Are carbodiphosphoranes better ligands than *N*-heterocyclic carbenes for Grubb's catalysts?†

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Theoretical investigations suggest that substitution of an *N*-heterocyclic carbene by a carbodiphosphorane in the Grubb's catalyst for olefin metathesis might lead to enhanced reactivity.

1R **2R'**

Scheme 1 Carbodiphosphoranes (CDP, left) and saturated *N*-heterocyclic carbenes (NHC, right) investigated (R = Me, Ph; R′ = Me, Mes where Mes = mesityl).

Recent experimental and theoretical studies about the bonding situation and reactivity of carbodiphosphoranes $C(PR_3)_2$ have renewed the interest in this exceptional class of compounds.[1–3] Carbodiphosphoranes (CDP) are best described in terms of a divalent carbon(0)-atom stabilized by two phosphane groups in contrast to *N*-heterocyclic carbenes (NHCs) which are divalent carbon(II)-compounds (Scheme 1).[2] A theoretical investigation of the ligand properties of CDPs showed that they are capable of acting as σ- and π-donor ligands.[4] We decided to study possible implications of this finding for catalytic processes where strong donor ligands play an important role. Olefin metathesis is an obvious choice as a test case because the initial steps of the metathesis reaction with a 2nd generation Grubb's catalyst which bears an NHC ligand are known from earlier investigations.[5–7]

An appealing theoretical explanation for the enhanced reactivity of Grubb's catalysts bearing NHC-ligands instead of phosphane-ligands based on arguments concerning ligand rotation has recently been given by Straub.[8,9] Using his model as a starting point, we calculated[10] the corresponding energy profiles with model and real CDP- and NHC-ligands (Scheme 2). We focused on three main factors for a promising catalyst:

(1) Endergonic dissociation of the phosphane in the first step (**A-L** → **B-L**). In contrast to earlier assumptions, a higher barrier has been found favourable.[11,12]

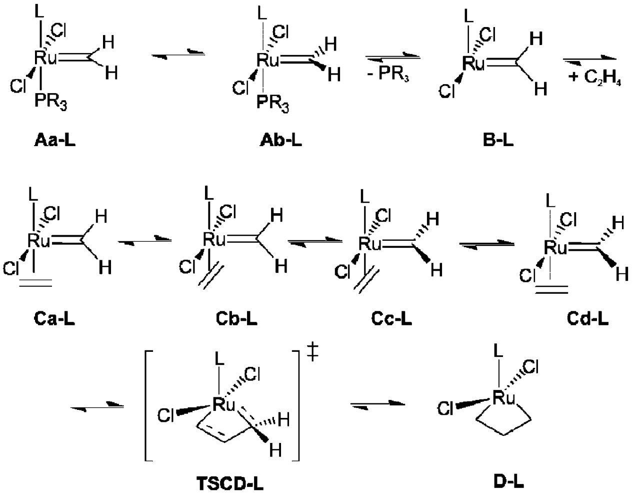
(2) Existence of active and inactive carbene conformations in the π-complex with the olefin **C-L**. A good catalyst should stabilise the active conformation (**Cc-L**).[8]

(3) Formation of a stable ruthenacyclobutane (**D-L**).[8]

The energy profiles for reactions **I** and **II** of the complexes **A-L** bearing model ligands with ethene are shown in Fig. 1. The first step starting from the energetically comparable conformers **Aa-L** or **Ab-L** shows the fulfillment of the first criterion defined above: the dissociation of the phosphane ligand (**A-L** → **B-L**) is more endergonic for **A-1Me** compared to **A-2Me**. The barrierless[13] olefin addition **B-L** → **C-L** yields an intermediate for which four different conformations **Ca-L–Cd-L** must be considered.[8,9] Conformer **Cd-L** is not a stationary point but rearranges directly to **D-L** as has been found earlier.[8]

The conformer **Cc-L** which was proposed to be the active conformer,[8] is lowest in energy with an even stronger stabilisation in the CDP-complex **Cc-1Me** (second criterion). Although the transition state **TSCD-1Me** is slightly higher in energy than **TSCD-2Me** the resulting ruthenacyclobutane **D-1Me** is more stable than its NHC-congoner **D-2Me** (third criterion).

