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Insertion of a N-Heterocyclic Carbene (NHC) into a Platinum−Olefin Bond

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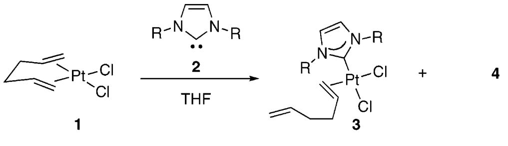
Summary: The insertion of a N-heterocyclic carbene (NHC) into a coordinated olefin moiety is observed for a Pt-based system. Important intermediates along the reaction pathway have been isolated and fully characterized. Computational work supports a proposed mechanistic pathway involving external attack at the olefin by a NHC ligand rather than an intramolecular migratory insertion route.

Since the reported synthesis and X-ray structure determination of *N*,*N*-bis(adamantyl)imidazol-2-ylidene (IAd),[1] the use of N-heterocyclic carbenes (NHCs) in catalysis has experienced a veritable explosion. These catalytic uses range from their now well-known role as ligands in ruthenium-based olefin metathesis[2] and palladium cross-coupling chemistry[3] to their efficient performance as organocatalysts in transesterification[4] and related transformations.[5]

As part of a program focusing on the reactivity of NHCs with late-transition-metal complexes,[6] we recently undertook a study dealing with Pt precursors. The work of Markó and co-workers in this area has clearly demonstrated that Pt−NHC-containing compounds exhibit excellent activity in the hydrosilylation of olefins.[7] Cavell and co-workers have also reported unusual reductive elimination of NHC-containing fragments from Pt centers.[8] Other than these important studies, very little has been reported of the chemistry of NHCs bound to Pt. We now present some of our findings involving "simple" ligand substitution reactions of NHCs for coordinated olefin positions.

For a straightforward Pt precursor we selected (1,5-hexadiene)$PtCl_2$ (**1**), in which the olefinic linkages are known to be labile.[9] We reasoned that this precursor would be an excellent source of the $PtCl_2$ moiety. Indeed, the olefin can be replaced by one or two NHCs, depending on the ligand steric hindrance.

Reaction of equimolar amounts of **1** and *N*,*N*-bis(2,6-diisopropylpheny)imidazol-2-ylidene (**2**; IPr) gives rise to the substitution of one coordinated double bond by IPr and affords complex **3** in 80% yield (eq 1).



(1)

R = 2,6(diisopropyl)phenyl

^{1}H and ^{13}C NMR data show the presence of both a coordinated double bond (^{1}H, 4.48, 4.12, and 3.79 ppm, J_{Pt-H} = 64−68 Hz; ^{13}C, 88.7 and 67.9 ppm) and an unbound olefin (^{1}H, 5.55, 4.87, and 4.83 ppm; ^{13}C, 137.5 and 114.9 ppm). An upfield shift of the IPr carbenic carbon at 144.0 ppm indicates its coordination. As a platinum-containing by product of reaction 1, the white precipitate **4** was isolated in 6% yield; its ^{1}H NMR shows the presence of one coordinated double bond at 4.30, 3.70, and 2.81 ppm (J_{Pt-H} = 69−75 Hz). No signal of the free olefin can be observed, and a multiplet with a very high J_{Pt-H} value of 132 Hz appears at 2.22 ppm. ^{13}C NMR DEPT correlation data strongly suggest the presence of a Pt−C single bond.

To unequivocally establish the identity of by product **4**, a single-crystal diffraction study was performed on crystals grown by slow evaporation of a saturated $CHCl_3$ solution. As shown by the ball and stick representation depicted in Figure 1, by product **4** is the result of the formal insertion of IPr into one coordinated double bond of hexadiene.

When reaction 1 was carried out with excess IPr (1.4 equiv), the isolated yield of the insertion product **4** increased to 40%.

