CO$_2$ Activation **Hot Paper**

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Capture of CO$_2$ by a Cationic Nickel(I) Complex in the Gas Phase and Characterization of the Bound, Activated CO$_2$ Molecule by Cryogenic Ion Vibrational Predissociation Spectroscopy

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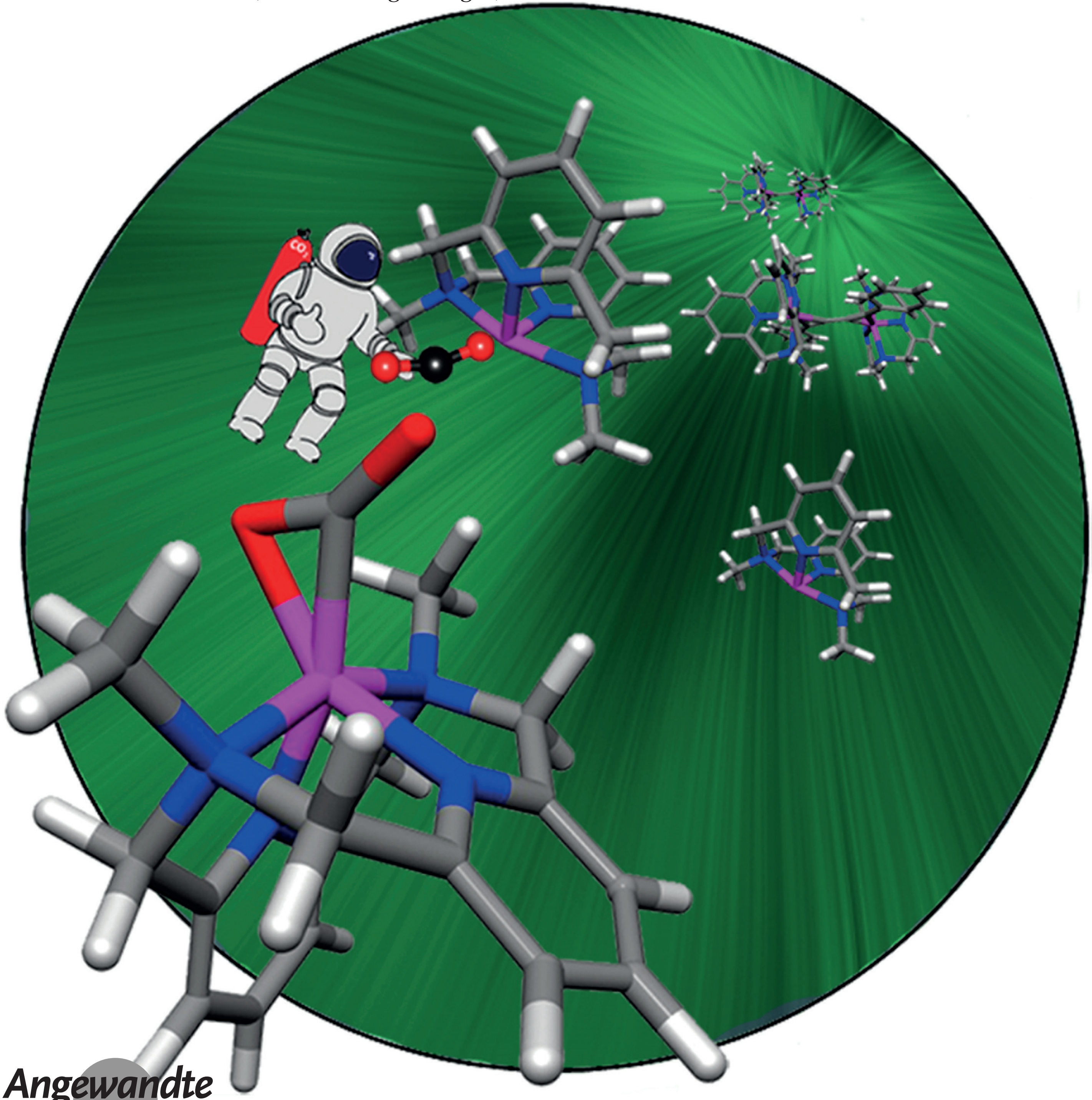

