two are very similar, the imidazolium being slightly closer to Pd in **PC7**. The transition structures **TS7** and **TS5** are likewise very similar in geometry, as are the products. However, the potential energy profile for the reaction (Figure 7) reveals a stabilization energy of 25.0 kcal $mol^{-1}$ for **PC7** (cf. 17.2 kcal $mol^{-1}$ for **PC5**) and a transition structure that lies 27.3 kcal $mol^{-1}$ below the products.[66] The product of oxidative addition lies 39.9 kcal $mol^{-1}$ below the reactants. Thus, oxidative addition to give **7** is also predicted to occur with no barrier, but with a much greater exothermicity than that to give **5**. This is an important result, as it shows that oxidative addition of imida-

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(65) Sakaki, S.; Biswas, B.; Sugimoto, M. *J. Chem. Soc., Dalton Trans.* **1997**, 803.

(66) At the level of geometry optimisation (B3LYP/LANL2DZ), the precursor complex is slightly lower in energy than the transition structure.

(67) Fraser, P. J.; Roper, W. R.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1974**, 102.

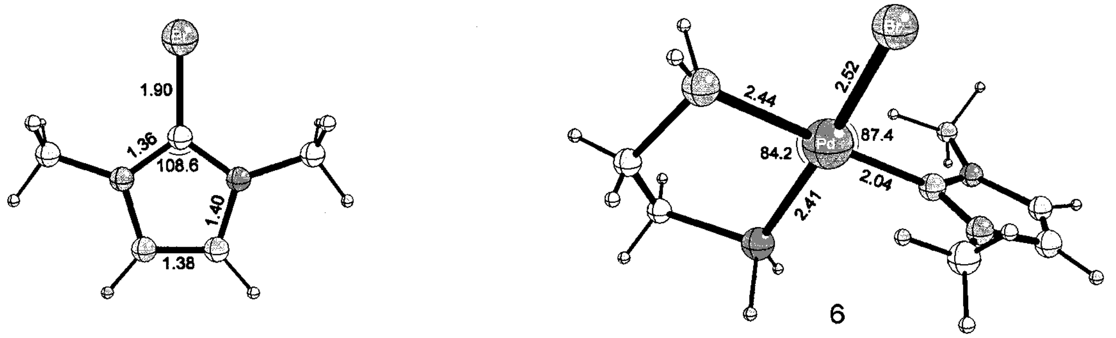


**Figure 5.** Optimized geometries of 2-bromo-1,3-dimethylimidazolium and the product of oxidative addition to Pd(dpe), **6**.

zolium to an actual $Pd^0$ complex may be strongly favored over reductive elimination.

Oxidative addition to $Pd(PMe_3)_2$ was also studied to see if the reaction would be possible without the benefit of chelation. The optimized geometries of the stationary points are shown in the right column in Figure 6. As expected, the P−Pd−P angles in the precursor complex, transition structure, and product are greater than those in the chelated analogues shown on the left of Figure 6. In the precursor complex **PC8**, the imidazolium is slightly farther away from the Pd center than in **PC7**, but the Pd−ligand bond lengths in **TS8** and **8** are almost identical to those in **TS7** and **7**. The potential energy profile (Figure 7) shows a stabilization energy of 6.8 kcal $mol^{-1}$ for **PC8** and a transition structure that lies 9.0 kcal $mol^{-1}$ below the reactants. The reaction is therefore predicted to occur with no energy barrier, with the product lying 18.7 kcal $mol^{-1}$ below the reactants. Accordingly, it should be possible to carry out oxidative addition of the imidazolium cation to an appropriate $Pd^0L_2$ complex, even without the aid of a chelating phosphine.

**2.6. Summary of Theoretical Studies.** The results of the density functional studies show that those factors affecting conventional oxidative addition likewise affect oxidative addition of imidazolium cations. The factors that are predicted to favor oxidative addition for the group 10 metals can be summarized as follows:

(i) Oxidative addition of imidazolium cations to $Pt^0$ and $Ni^0$ is more exothermic than that to $Pd^0$, and $Ni^0$ will react with a lower energy barrier.

(ii) A cis-chelating ligand on the $M^0$ complex both increases the exothermicity of the reaction and lowers the activation barrier relative to monodentate ligands.

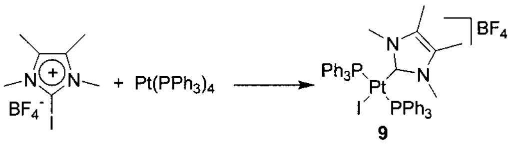
(iii) Addition of 2-H imidazolium groups is easier and more exothermic than addition of the 2-alkylimidazolium moiety. A halo-imidazolium group should further lower the barrier and increase the exothermicity.

(iv) A compact, strongly basic phosphine lowers the activation barrier and increases the exothermicity of the reaction.

From this it can be seen that the ideal candidate for oxidative addition of imidazolium would consist of a highly basic, chelating phosphine ligated to $Pt^0$ or $Ni^0$. However, the theoretical results show that not all of these conditions should be required, and that $Pd^0$ in combination with basic phosphines, even unidentate, may be able to oxidatively add the 2-H imidazolium cation.

## 3. Oxidative Addition: Experimental Studies

As, based on the theoretical studies, oxidative addition of a 2-haloimidazolium moiety was expected to be facile, and as Stone et al.[67] had previously reported the oxidation addition of 2-halothiazolium salts, 2-iodo-1,3,4,5-tetramethylimidazolium tetrafluoroborate was prepared following the method of Arduengo.[68] When the iodoimidazolium salt was suspended in a THF solution of $Pt(PPh_3)_4$ and heated to 60 °C, the iodo Pt−carbene complex $[PtI(tmiy)(PPh_3)_2]BF_4$ (**9**) (tmiy = 1,3,4,5-tetramethylimidazolin-2-ylidene) was formed in 89% yield (reaction 3). The $^{31}P$ NMR spectrum of **9**, which contains a singlet at 13.8 ppm with Pt satellites ($J_{P-Pt}$ = 1234 Hz), indicates a trans arrangement of the phosphine ligands. Evidently, isomerization of the cis complex that would initially result from oxidative addition has occurred. Isomerization of related Pt−carbene complexes has been previously reported.[55,69]