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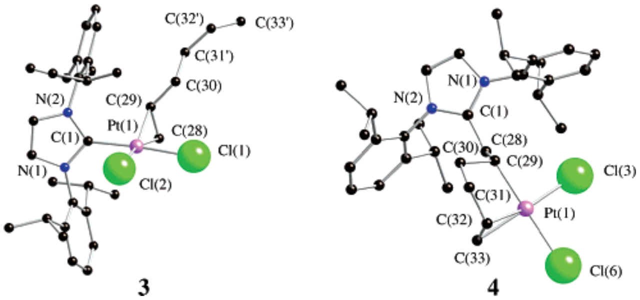
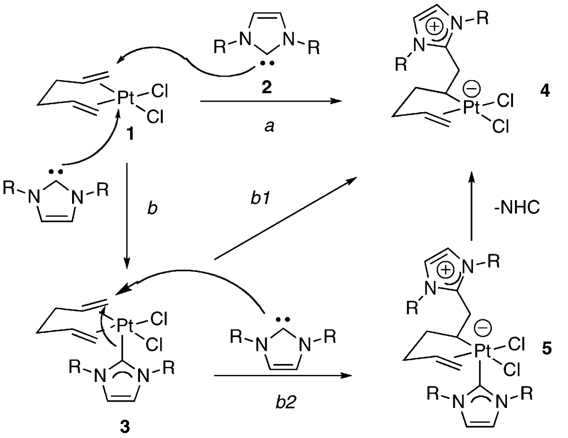


3 **4**

Figure 1. Ball-and-stick representations of **3** and **4**. Selected bond distances (Å) are as follows. **3**: Pt−C(1) = 1.9993(13), Pt−Cl(1) = 2.3563(4), Pt−Cl(2) = 2.3043(4), C(32′)−C(33′) = 1.326(4). **4**: Pt−C(29) = 2.071(5), Pt−Cl(3) = 2.3075(15), Pt−Cl(6) = 2.470(2).

Scheme 1. Possible Mechanisms for Reaction 1



Attempts to increase further the yield by overnight reaction have thus far failed.

DFT calculations were performed in order to gain insights into the mechanism of this reaction. Three possible pathways were considered for the attack of a NHC molecule onto a C═C double bond of the diene (Scheme 1).

Path *a* assumes intermolecular attack of a NHC molecule onto one of the C═C bonds of **1**. The alternative paths *b* assume displacement of a C═C double bond in **1** by a NHC molecule to give **3**. Complex **3** can undergo intramolecular attack of the coordinated NHC ligand at the nearby C═C double bond (path *b1*) or intermolecular attack of a second NHC molecule at the coordinated C═C double bond (path *b2*).

An energy diagram involving the three reaction pathways is illustrated in Figure 2. Path *a* thus starts from **1**, and through transition state [**1-4**]′‡, and an energy barrier of $\Delta H^{‡} = 18$ kJ/mol, collapses into product **4′**, which is 166 kJ/mol more stable than **1**. The alternative pathways start from **3′**. The intramolecular path (*b1*) proceeds through transition state [**3-4**]′‡, with an energy barrier of $\Delta H^{‡} = 167$ kJ/mol, and collapses into **4′**, while the intermolecular attack (*b2*) proceeds through transition state [**3-5**]′‡, with an energy barrier of $\Delta H^{‡} = 32$ kJ/mol, and collapses into **5′**, which is 108 kJ/mol lower in energy than **3′**. Dissociation of the NHC ligand from **5′** is an endothermic step, by 198 kJ/mol, and gives the final complex **4′**.

Figure 2 clearly shows that, according to the calculations, the preferred reaction pathway is an *intermolecular*, rather than an *intramolecular*, process. Although a NHC ligand binds strongly to the platinum−diene fragment, the activation energy for an intramolecular process is 1 order of magnitude larger than the activation energy for intermolecular processes.

In light of the DFT calculation results, it appears that **3** is the intermediate leading to final insertion product **4**. The intramolecular process requires 2 equiv of free IPr to achieve insertion of IPr onto the coordinated double bond, although the overall processs is catalytic in the second equivalent of the NHC. This explanation would account for the increased yield observed when the reaction is performed with excess IPr. It is worth noting that the energy required to go from **5′** to **4′** is more than the activation barrier from **5′** to **3′**. Thus, an equilibrium between **3′** and **4′** is likely to be present. This might explain the impossibility of increasing the yield of **4** by increasing the reaction time. To explore if the behavior of IPr toward

