

Replacement of N-heterocyclic carbenes by N-heterocyclic silylenes at a Pd(0) center: Experiment and theory

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Received 3 March 2005; accepted 16 March 2005

Available online 4 June 2005

Abstract

Via NMR-spectroscopy the relative reactivity of N-heterocyclic silylenes (NHSi) and carbenes (NHC) was studied. Reaction of sterically crowded bis-N-heterocyclic Pd(0) carbene complexes with free N-heterocyclic silylenes led to complete displacement of the N-heterocyclic carbene, which is unexpected knowing that usually a silylene is a weaker bound ligand compared to a carbene. High-level DFT calculations on a small model system and the experimentally used complexes confirm the experimental findings and indicate that steric interactions play an important role in the substitution reaction.

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Keywords: N-Heterocyclic carbene; N-Heterocyclic silylene; DFT calculations; Palladium; Steric repulsion

1. Introduction

Coordination chemistry directed towards catalysis has been boosted in recent years by the discovery of N-heterocyclic carbenes being powerful ligands [1]. Considering the electronic characteristics of this class of compounds the higher homologues N-heterocyclic silylenes (NHSi) and germylenes (NHGe) are also of interest and have therefore been studied experimentally [2–6] and theoretically [7–11]. We recently reported the formation of homoleptic palladium complex **1** for which an equilibrium with a dinuclear species **2** and free NHSi **3** was observed by NMR (Scheme 1) [12]. This assign-

ment was supported by X-ray structures of related dimeric complexes bearing terminal phosphines reported by Fuerstner and us [12,13]. Our observation is in contrast to the corresponding nickel compound prepared by West and coworkers [14].

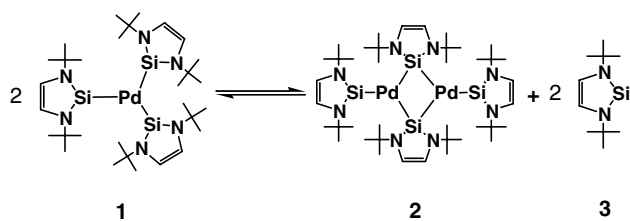
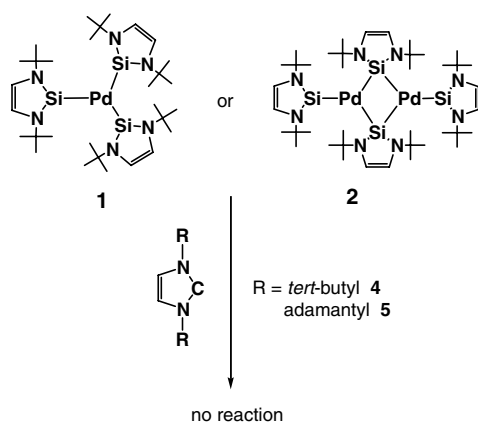
This prompted us to take a closer look at the chemical behavior of **1** on an experimental and theoretical basis. In a first set of experiments compounds **1** and **2** are treated with carbenes **4** (*t*Bu-Im) and **5** (Ad-Im). Unexpectedly, in both cases no reaction was detected (Scheme 2), although it is known from earlier experiments that phosphines can substitute a NHSi ligand in **1** with eventual formation of a mixed dinuclear complex [12].

In alternative experiments carbene complexes **6** and **7**, both generated in situ by phosphine exchange reactions with carbenes **4** and **5** starting from bis(tris(*tert*-butyl)phosphine)palladium(0) [15,16], were reacted with three equivalents of NHSi **3**. Additionally, complex **6** was isolated and then treated with NHSi **3** as