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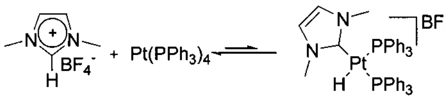
(3)

Single crystals suitable for an X-ray structure determination were grown by vapor diffusion of ether into a dichloromethane (DCM) solution of **9**. The X-ray study confirms a trans arrangement of the phosphine ligands and a nearly perfect square planar coordination geometry (Figure 8), the cations lying with their $[IPt(N_2C_3(methyl-CH)_4)]$ components disposed in the crystallographic mirror planes of space group *Pnma* (anionic $F_2BF_2$ disposed similarly). The Pt−C distance (1.995(5) Å) is similar to that found in other Pt−carbene complexes;[70,71] the carbene ligand skeleton is obligate planar and coplanar with Pd, I and normal to the $IPtP_2C$ plane.

The reactivity of $Pt(PPh_3)_4$ toward 1,3-dimethylimidazolium tetrafluoroborate was also investigated.[55] Heating equimolar quantities of the imidazolium salt and $Pt(PPh_3)_4$ in THF/acetone (60 °C) resulted in the formation of ca. 15% (NMR) of the oxidative addition product *cis*-$[PtH(dmiy)(PPh_3)_2]BF_4$ (**10**) (dmiy = 1,3-dimethylimidazolin-2-ylidene) relative to unreacted imidazolium and $Pt(PPh_3)_4$ (reaction 4). It was concluded that the low amount of **10** resulting was not a consequence of a high energy barrier to oxidative addition but, rather, a representation of the equilibrium concentration of the reactants and



10

(4)

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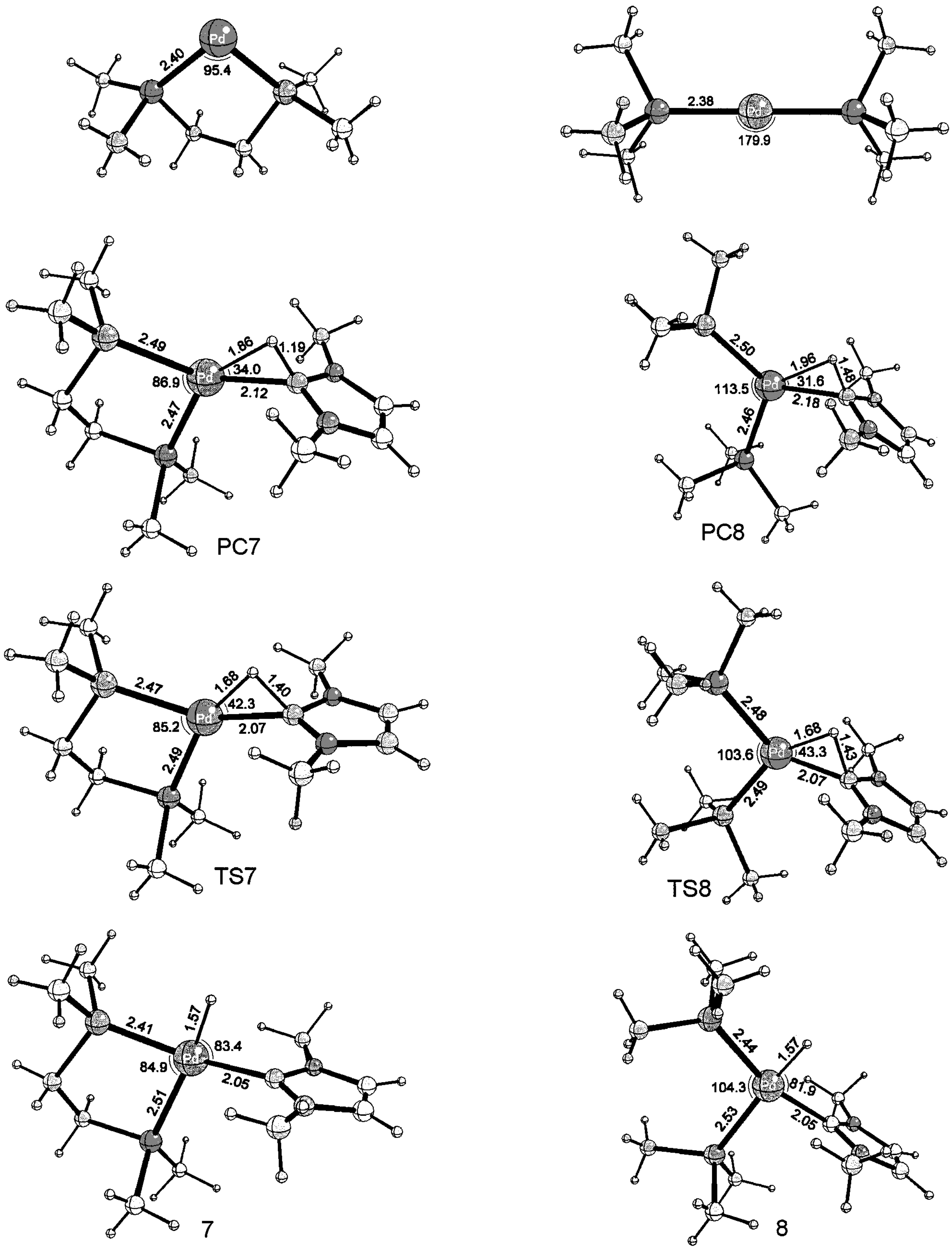

**Figure 6.** Optimized geometries corresponding to oxidative addition of 1,3-dimethylimidazolium to Pd(dmpe) and Pd($PMe_3$)$_2$.

product, so that the $\Delta G_{\mathrm{react}}$ value is therefore close to zero. Oxidative addition to Pt($PPh_3$)$_4$ requires concomitant dissociation of two phosphine ligands, which is expected to result in the reaction being less exothermic (or more endothermic). It was therefore anticipated that starting with the unsaturated 14-electron complex Pt($PPh_3$)$_2$ may be enough to drive the reaction to completion. Indeed, when Pt($PPh_3$)$_2$ was reacted with 1,3-dimethylimidazolium tetrafluoroborate in THF/acetone, complex *cis*-**10** was isolated pure in 63% yield as an air-stable white powder. Thus, by eliminating two phosphines from the coordination sphere of Pt, the equilibrium is driven substantially in the forward direction, allowing isolation of the product in good