Abstract: *We describe a systematic method for the preparation and spectroscopic characterization of a CO_2 molecule coordinated to an activated bisphenoidal nickel(I) compound containing a tetraazamacrocyclic ligand in the gas phase. The resulting complex was then structurally characterized by using mass-selected vibrational predissociation spectroscopy. The results indicate that a highly distorted CO_2 molecule is bound to the metal center in an η^2-C,O coordination mode, thus establishing an efficient and rational method for the preparation of metal-activated CO_2 for further studies using ion chemistry techniques.*

The capture and structural characterization of intermediates in the catalytic activation of small molecules is an important aspect of mechanistic organometallic chemistry.[1–5] An exciting recent development in this endeavor is the use of ambient ionization methods[6–8] to extract key precursor species from solution and then activate them using gas-phase ion chemistry techniques.[9–12] Once activated, substrate molecules can be introduced directly to the metal center so that the catalyst–substrate complex can be structurally characterized using mass-selected vibrational spectroscopy.[9,12–20]

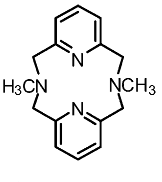

Figure 1. Structure of the ligand L-N$_4$Me$_2$.

We focus on CO_2 activation by Ni^I compounds. The reduction of a Ni^{II} phosphine complex by sodium under a CO_2 atmosphere led to the first documented observation of a covalently bound Ni–CO_2 species.[21] Subsequently, the activation of CO_2 has been carried out by using other Ni^0 and Ni^I phosphine compounds in the condensed phase, and Ni^I appeared to be the key oxidation state for the electrochemical reduction of CO_2.[22–25] The disproportionation mechanism for the conversion of CO_2 into CO and CO_3^{2-} with bimetallic Ni^I complexes has also been established using traditional methods of analysis.[26] Herein, we characterize the initial activation step in which a neutral CO_2 molecule coordinates to a single Ni^I center bound to the tetraazamacrocycle shown in Figure 1 in the gas phase, and thus demonstrate a rational, multi-step method to prepare and characterize such species.[27] The coordinatively unsaturated Ni^I complex was generated by collisional dissociation of the dinuclear precursor [{Ni^I(L-N$_4$Me$_2$)}$_2$(μ-C$_{16}$H$_{10}$)]$^{2+}$ (**1**) as described in Figure 2. In compound **1,** each Ni^I ion is coordinated to the four nitrogen donor atoms of the tetraazamacrocyclic diazapyridinophane ligand L-N$_4$Me$_2$. The distorted trigonal-bipyramidal coordination environment around each Ni^I ion is completed by a side-on-coordinated alkyne group of the bridging diphenyldiyne ligand as shown in Figure 2. The bare dication (**1**) was extracted from solution using a custom electrospray ion source interfaced to a cryogenic ion vibrational predissociation mass spectrometer described previously.[28,29] Millimolar solutions of [{Ni^I(L-N$_4$Me$_2$)}$_2$(μ-C$_{16}$H$_{10}$)](BF$_4$)$_2$ were prepared in dry and oxygen-free acetonitrile in a nitrogen-purged glove box. The resulting mass spectra for various source conditions are summarized in the Supporting Information, Figures S1 and S2. The ion distribution strongly depends on the capillary-to-skimmer voltage in the first differential pumping stage of the instrument.[8] With increasing voltage, the intensity of the signal for dinuclear **1** decreases while more mononuclear **2** + (C$_{16}$H$_{10}$) is formed, which corresponds to retention of the bridging ligand. A further increase in the voltage then leads to dissociation of the diyne ligand to generate the desired bisphenoidal (also termed disphenoidal or seesaw) Ni^I compound **2**. This mononuclear species is both electron-rich and has an open coordination site, so that it is able to react with substrate molecules. The ions were then transferred to a temperature-controlled radiofrequency ion trap where the reaction with CO_2 took place under the conditions described in detail in the Supporting Information. The highest temperature at which significant amounts of **2** + CO_2 could still be formed was 225 K. The raw, temperature-dependent mass spectra are shown in Figure S3.

