Unexpected Trimerization of Pyrazine in the Coordination Sphere of Low-Valent Titanocene Fragments

Thomas Jung,[†] Rüdiger Beckhaus,[*,†] Thorsten Klüner,[*,‡] Sebastian Höfener,[§] and Wim Klopper[*,§]

Inorganic Chemistry and Theoretical Chemistry, Institute of Pure and Applied Chemistry, Carl von Ossietzky University, D-26111 Oldenburg, Germany and Institute of Physical Chemistry, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

Abstract: The titanium mediated trimerization of pyrazine leads to the formation of a tris−chelate complex employing a 4a,4b,8a,8b,12a,12b-hexahydrodiyprazino[2,3-*f*:2′,3′-*h*]quinoxaline ligand ($HATH_6$, **3**). The driving force in the formation of the $(Cp*_2Ti)_3(HATH_6)$ complex **2** is attributed to the formation of six Ti−N bonds. We show that density functional theory (DFT) fails to predict quantitatively correct results. Therefore, post-Hartree−Fock methods, such as second-order Møller−Plesset perturbation theory (MP2), in combination with coupled-cluster (CC) methods must be used. Both MP2 and CCSD(T) levels of theory provide endothermic trimerization energies, showing that the plain pyrazine trimer is not stable with respect to decomposition into its monomers. Complete basis set (CBS) results for the MP2 level of theory were computed using explicitly correlated wave functions. With these, we estimate the CCSD(T) CBS limit of the hypothetical trimerization energy to be +0.78 eV. Thus, the trimerization is facilitated by the formation of six Ti−N bonds with a calculated formation energy of −1.32 eV per bond.

Introduction

One of the general advantages of organometallic compounds is their ability to stabilize highly reactive, short-lived organic molecules and fragments in the coordination sphere of transition metals. Some remarkable examples are arynes and aryne complexes,[1] vinylidenes and vinylidene complexes,[2] and cyclobutadiene and its complexes.[3] In the course of our investigations concerning the self-assembled formation of multinuclear highly ordered complexes, employing low-valent early transition-metal complexes and aromatic bis-azines as bridging ligands, different reaction patterns have been found.[4] In these investigations, the formation of well-

Scheme 1. Formation of $(Cp*_2Ti)_3(HATH_6)$ (**2**)
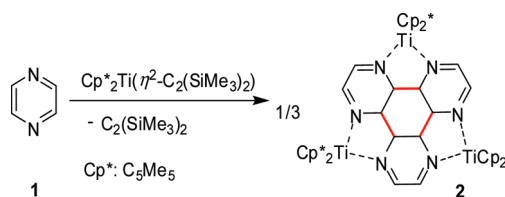
defined molecular squares or rectangles,[5] dehydrogenative[6,7] as well as C−C coupling reactions induced by the primary formation of radical anions have been observed (Scheme 1).[8]

The formation of the trinuclear titanium complex **2** by a spontaneous 3-fold C−C coupling of three pyrazine molecules (**1**) inspired us to investigate theoretically the hypothetical C−C coupling reaction of three pyrazine molecules (Scheme 2), forming the 4a,4b,8a,8b,12a,12b-hexahydrodiyprazino[2,3-*f*:2′,3′-*h*]quinoxaline ligand ($HATH_6$, **3**).
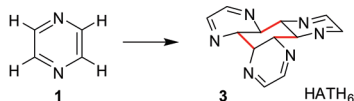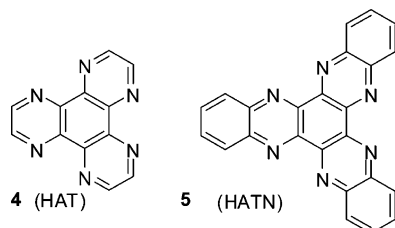
To the best of our knowledge, the nonaromatic molecule $HATH_6$ (**3**) is still unknown, in contrast to the well-known aromatic hexaazatriphenylen ligand (HAT) (**4**). However,

* Corresponding authors. Telephone: +49 441 798 3656 (R.B.); +49 441 798 3681 (T.K.); and +49 721 608 7263 (W.K.). Fax: +49 441 798 3851 (R.B.); +49 441 798 3964 (T.K.); and +49 721 608 3319 (W.K.). E-mail: ruediger.beckhaus@uni-oldenburg.de (R.B.); thorsten.kluener@uni-oldenburg.de (T.K.); and klopper@chem-bio.uni-karlsruhe.de (W.K.).

† Inorganic Chemistry, Carl von Ossietzky University.

‡ Theoretical Chemistry, Carl von Ossietzky University.