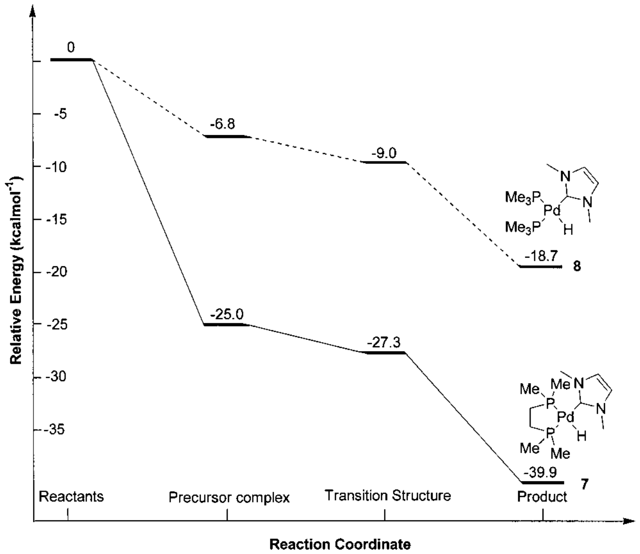

**Figure 7.** Potential energy profile for the oxidative addition of 1,3-dimethylimidazolium to Pd(dmpe) and Pd($PMe_3$)$_2$.

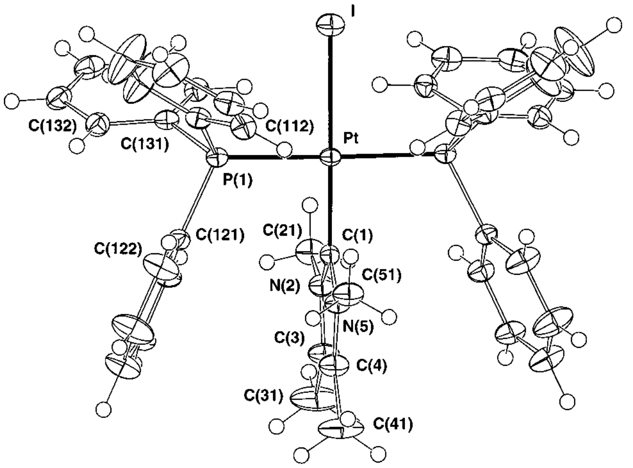

**Figure 8.** Projection of **9**, normal to the coordination plane. Thermal ellipsoids with 50% probability are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Selected bond lengths (Å) and angles (°): Pt−I 2.6449(5), Pt−C(1) 1.995(5), Pt−P(1) 2.315(1), C(1)−N(2) 1.343(6), C(1)−Pt−I 177.8(1), C(1)−Pt−P(1) 90.98(2), P(1)−Pt−I 89.08(2), P(1)−Pt−P(1′) 176.20(3).

yield. Complex **10** has been characterized by $^1$H, $^{13}$C, $^{31}$P NMR, high-resolution MS, and elemental analysis.

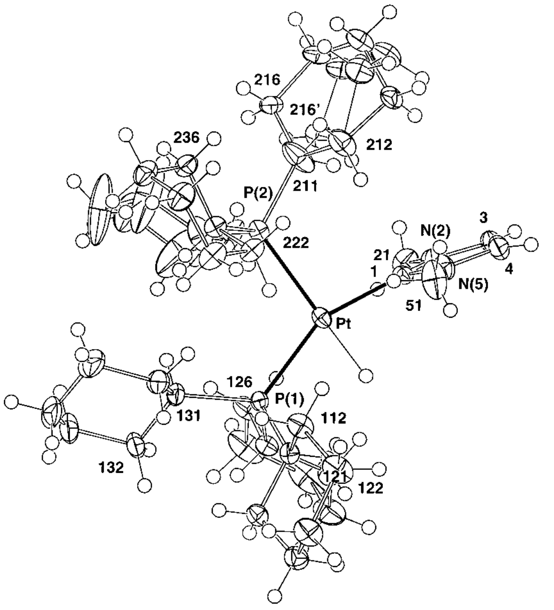

**Figure 9.** Projection of *cis*-**11**. Selected bond lengths (Å) and angles (°): Pt−C(1) 2.028(3), Pt−P(1) 2.3076(9), Pt−P(2) 2.3693(9), C(1)−Pt−P(1) 154.44(9), C(1)−Pt−P(2) 97.91(9), P(1)−Pt−P(2) 107.61(3).

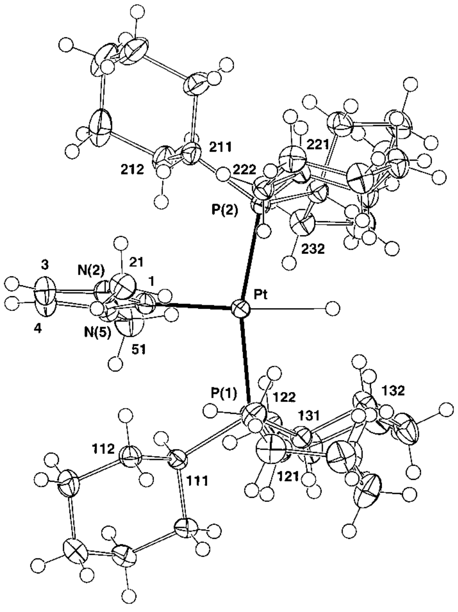

**Figure 10.** Projection of *trans*-**11**. Selected bond lengths (Å) and angles (°): Pt−C(1) 2.058(3), Pt−P(1) 2.3020(8), Pt−P(2) 2.2976(8), C(1)−Pt−P(1) 98.03(8), C(1)−Pt−P(2) 97.35(8), P(1)−Pt−P(2) 163.28(2).