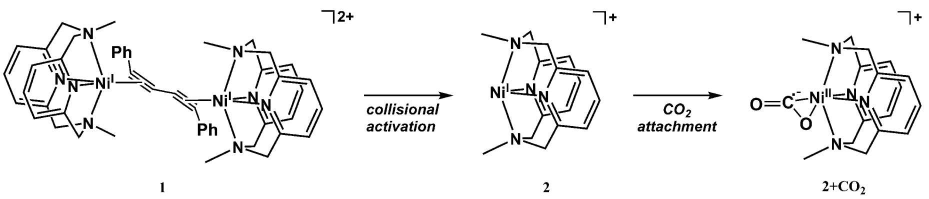

Figure 2. Conversion of the dinuclear Ni^I complex [{Ni^I(L-N$_4$Me$_2$)}$_2$(μ-C$_{16}$H$_{10}$)]$^{2+}$ (**1**) into its fragment [Ni^I(L-N$_4$Me$_2$)]$^+$ (**2**) by collisional activation and finally into its adduct with CO_2, [Ni(L-N$_4$Me$_2$)(CO_2)]$^+$ (**2** + CO_2).

Mass-selected photodissociation was carried out using the Yale photofragmentation mass spectrometer described in detail elsewhere.[28,29] The vibrational predissociation spectrum of **2** + CO_2 was obtained by monitoring the photoinduced dissociation of the CO_2 molecule, which was the only observed loss channel. The resulting spectrum of **2** + CO_2 is displayed in Figure 3a. It is remarkably simple, being dominated by only one very strong absorption at 1923 cm^{-1} in the fingerprint region. This band lies energetically far below that associated with the antisymmetric stretching vibration of an isolated CO_2 molecule at 2375 cm^{-1} (arrow in Figure 3a). The other strong absorptions appear around 3000 cm^{-1}, in the region expected for C–H stretching fundamentals, and have dense, but resolved multiplet structures. The spectra were not observed to depend on temperature over the range of 150–225 K, and the internal energy

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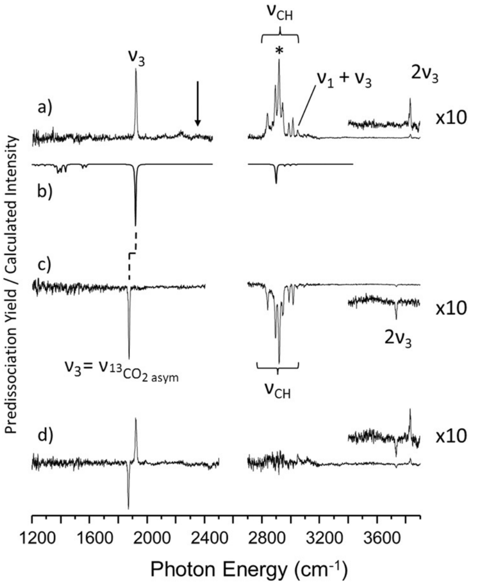

Figure 3. a) Vibrational predissociation spectrum of $[Ni(L\text{-}N_4Me_2)(CO_2)]^+$, b) its calculated spectrum (PBE1PBE/cc-pVDZ for C, H, N, O and the Stuttgart 1997 ECP for Ni), c) the vibrational predissociation spectrum of its $^{13}CO_2$ analogue, and d) the difference spectrum between (a) and (c) normalized to the intensity of the feature marked with *.

available at 150 K is sufficient to enable single photon dissociation even for a calculated binding energy of $D_o = 2900\ cm^{-1}$ (including BSSE and zero-point corrections, see Table S6). The linearity of the photofragmentation at $1923\ cm^{-1}$ as a function of laser pulse energy establishes that it arises from a single photon absorption.

