

## Rotational Spectroscopy

International Edition: DOI: 10.1002/anie.201511646  
German Edition: DOI: 10.1002/ange.201511646Highly Unsaturated Platinum and Palladium Carbenes PtC<sub>3</sub> and PdC<sub>3</sub> Isolated and Characterized in the Gas Phase

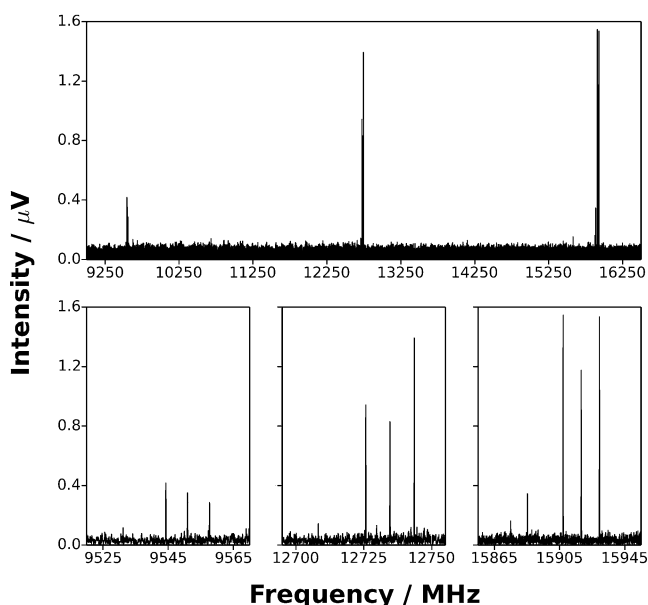
Dror M. Bittner, Daniel P. Zaleski, David P. Tew, Nicholas R. Walker,\* and Anthony C. Legon\*

**Abstract:** Carbenes of platinum and palladium, PtC<sub>3</sub> and PdC<sub>3</sub>, were generated in the gas phase through laser vaporization of a metal target in the presence of a low concentration of a hydrocarbon precursor undergoing supersonic expansion. Rotational spectroscopy and *ab initio* calculations confirm that both molecules are linear. The geometry of PtC<sub>3</sub> was accurately determined by fitting to the experimental moments of inertia of twenty-six isotopologues. The results are consistent with the proposal of an autogenic isolobal relationship between O, Au<sup>+</sup>, and Pt atoms.

The importance of industrial catalysis by platinum and palladium has prompted extensive studies of their gas-phase chemistry.<sup>[1]</sup> Each metal atom is known to initiate cleavage of the C–H and C=C bonds of hydrocarbon precursors. We believe that the present study provides the first pure rotational spectra of platinum and palladium carbenes isolated in the gaseous phase. PtC<sub>3</sub> and PdC<sub>3</sub> (each in a <sup>1</sup>Σ state) were generated through laser vaporization of solid Pt/Pd in the presence of a gas sample undergoing supersonic expansion and containing a low concentration (typically 1%) of a hydrocarbon precursor in a buffer gas of argon. Analysis of the rotational spectra reveals that each molecule has a linear geometry and an MCCC connectivity (where M is the metal atom). The results are a successful test of a model proposed by Pyykkö et al.<sup>[2]</sup> which suggests that platinum can be regarded as the isoelectronic and isolobal counterpart of a chalcogen for the purposes of predicting structure and reactivity trends.

A wide range of hydrocarbon precursors, each tested individually, were found to allow the generation of PtC<sub>3</sub> and

PdC<sub>3</sub>. For PdC<sub>3</sub>, the range of effective precursors includes C<sub>3</sub>H<sub>4</sub> (allene), C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, and C<sub>4</sub>H<sub>4</sub>O (furan). For PtC<sub>3</sub>, the range is narrower, including C<sub>3</sub>H<sub>4</sub> (allene), C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub>, all of which were found to be effective. Broadband microwave spectra of the target molecules were recorded between 6.5 and 18.5 GHz (Figure 1) using a spectrometer described