The unsaturated Pt$^0$ complex Pt($PCy_3$)$_2$ is also available by way of a straightforward synthesis.[72] It was therefore of interest to determine if this complex underwent oxidative addition of the imidazolium cation, as the bulky $PCy_3$ ligand has been shown to promote reductive elimination of methyl-imidazolium from Pd$^{II}$.[30] When Pt($PCy_3$)$_2$ and 1,3-dimethylimidazolium tetrafluoroborate were heated together in THF/acetone at 60 °C, [PtH(dmiy)($PCy_3$)$_2$]$BF_4$ (**11**) was formed in 60% isolated yield. A cis geometry for **11** was inferred from the $^{31}$P and $^1$H NMR data. The Pt−H resonance appears as a doublet of doublets at −7.95 ppm with Pt satellites ($J_{P-H} = 160$, 21 Hz, $J_{Pt-H} = 880$ Hz). When crystals of **11** were grown from DCM/pentane over a number of days, two different forms of crystals were obtained, trans and cis. An X-ray study of a prismatic specimen showed that phase to be *cis*-**11**, consistent with the spectroscopic data (Figure 9). A significantly distorted square planar core geometry is displayed, with a P−Pt−P angle of 107.61(3)°. This distortion from square planar geometry is attributed to the bulk of the $PCy_3$ ligands, which push each other apart, crowding the carbene ligand to such an extent that the P(2)−Pt−C angle is opened to 97.91(9)°. The crystal structure of **11** is thus consistent with the notion that bulky cis ligands will push cis carbene and hydrocarbyl groups together and facilitate reductive elimination.[30] The Pt−C distance (2.028(3) Å) is longer than that in **9**, reflecting steric crowding and a higher trans influence of $PCy_3$ relative to that of the iodide ligand. Also noticeable is the difference between the two Pt−P distances, the bond length trans to the hydride (2.3693(9) Å) being longer than Pt−P trans to the carbene (2.3076(9) Å), a reflection of the higher trans influence of the hydride ligand. A similar trend is observed in the theoretical geometries of the hydride complexes **5**, **7**, and **8**. An X-ray study of a specimen of the needle phase showed it

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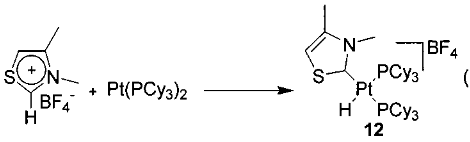
[72] Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 113.

to be *trans*-**11**, as shown in Figure 10. A distorted square planar core geometry is displayed, the distortion less than that found in *cis*-**11** due to the trans arrangement of the phosphines. The phosphine ligands are both bent away from the carbene ligand, reflecting the low steric demand of the hydride. The Pt−C distance (2.058(3) Å) is slightly elongated relative to that in *cis*-**11** due to the high trans influence of the hydride ligand. The formation of the trans isomer must result from a slow *cis*−*trans* isomerization in solution over the period of crystallization.

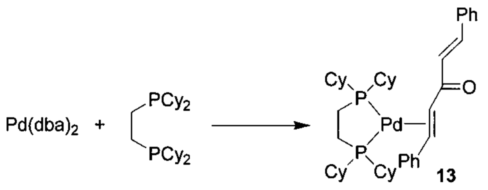
Crystal structures of hydrido carbene complexes are rare,[73,74] and the two structures above represent the first examples for the group 10 metals. The formation of **11**, which contains a very bulky phosphine, can be attributed to the greater tendency of Pt toward oxidative addition relative to Pd, the strong donor nature of $PCy_3$, and the low steric demand of the hydride ligand. Notably, the above results demonstrate for the first time that oxidative addition of the imidazolium cation to yield a M−hydride complex is possible. Oxidative addition of the imidazolium ion to give complexes **10** and **11** is the first example of oxidative addition of a C−H bond to a $Pt^0$ complex which does not contain a chelating ligand,[49−51] hitherto thought to be requisite for this reaction.[54]

Stone et al.[67] had previously reported oxidative addition of 2-halothiazolium cations to $M^0$, and the above theoretical studies have shown that this reaction probably occurs via the same mechanism of concerted oxidative addition as that of 2-H imidazolium addition. Consequently, it was decided to investigate the reaction of 3,4-dimethylthiazolium tetrafluoroborate with $Pt(PCy_3)_2$. The heating of a THF solution of these reactants to 60 °C afforded $[PtH(dmty)(PCy_3)_2]BF_4$ (**12**) (dmty = 3,4-dimethylthiazolin-2-ylidene), isolated in 23% yield as a yellow powder (reaction 5). A cis geometry is indicated by the spectroscopic data. The Pt−H resonance appears as a doublet of doublets ($J_{P-H}$ = 24, 159 Hz) centered at −7.49 ppm with Pt satellites ($J_{Pt-H}$ = 444 Hz). The formation of complex **12** confirms that the thiazolium cation shares similar reactivity with the imidazolium cation, in that it is also capable of oxidative addition—and probably reductive elimination—reactivity with metals. This is an important result, as it shows that hydrocarbyl complexes of thiazolin-2-ylidenes may also be prone to decomposition via carbene−hydrocarbyl coupling. Complexes of thiazole-based carbenes have recently been investigated as catalysts for C−C coupling.[26]



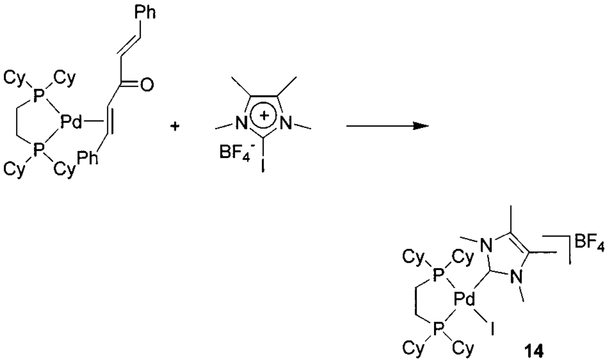
(5)

To study the oxidative addition behavior of $Pd^0$, complex **13** was prepared (reaction 6). Complex **13** contains the chelating phosphine 1,3-bis(dicyclohexylphosphino)ethane (dcype). Dissociation of the weakly coordinating dba ligand from **13** would generate the reactive $Pd^0(P\wedge P)$ fragment. The Pt analogue to this species has been used by Whitesides et al.[49−51] to carry out C−H bond oxidative addition of hydrocarbons. Complex **13** gives broad signals in the $^1H$ NMR spectrum at ambient temperature, ascribed to fluxional behavior of the dba ligand. At −40 °C, the signals sharpen and the coordinated olefinic protons appear as two multiplets at 4.83 and 5.01 ppm. The same behavior has been described for similar $Pd^0$−dba complexes.[75,76] Recrystallization of **13** from DCM/pentane afforded yellow crystals which were identified as $Pd(dcype)Cl_2$:dba 1:1 "solvate" by an X-ray study.[77] This complex is most likely formed after an initial oxidative addition of DCM,[78] indicating that **13** has a high reactivity toward oxidative addition.



