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Communications

Structure and Reactivity of an Allylpalladium N-Heterocyclic Carbene Enolate Complex

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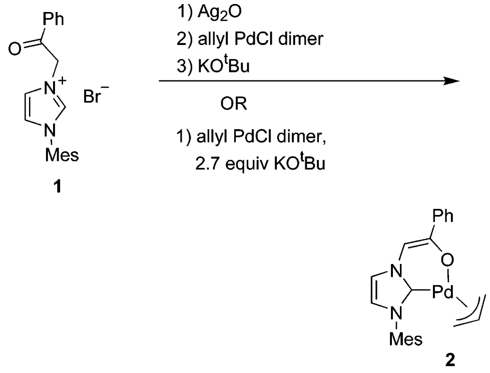
Summary: A novel anionic N-heterocyclic carbene was prepared and ligated to $[Pd(allyl)Cl]_2$ *to yield the complex (NHC-enolate)Pd(allyl). At elevated temperatures in acetonitrile, the allyl ligand undergoes a stereoselective* $\eta^3-\eta^1-\eta^3$ *isomerization in an associative process that is first order in* CD_3CN *with* $\Delta H^\ddagger = 13.5 \pm 0.7$ *kcal* mol^{-1} *and* $\Delta S^\ddagger = -17 \pm 2$ *eu. This complex reacts with electrophiles (HCl,* CH_3I*) at the enolate position.*

Since the first isolation of a free carbene by Arduengo,[1] N-heterocyclic carbenes (NHCs) have attracted increasing attention both as ancillary ligands in organometallic catalysis and as nucleophilic catalysts.[2−5] To date, they have found a variety of applications, most notably in cross coupling,[6−12] metathesis,[13] telomerization,[14,15] hydrogenation,[16] ethylene/CO copolymerization,[17] ring-opening polymerization,[18] and transesterification reactions.[19,20] These stable carbenes are potent σ-donor ligands analogous to phosphines. They differ from phosphines in that they form stronger metal bonds,[21−23] and their shape is more wedgelike than conical. Furthermore, carbene metal complexes are often more stable to air, water, and heat than their phosphine counterparts.[24−26]

Although a variety of neutral carbene ligands have been investigated, only a few examples of anionic ligands derived from carbenes are known.[27−33] Herein, we describe an anionic carbene enolate metal complex and some preliminary results on its reactivity.

The allyl Pd carbene enolate **2** was prepared by two methods (eq 1). Mesityl imidazole reacts with 2-bromoacetophenone to give **1**, which is converted to the silver carbene in the presence of Ag_2O.[34,35] Transmeta-



Mes = 2,4,6-trimethylphenyl

(1)

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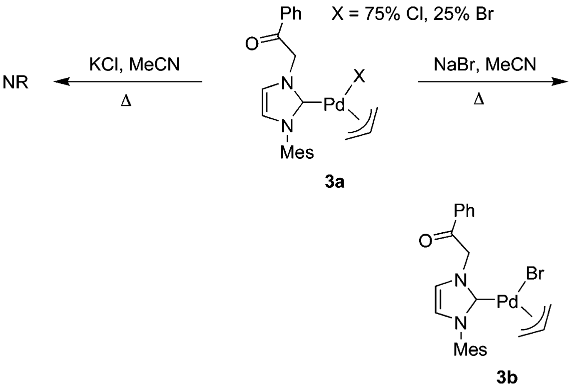
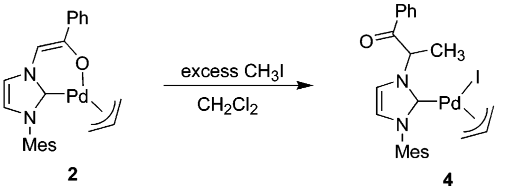
lation to palladium generates **3a**, which can be deprotonated with KO^{t}Bu to afford **2**. Alternatively, **2** can be made in one pot by mixing **1**, [Pd(allyl)Cl]$_2$, and KO^{t}Bu in ether and THF. This one-pot synthesis gives the product in higher yield, although it is slightly less pure. During the carbene transfer from Ag to Pd, some bromide was incorporated into the Pd complex; thus, **3a** is a mixture of 25% bromide and 75% chloride (by NMR and elemental analysis). To confirm this, we attempted two halide exchange reactions in refluxing acetonitrile. The mixture **3a** reacts quantitatively with NaBr in CH$_3$CN to yield the corresponding bromide **3b**; in contrast, **3a** did not react KCl under similar conditions (eq 2).



(2)

The reactivity of the allyl enolate **2** was investigated with electrophiles. When treated with HCl, **2** is protonated at the enolate to give **3a** (X = Cl). Excess HCl affords [Pd(allyl)Cl]$_2$ and the imidazolium chloride. When **2** is treated with excess MeI, alkylation of the enolate ensues to give **4** (eq 3). It is noteworthy that MeI does not react with the metal center in either **2** or **4**, which might be expected for these electron-rich species.[36,37]



(3)

Crystals suitable for X-ray analysis were formed by cooling a concentrated solution of **2** in ether with a drop of CH$_2$Cl$_2$ to −20 °C. Bond angles and lengths are similar to other reported (NHC)Pd(allyl) complexes (Figure 1).[15,38] The central carbon of the allyl is disordered at an 85:15 ratio. The allyl carbon trans to the carbene shows significant lengthening (9.1 pm) relative to the allyl carbon trans to the enolate. The most striking feature of the structure is that the square plane of the Pd, the carbene, and the enolate are all coplanar. For example, the N1−C4−C5−O dihedral angle is only 4°. NHCs typically adopt a structure orthogonal to or out of the Pd square plane. For an analogous neutral Pd(NHC-enamine)Cl$_2$ complex, Coleman noted that the imidazol-2-ylidene ring of the carbene tilted out of the Pd square plane by 38.5°.[39,40] The carbene enolate adopts a more planar geometry, which leads to bond angles larger than expected (e.g. C4−C5−O is 127.9°). The mesityl is situated nearly perpendicular to the heterocycle with an C2−N2−C12−C13 dihedral angle equal to 98°.

