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A theoretical study of the electronic effect of the ligand bite angle on the hydrosilylation reaction of ketones by Cu(I) diphosphine complexes

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ABSTRACT

Diphosphine ligands are commonly used for the catalytic hydrosilylation of ketones using Cu(I) complexes. The electronic effect of the P–Cu–P bite angle has been investigated by a theoretical DFT study. An increase of the P–Cu–P bite angle induces a stronger phosphorus lone pair/Cu-H σ* orbital interaction due to a better overlap between these orbitals. This increase in overlap affects structural and electronic properties of the copper hydride catalyst. Increasing the bite angle leads to a decrease of the Cu-P distances and an increases of the Cu-H distances. From an electronic point of view, the effect of an increasing bite angle leads to a weakening of the σ Cu-H orbital, and an increase of the hydride population. The increased polarization of the hydride leads to an easier electron transfer from the σ Cu-H bond to the carbon of the ketone.

1. Introduction

Asymmetric hydrosilylation of ketones provides an efficient route to chiral secondary alcohols. The first catalytic system based on rhodium was developed in the 70s [1–3]. Efficient systems using less expensive metals such as titanium [4–7], iron [8,9], manganese [10] or zinc [11–13] were successfully developed. In 1984, Brunner and Miehling reported the first asymmetric hydrosilylation using a copper-diphosphine catalyst [14]. Since, many catalytic systems based on a copper-diphosphine catalyst were developed [15–21]. The active species formed *in situ* is a copper (I) hydride. Lipshutz and co-worker describe the formation of the CuH species in a system combining a catalytic quantity of CuCl/NaOt-Bu/diphosphine and a stoichiometric quantity of hydrosilylant agent for 1,2 and 1,4 reductions [22–27]. At the same time, Carreira and co-workers [28], as well as Riant and co-workers [29–31] reported CuF_2 systems as interesting precursors to copper hydride.

The suggested catalytic cycle [17,20,21,32] is shown in Scheme 1, with the copper hydride interacting with a ketone leading to a four-membered transition state. The copper alkoxyde successively undergoes a σ-bond metathesis with the hydrosilylation agent to regenerate the Cu-H complex and a silyl ether product.

The selectivity, as well as the activity of the catalytic system is determined amongst others by the nature of the diphosphine ligand. It is postulated that one of the parameters influencing the catalytic activity of a XCu(I)Diphosphine catalyst is the size of the P-M-P bite angle β (Scheme 2). Dierkes and van Leeuwen [33] investigated a series of diphosphine ligands, from an experimental, as well as theoretical point of view, and surprisingly found the bite angles to be distributed in a very narrow range of about 3°. They conclude that the measured bite angle reflects the ligand preferences rather than the metal binding requirements. The ligand bite angle is expected to play an important role on the activity of the catalyst. If a ligand bite angle is close to the 'ideal' angle of the transition state, an increased reaction rate is expected, whereas the opposite is true if the bite angle is closer to the 'ideal' angle of the reactant [34]. Many studies have been performed to understand how catalytic activity is affected by this parameter [35–43], as illustrated by the correlation found between the ligand bite angle of rhodium catalysts and their activity in hydroformylation reactions [44]. Although the observation of good correlation, it was not possible to attribute this correlation purely to steric or electronic effects. Similar observations were made for Pd based cross-coupling reactions [45–49]. The bite angle can furthermore play a crucial role in the enantioselective outcome of a reaction [47,50].

To cover a wide range of different bite angles, all experimental studies consider a series of different diphosphine ligands. The observed differences in reactivity are therefore expected to be due to a combination of electronic (ligand-metal σ and π bonding) and steric effects.

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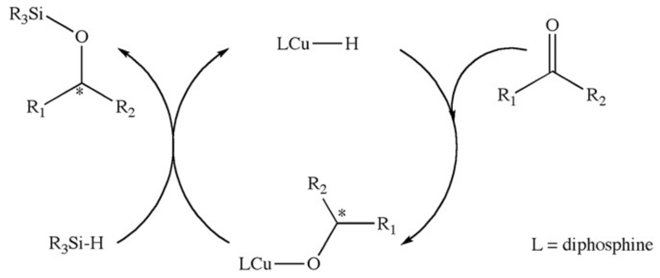


Scheme 1. Suggested catalytic cycle for the asymmetric hydrosilylation of ketones using Cu(I) catalysts.

