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ARTICLE TYPE

Pincer versus Pseudo-Pincer: Isomerism in Palladium(II) Complexes bearing κ^3*C*,*S*,*C* ligands

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In NHC pincer complexes incorporatig a hemilabile donor site, there exists an equilibrium between the true pincer form and a pseudopincer coordination isomer. The influence of the NHC moieties on this isomerism has been studied by DFT calculations.

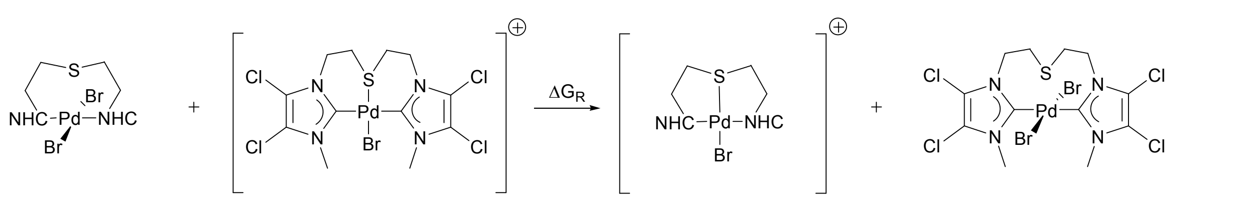
Tridentate, pincer and pincer-type ligands have gained increasing popularity due to the robustness and thermal stability the rigid, κ^3-*mer* or κ^3-(pseudo)-*mer* coordination geometry these ligands confer to their complexes. Transition metal complexes incorporation pincer ligands have been shown to be versatile and useful catalysts in organic synthesis.[1] Beyond catalysis, pincer complexes have also been utilized successfully for the development of new materials.[2] The fine-tuning of steric and electronic properties of pincer ligands - be it by modifications in the backbone or changes to the nature of the donor sites - has attracted considerable research interest, in order to provide coordination spheres for each and every application.[3] While catalysis often involves the coordinations sites on the metal centre not occupied by the pincer ligand, there are also cases in which partial decoordination of a hemilabile donor takes place. The advantage is the rapid creation of a coordinatively and electronically unsaturated metal centre, open for incoming substrates, while retaining the tethered donor functionality in the vicinity in order to allow for rapid recoordination and stabilisation of the active species. As a result, highly active, yet stable catalysts are obtained.[4] Frequently, the donor functionalities in the sidechains of the pincer ligands are the hemilabile sites,[5] but cases in which the central donor moiety exhibits hemilabile behaviour have been reported as well.[6] However, to control hemilabile behaviour, the governing geometric and electronic factors still need to be understood.[7]

N-heterocyclic carbenes (NHCs) have become ubiquitously employed ligands for transition metal catalysts due to their strong σ-basicity, the robustness of their complexes, and the ease with which they can be synthesized.[8] Their steric bulk and electronic properties can be fine-tuned rapidly by modifying the backbone and side chains,[9] and additional donor functionalities can be introduced in the side chains, which gives rise to chelating and pincer-type ligands. Donor moieties based on heteroatoms such as nitrogen, oxygen, phosphorous, and sulfur have been reported.[10,11] Especially the soft thioether functionalities are know to exhibit hemilabile behavior in their complexes.[12]

It has been shown that in the presence of coordinating counteranions, complexes of CSC pincer ligands are isolated either as κ^2-*trans*-*C*,*C* pseudo-pincer complexes or in their κ^3-*mer*-*C*,*S*,*C* pincer form.[13] The electron-donating abilities of the carbene moieties were suggested to have a pivotal influence on this isomerism. To study this electronic effect, we examined the electronic properties of NHCs with markedly different donor strenghts and the preference for either the pincer or the pseudo-pincer form by means of computational methods.

The relative Gibbs free energies ΔG of a neutral pseudopincer species **A** and the corresponding cationic pincer **C** and a bromide ion are difficult to obtain due to the significant impact of solvatation on the ion pair. Instead, the Gibbs free energy ΔG_R of the reaction of a pincer and pseudopincer complex was used as an indication of preference for the pincer form (Scheme 1). During this fictitious reaction, the number of ionic species stays constant throughout the reaction, and solvatation effects as well as the Gibbs free energy of the bromide counteranion can be neglected as they are almost identical for starting materials and products.

The resulting scale of pincer preference energy is arbitrary in the sense that the absolute values will depend on the choice of reference system. We decided to use complexes **B** and **D** featuring dichloroimidazolin-2-ylidene moieties as probe.



A **B** **C** **D**

Scheme 1 Homodesmotic pincer/pseudo-pincer exchange reaction

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This system was the most weakly donating ligand under scrutiny, and the respective complexes are known to prefer the pseudopincer form. A negative value for ΔG_R will thus signify a higher preference for the pincer form in comparison to the reference system. Both the pincer and pseudopincer forms of all examined complexes were optimised at the B3LYP/cc-pVDZ level of theory,[14,15,16] and their respective Gibbs free energies calculated at the same level of theory (see Supplementary Information for computational details).