§ Universität Karlsruhe (TH).

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Scheme 2. Formation of HATH₆ (**3**)

Chart 1.

the chemistry employing **4** is often limited by the low solubility and the laborious synthesis.[9] HAT derivatives are generally interesting ligands for different applications. The tris-chelating nitrogen heterocyclic molecule 1,4,5,8,9,12-hexaazatriphenylene (HAT) was often studied in the context of its coordination modes to metal ions,[10] photophysical properties,[11] liquid crystalline ordering,[12] light-harvesting functionality,[13] chirality,[14] and DNA related chemistry.[15] When employing quinoxaline instead of pyrazine in the reaction **1**→**2**, the formation of 1,6,7,12,13,18-hexaazatrinaphthylene (HATN, **5**) via the corresponding [(Cp₂Ti)₃(HATN)] complex is observed.[6] Under oxidative conditions, **5** can be obtained in quantitative yields. In attempts to use this oxidative workup procedure for **2**, no hints of **3** are found. Only traces of **4** are obtained (Chart 1).

The molecular symmetry of HAT derivatives leads to especially interesting building blocks creating self-assembled 3D frameworks.[16] Employing paramagnetic metal centers in

HAT-type complexes, magnetic properties of those derivatives,[17] including spin-frustrated behavior or antiferromagnetic couplings, are of interest.[18]

Under experimental conditions, **2** is characterized by the formation of an ideal cyclohexane ring in the chair conformation, exhibiting all hydrogens in axial positions. By comparing the experimental[8] structural parameters of the titanium complex **2** with the hypothetical molecule **3** (studied theoretically at the MP2/cc-pVTZ level), it is found that the enamide form **A** becomes dominant for **2**, whereas the diazadiene structure is preferred in **3** (Figure 1).

The dominating enamide form **A** for **2** becomes obvious by comparing the C−C and C−N distances in **2** and **3** (Figure 1).[8]

The Csp^3-Csp^3 bond lengths of the central cyclohexane rings of **2** and **3** are nearly identical (**2**: av. 1.53 Å; **3**: 1.52 Å). The Csp^2-Csp^2 bond lengths of **2** and **3** show slight differences (**2**: av. 1.41 Å; **3**: 1.47 Å). In the same way, the Csp^2-N distances are longer in **2** (av. 1.345 Å) than in **3** (1.29 Å).

Theoretical Study

To shed light on the energetics of the pyrazine trimerization, we calculated the corresponding reaction energy at various levels of theory. The results we obtained first are summarized in Table 1, where we report reaction energies for two different basis sets applying density functional theory (DFT) and ab initio quantum chemical methods. Regardless of the level of theory, we found the pyrazine trimerization to be energetically unfavorable with reaction energies in the range of 0.64 to 2.32 eV. Although this result is not unexpected as such, the large range of energies is quite disturbing. Analyzing our results in detail, we found that DFT generally
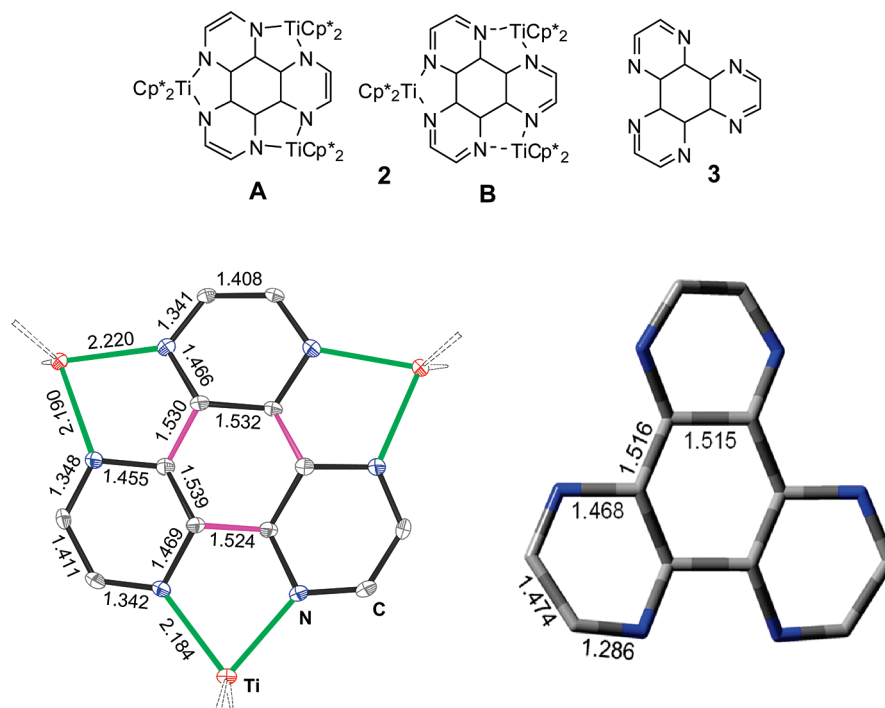

Figure 1. C−C and C−N distances (Å) in the titanium complex **2** (X-ray structure, left) and the hypothetical molecule **3** (right) (Ti red, N blue, C gray).