To identify the features in the $\mathbf{2} + CO_2$ vibrational spectrum that are due to the CO_2 molecule, we exploited the fact that contributions from many oscillators on the ligand that are remote from the coordination sites are not likely to be affected by isotopic substitution with $^{13}CO_2$. As such, the bands arising from CO_2 can be readily determined by subtracting the spectrum of $\mathbf{2} + {}^{13}CO_2$ from that of $\mathbf{2} + {}^{12}CO_2$ after normalization to the intensity of the largest feature in the C–H stretching region (marked by * in Figure 3a). The raw spectrum of the $\mathbf{2} + {}^{13}CO_2$ isotopologue and the difference spectrum with respect to $\mathbf{2} + {}^{12}CO_2$ are presented in Figure 3c and 3d, respectively. Most importantly, the strong feature at $1923\ cm^{-1}$ indeed shifts by the amount ($52\ cm^{-1}$ (expected) vs. $51\ cm^{-1}$ (experimental)) predicted for the antisymmetric stretching fundamental of CO_2, and can therefore be assigned to this mode. The considerable red shift ($422\ cm^{-1}$) of this transition relative to that in an isolated CO_2 molecule thus establishes that the CO_2 unit has undergone a significant perturbation upon attachment to **2**. The $0 \rightarrow 2$ overtone of the ν_3 vibration ($2\nu_3$ in Figure 3a) is also observed as the feature highest in energy at $3832\ cm^{-1}$, which is shifted by $98\ cm^{-1}$ in the $^{13}CO_2$ spectrum.

Electronic-structure calculations recovered the minimum-energy structure displayed in Figure 4 along with a few key structural parameters. The harmonic vibrational spectrum (fundamental frequencies scaled by 0.985) for this structure, which is included in Figure 3b, accurately reproduces the observed CO_2 asymmetric stretch at $1923\ cm^{-1}$ (unscaled harmonic value: $1956\ cm^{-1}$).

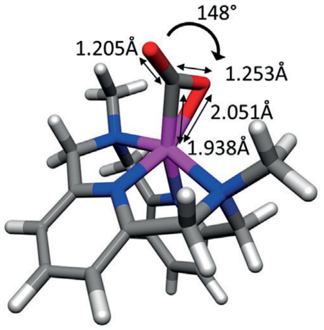

Figure 4. Calculated lowest-energy structure of $\mathbf{2} + CO_2$.

A comparison of the calculated structures for **2** and $\mathbf{2} + CO_2$ indicates that the N_{pyr}-Ni-N_{pyr} angle (pyr = pyridine) closes from 101° to 88° upon attachment of CO_2. At the same time, the CO_2 moiety is strongly bent (O-C-O angle: 148°) and attached in an η^2-C,O coordination mode (Ni–C: 1.938 Å; Ni–O: 2.051 Å) to the Ni atom in a skewed fashion such that the symmetry of the molecule is reduced from C_{2v} to C_s. The two C–O bond lengths are also different ($\Delta R = 0.048$ Å). The detailed nature of the complex is best viewed in the rotatable display in Figure S5.

Such a strongly bent CO_2 moiety is anticipated to arise from the partial accommodation of one extra electron in the molecular orbitals of the CO_2 group (isolated $CO_2^{-\bullet}$ is bent with an angle of 134°, which is quite close to the 133° found in the $[Ni(CO_2)(PCy_3)_2]$ complex).[21,30] This would, in turn, imply a formal change in the oxidation state of the Ni center from +1 to +2. Such a change would be expected to be apparent in the geometrical arrangement of the surrounding ligands. Although the rigid nature of the bent $L\text{-}N_4Me_2$ ligand does not allow a clear classification by visual inspection of the calculated structure, Reedijk et al. have introduced a method to quantify the nature of the coordination environment by the parameter τ.[31] The application of this formalism to $\mathbf{2} + CO_2$ is described in the Supporting Information. The calculated structure corresponds to a τ value of 0.27, which is more consistent with the formation of a distorted square-pyramidal coordination environment. Indeed, the structural changes described above (bending of the ligand scaffold and off-axis coordination of CO_2) can be interpreted as those imposed by the change from a Ni^I to a Ni^{II} oxidation state.

To gain a more quantitative understanding of the changes in the charge distribution of **2** upon CO_2 coordination, we also carried out a natural population analysis[32] of the charge densities in the **2** and $\mathbf{2} + CO_2$ ions. The differences in these charges indicate that charge is effectively transferred from the two aromatic pyridine rings (with differences of +0.17 and +0.34) as well as from the CH_2–$N(CH_3)$–CH_2 bridges (+0.11 and +0.14) to the carbon atom of the CO_2 center (−0.45) and the Ni atom (−0.33).

