3350 *J. Phys. Chem. A* **2004,** *108,* 3350−3355

# Reductive Nitrile Coupling in Niobium−Acetonitrile Complexes Probed by Free Electron Laser IR Multiphoton Dissociation Spectroscopy

**Björn M. Reinhard,*,[†,&] Anita Lagutschenkov,[†] Joël Lemaire,[‡] Philippe Maitre,[‡] Pierre Boissel,[‡] and Gereon Niedner-Schatteburg*,[†]**

*Fachbereich Chemie, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany, and Laboratoire de Chimie Physique, CNRS-UMR-8000, Université Paris XI, Bâtiment 350, 91405 Orsay Cedex, France*

*Received: November 3, 2003; In Final Form: February 3, 2004*

Experimental IR multiphoton dissociation spectra of cationic niobium−acetonitrile complexes with the formal stoichiometry $[Nb,nCH_3CN]^+$, $n = 4$, 5 (the notation $[Nb,nCH_3CN]^+$ was chosen in order to emphasize the formal stoichiometry of a cluster without implying any structural information), as provided by the Free Electron Laser at CLIO, Orsay, France, are compared to ab initio IR absorption spectra throughout the spectral "fingerprinting" range 780−2500 cm$^{-1}$. For $n = 4$ the vibrational spectrum in combination with the performed ab initio calculations provides strong evidence for a square-planar high-spin quintet $[Nb^I(NCCH_3)_4]^+$ complex. For $n = 5$, additional vibrational bands between 800 and 1550 cm$^{-1}$ are interpreted in terms of covalent C−C coupling in $[Nb,5CH_3CN]^+$. Screening on the basis of ab initio calculations leads to the assignment of the recorded spectrum to the metallacyclic species $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ with an electronic triplet state. The deduced processes upon 4-fold and 5-fold coordination of $Nb^I$ with $CH_3CN$ in the gas-phase are complexation only and reductive nitrile coupling, respectively. The minimum energy pathways of the reductive nitrile coupling reaction in $[Nb^I(NCCH_3)_n]^+$, $n = 4$, 5, investigated for singlet, triplet, and quintet states ($S = 0$, 1, 2) by density functional theory, account well for the observed (non)reactivity. In ground state (triplet, $S = 1$) $[Nb^I(NCCH_3)_5]^+$ the reaction is found to be exothermic and the activation barrier amounts to approximately 49 kJ mol$^{-1}$, whereas for ground state (quintet, $S = 2$) $[Nb^I(NCCH_3)_4]^+$ the corresponding reaction is endothermic and would require an activation of more than 116 kJ mol$^{-1}$.

## Introduction

Reactions that form new C−C bonds correspond to key steps in the catalytic synthesis of a variety of organic compounds. For instance the McMurry C−C coupling of two aldehydes or ketones yields vicinal diols when catalyzed by titanium at low temperatures.[1] Reductive nitrile C−C coupling can occur when nitrile complexes or metal halides in the presence of nitriles are reduced.[2,3] While some reactions of cationic niobium clusters with acetonitrile have been the subject of mass spectrometric studies under single collision conditions,[4] the structures of niobium−acetonitrile complexes and clusters are still unknown. Other than in bulk-phase solutions, the IR spectroscopy of isolated gas-phase complexes is not complicated by ligand−solvent interactions. However, IR spectroscopic studies of isolated gas-phase complexes face the inherent problem of low number densities, which do not allow application of traditional IR absorption techniques. In this work the vibrational spectra of niobium−acetonitrile complexes are investigated by IR multiphoton dissociation spectroscopy (IR-MPD)[5,6] instead. After absorption of an IR photon, internal vibrational relaxation (IVR)[7,8] within the excited complex randomizes the excitation energy out of the excited vibrational mode into the heat bath of all the accessible modes. IR-MPD spectroscopy relies on this ready coupling and that at least a single fragmentation channel of the complex is effectively activated. Although the IR-MPD technique can cope with the inherent problem of the low concentration of ions in the gas-phase, this technique suffers from the lack of common high-power tunable light sources for the full range of the chemical infrared. The spectral range of, e.g., line-tunable $CO_2$ lasers is limited to 930−1085 cm$^{-1}$, and modern optic parametric oscillators (OPOs) do not cover spectral ranges below ≈2200 cm$^{-1}$. It was shown before[9−13] that a free electron laser (FEL) is suitable to activate IR-MPD over a wide frequency range, yielding data that closely mimic IR absorption spectra.[14−15]

The performed FEL-IR-MPD experiments were supplemented with ab initio calculations which allow for an unambigious interpretation of the gas-phase IR spectra and as such provide a powerful tool for structure determination.

## Experimental and Computational Methods

The IR spectra were recorded at the "Centre Laser Infrarouge d'Orsay" (CLIO) FEL facility. The experimental setup at CLIO is based on a 10−50 MeV electron accelerator and has a very large wavelength range in the infrared from 3 to 75 $\mu$m, which is continuously tuneable over a wide spectral range ($\Delta\lambda/\lambda \approx 2.5$). The FEL temporal structure is composed of sequences of macropulses with a duration of 8 $\mu$s at a repetition rate of 25 Hz. Each of these macropulses contains 500 micropulses, which are only a few picoseconds long. The FEL laser light was focused into the center of a 1.25-T Fourier-transform ion cyclotron resonance (FT-ICR) ion trap by a spherical mirror of

---

* To whom correspondence should be addressed. E-mail: B. M. Reinhard, bmr@chemie.uni-kl.de; G. Niedner-Schatteburg, gns@chemie.uni-kl.de.