(6)

Complex **13** was found to react with 2-iodo-1,3,4,5-tetramethylimidazolium tetrafluoroborate under conditions analogous to those used with $Pt(PPh_3)_4$ to yield $[PdI(tmiy)(dcype)]BF_4$ (**14**) in 72% yield (reaction 7). It was therefore decided to study its reactivity toward 1,3-dimethylimidazolium tetrafluoroborate. When **13** was treated at room temperature with an equimolar quantity of the imidazolium salt, no change was evident by NMR. When excess imidazolium was added (4 equiv added to push the equilibrium in favor of oxidative addition), a reaction took place that resulted in decomposition and formation of Pd metal and free dba. The fate of the other organic groups could not be reliably determined by NMR. Therefore, it cannot be confidently stated at this stage whether **13** oxidatively adds the imidazolium ion and then subsequently decomposes, or whether it decomposes from $Pd^0$ by some interaction of the imidazolium ion. It is known, however, that hydrido Pd complexes are less stable than their Pt equivalents.[79] Further work on the oxidative addition of imidazoliums to Pd and Ni is underway.



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(77) Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Acta Crystallogr., Sect. C* **1994**, *50*, 217 reports the unsolvated form. In this work, $[(dcype)PdCl_2]\cdot$dba, $C_{43}H_{62}Cl_2OP_2Pd$, $M_r = 834.2$, is orthorhombic, space group $Pna2_1$, $a = 13.4790(7)$ Å, $b = 19.785(4)$ Å, $c = 15.697(3)$ Å, $V = 4186$ Å$^3$, $D_c = 1.324$ g cm$^{-3}$ ($Z = 4$), $T \approx 153$ K; 78 429 total reflections (full sphere) were merged after "empirical"/multiscan absorption correction ($\mu_{Mo} = 6.8$; specimen 0.60 × 0.30 × 0.22 mm, "$T$"$_{min, max}$ = 0.66, 0.80) to 10 658 ($R_{int}$ = 0.030) unique ($x_{abs}$ being found indeterminate of chirality), 8402 ($F > 4\sigma(F)$) used in full-matrix least-squares refinement ($R = 0.044$, ($R_w = 0.050$; $|\Delta\rho_{max}| = 2.3(1)$ e Å$^{-3}$.) One Cy ring was disordered over two sets of sites (occupancy, 0.758(7) and complement); the olefinic carbons of dba were also modeled as disordered over two sets of (trans) sites of equal occupancy. Results of the two determinations are generally harmonious.

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**Table 1.** Crystal Data, Collection, and Refinement Parameters for Complexes **9**, *cis*-**11**, and *trans*-**11**

| crystal data | **9** | *cis*−**11** | *trans*−**11** |
|---|---|---|---|
| solvation component | $2CH_2Cl_2$ | $2CH_2Cl_2$ | |
| formula | $C_{45}H_{46}BCl_4F_4IN_2P_2Pt$ | $C_{43}H_{79}BCl_4F_4N_2P_2Pt$ | $C_{41}H_{75}BF_4N_2P_2Pt$ |
| molecular weight | 1227.4 | 1109.8 | 939.9 |
| crystal size (mm) | 0.2 × 0.17 × 0.1 | 0.12 × 0.10 × 0.07 | 0.45 × 0.12 × 0.10 |
| crystal system | orthorhombic | triclinic | monoclinic |
| space group | *Pnma* | $P\bar{1}$ | $P2_1/n$ |
| $a$ (Å) | 18.989(1) | 11.5338(7) | 12.245(3) |
| $b$ (Å) | 15.970(1) | 15.0977(9) | 16.533(4) |
| $c$ (Å) | 15.586(1) | 15.1892(9) | 21.360(4) |
| α (°) | | 85.795(2) | |
| $\beta$ (°) | | 75.590(2) | 96.348(5) |
| $\gamma$ (°) | | 75.522(2) | |
| $V$ (Å$^3$) | 4726 | 2480 | 4298 |
| $Z$ | 4 | 2 | 4 |
| $\rho_c$ (g cm$^{-3}$) | 1.725 | 1.486 | 1.453 |
| | Data Collection and Refinement Parameters[a] | | |
| $\mu$ (cm$^{-1}$) | 39.7 | 31.6 | 33.9 |
| $2\theta_{max}$ (°) | 75 | 76 | 76 |
| total reflctns | 97 594 | 51 715 | 87 494 |
| indepdnt reflctns | 12 903 | 25 611 | 22 535 |
| “observed” reflctns | 8555 ($F > 4\sigma(F)$) | 16 855 ($F > 4\sigma(F)$) | 15 025 ($F > 4\sigma(F)$) |
| “$T$” (min, max) | 0.51, 0.77 | 0.63, 0.78 | 0.48, 0.76 |
| $R$, $R_w$ | 0.045, 0.053 | 0.045, 0.039 | 0.038, 0.040 |

[a] Full spheres of CCD area detector data ($T \approx 153$ K), merged after empirical/multiscan absorption correction. Anisotropic thermal parameters form refinement (non-H atom), $(x, y, z, U_{iso})_H$ constrained at estimated values (hydrido-H observed in difference maps for **11**). Reflection weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$; neutral atom complex scattering factors. Monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å. In **9**, residues modeled as $CH_2Cl_2$ were modeled as disordered over two sets of sites, occupancy 0.750(7) and complement. In *cis*-**11**, one Cy ring was disordered over two sets of sites, occupancies 0.5, with three of the $BF_4$ fluorines rotationally disordered over two sets of sites, occupancy 0.729(3) and complement.