The formation of covalent Ni–C and Ni–O bonds in the $\mathbf{2} + CO_2$ adduct raises the question as to how these interactions compare to those that occur when CO_2 is coordinated to a Ni^{II} precursor complex. We therefore prepared the CO_2 adduct of the $[Ni^{II}(L\text{-}N_4Me_2)]^{2+}$ ion (**3**), $\mathbf{3} + CO_2$, and show its

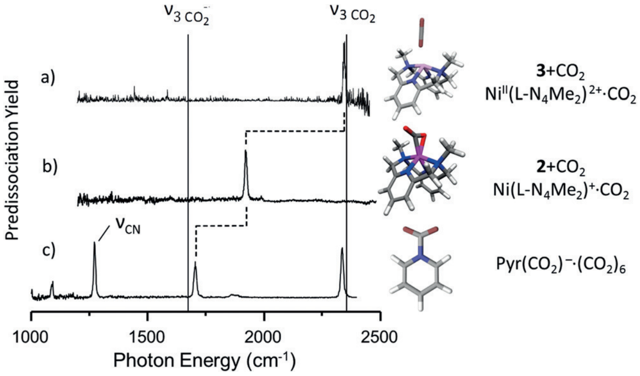

Figure 5. CO_2 predissociation spectra of **3** (a), **2** (b), and $Pyr(CO_2)^{-\bullet}\cdot(CO_2)_6$ (c).[33]

vibrational predissociation spectrum in Figure 5 a along with that obtained here for **2** + CO_2 (Figure 5 b) and the previously reported spectrum of the radical carbamate anion, $Pyr(CO_2)^{-\bullet}(CO_2)_6$ (Figure 5).[33] All three systems display remarkably clean spectral signatures of the degree to which CO_2 is activated by the extent of reduction. The CO_2 ν_3 band in **3** + CO_2 is essentially unperturbed compared to that of isolated CO_2, whereas the analogous transition in the carbamate (1650 cm^{-1}) occurs close to the band in the isolated $CO_2^{-\bullet}$ radical anion (1660 cm^{-1}).[33] In the **3** + CO_2 system, the CO_2 molecule is predicted to attach end-on to the Ni center, resulting in a small angle, almost parallel between the axis of the linear CO_2 moiety and the C_2 axis of the unperturbed molecule.

Whereas the occurrence of bisphenoidal structures is quite established in condensed-phase main-group chemistry, this coordination environment is very unlikely to be observed in transition-metal complexes in the ground state. Therefore the gas-phase preparation demonstrated here, which led to the formation of the reactive electron-rich nickel(I) species **2**, may enable a general way to access new reactions. Herein, we exploited this capability to confirm that the nickel(I) oxidation state is crucial to the activation of CO_2. The application of this approach to follow the activation of other small molecules such as D_2 and N_2 (see Table S6) warrants further exploration.