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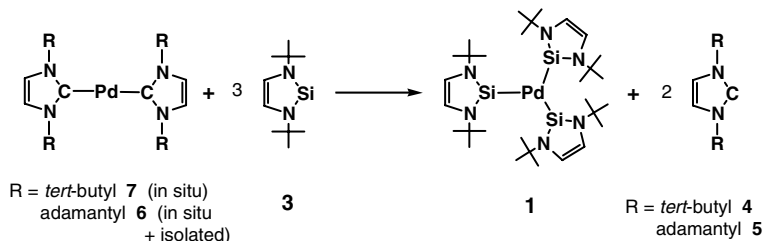
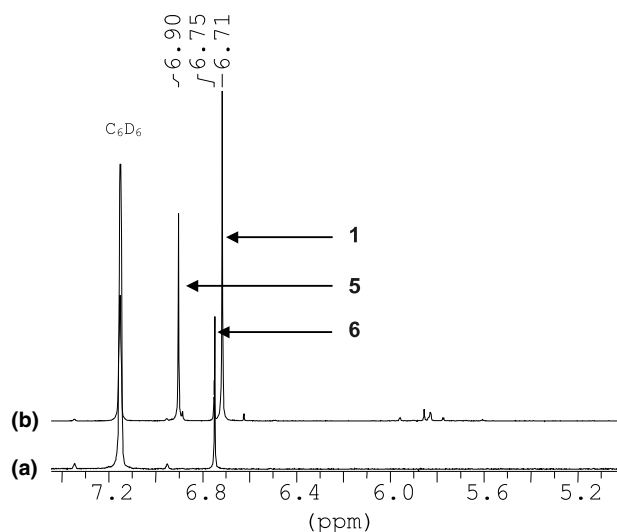
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Scheme 1. Equilibrium between **1** and binuclear species **2**.Scheme 2. Attempted conversion of Pd–NHSi complexes **1** and **2** with free NHC **4** and **5**.

described above. NMR monitoring revealed in both sets of reaction the N-heterocyclic carbenes being exchanged rapidly to form complex **1** without any formation of stable NHC containing intermediates (Scheme 3; Fig. 1).

To our knowledge this is the first time a complete replacement of NHCs in a Pd(0) system has been observed [17]. Previously, Nolan and coworkers found an equilibrium between Ni(*t*Bu-Im)(CO)₂ and Ni(CO)₄ [21]. From studies by Caddick and Cloke it is known that phosphines (P(*o*-tolyl)₃, PCy₃) are able to substitute one NHC ligand in **7** [22]. Since NHSis are known to have similar bonding properties to phosphines [23] and to form weaker metal–ligand bonds than NHCs [10], the formation of **1** is a surprising observation. To evaluate the substitution pathways and to investigate the reason for the unusual stability of the silylene complex

Scheme 3. Reaction of Pd–NHC complexes **6** and **7** with free NHSi **3**.Fig. 1. NMR spectrum of **6** before (a) / after (b) addition of NHSi **3**.

1 in the presence of NHCs, we undertook high-level DFT calculations.

2. DFT calculations

Generally, NHCs are known to be strong σ -donors with only weak π -back-bonding [9,10,24]. Compared to them NHSi are expected to have comparable properties with slightly enhanced π -back-bonding [10]. While there are many examples of quantum-chemical studies on NHC complexes [25], until now only a few theoretical reports on NHSi metal complexes have appeared [10,26,27].

This study has been directed towards the thermochemistry of the reaction observed by NMR to gain further insight into the pathway. All structures were optimized at the Becke3LYP/6-31G(d) level of theory. In the first part a model system was chosen consisting of NHC and NHSi ligands bearing methyl substituents, followed by calculations with the experimentally used complexes with *tert*-butyl substituents. This approach provides the opportunity to get a deeper understanding of the influence the steric demand of N-heterocyclic ligands has on the reactivity of the metal.

2.1. Model system calculations

Since there is only little known about the bonding properties of NHSis to Pd(0) we compared the bond strengths of a NHC, NHSi and a phosphine ligand by a model reaction, the coordination to the mono-NHC Pd fragment **8** leading to various disubstituted complexes (Scheme 4).

As expected, the free energy difference released by the coordination of a NHC ligand ($\Delta G = -35.2$ kcal/mol) is clearly higher compared to a NHSi ($\Delta G = -27.2$ kcal/mol). A similar trend was found for the dissociation energy of (NHC)MCl and (NHSi)MCl (M = Cu, Ag, Au) [10]. The weakest bond to palladium is established by trimethylphosphine ($\Delta G = -21.7$ kcal/mol). An earlier publication reported a dissociation energy of $\Delta E = 41.3$ kcal/mol for the NHC in a (NHC)Pd⁰(PH₃) complex (NHC = –NH–CH=CH–NH–C–) and an about 11 kcal/mol lower energy for the release of PH₃ [28].

