Normal and Abnormal Bonding of N-Heterocyclic Carbenes: Impact on Stability, Reactivity, and Catalysis

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N-heterocyclic carbenes (NHCs), typically derived from imidazolium salts, have provided highly powerful ligands for catalysis. Recently, abnormal C4 bonding rather than normal C2 bonding has been discovered as a new carbene bonding mode. We were interested in comparing the consequences of these two bonding modes on the metal center. Therefore we synthesized related palladium complexes 1 and 2 containing similarly cis chelating dicarbenes that bind via C2 and C4 respectively.

Complex 1 was obtained by the palladation of the potentially chelating diimidazolium ligand precursor with Pd(OAc)₂. We observed that adding a base favors the formation of tetracarbene over biscarbene palladium complexes, whereas without base, the concentration of reactants influences the selectivity for bridging bimetallic versus chelating monometallic species. The C4-bound carbene complex 2 was synthesized by palladation of the C2-protected diimidazolium salt precursor with Pd(OAc)₂.

X-ray photoelectron spectroscopy analyses of compounds 1 and 2 provide evidence that the electron density at the palladium center is markedly higher in C4- than in C2-bound carbene complexes. In addition reactivity studies of these complexes towards Lewis acids (AgBF₄, AgOAc), Brønsted acids (H₂SO₄, H₃PO₄, HOAc) and chlorine revealed that the palladium center in 2 is a stronger Lewis base than in 1. The abnormal carbene bonding mode induces new reaction patterns such as the formation of a Pd–Ag adduct or an unusual dimer which displays short Pd⋯Pd contacts.

To firmly probe the influence of the electronic factors of the carbene bonding mode we prepared two related NHC palladium complexes 3 and 4 with identical steric environment, containing cis chelating dicarbenes bound via C2 and C4 respectively.

XPS analyses and reactivity studies toward H₂SO₄, AgBF₄ and Cl₂ confirmed that C4-bound dicarbenes considerably increase the electron density at the metal center. We have exploited these bonding properties in alkene hydrogenation catalysis and showed that C4-bound NHCs are significantly more active catalysts than their normally bound analogues. More detailed catalytic studies revealed that alkenes hydrogenation with the C4-bound complex 2 is heterogeneous and depends on the formation of palladium nanoparticles.

In addition we synthesized new C2- and C4-bound NHC platinum complexes, similar to the palladium complexes. The C2-bound platinum complexes are formed according to established palladation procedures but modifications of the synthetic method was required to obtain the abnormal platinum complexes.

Members of the jury:
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