[†] Technische Universität Kaiserslautern.

[‡] Université Paris XI.

[&] Present address: Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720.

10.1021/jp037337i CCC: \$27.50

1 m focal length (estimated laser spot size ≈400 μm).[16] The open design of the ICR cell in use provides good optical access to its center, facilitating spectroscopic investigations of ions stored within it. Atomic $Nb^I$ monocations were generated by a Nd:YAG laser driven ablation off a niobium target adjacent to the ICR cell. Acetonitrile ($CH_3CN$) was admitted into the cell through a pulsed valve at $3.5 \times 10^{-6}$ mbar for 200 ms. Subsequently, $Nb^I$ ions were allowed to form complexes with $CH_3CN$ for 1 s, and those complexes with the formal stoichiometry $[Nb,nCH_3CN]^+$ were mass-selected by resonant frequency ejection techniques. Exposure to FEL-IR radiation for 2 s led to multiphoton absorption and complex fragmentation when resonant with a fundamental vibration. Fragment ion intensities and parent ion "dips" were recorded as a function of the FEL wavelength in order to obtain the experimental IR-MPD spectra. The IR-MPD spectra were recorded at average FEL powers of approximately 280 and 400 mW, respectively.

If not stated otherwise, ab initio IR absorption spectra were calculated at the B3LYP level of theory and for singlet ($S = 0$), triplet ($S = 1$), and quintet ($S = 2$) spin states. This method was chosen as several calibration calculations have proven that this functional yields accurate geometries and vibrational frequencies in transition-metal compounds.[17,18] Ahlrichs polarized triple-ζ basis sets were applied for C,N,H.[19] A relativistic effective core potential[20] and Ahlrichs polarized triple-ζ basis set described the Nb (1s−3d) and valence electrons, respectively. By comparison of B3LYP/TZVP calculated IR frequencies of the free acetonitrile molecule with experimental data,[21] a uniform frequency scaling factor of ∼0.98 was determined. (For unscaled frequencies, please refer to the supporting information.) Zero point energy (ZPE) corrected energy differences are referred to as $\Delta E_0$.

To determine activation barriers for the reductive nitrile coupling reaction we parametrically varied the C−C distance between the nitrile carbons of two adjacent acetonitrile ligands $CH_3CN$, while all other coordinates were freely optimized. All calculations were performed with the TURBOMOLE[22] program package.

## Results and Discussion

### A. IR-MPD Spectra of Niobium−Acetonitrile Complexes $[Nb,nCH_3CN]^+$, $n = 4-5$.

All of the recorded vibrational bands of complexes with the formal stoichiometry $[Nb,4CH_3CN]^+$ (Figure 1) are close to the vibrations of the free $CH_3CN$ molecule[21] except for the $\delta^{rock}(CH_3)$ mode at 1090 $cm^{-1}$, which is somewhat blue-shifted (by ∼40 $cm^{-1}$). The ν(CN) band is perturbed due to a Fermi-like resonance with the $\delta(CH_3) + \nu(CC)$ combination band, which is known from free acetonitrile to appear at 2300 $cm^{-1}$.[23] In the ν(CC) stretch mode region (below 1000 $cm^{-1}$) the recorded level is down to noise level, which is due to a decrease in FEL power at the end of its scan range. At first glance the experimental spectrum does not yield strict evidence of anything beyond coordination of four $CH_3CN$ to a single $Nb^I$ monocation.

To substantiate this assertion, we calculated the IR absorption spectra of several optimized $[Nb,4CH_3CN]^+$ complex structures of assumed spin states ($S = 0, 1, 2$). Among the investigated complex structures were structures with nonreactive first and also second shell coordination as well as cluster structures resulting from potential intracluster reactions (for all of these IR absorption spectra cf. supporting information, Figure S1). The calculated IR absorption spectrum of quintet ($S = 2$) $[Nb^I(NCCH_3)_4]^+$, with four first shell acetonitrile ligands bound directly to the niobium monocation, matches the experimental spectrum best. $Nb^I$-acetonitrile complexes with three first shell and one second shell acetonitrile ligand, as well as singlet $[Nb^I(CH_3C{=}N)_3(NCCH_3)]^+$, which contains one acetonitrile ligand and one 2,4,6-trimethyltriazine ligand $(CH_3C{=}N)_3$ bound to $Nb^I$, also show a basic correspondence to the experimental spectrum in all spin states $S = 0, 1, 2$ (cf. Figure S1). However, as these complexes are energetically clearly disfavored by >100 kJ $mol^{-1}$ with regard to $[Nb^I(NCCH_3)_4]^+$, their existence on the time scale of the performed experiments (several seconds) is extremely improbable.