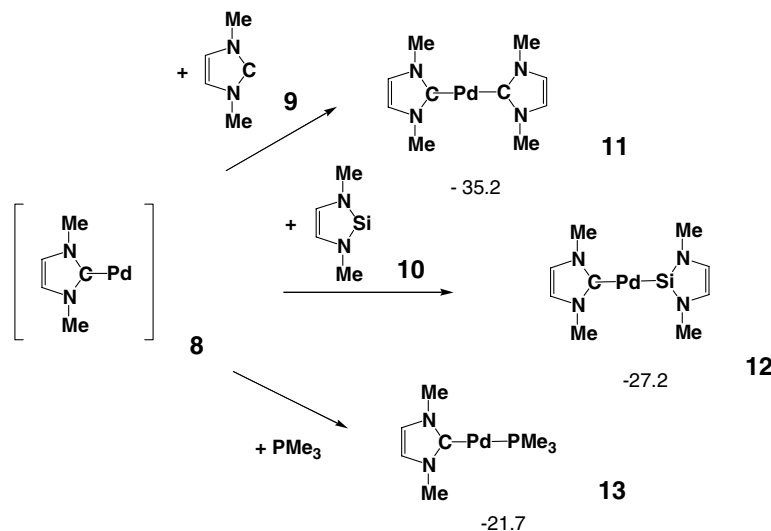
In the next step the NMR reaction was investigated (Scheme 5). In this part we are only looking at the energetic situation, structural aspects of the complexes are discussed below in connection with the *tert*-butyl system.

It was assumed that the exchange reaction proceeds via a step-wise exchange of NHC ligands by NHSi. Such a mechanism is well known from the reaction of Pd(0)–phosphine complexes with free NHC [15,16,22]. Starting from the bis-NHC complex **11** it can be clearly seen that an associative mechanism, i.e., the addition of one NHSi **10** leading to intermediate **15** ($\Delta G = +5.3$ kcal/mol), is the energetically favored reaction pathway for a ligand exchange. Due to the high bond strength of the NHC **9**, a dissociation is very unlikely ($\Delta G = +35.2$ kcal/mol). The same is true for the formation of a three-coordinated NHC-complex **14** ($\Delta G = +10.7$ kcal/mol). Stepwise ligand exchange leads to the tris-NHSi complex **18** which

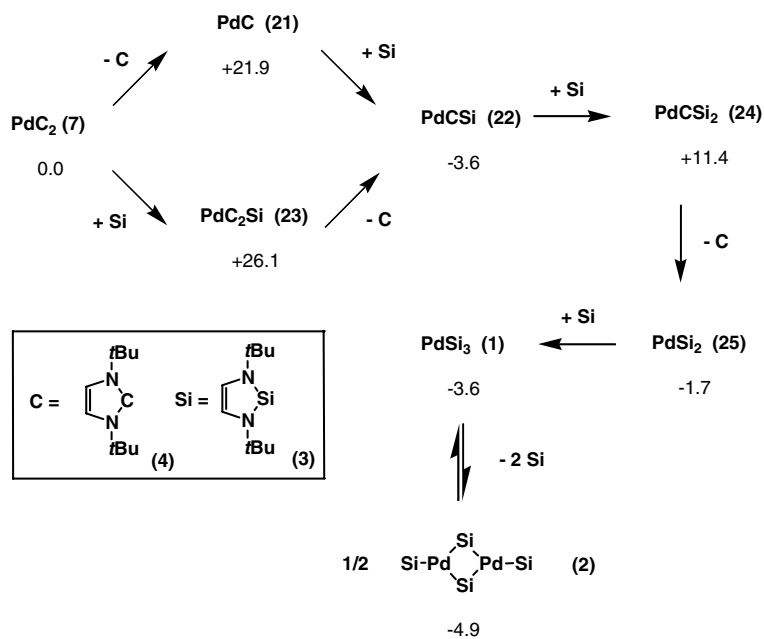
was detected by NMR. The energetically most unfavorable structure during this process is Pd(NHSi)₂ **17**. It is +20.4 kcal/mol higher in energy which also serves as a lower limit for the barrier of the overall reaction. In the case of the small methyl substituted NHSi ligands even the coordination of four silylenes is possible (Structure **19**). The binuclear complex **2** with bridging silylene elements was predicted earlier from NMR studies [12]. The DFT calculations confirm that the formation of the proposed binuclear structure in the equilibrium is possible, since the model complex **20** is almost isoenergetic with **18**. In summary, in two-coordinated complexes the more strongly bound NHC compared to the NHSi leads to a higher stability. Thus, Pd(NHC)₂ **11** is 8.0 kcal/mol lower in energy than Pd(NHC)(NHSi) **12** and 20.4 kcal/mol lower than Pd(NHSi)₂ **17**. The situation is more complex looking at the threefold coordinated complexes. Here, the sum of electronic factors and steric interactions leads to the situation that silylene complex **16** becomes more favorable than **14** or **15**. Due to the longer Pd–Si and Si–N distances and the smaller N–Si–N angles compared to the corresponding parameters in a NHC ligand, steric interactions between the ligands are significantly decreased in the case of a NHSi. This seems to be the reason why a NHSi is able to replace a NHC despite the lower bond strength. However, DFT calculations using the small methyl substituted model system can not explain the experimental results of the *tert*-butyl substituted ligands. Therefore we had to look at the real system.