Acknowledgements

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[1] E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, *Chem. Soc. Rev.* **2009**, *38*, 89.
[2] A. J. Morris, R. T. McGibbon, A. B. Bocarsly, *ChemSusChem* **2011**, *4*, 191.
[3] M. W. Kanan, D. G. Nocera, *Science* **2008**, *321*, 1072.
[4] O. Eisenstein, J. D. Blakemore, N. D. Schley, D. Balcells, J. F. Hull, G. W. Olack, C. D. Incarvito, G. W. Brudvig, R. H. Crabtree, *J. Am. Chem. Soc.* **2010**, *132*, 16017.
[5] R. H. Grubbs, W. Tumas, *Science* **1989**, *243*, 907.
[6] G. B. S. Miller, T. K. Esser, H. Knorke, S. Gewinner, W. Schollkopf, N. Heine, K. R. Asmis, E. Uggerud, *Angew. Chem. Int. Ed.* **2014**, *53*, 14407; *Angew. Chem.* **2014**, *126*, 14635.
[7] R. H. Perry, K. R. Brownell, K. Chingin, T. J. Cahill, R. M. Waymouth, R. N. Zare, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 2246.
[8] P. B. Armentrout, *Top. Curr. Chem.* **2003**, *225*, 233.
[9] D. Schroder, H. Schwarz, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 18114.
[10] D. K. Böhme, H. Schwarz, *Angew. Chem. Int. Ed.* **2005**, *44*, 2336; *Angew. Chem.* **2005**, *117*, 2388.
[11] N. Dietl, T. Wende, K. Chen, L. Jiang, M. Schlangen, X. Zhang, K. R. Asmis, H. Schwarz, *J. Am. Chem. Soc.* **2013**, *135*, 3711.
[12] S. M. Lang, A. Frank, T. M. Bernhardt, *J. Phys. Chem. C* **2013**, *117*, 9791.
[13] A. J. Ingram, A. B. Wolk, C. Flender, J. L. Zhang, C. J. Johnson, U. Hintermair, R. H. Crabtree, M. A. Johnson, R. N. Zare, *Inorg. Chem.* **2014**, *53*, 423.
[14] E. Garand, J. A. Fournier, M. Z. Kamrath, N. D. Schley, R. H. Crabtree, M. A. Johnson, *Phys. Chem. Chem. Phys.* **2012**, *14*, 10109.
[15] A. Škríba, J. Schulz, J. Roithová, *Organometallics* **2014**, *33*, 6868.
[16] A. B. Wolk, C. M. Leavitt, J. A. Fournier, M. Z. Kamrath, G. B. Wijeratne, T. A. Jackson, M. A. Johnson, *Int. J. Mass Spectrom.* **2013**, *354*, 33.
[17] X. B. Wang, L. S. Wang, *Rev. Sci. Instrum.* **2008**, *79*, 073108.
[18] C. Hock, J. B. Kim, M. L. Weichman, T. I. Yacovitch, D. M. Neumark, *J. Chem. Phys.* **2012**, *137*, 244201.
[19] A. Svendsen, U. J. Lorenz, O. V. Boyarkin, T. R. Rizzo, *Rev. Sci. Instrum.* **2010**, *81*, 073107.
[20] A. Fedorov, E. P. A. Couzijn, N. S. Nagornova, O. V. Boyarkin, T. R. Rizzo, P. Chen, *J. Am. Chem. Soc.* **2010**, *132*, 13789.
[21] M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, M. Manassero, *J. Chem. Soc. Chem. Commun.* **1975**, 636.
[22] R. Beck, M. Shoshani, J. Krasinkiewicz, J. A. Hatnean, S. A. Johnson, *J. Chem. Soc. Dalton Trans.* **2013**, *42*, 1461.
[23] Y. E. Kim, J. Kim, Y. Lee, *Chem. Commun.* **2014**, *50*, 11458.
[24] J. D. Froehlich, C. P. Kubiak, *Inorg. Chem.* **2012**, *51*, 3932.
[25] J. D. Froehlich, C. P. Kubiak, *J. Am. Chem. Soc.* **2015**, *137*, 3565.
[26] B. Horn, C. Limberg, C. Herwig, B. Braun, *Chem. Commun.* **2013**, *49*, 10923.
[27] F. Bottino, M. Digrazia, P. Finocchiaro, F. R. Fronczek, A. Mamo, S. Pappalardo, *J. Org. Chem.* **1988**, *53*, 3521.
[28] M. Z. Kamrath, R. A. Relph, T. L. Guasco, C. M. Leavitt, M. A. Johnson, *Int. J. Mass Spectrom.* **2011**, *300*, 91.
[29] A. B. Wolk, C. M. Leavitt, E. Garand, M. A. Johnson, *Acc. Chem. Res.* **2014**, *47*, 202.
[30] J. Almlöf, A. Lund, K.-Å. Thoumas, *Chem. Phys. Lett.* **1974**, *28*, 179.
[31] A. W. Addison, T. N. Rao, J. Reedijk, J. Vanrijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349.
[32] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735.
[33] M. Z. Kamrath, R. A. Relph, M. A. Johnson, *J. Am. Chem. Soc.* **2010**, *132*, 15508.

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