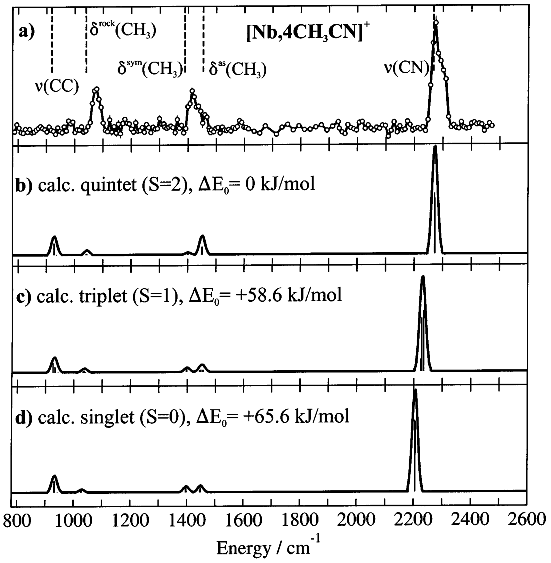

**Figure 1.** IR spectra of the $[Nb,4CH_3CN]^+$ complex: (a) experimental FEL-IR-MPD spectrum recorded with an average FEL power of approximately 280 mW = 11.2 mJ/macropulse at 25 Hz; (b−d) calculated spectra (solid lines: calculated vibrations) of $[Nb^I(NCCH_3)_4]^+$ in various spin states (full width at half-maximum (fwhm) of 10 $cm^{-1}$ assumed). Dashed lines in (a) indicate normal modes of the free $CH_3CN$ molecule. The FEL-IR-MPD spectrum (a) contains no indication of any reactivity beyond coordination and matches the calculated IR absorption spectra of quintet ($S = 2$) $[Nb^I(NCCH_3)_4]^+$ (b) best. In the IR absorption spectra of the triplet (c) and singlet (d) the ν(CN) bands are red-shifted with regard to (a).

B3LYP/TZVP calculations of $[Nb^I(NCCH_3)_4]^+$ in the assumed spin states ($S = 0, 1, 2$) reveal distinct geometries of different relative stabilities. The 4-fold coordination of $Nb^I$ is most stable when square-planar and high-spin quintet ($S = 2$, $\Delta E_0 = 0$ kJ $mol^{-1}$). It is a distorted tetrahedral when triplet ($S = 1$, $\Delta E_0 = +58.6$ kJ $mol^{-1}$) and a tetrahedral when low-spin singlet ($S = 0$, $\Delta E_0 = +65.6$ kJ $mol^{-1}$). We further confirmed the preference of the high-spin quintet against the triplet and singlet by energy calculations at the MP2/TZVP level of theory, which suggest that the quintet remains energetically favored to the triplet and singlet by 68.6 and 54.2 kJ $mol^{-1}$, respectively. On the basis of these energies it becomes unlikely that also $[Nb^I(NCCH_3)_4]^+$ isomers with an electronic singlet or triplet state contribute to the recorded IR-MPD spectrum. Moreover, the predicted red-shift of the ν(CN) stretch vibration that anticorrelates with total spin justifies the assignment of the experimental spectrum to the square-planar high-spin quintet ($S = 2$) complex $[Nb^I(NCCH_3)_4]^+$. While the experimental IR-MPD spectrum by itself does not suffice to pinpoint a particular structure, its interpretation in the light of concomitant ab initio calculations is conclusive. In total we find strong evidence for the square-planar high-spin complex without evidence for any other isomer.

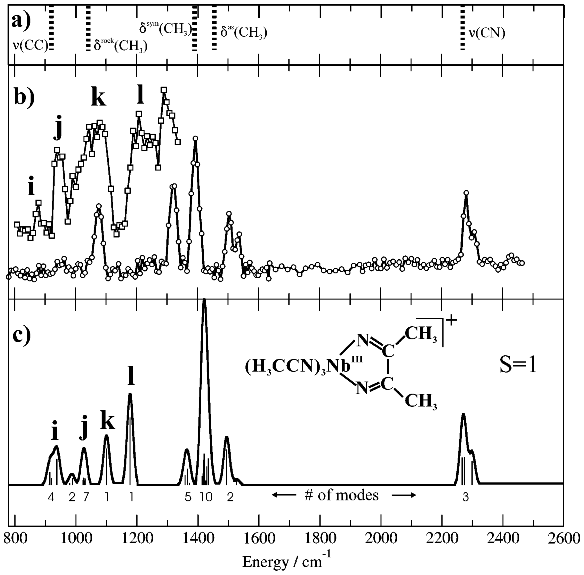

**Figure 2.** IR spectra of the $[Nb,5CH_3CN]^+$ complex: (a) IR bands of the free $CH_3CN$ molecule; (b) FEL-IR-MPD spectra of $[Nb,5CH_3CN]^+$ recorded with an average power (see text) of $\leq 280$ mW = 11.2 mJ/macropulse at 25 Hz (bottom trace, open circles) and recorded with an average power of 400 mW = 16.0 mJ/macropulse at 25 Hz (top trace, open squares); (c) calculated spectrum of triplet $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$. Details as in Figure 1. Spectra of other structures and spin states (cf. supporting information) deviate strongly from (b).

The IR-MPD spectrum of $[Nb,5CH_3CN]^+$ (Figure 2b, bottom trace, open circles) is more complex than that of $[Nb^{I}(NCCH_3)_4]^+$. Additional vibrational bands, shifted away from those of the acetonitrile monomer (cf. Figure 2a), appear between 800 and 1550 cm$^{-1}$. These new bands can neither be assigned to shifted $\delta(CH_3)$ deformation vibrations nor to shifted $\nu(CC)$ stretching vibrations of the gas-phase $CH_3CN$. In principle various reasons are conceivable for the new vibrational bands: They might arise from second-shell $CH_3CN$ molecules in $[Nb,5CH_3CN]^+$ or, alternatively, from a chemical modification due to an internal reaction, which is yet to identify.