2.2. Real system calculations

DFT calculations were repeated for important structures now bearing *tert*-butyl groups since the steric demand strongly depends on the substitution on the



Scheme 4. Coordination of a NHC, a NHSi and a phosphine to a Pd mono-NHC complex (B3LYP/6-31G(d); free energy values at 298.15 K in kcal/mol).

Scheme 7. Calculated structures in the substitution reaction in the *tert*-butyl system (B3LYP/6-31G(d); free energy values at 298.15 K in kcal/mol).

[31] found in a theoretical study about the pK_a of carbenes that **4** is only slightly more basic than **9**. The lability of sterically encumbered NHC ligands was proven in some experimental studies [21,22,32,33]. In particular,

Caddick and Cloke [34] reported a dissociation enthalpy of 25.6 kcal/mol for ligand **4** in the Pd(II) complex *trans*-[Pd(*t*Bu-Im)₂(4-Me-C₆H₄)Cl]. Our calculations predict a ΔH of 36.2 kcal/mol for the dissociation of one carbene

Table 1

Selected geometric parameters (bond distances in Å, bond angles in °; E denotes the group14 atom of the N-heterocyclic ligand (C or Si), μ bridging atoms)

	1	NHSi 3	NHC 4	7	21
Pd–E	2.35–2.37 (Si)	–	–	2.11 (C)	2.01 (C)
E–N	1.78 (Si)	1.78 (Si)	1.37 (C)	1.38 (C)	1.38 (C)
E–Pd–E	118.1–121.7 (Si)	–	–	180.0 (C)	–
N–E–N	88.5–88.6 (Si)	86.5 (Si)	102.5 (C)	103.3 (C)	104.3 (C)
	22	23	24	25	
Pd–C	2.17	2.21/2.33	2.32	–	
Pd–Si	2.25	2.39	2.33/2.36	2.32	
C–N	1.37	1.38–1.39	1.38	–	
Si–N	1.77	1.81	1.80	1.77	
C–Pd–C	–	136.3	–	–	
C–Pd–Si	180.0	107.6/116.0	121.6/134.2	–	
Si–Pd–Si	–	–	104.1	179.6	
N–C–N	104.0	102.6/102.8	103.0	–	
N–Si–N	89.1	86.7	87.8/87.9	89.4	
	2				
Pd–Pd	2.77				
Pd–Si _{terminal}	2.32				
Pd–Si _{μ}	2.48				
Si _{terminal} –N	1.78				
Si _{μ} –N	1.79				
Pd–Si–Pd	68.0				
Pd–Pd–Si _{terminal}	180.0				
Si _{μ} –Pd–Si _{μ}	112.0				
Si _{μ} –Pd–Si _{terminal}	124.0				
N–Si _{terminal} –N	88.7				
N–Si _{μ} –N	88.6				

4 in the biscarbene complex **7**. Although the electronic situation in both complexes is not directly comparable, this result seems reasonable since the steric demand in our two-coordinated complex is reduced compared to a four-coordinated complex. Our value compares well with a bond dissociation energy of 39 ± 3 kcal/mol of **4** determined experimentally in a Ni(0)-complex [21]. Relative to carbene complex **7** a stronger metal–ligand bond is established by the NHSi in **22** with a calculated strength of $\Delta G = 25.5$ kcal/mol, an up to now unknown behavior of N-heterocyclic ligands.