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Table 1. Endothermic Trimerization Energy (in eV) As Obtained at Various Levels of Theory (Full Geometry Optimization)[a]

basis	method	ΔE/eV
cc-pVDZ	B3LYP[26–29]	1.98
	PBE[30]	1.43
	PW91[31,32]	1.40
	PBE1W[33]	1.77
	MPWLYP1W[33]	2.15
	HF	1.90
	MP2	1.04
	CCSD//MP2	0.64
	CCSD(T)//MP2	0.68
cc-pVTZ	B3LYP[26–29]	2.32
	PBE[30]	1.70
	PW91[31,32]	1.70
	PBE1W[33]	2.07
	MPWLYP1W[33]	2.55
	MPWB1K[34–36]	1.42
	HF	2.01
	MP2	1.11
	CCSD//MP2	0.71

[a] The CCSD and CCSD(T) results were obtained at the corresponding MP2/cc-pVDZ and MP2/cc-pVTZ geometries (denoted as //MP2). Only valence orbitals were correlated.

fails to predict accurate results for this endothermic reaction, underestimating the stability of the pyrazine trimer by up to 1.5 eV.[19–22] Note that the very popular B3LYP hybrid exchange-correlation functional seems to give the worst results of any mean-field method, including Hartree–Fock (HF). Recent functionals such as PBE1W and MPWLYP1W do not improve the situation, although the MPWB1K functional turns out to be superior to other exchange-correlation functionals. Taking our CCSD and CCSD(T) calculations as a reference, MP2 gives much more accurate energies than that of HF or DFT, although an error of about 0.5 eV remains. To further analyze this phenomenon and to estimate the MP2 reaction energy at the complete basis set (CBS) limit, we subsequently performed MP2-F12 calculations in which we found an endothermic trimerization energy of 1.14 eV (Table 2).

The trimerization of pyrazine is endothermic by about 0.64–0.68 eV at the coupled-cluster level in a small double-ζ basis (CCSD/cc-pVDZ and CCSD(T)/cc-pVDZ values). In this same basis, the MP2 value amounts to 1.04 eV, and hence, our best estimate for the trimerization energy is 0.78 eV. This value is expected to represent the CCSD(T) basis set limit. In view of the large variation in the DFT results, we conclude that an accurate treatment of electron correlation is crucial to obtain quantitatively correct results. Here, accuracy refers to both excitation level (up to connected triples) and one-particle basis set (F12 approach).

For a realistic treatment of the whole reaction, the pyrazine trimerization was furthermore studied in the presence of three equivalents of $TiCl_2$, leading to **6**, which serves as a model compound for **2** in which the Cp* ligand is substituted by chlorides. This choice is motivated by computational savings and validated by previous experimental studies.[23]

In view of the large computational effort, we restricted these calculations to MP2 studies using a cc-pVDZ basis set. Although the error in the trimerization energy is at least 0.3–0.4 eV, as suggested by the results reported in Tables 1 and 2, the qualitative interpretation of our results is straightforward. Due to the formation of six Ti–N bonds, the reaction of **1**→**6** becomes strongly exothermic, exhibiting a reaction energy of about −8.70 eV, assuming a high-spin configuration of maximum multiplicity. This results in a formation energy of about −1.32 eV (127 kJ mol^{-1}) per Ti–N bond (calculated from (8.70 − 0.78 eV)/6), which is a reasonable value in good agreement with rare experimental values for titanium(II) complexes employing π-acceptor ligands, as shown for $Cp_2Ti(\eta^2$-PhN=NPh) (144 ± 12 kJ mol^{-1}).[24] In the case of titanium(IV) amido derivatives, higher mean bond enthalpies are found (e.g., 334 ± 10 kJ mol^{-1} for $Cp_2Ti(NC_8H_6)_2$).[25] Thus, despite the fact that the pyrazine trimerization is energetically unfavorable, we predict a strong stabilization of the trinuclear titanium complex **2**.