We calculated the IR absorption spectra of various coordination complexes—including structures with second-shell coordination—and of products of potential intracluster reactions. The IR absorption spectra were computed for the B3LYP/TZVP optimized complex structures in the electronic singlet, triplet, and quintet states, respectively. A comprehensive list of IR absorption spectra is provided in Figure S2 of the supporting information. There is no single calculated spectral prediction in terms of conceivable combinations of coordination and spin state that would resemble all of the band patterns of the initially recorded spectrum (Figure 2b, bottom trace). The absorption spectra of coordination complexes with first- and second-shell acetonitrile ligands resemble closely that of the coordination complexes with only first-shell acetonitrile ligands. The spectra of these complexes do not show any vibrational bands apart from those of the free acetonitrile shifted by small margins as observed for $[Nb^{I}(NCCH_3)_4]^+$ before (cf. Figure 1). Therefore it is most probable that the experimentally observed vibrational bands between 800 and 1550 cm$^{-1}$ indicate a covalent bond modification within the complex of the formal stoichiometry $[Nb,5CH_3CN]^+$.

Systematic screening on the basis of calculated IR absorption spectra led us to an assignment of the recorded spectrum in terms of a metallacyclic species $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ (inset to Figure 2c) with a triplet state ($S = 1$). The calculated and experimental spectra agree in the position and shape of the $\nu(CN)$ mode at 2290 cm$^{-1}$ and, most importantly, in the structured region between 1300 and 1550 cm$^{-1}$. In the low-energy region (below 1200 cm$^{-1}$) there are some deviations, however. In the spectrum which covers the spectral range from 780 to 2500 cm$^{-1}$ (cf. bottom trace in Figure 2b, open circles), some of the predicted bands i−l**,** most notably band l**,** are missing. The average FEL power for this spectrum was approximately 280 mW throughout most of the scan range. For technical reasons it is difficult to maintain constant FEL power over such a broad range, and the FEL power at the low-energy region of this spectrum was actually somewhat lower (only ~200 mW). However, after the FEL conditions were optimized for the range 800−1350 cm$^{-1}$, we managed to record a spectrum in this narrow spectral range with an average FEL power of approximately 400 mW (cf. upper trace in Figure 2b, open square symbols). Under these conditions IR absorption of all predicted bands i−l led to fragmentation and gave rise to a recordable signal intensity. Thus, the IR-MPD spectrum recorded at the higher photon flux matches the calculated absorption spectrum of $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ in an electronic triplet state ($S = 1$) and affirms the assignment of the experimental IR-MPD spectrum to the metallacyclic species. Please note that the enhancement of the IR-photon flux between 800 and 1200 cm$^{-1}$ was possible only at the expense of inferior spectral resolution.

The fact that the low photon flux IR-MPD spectrum of $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ contains only band k, while bands i, j, and l are absent, indicates strongly mode specific absorption and fragmentation dynamics. It is well-known that both multiphoton absorption as well as concomitant fragmentation depend on a series of molecular and mechanistic details, which can be very diverse for different modes.[24] For instance, the absence of single bands in the low-energy region of the spectrum at lower photon flux might arise from a lack of high state density as is necessary to achieve efficient multiphoton dissociation of anharmonic modes. In this case, significantly higher FEL powers are needed to induce fragmentation. In addition, a heavy atom effect[25,26] in $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ might also account for the absence of single bands in the spectrum recorded at lower photon flux. The central, heavy $Nb^{III}$ atom might hinder an effective energy flow among excited and fragmenting modes, requiring very high photon fluxes in order to achieve fragmentation. The investigation of such mode-specific fragmentation efficiencies as a function of photon flux in the low-energy region of the IR-MPD spectrum of $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ would certainly reveal important information about the multiphoton absorption induced fragmentation process and will be subject of future experimental studies.

### B. Coordination versus Reactive Nitrile Coupling in $[Nb,nCH_3CN]^+$, $n = 4$, 5.

The recorded IR-MPD spectra of $[Nb,nCH_3CN]^+$, $n = 4$, 5, yield convincing spectroscopic evidence of an internal reaction in the case of $n = 5$, as opposed to nonreactive coordination in the case of $n = 4$. By comparison with the calculated IR absorption spectra (cf. Figure 2), the IR-MPD spectrum for $n = 5$ was assigned to the metallacyclic species $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ in an electronic triplet state ($S = 1$), whereas in case of $n = 4$ the IR-MPD spectrum was assigned to the coordination complex $[Nb^{I}(NCCH_3)_4]^+$ in an electronic quintet state ($S = 2$). Both entities, $n = 4$ and $n = 5$, have been assembled stepwise in the gas-phase. Therefore the observed