All recalculated structures of the NMR reaction are depicted in Scheme 7. Corresponding geometric parameters are given in Table 1; three-dimensional representations can be found in Fig. 2. It should be noted, that in this part Pd(0)-complexes with four ligands have not been considered since extremely high steric interactions between the *tert*-butyl substituents lead to unstable moieties.

As reported before, the influence on the geometry of the N-heterocyclic ligand by the coordination to the metal is small, only the N–E–N angle (E = C, Si) increases slightly [14,35,36]. Structures **23** and **24** reveal an interesting detail. Due to the high steric constraint the environment of one (**23**) or two (**24**) silicon atoms is distorted towards a tetrahedral coordination. Consistently, Pd–E and E–N bond lengths are elongated in these complexes (E = C, Si). Small deviations from the trigonal-planar coordination of the silicon atom in NHSi-ligands have also been observed in a crystal structure of a crowded nickel–NHSi complex [29]. Compared to that the coordination around the silicon atoms of the bridging NHSis in structure **2** can be regarded as distorted, but clearly tetrahedral. Surprisingly, there are only minor differences in the ring geometry relative to a terminal NHSi. This is consistent with a pure silylene character of the bridging silicon atoms, which was also found in only small differences in ^{29}Si NMR shifts of both NHSi in **2** [12].

In the *tert*-butyl case a dissociative mechanism in the carbene–silylene replacement process becomes more favorable than the addition of a NHSi by 4.2 kcal/mol comparing the ground states **21** and **23**. The structure **22** after exchange of one ligand is calculated to be remarkable stable (ΔG of -3.6 kcal/mol relative to **7**). The same is true for homoleptic structures **25** and **1**, the latter being the observed product. The reason is the decrease in steric interactions between the *tert*-butyl groups due to longer Pd–E and E–N bonds compared to that in a NHC (E = C, Si). The high steric constraint in the NHC complex **7** reduces the bond strength of the Pd–C bond and therefore allows NHSis to replace the NHCs. The bulkiness of NHC ligand **4** is also responsible for the above mentioned distorted coordination of the NHSi ligands in complexes **23** and **24** which are energetically unfavorable. Relative to educt **7** homolep-