The free energy changes for the reactions **I–IV** are summarised in Table 1. Note that the absolute energies for the dissociation energies are likely too high. A systematic study of theoretically predicted bond energies has shown that MP2 gives values which are too large, typically by 15–25%.[14] The calculated value for the bond dissociation energy of the PCy_3 ligand in compound **B-1Ph** is 33.5 kcal mol^{-1} (reaction **III**,



Reaction No.	I	II	III	IV
L	**1Me**	**2Me**	**1Ph**	**2Mes**
PR_3 with R =	Me	Me	Cy	Cy

Scheme 2 Reaction scheme and numbering (Cy = cyclohexyl).

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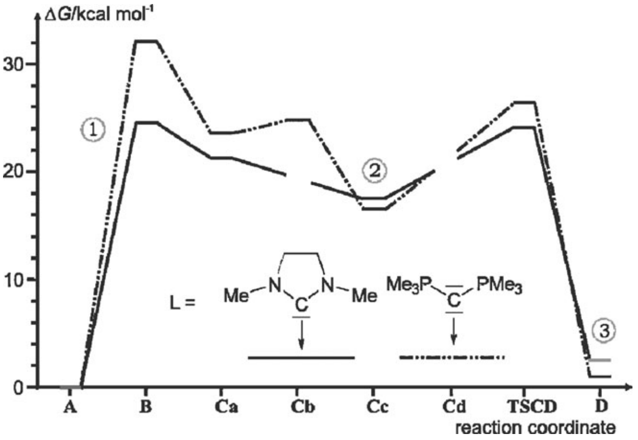

Fig. 1 Energy profile of the initial steps of olefin metathesis starting with **A-L**-complexes where **A** = [$Cl_2Ru({=}CH_2)(PMe_3)$] and L = **1Me**, **2Me**. Free energy changes (ΔG) at the MP2/TZVPP//BP86/SVP level of theory given relative to the starting materials in kcal mol^{-1}.

Table 1). Experimental studies have shown that the dissociation energy is <24 kcal mol^{-1}.[11,12] However, the trend which is predicted by the MP2 values for the reaction profiles of the different ligands should be correct.[14]

The data for the model and real CDP **1Me** and **1Ph** (reactions **I** and **III**, respectively) are very similar. Differences between the latter systems concern the conformation **Cb-1Ph** which is not a stationary point on the PES. A high dissociation barrier (**A-1Ph** → **B-1Ph**), a low-lying conformer **Cc-1Ph** and a stable ruthenacyclobutane **D-1Ph** show that the results derived for the model system can be transferred to the experimentally more interesting ligand **1Ph**.

A comparison of reactions **II** and **IV**, employing the NHC-ligands **2Me** and **2Mes** respectively, shows important differences (Table 1). The barrier for the loss of the PR_3-ligand (**A-L** → **B-L**) is significantly higher for the real NHC-ligand. Also the active conformation **Cc-2Mes** is higher in energy compared to **Cc-2Me**. Another indicator for the non-equivalent behaviour of **2Me** and **2Mes** as ligands is the relative energy of ruthenacyclobutane **D-2Mes** which is much higher than for **D-2Me**. This indicates that **2Me** is not a suitable model for the reactivity of **2Mes**. The results of the last two paragraphs suggest similar donor properties for **1Me** and **1Ph** and a higher donor strength of **2Mes** compared to **2Me**.

Table 1 Free energy changes (ΔG)[a] for reactions **I–IV** according to Scheme 2 given in kcal mol^{-1} relative to (**Aa-L** + ethene)

Reaction	I	II	III	IV
Aa	0.0	0.0	0.0	[b]
Ab	−0.6	−2.1	[b]	0.0
B	32.3	24.7	33.5	34.2
Ca	23.8	21.3	23.9	→ **D**[c]
Cb	24.9	→ **Ca**[c]	→ **Ca**[c]	31.3
Cc	16.5	17.6	15.0	27.9
Cd	→ **D**[c]	→ **D**[c]	→ **D**[c]	→ **D**[c]
TSCD	26.2	24.0	[d]	[d]
D	1.0	2.8	1.8	11.5

[a] Values at MP2/def2-TZVPP//BP86/SVP-level of theory. [b] No stationary point found. [c] Optimisations starting from structures of these conformations ended in minima corresponding to the conformations given in the table. [d] Transition structure search unfeasible.