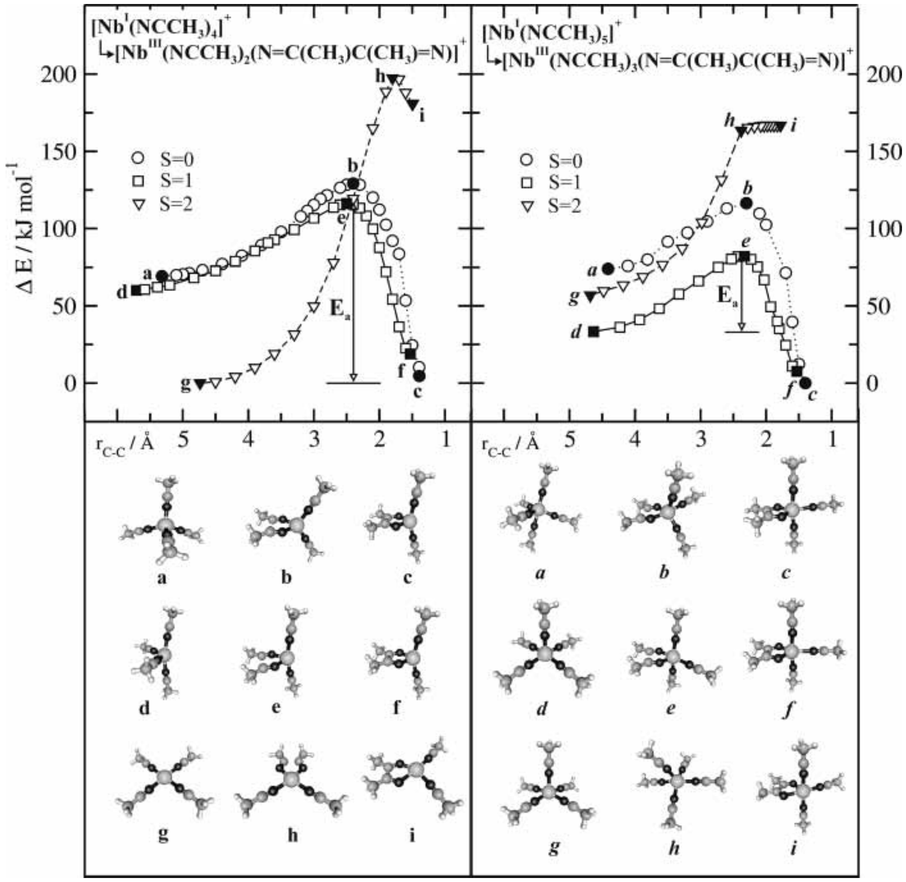

**Figure 3.** B3LYP reaction coordinates and structures along the $r_{C-C}$ reaction coordinate for the intramolecular reductive nitrile coupling reaction in $[Nb^I(CH_3CN)_n]^+$, $n = 4$ (left) and $n = 5$ (right), with total spin $S = 0, 1, 2$.

$[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ species must have formed from $[Nb^I(NCCH_3)_5]^+$ according to the redox reaction (1).

$$[Nb^I(NCCH_3)_5]^+ \rightarrow [Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+ \quad (1)$$

In the course of this reaction, two adjacent acetonitrile ligands react with each other and with $Nb^I$ to form two covalent Nb−N bonds and an interlinking C−C bond yielding a five-membered heterocycle. While the two $CH_3CN$ ligands are reduced in the course of this reaction, quintet $Nb^I$ is oxidized to triplet $Nb^{III}$.

To elucidate the size-dependent reactivity of $[Nb^I(NCCH_3)_n]^+$, $n = 4, 5$ (coordination only and reductive nitrile coupling, respectively), the reaction energetics and reaction barriers of the C−C coupling reaction were investigated by means of DFT calculations. The diabatic minimum energy pathways that connect the reactants and the products of the reductive nitrile coupling reaction were calculated as a function of the reaction coordinate (distance between two nitrile carbons) and for various spin states ($S = 0, 1, 2$) of $[Nb^I(NCCH_3)_n]^+$, $n = 4, 5$, at the B3LYP/TZVP level of theory. The obtained minimum energy pathways together with selected complex structures are shown in Figure 3. Relative energies $\Delta E$ (in kJ mol$^{-1}$) are plotted against the carbon−carbon distance $r_{C-C}$ between the nitrile carbons of two adjacent acetonitrile ligands $CH_3CN$. For quintet ground state $[Nb^I(NCCH_3)_4]^+$ the reductive nitrile coupling reaction **g** → **i** is strongly endothermic by $\Delta E = +180.8$ kJ mol$^{-1}$ ($\Delta E_0 = +186.6$ kJ mol$^{-1}$) and requires an activation energy of $E_a(\mathbf{g} \rightarrow \mathbf{i}) = +197.8$ kJ mol$^{-1}$. In contrast, the C−C coupling reactions **a** → **c** and **d** → **f** in the singlet and triplet $[Nb^I(NCCH_3)_4]^+$ states are exothermic by $\Delta E = -64.7$ kJ mol$^{-1}$ ($\Delta E_0 = -52.4$ kJ mol$^{-1}$) and $\Delta E = -41.0$ kJ mol$^{-1}$ ($\Delta E_0 = -31.8$ kJ mol$^{-1}$), respectively, and have significantly lower activation energies of $E_a(\mathbf{a} \rightarrow \mathbf{c}) = +60.2$ kJ mol$^{-1}$ and $E_a(\mathbf{d} \rightarrow \mathbf{f}) = +56.1$ kJ mol$^{-1}$.

In the case of quintet $[Nb^I(NCCH_3)_5]^+$ the C−C coupling reaction coordinate is practically nonreactive. No stable minimum could be located for quintet $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$, which instead decomposes into quintet $[Nb^I(NCCH_3)_5]^+$ in a barrierless reaction. In contrast for the singlet and most importantly for the ground-state triplet $[Nb^I(NCCH_3)_5]^+$ the reductive nitrile coupling reactions ***a*** → ***c*** and ***d*** → ***f*** are exothermic by $\Delta E = -74.0$ kJ mol$^{-1}$ ($\Delta E_0 = -61.9$ kJ mol$^{-1}$) and $\Delta E = -25.7$ kJ mol$^{-1}$ ($\Delta E_0 = -15.5$ kJ mol$^{-1}$), respectively. The corresponding calculated activation energies are $E_a(\boldsymbol{a} \rightarrow \boldsymbol{c}) = +42.6$ kJ mol$^{-1}$ and $E_a(\boldsymbol{d} \rightarrow \boldsymbol{f}) = +49.1$ kJ mol$^{-1}$.