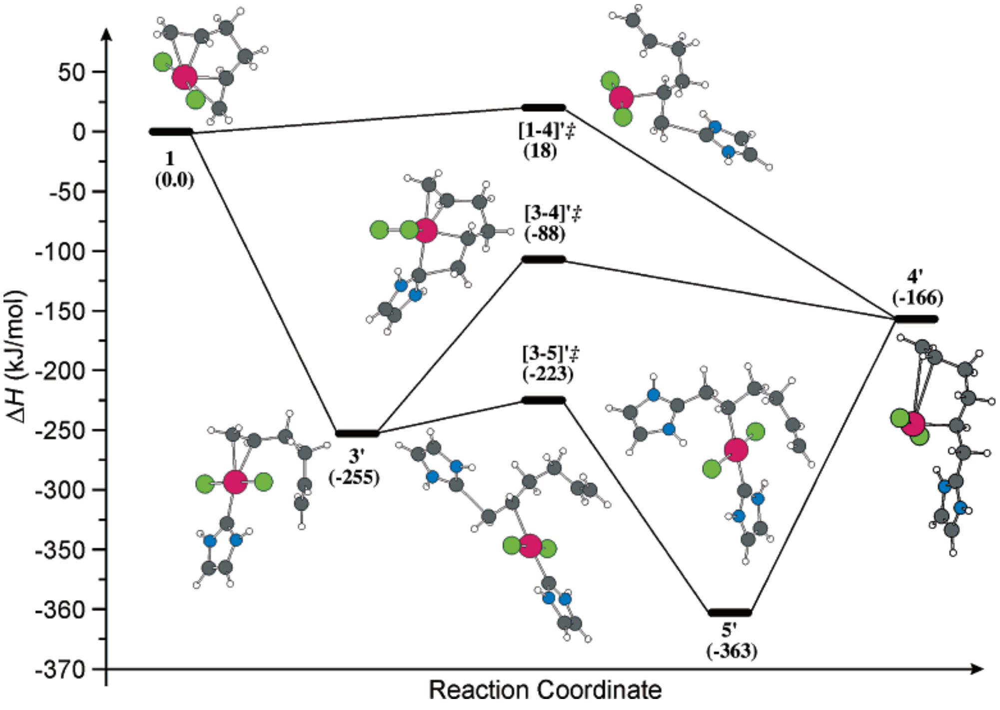
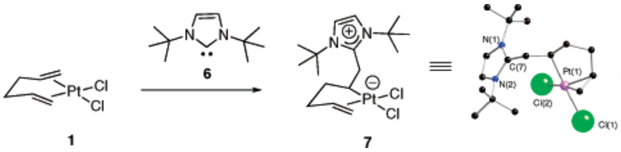


Figure 2. Energy diagram of reaction 1 pathways.

coordinated olefin is general for other NHC ligands, the reaction between **1** and a 2-fold excess of ItBu (**6**) was performed (eq 2).



(2)

The ItBu insertion product **7** was obtained in 55% yield. ^{1}H and ^{13}C NMR spectra show the same features as for **4**. A single-crystal diffraction study unambiguously confirms the atom connectivity.

The noninnocent behavior of coordinated NHC with metal centers or adjacent ligands has been documented,[10] as have examples where a TM−NHC bond (TM = transition metal) displays lability.[11] Cavell has proposed a similar insertion behavior with Pd(0) and Ni(0).[12] Kirchner has reported the insertion behavior of a NHC in ruthenium−acetylide systems,[10a] but to our knowledge this is the first system where the insertion intermediate and product have been isolated and fully characterized. This insertion also appears to be catalytic in the second equivalent of NHC employed. This behavior has dire consequences for Pt-based catalysis, as deactivation in this manner would presumably lead to inactive species. Judicious selections of Pt precursor and NHC become key issues in inhibiting this reactivity manifold. The exact driving force and factors influencing this insertion behavior are presently being further explored in our laboratories.

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Supporting Information Available: Text and figures giving experimental details, a detailed discussion of the computational treatment, NMR, mass spectra and CIF files giving crystal data for complexes **3**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and can be obtained on request, free of charge, by quoting the publication citation and the deposit numbers 639902 (**3**), 639901 (**4**), and 639903 (**7**).

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