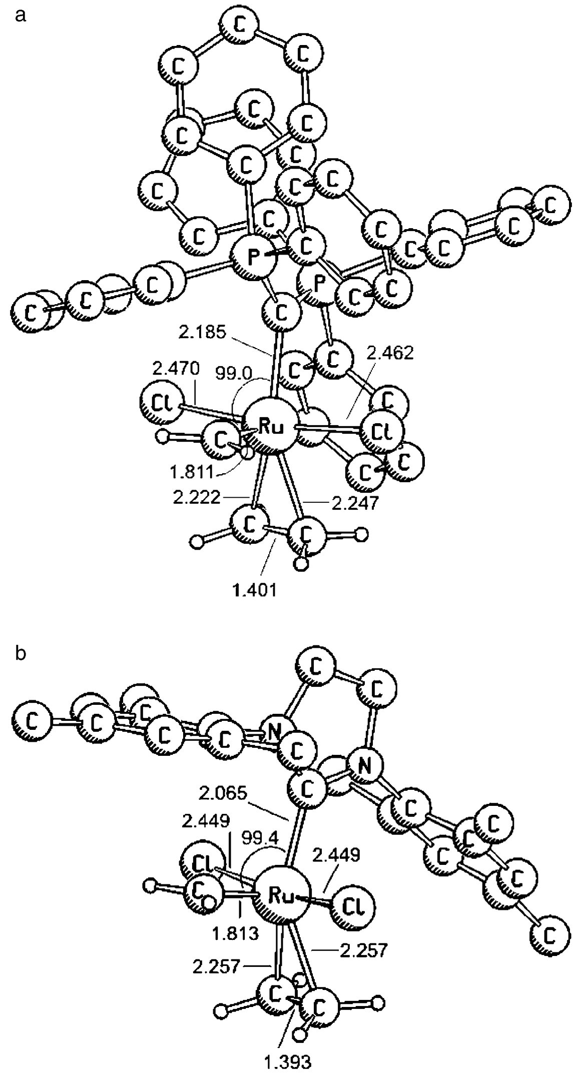

Fig. 2 Calculated geometries of **Cc-1Ph** and **Cc-2Mes** with selected bond length (in Å) and bond angles (in °) at BP86/SVP.

The most important conclusion which can be drawn from the data shown in Table 1 is that the real CDP-complex matches the energetic key features proposed for a good catalyst in olefin metathesis. As **1Ph** is available through well-known synthetic procedures,[15] it could be worthwhile to use this ligand in an experimental investigation of olefin metathesis reactions.

Since the steric requirements and the orientation of the ligand in the complexes are important for the catalytic activity we show the calculated geometries of the CDP complex **Cc-1Ph** and **Cc-2Mes** (Fig. 2). It becomes obvious that the structural features are similar which in both cases can be fine-tuned by the choice of the substituents.

After completion of this work a very interesting paper by Kennepohl and coworkers[16] was published which reports about experimental and theoretical investigations of the charge donation of phosphine and NHC ligands in Grubbs catalysts. It was found that the ruthenium atom in the complex which carries a NHC ligand is more positively charged than in the complex which carries a phosphine ligand. Therefore, it was concluded that NHC ligands are poorer donors than phosphine ligands even though they form stronger bonds. The authors suggest that the lower electron density at the metal center for the NHC-bound complexes should play an important role in defining the relative reactivities.[16] If this assumption is correct, the catalytic activity of the CDP-bound complexes might indeed be higher than that of the NHC-bound species. The NBO atomic partial charge at Ru in the CDP complex **Ab-1Me** (+0.15 e) is slightly larger than in the NHC complex **Ab-2Me** (+0.11 e).

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