Both in $[Nb^I(NCCH_3)_4]^+$ and $[Nb^I(NCCH_3)_5]^+$ complexes the reductive nitrile coupling reaction takes place on the triplet and singlet potential energy surfaces (PESs), whereas the quintet PESs are essentially nonreactive. Although the PESs for a particular spin state are similar in $[Nb^I(NCCH_3)_n]^+$, $n = 4-5$, it is important to note that the energies of the triplet and singlet PESs relative to the quintet PESs are reversed and that the quintet is the ground state only for $[Nb^I(NCCH_3)_4]^+$. This finding has important consequences on the reactivity of the 4- and 5-fold coordinated species and accounts for their different chemical behavior, as observed in the experiments: For ground-state triplet $[Nb^I(NCCH_3)_5]^+$, the reductive nitrile coupling reaction is exothermic and, most notably, the activation barrier amounts to approximately 49 kJ mol$^{-1}$, which Arrhenius-like

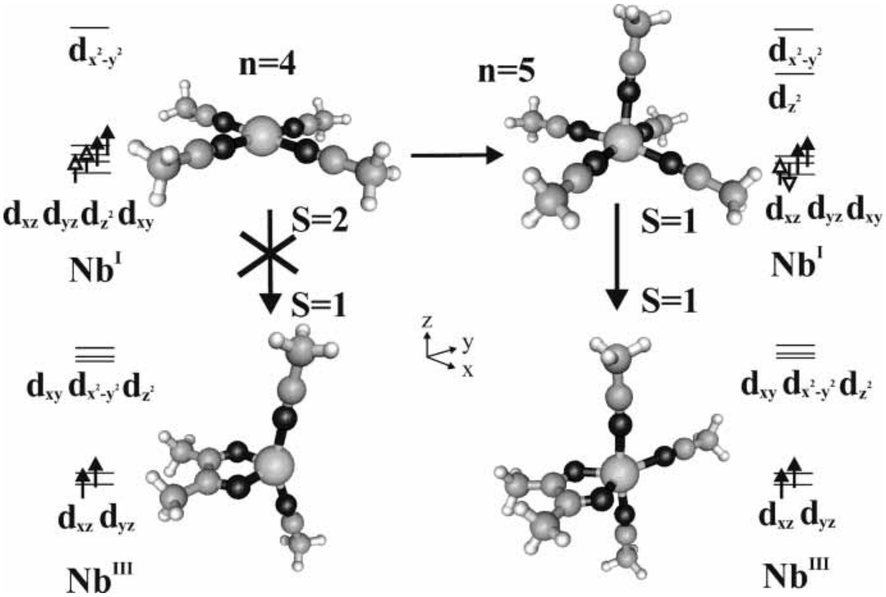

**Figure 4.** Proposed reaction scheme for $[Nb^I(CH_3CN)_n]^+$, $n = 4$, 5. For $n = 4$ the square-planar high-spin complex is stable. Addition of a fifth $CH_3CN$ ligand induces spin change and subsequent C−C coupling (see text).

kinetics readily overcomes on a submillisecond time scale. (Preexponential factors $A$ (in $k = Ae^{-E_a/kT}$) for gas-phase first-order kinetics R → P (R = Reactant, P = Products) are typically of the order of $(1 \times 10^{12})-(1 \times 10^{14})$ $s^{-1}$.[44] In the present case this leads to rate constants $k$ (at 300 K) between 2940 and 29.40 $\times$ $10^4$ $s^{-1}$, corresponding to average lifetimes $\tau = 1/k$ of R between $\tau = 0.34$ ms and $\tau = 3.4$ $\mu$s, respectively.) In contrast, in $[Nb^I(NCCH_3)_4]^+$ the C−C coupling reaction requires a change of spin if this species starts in its (quintet) ground state. However, it has been demonstrated before that in organometallic chemistry gas-phase reactions can involve a change in spin multiplicity.[27−31] Formally, spin forbidden reactions have been observed to occur in various transition-metal systems. To name only a few, we refer to the recombination reactions of neutral $M(CO)_x$ complexes with CO (M = Fe, $x = 2-4$;[32,33] M = Cr, $x = 2-5$;[34−37] M = Co, $x = 1-3$[38]), C−S bond activation of carbon disulfide by an atomic vanadium cation,[39] and C−H activation by $FeO^+$. The latter has been previously investigated experimentally[40] and theoretically[41−43]. Spontaneous spin flipping might occur in transition-metal complexes, provided that the PESs of different multiplicity have an opportunity to interact—the completion of this requirement depends on the chemical nature of the metal ion and the ligands, the number of attached ligands, and the coordination geometry. The particular interaction of diabatic niobium−acetonitrile PESs surely depends on the complex size.