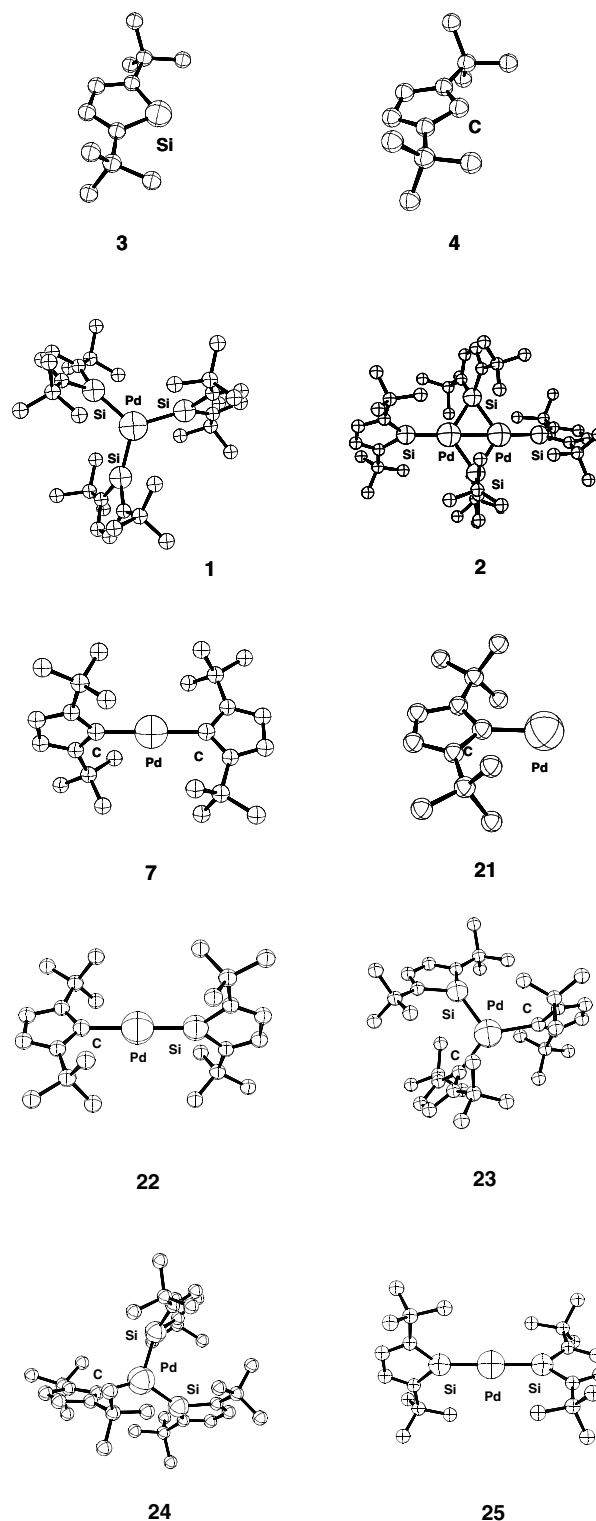


Fig. 2. Three-dimensional representations of calculated structures in the *tert*-butyl system (hydrogen atoms have been omitted for clarity).

tic silylene complexes **1** and **25** are favored, especially the formation of **1** is exergonic by -3.6 kcal/mol. This result is consistent with the initially unexpected formation of NHSi complexes from NHC complexes. Finally,

the formation of the dimer **2** relative to **1** is slightly exergonic with -1.3 kcal/mol.

3. Conclusions

In summary, the present study reveals that the classification of NHCs as a stronger bound ligand compared to NHSi needs more careful consideration. The energy of a NHC–metal bond is strongly influenced by the steric bulk on the nitrogen atom. In the present case this is the reason why the silylene shown above is able to replace the corresponding carbenes at a Pd(0) center because of the 3.6 kcal/mol higher overall bond strength. Due to longer Pd–Si and Si–N bond lengths and a lower N–Si–N angle steric interactions are clearly reduced, which in case of a *tert*-butyl substituent at the nitrogen atoms allows three NHSi ligands to bind to the metal center. Furthermore, an equilibrium of this complex is established in solution with a bridged dinuclear species to further decrease the steric bulk. The latter structure was proposed from NMR studies and its existence could be confirmed by DFT calculations.

4. Experimental

All manipulations were carried out in an argon-filled glovebox. Solvents were dried prior to use and degassed. ^1H NMR spectra were recorded at 400 MHz in d_6 -benzene at RT on a Bruker DPX 400. The free NHSi **3** [37], NHC **4** and **5** [38,39], as well as the NHSi–Palladium [12] and NHC–palladium-complexes [15,16] were prepared according to literature procedures. NMR experiments: both reactants were dissolved in about 0.3 ml of d_6 -benzene. The metal-complex solution was transferred to an NMR tube and sealed with a septum. The second educt was filled in a syringe and subjected into the NMR tube shortly before starting the NMR measurement. After a short shaking period the spectra were recorded. The resulting NMR spectra have been compared with the known shifts of the educts and known homoleptic complexes. The experiments were carried out with various equivalents of reagents. In all cases the same results could be observed.

5. Computational details

All calculations were performed with GAUSSIAN 98 [40]. The density functional hybrid model Becke3LYP [41–44] was used together with the valence double- ζ basis set 6-31G(d). Palladium was treated by a small core Hay–Wadt VDZ effective core potential (ECP) [45]. No symmetry or internal coordinate constraints were

applied during optimizations. All reported intermediates were verified as true minima by the absence of negative eigenvalues in the vibrational frequency analysis. Approximate free energies were obtained through thermochemical analysis of the frequency calculation, using the thermal correction to Gibbs free energy as reported by Gaussian. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. All energies reported in this paper, unless otherwise noted, are free energies at 298 K and 1 atm. Frequencies remain unscaled.

Acknowledgements

We are grateful to the Leibniz-Rechenzentrum Muenchen for providing computer time and financial support of the Fonds der Chemischen Industrie. We thank Dr. Christian Gstöttmayr for helpful discussions. A.Z. thanks the “Gesellschaft der Freunde und Förderer der Technischen Universität Dresden” for a generous travel grant.

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