## 4. Conclusions

Theoretical density functional studies have shown which factors can be expected to favor oxidative addition of the imidazolium cation to zerovalent group 10 metals. Pt and Ni should react most readily; however, the results suggest that with appropriate supporting ligands and under appropriate reaction conditions, all three of the metals should undergo oxidative addition. The prediction that oxidative addition can occur has been confirmed by experiment for the first time, and three new hydrido Pt−carbene complexes have been prepared by this reaction.

These results confirm that a potentially important method of limiting decomposition of M−carbene catalysts will be to operate in imidazolium-based ionic liquids. For this reason, catalysts based on heterocyclic carbene complexes should be particularly suited to reactions in ionic liquids. Studies on the application of Ni−carbene complexes for olefin dimerization in an imidazolium-based ionic liquid will be reported shortly. Furthermore, these results show unambiguously for the first time the “noninnocent” role of ionic liquid solvents—the imidazolium cation can react with low-valent metal complexes to generate a carbene complex in situ. While interaction of the imidazolium cation with $Pd(OAc)_2$ has been shown to yield carbene complexes,[46] this work shows that a basic metal salt is not necessarily required to deprotonate the imidazolium. Thus, when group 10 metal complexes, particularly $M^0$ complexes, are used in imidazolium-based ionic liquids, the possibility that carbene complexes are generated and act as the active species must be considered. The large excess of imidazolium present under these conditions can be expected to drive the oxidative addition reaction. Furthermore, the supporting ligands studied herein and found using both theoretical and experimental methods to promote oxidative addition are commonly used ligands in catalysis. It is noted that oxidative addition of an imidazolium ion would generate a reactive metal hydride that could initiate many catalytic cycles involving unsaturated substrates.

## 5. Experimental Section

**5.1. General Comments.** All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox. All solvents were purified and dried by standard procedures and distilled under nitrogen immediately before use. Nuclear magnetic resonance 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 and MS were carried out by the Central Science Laboratory, University of Tasmania. X-ray structure determinations are summarized in Table 1. $Pt(PPh_3)_4$,[80] $Pt(PPh_3)_2$,[81] and $Pt(PCy_3)_2$[72] were prepared by literature methods.

**5.2. Synthesis. 2-Iodo-1,3,4,5-tetramethylimidazolium Tetrafluoroborate.** This compound was prepared via a method similar to that used by Arduengo et al.[68] to prepare related imidazolium salts. The free carbene tmiy (2.03 g, 16.3 mmol) was dissolved in THF (20 mL), and a solution of iodine (4.15 g, 16.3 mmol, 40 mL of THF) was added dropwise over 1 h. After addition, the solution was stirred for a further 30 min before the precipitate was collected by filtration. The product was washed with THF followed by ether and then dried in vacuo to yield 2-iodo-1,3,4,5-tetramethylimidazolium iodide. The iodide (1.71 g, 4.52 mmol) was suspended in water/MeOH (1:3), and an aqueous solution of $AgBF_4$ was added (prepared by stirring 0.52 g (2.24 mmol) of $Ag_2O$ in water with 0.79 g of 50% $HBF_4$). The solids were collected on a filter paper and extracted with THF followed by DCM. The organics were then removed in vacuo, and the product was washed with THF/ether. $^1$H NMR (200 MHz, DMSO-$d_6$): $\delta$ 3.75 (s, 6H, NC*H*$_3$), 2.32 (s, 6H, CC*H*$_3$). $^{13}$C NMR (50 MHz, DMSO-$d_6$): $\delta$ 129.6 ($H_3$C*C*CCH$_3$), 100.1 (*C*I), 36.4 (N*C*H$_3$), 9.1 (H$_3$*C*CCCH$_3$).

**3,4-Dimethylthiazolium Tetrafluoroborate.** Thiazole (4.81 g, 0.0485 mol) and MeI (4 mL, 0.06 mol) were added to a reaction bomb along with 10 mL of THF and heated to 90 °C for 2 days. A solid yellow cake was obtained that was collected on a Schlenk filter and washed with THF (50 mL). The compound was dried in vacuo to yield a yellow powder, 3,4-dimethylthiazolium iodide. Yield: 11.9 g (100%). The iodide (6.30 g, 0.0261 mol) was taken up in EtOH/MeOH (50/50,

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100 mL), and a MeOH solution of $AgBF_4$ (prepared from 3.20 g, 0.0138 mol of $Ag_2O$ and 3.4 mL of 50% $HBF_4$ solution) was added. The solution was dried over molecular sieves and filtered to remove AgI, and the solvent was removed in vacuo until ca. 20 mL remained. Ether (20 mL) was added, and the solvent was decanted. The remaining oil was washed with ether, dried in vacuo, and washed again with ether. Drying in vacuo over a warm water bath gave a white powder. Yield: 2.79 g (53%). $^1$H NMR (200 MHz, $D_2O$): $\delta$ 9.75 (s, 1H, SC(*H*)N), 7.76 (s, 1H, SC*H*), 4.10 (s, 3H, NC*H*$_3$), 2.54 (s, 3H, CC*H*$_3$). $^{13}$C NMR (50 MHz, $D_2O$): $\delta$ 160.5 (S*C*N), 123.0 (N*C*CH$_3$), 116.0 (S*C*), 42.5 (N*C*H$_3$), 15.3 (C*C*H$_3$).