Hence, our quantum chemical calculations reveal how Ti-based coordination chemistry can be used to stabilize a pyrazine trimer species, which corresponds to a highly endothermic reaction in a gas phase. Further experimental and theoretical studies will explore this new potential of possible reactivity.

Conclusions

The formation of the pyrazine trimerization product in form of the trinuclear titanium complex **2** illustrates in a spectacular manner the advantages of organometallic synthesis. Due to the formation of six moderately strong Ti–N bonds, the pyrazine trimer is stabilized, although a trimerization of pyrazine as such is an energetically unfavorable process, that is, an endothermic reaction. As our large-scale high-quality ab initio calculations reveal, such a trimerization is energetically clearly unfavorable, exhibiting a hypothetical formation energy of +0.78 eV. It should be noted that the pyrazine trimerization reaction turns out to be a prominent example of a complete failure of popular DFT functionals. Along these lines, PBE and PW91 results are virtually identical and strongly overestimate the endothermic reaction energy by almost 1 eV. The widely used hybrid functional B3LYP exhibits an even larger error of about 1.5 eV, which is worse than Hartree–Fock. The best DFT result has been obtained using the MPWB1K functional still resulting in an error of about 0.7 eV with respect to our coupled-cluster calculations. Thus, the pyrazine trimerization reaction turns out to be a prominent example in which an accurate correlation treatment is mandatory. Our large-scale correlation calculations, which explore the limits of currently available computing resources, allow for a systematic and highly accurate calculation of the pyrazine trimerization energy. Eventually, we demonstrate

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Table 2. Endothermic Trimerization Energy (in eV) as Obtained at the Frozen-core MP2-F12 Level[a]

basis	CABS	MP2 fitting basis	JK fitting basis	Hartree−Fock	MP2	MP2-F12
def2-TZVP	def2-SVP	def2-QZVPP	def2-QZVPP	2.30	2.11	1.33
def2-TZVP	def2-TZVP	def2-QZVPP	def2-QZVPP	2.30	2.11	1.31
aug-cc-pVTZ	cc-pVTZ	aug-cc-pVQZ	aug-cc-pVTZ	2.15	0.94	1.06
aug-cc-pV5Z	cc-pVTZ	aug-cc-pV5Z	aug-cc-pV5Z	2.19	1.13	1.14

[a] Using Ansatz 2B and a Slater-type geminal exponent of $\gamma = 1.4$ a$_0^{-1}$. The frozen-core MP2/cc-pVTZ equilibrium structures were used for all calculations. An MP2 fitting basis was used as complementary auxiliary basis set (CABS).

Table 3. MP2 Valence Shell Correlation Energies (in Hartree) for the Benzene Molecule with Various Basis Sets[d]

basis	basis size	ΔE_{MP2}	%[a]	$\Delta E_{MP2\text{-}F12}$ fixed[b]	%[a]	$\Delta E_{MP2\text{-}F12}$ optimized[c]	%[a]
aug-cc-pVTZ	414	−0.9645	91.2	−1.0505	99.3	−1.0534	99.6
aug-cc-pV5Z	1242	−1.0358	97.9	−1.0571	100.0	−1.0573	100.0
aug-cc-pV6Z	1896	−1.0446	98.8	−1.0576	100.0	−1.0576	100.0
def2-TZVP	222	−0.9325	88.2	−1.0432	98.6	−1.0483	99.1
def2-QZVPP	522	−1.0081	95.3	−1.0544	99.7	−1.0555	99.8

[a] The percentage with respect to the estimated MP2 basis set limit. [b] The F12 amplitudes were held fixed according to the rational generator approach. [c] The F12 amplitudes were optimized variationally. [d] The limit is estimated to be −1.0576 ± 0.0005 E$_h$.[58]

in a quantitative manner how the formation of a pyrazine trimer as a trinuclear titanium complex can be rationalized.