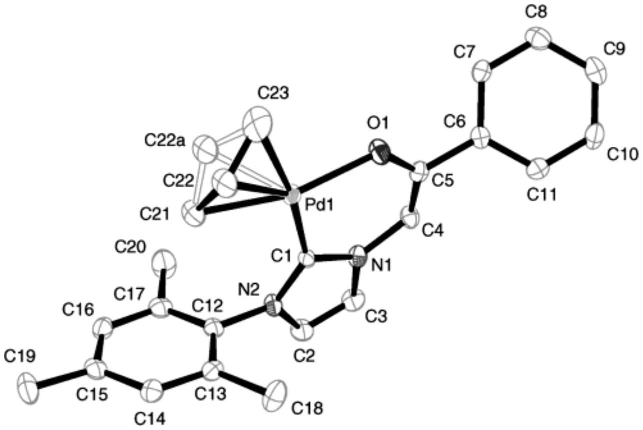


Figure 1. ORTEP diagram of **2**. Selected bond lengths (Å) and angles (deg): Pd−C1, 2.022(4); Pd−O, 2.062(3); Pd−C21, 2.113(4); Pd−C22, 2.133(5); Pd−C23, 2.204(4); C1−N1, 1.374(5); C1−N2, 1.358(5); N1−C4, 1.426(5); C4−C5, 1.336(6); C5−O, 1.323(5); C1−Pd−O, 91.70(14); C1−Pd−C21, 103.61(17); O−Pd−C23, 96.83(16); N1−C1−N2, 103.4(3); N1−C4−C5, 125.4(4); C4−C5−O, 127.9(4).

The allyl ligand of **2** exhibits dynamic behavior in CD$_3$CN solution. At room temperature, the ^{1}H NMR spectra shows five distinct allyl proton resonances in a variety of solvents. When **2** is heated to 110 °C in CD$_3$CN, the allyl protons cis to the carbene[41] coalesce, while the other three peaks remain sharp.[42] These results are consistent with an $\eta^3-\eta^1-\eta^3$ allyl isomerization[43−53] that selectively takes place via formation of a

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(36) In a recent study of MeI oxidative addition to Rh(CO)L$_2$I, Haynes found that, when L = NHC, oxidative addition is slower than when L = phosphine. Haynes argued that this was due to a greater steric bulk of the carbene, and this may also be the case for these Pd carbenes.

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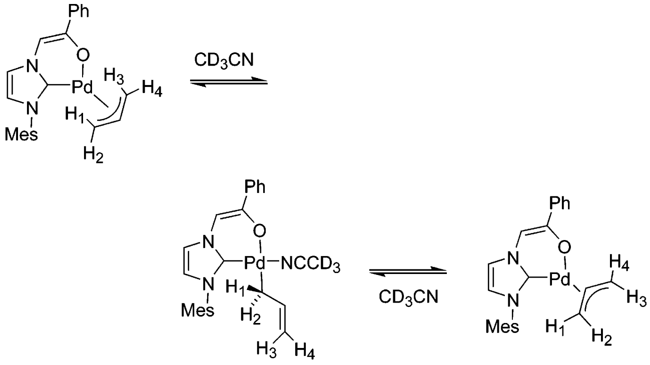
Scheme 1. Proposed Associative Allyl Isomerization



σ-allyl cis to the carbene (Scheme 1). In contrast to the results in CD_3CN, there was no evidence for fluxional behavior of the allyl ligand in d_8-toluene from 20 to 110 °C. Selective syn/anti allyl exchanges are known for a variety of Pd allyls, and the selectivity has been attributed to either the trans effect or sterics.[54−58] Pregosin found that for a variety of cationic Pd bis-phosphine complexes, the σ-allyl forms cis to the least sterically demanding ligand. For this Pd carbene enolate, however, the σ-allyl forms cis to the bulkier mesityl group. Because the selectivity is counter to steric considerations, the origin of the selectivity most likely arises from the greater trans effect of the carbene. This is consistent with the findings of Helmchen and others that the σ-allyl forms cis to the stronger σ-donor ligand.[56]

An Eyring plot of the allyl exchange rates in CD_3CN gave $\Delta H^\ddagger = 13.5 \pm 0.7$ kcal mol^{-1} and $\Delta S^\ddagger = -17 \pm 2$ cal mol^{-1} K^{-1}. The negative entropy of activation is indicative of an associative mechanism. To test this, we investigated the kinetics of the isomerization of **2** as a function of CD_3CN concentration in d_8-toluene at 71.6 °C. The rate of isomerization was first order in acetonitrile concentration, consistent with an associative mechanism (Scheme 1) where association of CD_3CN induces an $\eta^3-\eta^1$ conversion. Rotation around the C−C bond and subsequent η^3-allyl binding gives the complex in which H_1 (previously anti) has become syn. This mechanism agrees with the mechanism proposed recently by Szabó on the basis of theoretical calculations.[59]

In conclusion, we synthesized an allyl Pd species with a conjugated anionic chelating NHC and found that it undergoes selective $\eta^3-\eta^1-\eta^3$ allyl exchange via an associative mechanism. We are currently investigating this novel ligand class and its application to a variety of catalytic processes.

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Supporting Information Available: Text and figures giving complete experimental details, including synthesis, allyl exchange data, and NMR spectra, and tables giving X-ray crystallographic data; X-ray data are also available as CIF files. This material is available free of charge via the Internet at http://acs.pubs.org.

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