**[PtI(tmiy)(PPh$_3$)$_2$]BF$_4$ (9).** 2-Iodo-1,3,4,5-tetramethylimidazolium tetrafluoroborate (0.0403 g, 0.119 mmol) and Pt(PPh$_3$)$_4$ (0.144 g, 0.116 mmol) were taken up in THF (30 mL) and heated to 65 °C for 24 h. The solvent was removed until ca. 2 mL remained, ether (10 mL) was added, and the solvent was decanted off the precipitate. After washing with THF/ether (2 mL/10 mL) and ether (2 × 5 mL), the product was dried in vacuo to give a white powder. Yield: 0.109 g (89%). Anal. Calcd for $C_{43}H_{42}N_2IP_2PtBF_4$: C, 48.83; H, 4.00; N, 2.65. Found: C, 48.09; H, 4.24; N, 2.42. MS (LSIMS): *m*/*z* (relative intensity) 970 [M]$^+$ (11); 708 [M − PPh$_3$]$^+$ (10); 580 [M − PPh$_3$I]$^+$ (25). $^1$H NMR (200 MHz, $CD_2Cl_2$): $\delta$ 7.6−7.4 (m, 30H, phenyl*H*), 3.11 (singlet with Pt satellites, $J_{\mathrm{Pt-H}} = 3$ Hz, 6H, NC*H*$_3$), 1.62 (s, 6H, CC*H*$_3$). $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$: 134.3 (singlet with Pt satellites, $J_{\mathrm{Pt-C}} = 6$ Hz, phenyl*C*), 131.6 (phenyl*C*), 128.9 (m, phenyl*C*), 128.7 (singlet with Pt satellites, $J_{\mathrm{Pt-C}} = 5$ Hz, *C*═*C*), 127.0 (phenyl*C*), 34.3 (N*C*H$_3$), 8.6 (C*C*H$_3$). $^{31}$P NMR (161 Hz, $CD_2Cl_2$): $\delta$ 13.8 (singlet with Pt satellites, $J_{\mathrm{P-Pt}} = 1234$ Hz).

**[PtH(dmiy)(PPh$_3$)$_2$]BF$_4$ (10).** Pt(PPh$_3$)$_2$ (0.247 g, 0.343 mmol) was dissolved in 10 mL of THF, and a solution of 1,3-dimethylimidazolium tetrafluoroborate (0.126 g, 0.68 mmol) in 10 mL of acetone was added. The heterogeneous solution was stirred at 60 °C for 18 h and filtered through Celite. The solvent was removed in vacuo, and the residue was taken up in 2.5 mL of DCM and extracted with water (3 × 4 mL). The solvent was then removed in vacuo, and the product was washed further with water (2 × 4 mL) and ether (2 × 5 mL). Drying in vacuo gave a white powder. Yield: 0.196 g (63%). Anal. Calcd for $C_{41}H_{39}N_2P_2PtBF_4$: C, 54.50; H, 4.35; N, 3.10. Found: C, 54.32; H, 4.32; N, 3.02. HRMS (LSIMS): *m*/*z* calcd for $C_{41}H_{39}N_2P_2$195Pt, 816.22361; found, 816.22419. MS (LSIMS): *m*/*z* (relative intensity) 816 [M]$^+$ (100); 719 [Pt(PPh$_3$)$_2$]$^+$ (50); 553 [M − PPh$_3$H]$^+$ (80); 455 [PPh$_3$]$^+$ (25). $^1$H NMR (200 MHz, $CD_2Cl_2$): $\delta$ 6.79 (singlet with Pt satellites, $J_{\mathrm{Pt-H}} = 6$ Hz, 2H, *H*C═C*H*), 3.50 (singlet with Pt satellites, $J_{\mathrm{Pt-H}} = 2$ Hz, 6H, NC*H*$_3$), −5.23 (dd with Pt satellites, $J_{\mathrm{P-H}} = 19$, 176 Hz, $J_{\mathrm{Pt-H}} = 511$ Hz, 1H, Pt*H*). $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ 134.3 (d, $J = 12$ Hz, Ph*C*), 133.6 (d, $J = 12$ Hz, Ph*C*), 131.2 (s, br, Ph*C*), 128.8 ("t", $J = 11$ Hz, Ph*C*), 122.9 (s with Pt satellites, $J_{\mathrm{P-C}} = 4$ Hz, $J_{\mathrm{Pt-C}} = 16$ Hz, H*C*═*C*H), 37.6 (s with Pt satellites, $J = 20$ Hz, N*C*H$_3$). $^{31}$P NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 24.0 (d with Pt satellites, $J_{\mathrm{P-P}} = 18$ Hz, $J_{\mathrm{P-Pt}} = 654$ Hz), 20.1 (d with Pt satellites, $J_{\mathrm{P-P}} = 18$ Hz, $J_{\mathrm{P-Pt}} = 663$ Hz).

**[PtH(dmiy)(PCy$_3$)$_2$]BF$_4$ (11).** This was prepared in the same manner as **10** from Pt(PCy$_3$)$_2$ (0.099 g, 0.13 mmol) and 1,3-dimethylimidazolium tetrafluoroborate (0.0248 g, 0.134 mmol) to give a white solid. Yield: 0.074 g (60%). Anal. Calcd for $C_{41}H_{75}N_2P_2PtBF_4$: C, 52.39; H, 8.04; N, 2.98. Found: C, 52.29; H, 8.03; N, 2.89. MS (LSIMS): *m*/*z* (relative intensity) 852 [M]$^+$ (65), 756 [M − dmiyH]$^+$ (10), 571 [M − PCy$_3$H]$^+$ (100), 281 [HPCy$_3$]$^+$ (15). $^1$H NMR ($CD_2Cl_2$, 400 MHz): $\delta$ 7.16 (s with Pt satellites, $J_{\mathrm{Pt-H}} = 4$ Hz, 2H, *H*C═C*H*), 3.67 (s, 6H, NC*H*$_3$), 1.0−2.2 (m, 66H, Cy*H*), −7.95 (dd with Pt satellites, $J_{\mathrm{P-H}} = 160$, 21 Hz, $J_{\mathrm{Pt-H}} = 880$ Hz, 1H, Pt*H*). $^{13}$C NMR ($CD_2Cl_2$, 100 MHz): $\delta$ 123.1 (d with Pt satellites, $J_{\mathrm{P-C}} = 3$ Hz, $J_{\mathrm{Pt-C}} = 16$ Hz, H*C*═*C*H), 38.0−38.5 (m, Cy*C*), 37.7 (s, N*C*H$_3$), 30.8 (s with Pt satellites, Cy*C*), 30.7 (s, Cy*C*), 27.9−27.7 (m, Cy*C*), 26.6, 26.3 (s, Cy*C*). $^{31}$P NMR (162 MHz, $CD_2Cl_2$): $\delta$ 29.1 (d with Pt satellites, $J_{\mathrm{P-P}} = 18$ Hz, $J_{\mathrm{P-Pt}} = 1265$ Hz), 29.7, 29.8 (two doublets attributed to two conformations of the bulky PCy$_3$ ligand, with Pt satellites, $J_{\mathrm{P-P}} = 18$ Hz, $J_{\mathrm{P-Pt}} = 990$ Hz).