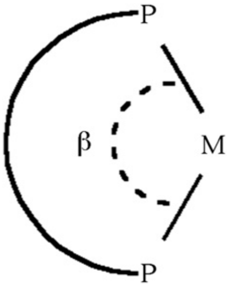
In this paper, the goal is to study a single specific part of the ligand bite angle effect, focussing more specifically on the electronic effect of a change in bite angle. To do so, a system needs to be set up for which the bite angle is allowed to change without an important change in steric effect. Ideally this situation can be approximated by changing the bite angle without altering the nature of the ligand. For changes in bite angle of about 8° around the optimal bite angle, a limited change in steric effect can be assumed. Changing the bite angle of a ligand, without changing the nature of any of the system's components, is difficult to achieve experimentally [51] (although some experiments have been executed using the CnTunaPhos diphosphines [52]), and hence computational modelling is required. This approach is therefore adopted in this paper. In previous contributions, the nature of hydrosilylation reactions of ketones using Cu(I) diphosphine hydride catalysts was investigated. This system was therefore chosen as a model system.

To study the electronic effect of a change in bite angle $C_4H_4(PR_2)_2$ ligands were considered (Fig. 1). By considering different phosphorus substituents (R = −H, −CH_3, −Ph), trends were confirmed. $HCu(PMe_3)_2$ is chosen as a reference system, as comparable bonding is observed in different alkyl and aryl phosphine ligands [53].

For each ligand, the active copper hydride species was optimized. To study the impact of the bite angle on the electronic structure of the active catalyst, the P-M-P angle was then varied by increments of 1° around the optimal structure. For each different bite angle, all of the other structural parameters (bond lengths, angles, and torsional angles) were re-optimized. In a second part of the paper, the incidence of the bite angle on the first step of the catalytic cycle is investigated. In a similar approach the variation of the activation barrier as a function of the bite angle is studied, using acetone as carbonyl group.

2. Computational details

All structures were fully optimized using Becke's three parameters exchange functional [54] and the correlation functional of Lee, Yang and Parr (B3LYP) [55], as implemented in the Gaussian 03 [56] series of programs. Frequency calculations were performed to characterize the nature of minima and transition states, and to determine their entropies and free energies based on a statistical thermodynamics treatment. The Cu atom was described using an effective core potential to represent all but the valence n*d* and (n + 1)*s* and outer core n*s* and n*p* electrons [57–59]. The latter were described with a triple zeta contraction of the original double zeta basis set, this combination is referred to as the LANL2DZ basis set. All non-metal atoms were described using the standard 6−31G(d,p) basis set (with only the five spherical harmonic d functions). Atomic charges were calculated using the NBO method [60–63]. Orbital interactions were also investigated using this latter method, requiring a bonding model for the systems studied. As Cu(I) species are d^{10} species, an optimal Lewis-like NBO bonding scheme is achieved, describing the hydride bonding as a σ bond involving the 1s H and the 4s Cu atomic orbitals. The phosphorus groups are linked to the Cu-H entity by interaction of the phosphorus lone pair and the σ* Cu-H bond and possible π backbonding from occupied Cu *d* orbitals towards unoccupied ligand σ*P-C orbitals.[1] Such a model, furthermore explains the relatively weak bonding of the phosphorus groups to the Cu-H entity [32]. In these complexes, all electrons are paired yielding a spin multiplicity of one.



Scheme 2. Bite angle.

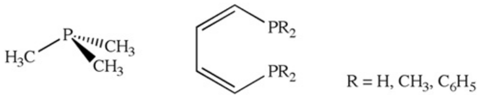


Fig. 1. PMe_3 ligand used as reference copper ligand and diphosphine ligands considered in this study.

Energies due to deviation of the ideal Lewis-like structure, and thus interactions with σ* orbitals can be estimated by second-order NBO perturbation analysis [53]. The stabilization energy $E(2)$ associated with delocalization from a donor orbital *i* to an acceptor orbital *j* can be estimated as $E(2) = \Delta E_{ij} = q_i \times F(i,j)^2/(\varepsilon_j - \varepsilon_i)$. In this expression, q_i is the donor orbital occupancy, ε_j and ε_i are the respective orbital energies, and $F(i,j)$[2] is the off-diagonal Fock matrix element expressed in the NBO basis. The latter is a resonance integral, measuring how much energy is gained by sharing electrons between orbitals *i* and *j*. In practice, this term can be interpreted as measuring the extent of overlap between orbitals. Interaction energies are obtained by summing up all second−order perturbative interactions between donor orbitals and acceptor orbitals.

3. Results and discussion

3.1. Influence of the bite angle on the Cu(I) hydride catalyst

In a first part of this paper, the effect of an increasing bite angle on the structural, electronic and energetic properties of the copper (I) hydride species are investigated. The diphosphine ligands considered in this study are represented in Fig. 1. Fig. 2 shows the bite angle, as well as the Cu-P and Cu-H distances for the optimized copper hydride diphosphine species at the above mentioned level of theory. As shown by this figure the bite angle decreases when considering a diphosphine instead of two single monophosphines. As expected, the organic backbone linking the two phosphorus

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[1] Forcing the Cu atom to adopt a sp^2 hybridization and an interaction with the phosphorus lone pairs through σ donation, leads to unrealistic NBO models characterized by high delocalization and unrealistic lewis-like structures.

[2] This value is given in the output using the NBO keyword in Gaussian03.