Carbene Ligands

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Platinum-Mediated Oxidative Addition and Reductive Elimination of Imidazolium Salts at C4 and C5**

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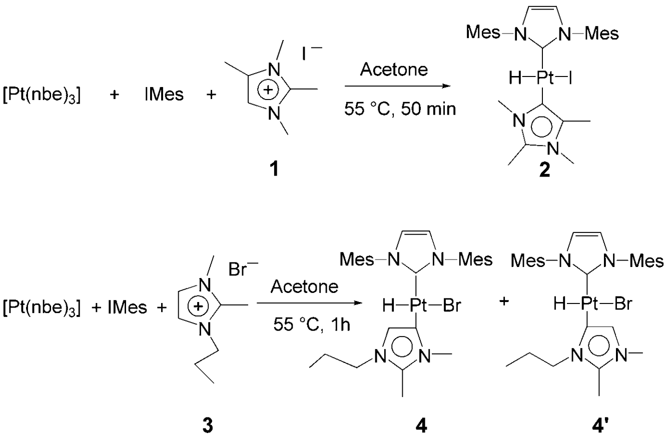
Nucleophilic N-heterocyclic carbenes (NHCs) have attracted considerable interest as ligands in organometallic chemistry and catalysis.[1] This attention is largely because of the unique combination of strong σ-donor, poor π-acceptor, and steric properties.[2] Typical transition-metal NHC complexes show “normal” binding at C2 because of the acidity of the C2 proton in the precursor azolium salt.[3] “Abnormal” metalation at C5 of the NHC ring was first reported in elegant studies by Crabtree and co-workers for pyridyl- and picolyl-NHC dihydride complexes of Ir^{III};[4] blocking C2 with a substituent, such as Me or Ph groups, will also encourage binding at C5.[5] Nolan and co-workers have recently reported the structure and interesting catalytic reactivity of $[PdCl_2(NHC)_2]$ complexes containing NHC ligands bound the “wrong way” that are derived from imidazolium salts.[6] In both these studies, the carbene bound at C4/5 was generated through deprotonation by the addition of a base or use of basic ligands on the metal.

In previous studies on metal–carbene complexes, we identified a facile reductive-elimination process, in which the carbene is lost as an imidazolium salt.[7] Conversely, it was found that imidazolium salts (ionic liquids) add oxidatively to low-valent metal centers through C2 activation.[7–9] The combination of these two redox steps lead to a new atom-efficient catalytic reaction for the substitution of azolium salts at C2.[10] The nature of this reaction and its wider implications is of major interest; for example, ionic liquids may add oxidatively to metal complexes dissolved within them, which generates catalytically active (hydrido)metal(carbene) complexes, and ionic liquids may also be incorporated into the reaction products, thus both problems and opportunities are presented.[11]

Herein, we report a novel extension to our investigations on this redox behavior. Platinum hydride complexes have been synthesized that bear NHC ligands in an abnormal binding mode through the oxidative addition of imidazolium salts with the C2 position blocked by a methyl group.

Complexes **2**, **4**, and **4′** were prepared in one-pot reactions by mixing $[Pt(norbornene)_3]$,[12] 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes), and either 1,2,3,4-tetramethylimidazolium iodide (**1**), in the case of **2**, or 1,2-dimethyl-3-propylimidazolium bromide (**3**), in the case of **4** and **4′**, in a molar ratio of 1:1:1.8 (Scheme 1). The reactions yielded the desired products after washing the crude residues with *n*-hexane and extraction with THF. It is proposed that the reactions proceed through the initial



Scheme 1. Oxidative addition at C4 and C5 in imidazolium cations to a Pt^0 center. nbe = norbornene.

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formation of a $[Pt(IMes)(norbornene)_2]$ complex, which then undergoes oxidative addition of the C4,5–H bond of the imidazolium salt. This one-pot reaction provides a potentially valuable route to "wrong-way" (hydrido)metal(carbene) complexes, which may have applications in catalysis.

Complexes **4** and **4′** were characterized by ^1H and ^{13}C NMR spectroscopic analysis, which revealed a mixture of two isomers in a ratio of 3:1. The platinum center in the minor component **4′** is connected to C4, which is the carbon atom closest to the *N*-propyl chain, whereas the platinum center in the major component **4** is connected to C5, which is the carbon atom adjacent to the *N*-methyl group. Steric influences may produce the observed regioselectivity.

The hydride ligands in **4** and **4′** appear in the ^1H NMR spectra (CD_2Cl_2) at $\delta = -18.29$ ppm (^1J(Pt-H) = 1714 Hz) and $\delta = -18.31$ ppm (^1J(Pt-H) = 1711 Hz), respectively. The ^{13}C NMR spectra of **4** and **4′** show characteristic signals from C2 of the IMes unit at $\delta = 180.9$ and 180.7 ppm, respectively, and from C4 and C5 of the abnormal carbene moiety at $\delta = 124.4$ and 151.6 ppm for **4**, respectively, and at $\delta = 152.4$ and 126.3 ppm for **4′**, respectively. The presence of a metal-bound carbene is also indicated by the $^{13}C\{^1H\}$ NMR spectra, in which the signals from C4 and C5 in **4** and **4′** are shifted downfield relative to **3**. The ^{13}C NMR resonances for C4 and C5 are comparable with previously reported abnormally bound carbenes.[5,13]