To avoid the influence of variations in steric bulk associated with changing the substituents at nitrogen and to limit computational cost, NHC side chains were simplified to sterically unassuming methyl groups, and the effect of five vastly different NHC backbones (cf. figure 2) was examined, two of which have already been studied experimentally.[13]

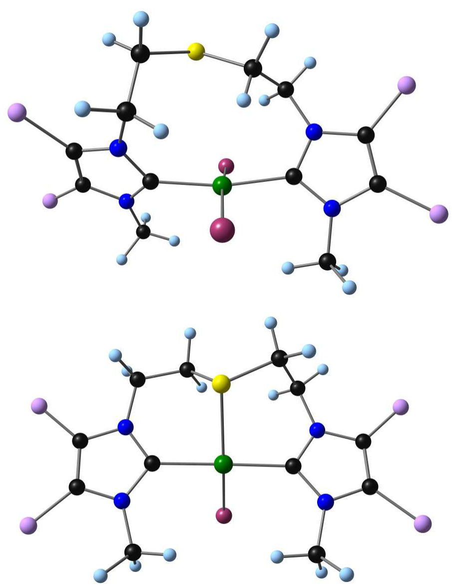

Fig. 1 Optimised pseudo-pincer and pincer geometries based on the dichloromidazolin-2-ylidene moiety

The optimised structures are comparable to the reported molecular structures.[13] All complexes have a distorted square planar coordination geometry of the palladium center (Figure 1). In the pincer complexes, the metallacycles adopt a distorted boat conformation and the planes defined by the NHC rings are almost coplanar, while they showed a twist of 26-43° in the corresponding pseudopincer forms. From these optimized structures, ΔG_R can be obtained.

No experimental donor strength values are available for the ligands in the calculated complexes. However, it has been shown that the Kohn-Sham eigenvalue of the σ-lone pair orbital ε(σ-HOMO) correlates well with the donor strength.[17] To limit computational cost, orbital energies were calculated for truncated ligands at the B3LYP/auc-cc-pVTZ//B3LYP/cc-pVDZ level (Figure 2).[14,16,18] In all cases, the highest orbital with σ-symmetry was found to be the lone pair at $C_{carbene}$ (Figure 3).

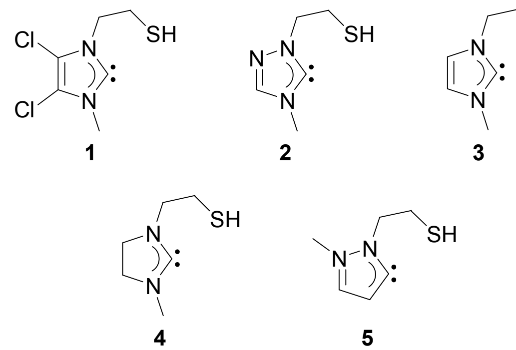

Fig. 2 Truncated ligands with different NHC moieties

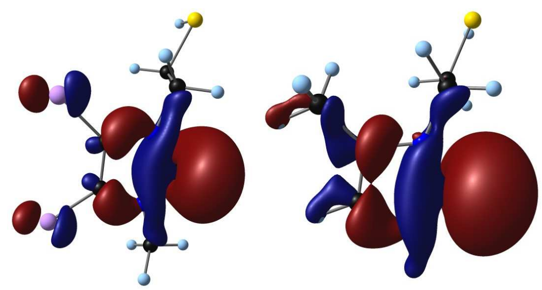

Fig. 3 σ-HOMO of NHCs **1** (HOMO-1) and **5** (HOMO)

Orbital energies for the σ-lone pair orbital were found to range from -6.56 to -5.52 eV, and confirmed the expected increase in donor strength from **1** to **5** (Table 1). The preference for the pincer form, represented by ΔG_R of the test reaction, increased in the same order, and Figure 4 shows the strong correlation between donor strength and ΔG_R (R^2 = 0.9931).

Table 1. ε(σ-HOMO) of the truncated ligand and ΔG_R

NHC moiety	ε(σ-HOMO) [eV]	ΔG_R [kJ/mol]
Cl_2-imidazole	-6.56	0.0
1,2,4-triazole	-6.52	-5.4
Imidazole	-6.12	-26.5
Imidazoline	-5.94	-32.8
Pyrazole	-5.52	-57.0

It is apparent that more strongly donating carbene moieties in the CSC ligand favour the pincer form. The cationic pincer complexes are better stabilised by stronger NHCs than the neutral pseudopincer form, and this difference in stabilization increases with the donor strength. Additionally, entropy and solvation also favour the formation of the ionic pincer over the pseudopincer form. On the other hand, the neutral pseudopincer complexes are preferred if the NHC moieties transfer less electron density towards the metal atom due to the fact that bromide is a better ligand than the thioether.

In a more formalistic approach, the $[PdBr(NHC)_2]^+$ fragment can be understood as a Lewis acid interacting with a either the thioether moiety or a bromido ligand as a Lewis base. The internal charge redistribution in the Lewis acid upon charge transfer from the Lewis base is energetically more favourable with more weakly donating NHC moieties, which allows the coordination of the more strongly donating bromido ligand.[19]

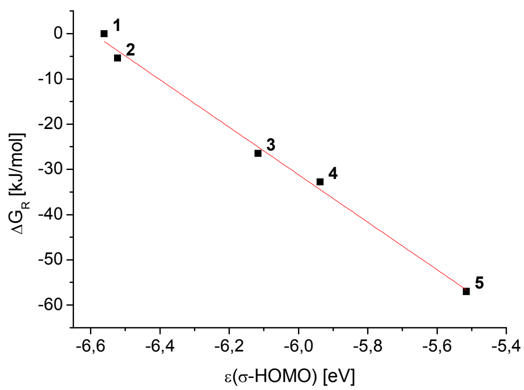

Fig. 4 Correlation ε(σ-HOMO) [eV] and ΔG_R [kJ/mol]

In summary, the relationship between donor strength and pincer/pseudo-pincer isomerism has been unambigously demonstrated in good agreement with experimental observations. Calculated or experimentally determined ε(σ-HOMO) values can thus serve as indication for the hemilability of the central donor site in similar complexes, allowing for a more rational ligand design and the synthesis of taylor-made pincer complexes.

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Notes and references

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