Experimental Section

Synthesis. The trinuclear complex **2** was prepared by reaction of Cp*$_2$Ti(η^2-C$_2$(SiMe$_3$)$_2$) with pyrazine in a 1:1 ratio, as described earlier.[8]
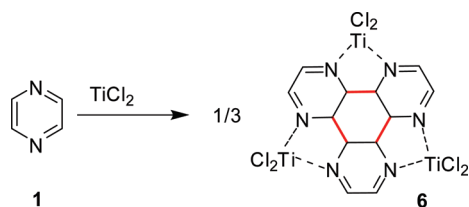
Pyrazine Trimerization 1→3. Almost all calculations concerning the energetics of the pyrazine trimerization **1→3** were performed using the Gaussian03[37] quantum chemistry program package. Only the explicitly correlated MP2-F12 calculations were performed with an experimental version of the Turbomole v5.10 code.[38] Using correlation-consistent basis sets of cc-pVDZ and cc-pVTZ-quality,[39] we applied different DFT approaches, including the B3LYP, PBE, PW91, PBE1W, MPWLYP1W, and MPWB1K functionals for exchange and correlation. For a more accurate treatment of electron correlation, we performed conventional ab intio calculations at the MP2 level. The energy of the trimerization reaction was calculated performing full geometry optimizations of reactants and products for each basis set and level of theory. In order to improve our prediction of the energetics further, we performed CCSD and CCSD(T) calculations using the MP2-optimized structures for each basis set.

Explicitly Correlated Calculations. To explore errors due to truncation of the one-particle basis set, we performed MP2-F12 calculations[40,41] in the basis sets def2-TZVP,[42] aug-cc-pVTZ,[39,43] and aug-cc-pV5Z.[39,43] For the trimer, the latter basis comprises as many as 3 246 contracted basis functions, and, apart from the purpose of calculating accurate second-order trimerization energies, the MP2-F12/aug-cc-pV5Z calculations were also performed to assess the performance of our newly developed code.[44,45] The MP2-F12 calculations were performed using ansatz 2B[40] with a complementary auxiliary basis set (CABS) to approximate three electron integrals.[46] Two electron integrals were approximated using robust density fitting.[47] A Slater-type geminal[48] with exponent $\gamma = 1.4$ a$_0^{-1}$ was used as explicitly correlated two-particle basis function (represented by a six-term Gaussian expansion[49]). To circumvent two-electron

integrals involving commutators of kinetic energy and Fock operators, we applied an approach similar to that of Kedžuch and co-workers.[50] The F12 amplitudes were held fixed, following the rational generator approach of Ten-no.[51] The MP2-F12 model has been implemented in the module RICC2 of Turbomole developed by Hättig and co-workers.[52,53] As CABS, we used the def2-SVP, def2-TZVP, and cc-pVTZ cbas sets of Weigend et al.[54,55] that usually are used for Coulomb fitting in RI-MP2 theory (MP2 fitting basis). For the density fitting approach itself within both the MP2 and F12 parts, we used the def2-QZVPP and aug-cc-pVXZ (X = Q, 5) cbas sets of Hättig.[56] To represent the Fock operator within the MP2-F12 calculation of the correlation energy, we used the JK fitting basis sets (jkbas) of Weigend.[57]

To be able to judge the quality of the explicitly correlated calculations, we have added results for benzene of which the MP2 complete basis set limit is well-known (Table 3).[58] These calculations were carried out using the Slater exponent $\gamma = 1.5$ a$_0^{-1}$ and the Coulomb fitting basis def2-QZVPP as CABS. The geometry was taken from ref 58. Table 3 shows that 99.95% of the valence shell correlation energy of benzene is recovered at the MP2-F12/aug-cc-pV5Z level using fixed amplitudes, and we expect that the MP2-F12/aug-cc-pV5Z calculations of the reaction energy of the trimerization of pyrizine are equally accurate.

As usual, the convergence of the conventional results is rather slow, even in the augmented sextuple-zeta basis with more than 1 800 contracted basis functions, less than 99% of the MP2 correlation energy limit is obtained. Table 3 demonstrates clearly a significantly improved convergence behavior when explicit correlation is taken into account in the wave function. Even using fixed amplitudes, the MP2-F12 calculation in a small def2-TZVP basis with only 222 contracted basis functions is almost as accurate as the standard MP2 calculation in an aug-cc-pV6Z basis. When the F12 amplitudes are optimized variationally, the small basis even outperforms this conventional result. Nevertheless, the differences among fixed and variationally optimized F12 amplitudes are small. Hence, for larger systems such as the pyrazine trimer, the fixed amplitudes approach is favorable because fixing the amplitudes results in much lower com-

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Scheme 3. Formation of **6**

Pyrazine Trimerization 1→6. All calculations for the trimerization reaction **1→6** were performed at the MP2 level of theory with full geometry optimization employing for Ti a Karlsruhe[40,41] DZ basis set augmented by one polarization set of f-type functions with an exponent of 0.8 a_0^{-2}. All remaining atoms were represented using a cc-pVDZ set. In all calculations of Ti-containing compounds, maximum-spin multiplicity was assumed, that is, $TiCl_2$ was calculated in a triplet state, which could be verified by subsequent calculations, while the complex **6** was treated as a septet.

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