In $[Nb^I(NCCH_3)_4]^+$ a "hop" from the nonreactive quintet to the triplet PES in the vicinity of the crossing at $r_{C-C} \approx 2.3$ Å would require an activation energy $E_a$ of at least 116 kJ $mol^{-1}$. However, the geometry of the quintet ($S = 2$) complex differs distinctly from those of the $S = 1$ (triplet) and $S = 0$ (singlet) complexes when close to the crossings of the minimum energy paths (cf. Figure 3), where the transition probability[45,46] between different PESs is maximal. Structures **b** ($S = 0$) and **e** ($S = 1$) each contain two acetonitrile ligands perpendicular to the plane formed by the remaining two acetonitrile ligands and the niobium ion, whereas all complexes of the $S = 2$ path are planar. Due to these significant differences in the geometries of quintet and both singlet and triplet $[Nb^I(NCCH_3)_4]^+$ complexes, the transition probability from quintet to singlet and triplet states is negligible. Consequently the reaction coordinate of the quintet is essentially nonreactive due to an activation energy $E_a$ of significantly more than 116 kJ $mol^{-1}$ (estimated). Even if intersystem crossings were feasible in $[Nb^I(NCCH_3)_4]^+$ and the reaction could proceed from **g** to **c** in Figure 3, the reaction would still be endothermic by $\Delta E_0 = +13.2$ kJ $mol^{-1}$.

The findings from the IR-MPD experiments and from the B3LYP/TZVP calculations together allow for an interpretation of the observed (non)reactivity of niobium−acetonitrile complexes (cf. Figure 4). The planar, high-spin quintet ($S = 2$) complex $[Nb^I(NCCH_3)_4]^+$ is stable against reductive nitrile coupling (into low-spin products). Upon attachment of the fifth acetonitrile ligand, however, the $d_{z^2}$ orbital is forced to rise in energy and the triplet state becomes energetically favored in $[Nb^I(NCCH_3)_5]^+$. As the reductive nitrile coupling reaction takes place on the triplet PES, triplet $[Nb^I(NCCH_3)_5]^+$ reacts under spin conservation into the metallacyclic species $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$.

## Conclusions

We have recorded the FEL-IR-MPD spectra of mass selected cationic niobium−acetonitrile complexes with the formal stoichiometry $[Nb,nCH_3CN]^+$, $n = 4$, 5, in the spectral range 780−2500 $cm^{-1}$. In case of $n = 4$ the recorded vibrational bands are close to those of the free $CH_3CN$ molecule and the experimental spectrum does not contain any evident indication of a potential reaction beyond coordination. By comparison with IR absorption spectra, calculated with the B3LYP functional, the recorded IR-MPD spectrum is assigned to high-spin (quintet, $S = 2$), planar $[Nb^I(NCCH_3)_4]^+$. In the case of $n = 5$, however, new vibrational bands shifted away from those of the acetonitrile monomer are observed between 800 and 1550 $cm^{-1}$. These new bands cannot be assigned to shifted $\delta(CH_3)$ deformation vibrations or to shifted $\nu(CC)$ stretching vibrations of the gas-phase acetonitrile monomer but provide clear evidence of a chemical modification within $[Nb,5CH_3CN]^+$ due to an intramolecular reaction. Based on the B3LYP calculated IR absorption spectra, the recorded spectrum is assigned to the metallacyclic species $[Nb^{III}(NCCH_3)_3(N{=}C(CH_3)C(CH_3){=}N)]^+$ (triplet, $S = 1$). This is indicative of a spontaneous intramolecular reductive nitrile coupling reaction to have occurred in $[Nb^I(NCCH_3)_5]^+$. The calculated reaction coordinates provide an explanation of the experimentally observed differences in reactivity between ground state $[Nb^I(NCCH_3)_4]^+$ and $[Nb^I(NCCH_3)_5]^+$. The reductive nitrile coupling reaction is exothermic and accessible ($E_a = 49$ kJ mol$^{-1}$) only in $[Nb^I(NCCH_3)_5]^+$, whereas in $[Nb^I(NCCH_3)_4]^+$ the reaction is found to be endothermic and retarded by a significantly higher activation barrier ($E_a \gg 116$ kJ mol$^{-1}$).

**Acknowledgment.** We have benefited from the program "Enhancing access to research Infrastructures" of the European Community. We thank the Fraunhofer Gesellschaft for a generous grant of computer time at the Linux Cluster of the Institute of Technomathematics in Kaiserslautern. We also thank Dr. H.-J. Krüger for valuable discussions on inorganic coordination compounds. Helpful discussions with Dr. S. S. Xantheas are gratefully acknowledged.