**[PtH(dmty)(PCy$_3$)$_2$]BF$_4$ (12).** This was prepared in the same manner as **10**, from Pt(PCy$_3$)$_2$ (0.080 g, 0.10 mmol) and 3,4-dimethylthiazolium tetrafluoroborate (0.087 g, 0.43 mmol) to yield a yellow powder. Yield: 0.022 g (23%). Anal. Calcd for $C_{41}H_{74}NSP_2PtBF_4$: C, 51.46; H, 7.79; N, 1.46. Found: C, 51.33; H, 8.38; N, 1.38. MS (LSIMS): *m*/*z* (relative intensity) 869 [M]$^+$ (80), 755 [Pt(PCy$_3$)$_2$]$^+$ (55), 588 [Pt(PCy$_3$)$_2$ − Cy]$^+$ (100), 504 [Pt(PCy$_3$)$_2$ − 2Cy]$^+$ (25), 281 [HPCy$_3$]$^+$ (70). $^1$H NMR (200 MHz, $CD_2Cl_2$): $\delta$ 7.27 (s with Pt satellites, $J_{\mathrm{Pt-H}} = 7$ Hz, 1H, SC*H*), 3.96 (s, 3H, NC*H*$_3$), 2.44 (s, 3H, CC*H*$_3$), 0.8−2.2 (m, 66H, Cy*H*), −7.49 (dd with Pt satellites, $J_{\mathrm{P-H}} = 24$, 159 Hz, $J_{\mathrm{Pt-H}} = 444$ Hz, 1H, Pt*H*). $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ 38.2 (N*C*H$_3$), 35.9 (d, Cy*C*), 30.6 (Cy*C*), 30.4 (m, Cy*C*), 27.6 (m, Cy*C*), 27.2 (Cy*C*), 26.5 (d, Cy*C*), 14.6 (C*C*H$_3$). $^{31}$P NMR (161 Hz, $CD_2Cl_2$): $\delta$ 28.9 (d, with Pt satellites, $J_{\mathrm{P-P}} = 15$ Hz, $J_{\mathrm{Pt-P}} = 1278$ Hz), 27.0 ("t" attributed to conformations of the PCy$_3$ ligand, with Pt satellites, $J_{\mathrm{P-P}} = 15$ Hz, $J_{\mathrm{Pt-P}} = 985$ Hz).

**Pd(dcype)(dba) (13).** Pd(dba)$_2$ (0.59 g, 1.03 mmol) and dcype (0.44 g, 1.04 mmol) were dissolved in toluene (30 mL) and stirred for 3 days. The solvent was removed in vacuo, and the residue was taken up in THF (25 mL) and filtered through Celite. The THF was removed in vacuo until ca. 5 mL remained, and pentane (20 mL) was added to precipitate the product. The solvent was decanted off, the solid washed with pentane/ether (10 mL/10 mL, 3×), and the product dried in vacuo to give an orange powder. Yield: 0.426 g (54%). MS (LSIMS): *m*/*z* (relative intensity) 763 [M]$^+$ (20), 528 [M − dba]$^+$ (100), 445 [M − dba − Cy]$^+$ (33), 363 [M − dba − 2Cy]$^+$ (35), 281 [M − dba − 3Cy]$^+$ (28). $^1$H NMR (200 MHz, $CD_2Cl_2$, −40 °C): $\delta$ 6.8−7.8 (m, 12H, Ph*H*, *H*C═C*H*), 5.01 (m, 1H, *H*C═CH), 4.83 (m, 1H, HC═C*H*), 0.5−2.2 (br, m, 48H, Cy*H*, PC*H*$_2$). $^{13}$C NMR (50 MHz, $CD_2Cl_2$, −60 °C): $\delta$ 129.7, 129.6, 129.1 (Ph*C*), 25.9−27.9 (m, Cy*C*). $^{31}$P NMR (161 Hz, $CD_2Cl_2$, 15 °C): $\delta$ −1.29, −3.56 (s, br).

**[PdI(dcype)(tmiy)]BF$_4$ (14).** This complex was prepared by a method similar to that employed for the synthesis of **9**, from Pd(dcype)(dba) (**13**) (0.095 g, 0.12 mmol) and 2-iodo-1,3,4,5-tetramethylimidazolium tetrafluorborate (0.0426, 0.126) to afford an orange powder. Yield: 0.075 g (72%). Anal. Calcd for $C_{33}H_{60}N_2P_2IPdBF_4$: C, 45.72; H, 6.98; N, 3.23. Found: C, 45.47; H, 6.45; N, 3.44. MS (LSIMS): *m*/*z* (relative intensity) 779 [M]$^+$ (10), 655 [M − tmiy]$^+$ (65). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 3.76 (s, 6H, NC*H*$_3$), 2.23 (s, 6H, CC*H*$_3$), 1.2−2.2 (broad humps, 48H, Cy*H*, PC*H*$_2$). $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ 127.3 (*C*═*C*), 33.6 (N*C*H$_3$), 30.6, 29.4, 26.9 (br), 25.8 (Cy*C*, P*C*H$_2$), 8.2 (H$_3$*C*CC*C*H$_3$).

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**Supporting Information Available:** Complete listing of the optimized geometries with absolute energies of all stationary points, and a thermal ellipsoid plot of PdCl$_2$(dcype)·dba (PDF). X-ray parameters, fractional coordinates and displacement parameters, bond lengths and bond angles for complexes **9**, *cis*-**11**, *trans*-**11**, and PdCl$_2$(dcype)·dba (CIF). This material is available free of charge via the Internet at http://pubs/acs.org.

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