A mixture of crystalline needles (**4′**) and plates (**4**) was grown by slow diffusion of hexane into a saturated solution of the crude product in acetone. Only the needles were found to be suitable for single-crystal X-ray analysis, and they showed an abnormally bound Pt carbene complex (Figure 1). The crystal contains one acetone molecule and two Pt carbene complexes in the asymmetric unit. Both Pt carbene complexes in the crystal are identical within experimental error. The molecular structure of **4′**[14] shows a slightly distorted square-planar coordination around the Pt^{II} center, with *trans*-NHC moieties and hydride and bromide ligands occupying the remaining coordination sites. The Pt–C(carbene) bond lengths for the IMes ligand (Pt21–C21: 2.018(8) Å) and for the carbene ligand coordinated at C5 (Pt21–C223: 2.041(8) Å) are comparable and consistent with Pt–C single bonds.[5,6,13,15]

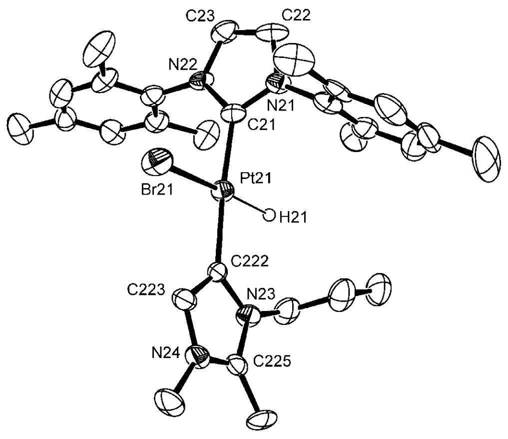
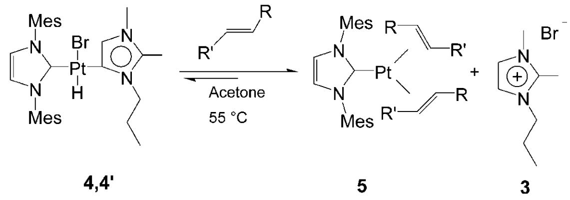


Figure 1. ORTEP diagram of **4′**. Some hydrogen atoms, the acetone molecule, and a molecule of **4′** are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt21-C21 2.018(8), Pt2-C222 2.041(8), Pt21-Br21 2.5622(9), Pt21-H21 1.8052, C21-Pt(21)-C222 175.6(3); C21-Pt21-Br21 91.4(2), C21-Pt21-H21 93.1, C222-Pt21-Br21 90.0(2), C222-Pt21-H21 85.2, Br21-Pt21-H21 173.2.

Although the mixture of **4** and **4′** is stable, both in the solid state and in solution with acetone at room temperature over two–three days, the mixture underwent reductive elimination[10,16,17] in the presence of alkenes (styrene or dimethyl fumarate) to regenerate **3** and form $[Pt(\eta^2\text{-alkene})_2(IMes)]$ complexes **5a** and **5b** (Scheme 2). Stirring a mixture of **4** and **4′** with five equivalents of dimethyl fumarate in acetone for three hours resulted in quantitative reductive elimination.[8] The equivalent reaction with styrene resulted in partial conversion with equilibrium concentrations of **4**, **4′**, **5**, and **3** being established.[16] The ^1H NMR spectrum of **5a** was identical to that observed for an authentic sample of $[Pt(\text{dimethyl fumarate})_2(IMes)]$ prepared by the reaction of $[Pt(cod)_2]$ (cod = cyclooctadiene), IMes, and dimethyl fumarate.



5a: R = R′ = COOMe *t* = 3 h 100%
5b: R = Ph, R′ = H *t* = 8 h 50%

Scheme 2. Reductive elimination of imidazolium salts at C4/5–H from "abnormal" carbene complexes.

The observed reductive-elimination behavior is consistent with the π-acceptor ability of alkenes, the distribution of electron density within the complex, and the Pt–alkene bond strength. Interestingly, reductive elimination of the "normal" carbene and the products that result from insertion of alkenes into the Pt–H bond (e.g., Pt hydrocarbyl complexes or imidazolium salts substituted at C4/5) were not observed. The behavior reported herein provides clear indication that the substitution of ionic liquids at C2 may not be enough to prevent their involvement in reactions for which they are the solvent.[18]

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[14] Crystal data for **4′**: $C_{58}H_{78}Br_2N_8Pt_2 \cdot C_3H_6O$, $M_r = 1495.36$ triclinic $P\bar{1}$, $a = 14.4027(3)$, $b = 14.4603(3)$, $c = 16.8198(4)$ Å, $\alpha = 75.582(1)$, $\beta = 68.713(1)$, $\gamma = 75.279(1)°$, $V = 3108.76(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.597\,Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 0.71073$, $T = 150(2)$ K, 57703 reflections collected, 14183 (R(int) 0.1635), F^2 refinement $R_1 = 0.0616$, $wR_2 = 0.1111$ for ($I > 2\sigma(I)$), 24 restraints, and 687 parameters. CCDC-265475 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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[18] Experimental details of the preparation, characterization of the complexes, and full details of the X-ray crystal structure of **4′** are available in the Supporting Information.