**Supporting Information Available:** Figure S1, IR absorption spectra and relative energies $\Delta E_0$ of various $[Nb,4CH_3CN]^+$ complex structures; Figure S2, IR absorption spectra and relative energies $\Delta E_0$ of various $[Nb,5CH_3CN]^+$ complex structures. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Corey, E. J.; Danheiser, R. L.; Chandrasekan, S. *J. Org. Chem.* **1976**, *41*, 260.
(2) Sattelberger, A. P.; Wilson, R. B., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 7111.
(3) Finn, P. A.; King, M. S.; Kilty, P. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 220.
(4) Berg, C.; Schindler, T.; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Chem. Phys.* **1995**, *102*, 4870.
(5) Dunbar, R. C. *Int. J. Mass Spectrom.* **2000**, *200*, 571.
(6) Duncan, M. A. *Int. J. Mass Spectrom.* **2000**, *200*, 545.
(7) Nesbitt, D. J.; Field, R. W. *J. Phys. Chem.* **1996**, *100*, 12735.
(8) Gruebele, M. *Adv. Chem. Phys.* **2000**, *114*, 193.
(9) Oomens, J.; Meijer, G.; von Helden, G. *J. Phys. Chem. A* **2001**, *105*, 8302.
(10) Oomens, J.; Bakker, J. M.; Sartakov, B. G.; Meijer, G.; von Helden, G. *Chem. Phys. Lett.* **2003**, *367*, 576.
(11) Lemaire, J.; Boissel, P.; Héninger, M.; Mauclaire G.; Bellec, G.; Mestdagh, H.; Simon, A.; Le Caër, S.; Ortega, J. M.; Glotin, F.; Maitre, P. *Phys. Rev. Lett.* **2002**, *89*, 273002.
(12) van Heijnsbergen, D.; von Helden, G.; Meijer, G.; Maitre, P.; Duncan, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1562.
(13) Jones, W.; Boissel, P.; Chiavarino, B.; Crestoni, M. E.; Fornarini, S.; Lemaire, J.; Maitre, P. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 2057.
(14) Bray, R. G.; Cox, D. M.; Hall, R. B.; Horsley, J. A.; Kaldor, A.; Kramer, G. M.; Levy, M. R.; Priestly, E. *J. Phys. Chem.* **1983**, *87*, 429.
(15) Crofton, M. W.; Price, J. M.; Lee, Y. T. In *Clusters of Atoms and Molecules II*; Haberland, H., Ed.; Springer-Verlag: Berlin, 1994.
(16) Maitre, P.; Le Caër, S.; Simon, A.; Jones, W.; Lemaire, J.; Mestdagh, H.; Héninger, M.; Mauclaire, G.; Boissel, P.; Prazeres, R.; Glotin, F.; Ortega, J. M. *Nucl. Instrum. Methods Phys. Res. Sect. A* **2003**, *507*, 541.
(17) Sodupe, M.; Branchadell, V.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Phys. Chem. A* **1997**, *101*, 7854.
(18) Bauschlicher, C. W., Jr.; Ricca, A.; Partridge, H.; Langhoff, S. R. In *Recent Advances in Density Functional Theory Part II*; Chong, D. P., Ed.; World Scientific Publishing: Singapore, 1997.
(19) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
(20) Andrae, D.; Haeussermann, M.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
(21) Dimitrova, Y. *J. Mol. Struct. (THEOCHEM)* **1995**, *343*, 25.
(22) Treutler, O.; Ahlrichs R. *J. Chem. Phys.* **1995**, *102*, 346.
(23) Koga, Y.; Kondo, S.; Saeki, S.; Person, W. B. *J. Chem. Phys.* **1984**, *88*, 3152.
(24) Lupo, D. W.; Quack M. *Chem. Rev.* **1987**, *87*, 181.
(25) Baer, T.; Hase, W. H. *Unimolecular Reaction Dynamics: Theory and Experiment*; Oxford University Press: New York, 1996, 12.
(26) Zhitneva, G. P. *Chem. Phys. Lett.* **1999**, *307*, 379.
(27) Armentrout, P. B. *Science* **1991**, *251*, 175.
(28) Weisshaar, J. C. *Acc. Chem. Res.* **1993**, *26*, 213.
(29) van Koppen, P. A. M.; Bowers, M. T.; Haynes, C. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1998**, *120*, 5704.
(30) Harris, N.; Cohen S.; Filatov, M.; Ogliaro, F.; Shaik, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 2003.
(31) Schröder, D.; Shaik, S.; Schwarz, H. *Acc. Chem. Res.* **2000**, *33*, 139.
(32) Ouderkirk, A. J.; Werner, P.; Schultz, N. L.; Weitz, E. *J. Am. Chem. Soc.* **1983**, *105*, 3354.
(33) Seder, T. A.; Ouderkirk, A. J.; Weitz E. *J. Chem. Phys.* **1986**, *85*, 1977.
(34) Seder, T. A.; Church, S. P.; Ouderkirk, A. J.; Weitz, E. *J. Am. Chem. Soc.* **1985**, *107*, 1432.
(35) Seder, T. A.; Church, S. P.; Weitz, E. *J. Am. Chem. Soc.* **1986**, *108*, 4721.
(36) Fletcher, T. R.; Rosenfeld, R. N. *J. Am. Chem. Soc.* **1986**, *108*, 1686.
(37) Fletcher, T. R.; Rosenfeld, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 2097.
(38) Rayner, D. M.; Nazran, A. S.; Drouin, M.; Hacket, P. A. *J. Phys. Chem.* **1986**, *90*, 2882.
(39) Rue, C.; Armentrout, P. B.; Kretschmar, I.; Schröder, D.; Harvey, J. N.; Schwarz, H. *J. Chem. Phys.* **1999**, *110*, 7858.
(40) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1973.
(41) Fiedler, A.; Schröder, D.; Shaik, S.; Schwarz H. *J. Am. Chem. Soc.* **1994**, *116*, 10734.
(42) Harris, N.; Shaik, S.; Schröder D.; Schwarz H. *Helv. Chim. Acta* **1999**, *82*, 1784.
(43) Shiota, Y.; Yoshizawa, K. *J. Chem. Phys.* **2003**, *118*, 5872.
(44) Wilkinson, F. *Chemical Kinetics and Reaction Mechanisms*; Van Nostrand Reinhold: Wokingham, 1980; p 124.
(45) Poli, R.; Harvey J. N. *Chem. Soc. Rev.* **2003**, *32*, 1.
(46) Plattner, D. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 82.