**Figure 1.** Top: The broadband rotational spectrum (showing the 9 GHz to 16.5 GHz region) averaged over 480 000 free induction decays (FIDs) and recorded while vaporizing a Pt source in the presence of CH<sub>4</sub> under the conditions described in the text. Bottom:  $J' \rightarrow J'' = 6 \rightarrow 5$  transitions of each of <sup>194</sup>PtC<sub>3</sub>, <sup>195</sup>PtC<sub>3</sub>, <sup>196</sup>PtC<sub>3</sub>, and <sup>198</sup>PtC<sub>3</sub> are displayed in the bottom-left panel.  $J' \rightarrow J'' = 7 \rightarrow 6$  and  $J' \rightarrow J'' = 8 \rightarrow 7$  transitions of the isotopologues listed above are shown in the bottom-center and bottom-right panels, respectively.

previously in detail.<sup>[3]</sup> Each spectrum was assigned and fitted to the Hamiltonian of a linear molecule using Western's program PGOPHER.<sup>[4]</sup> The low number of  $J' \rightarrow J''$  transitions within the bandwidth of the spectrometer required that centrifugal distortion constants be fixed at results calculated *ab initio* by an approach described previously.<sup>[5]</sup> Structure optimizations, reaction energies, and orbital energy level diagrams were calculated using the MOLPRO package<sup>[6]</sup> at the CCSD(T) level of theory.<sup>[7]</sup> The basis set combination employed the aug-cc-pwCV5Z basis set for each C atom and the aug-cc-pwCV5Z-PP basis set for each of Pt and Pd.<sup>[8]</sup> The ECP-28-MDF and ECP-60-MDF effective core potentials were used to account for scalar relativistic effects on Pd and

[\*] D. M. Bittner, Dr. D. P. Zaleski, Dr. N. R. Walker  
School of Chemistry, Bedson Building, Newcastle University  
Newcastle upon Tyne, Tyne and Wear, NE1 7RU (UK)  
E-mail: nick.walker@newcastle.ac.uk

Dr. D. P. Tew, Prof. Dr. A. C. Legon  
School of Chemistry, University of Bristol  
Bristol, BS8 1TS (UK)  
E-mail: a.c.legon@bristol.ac.uk

Dr. D. P. Zaleski  
Current address: Argonne National Laboratory  
Chemical Sciences and Engineering  
9700 S. Cass Ave., Bldg. 200, Lemont, IL 60439 (USA)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/anie.201511646>.

© 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Pt, respectively,<sup>[8]</sup> with all electrons included in the correlation treatment. Electric dipole moments and centrifugal distortion constants were calculated with the GAUSSIAN09 package<sup>[9]</sup> at the MP2 level of theory using a basis set combination consisting of aug-cc-pVTZ on C atoms and aug-cc-pVTZ-PP on Pd and Pt atoms.<sup>[8]</sup> Selected results of spectroscopic fits are shown in Table 1 with complete details for all isotopologues provided in the Supporting Information. The standard deviations of all fits are consistent with the measured linewidth (FWHM) of 120 kHz. Neither PtC<sub>2</sub> nor PdC<sub>2</sub> were identified despite a careful search of the spectra. Rotational transitions of both PtC<sup>[10]</sup> (measured previously) and PdC lie higher in frequency than the upper limit of the spectrometer. Where PdC<sub>3</sub> was generated from a furan precursor, intense transitions of PdCO<sup>[11]</sup> were detected in addition to those assigned to PdC<sub>3</sub>.

**Table 1:** Spectroscopic parameters of PtC<sub>3</sub> and PdC<sub>3</sub>.<sup>[a]</sup>

Species	$B_0$ [MHz]	$[D_j \times 10^2]^{[b]}$ [kHz]	$\chi_{aa}^{(105\text{Pd})}$ [MHz]	$\sigma$ [kHz]	$N$
<sup>194</sup> Pt <sup>12</sup> C <sup>12</sup> C <sup>12</sup> C	1592.94589(35)	[6.2]	–	5.0	3
<sup>194</sup> Pt <sup>13</sup> C <sup>13</sup> C <sup>13</sup> C	1486.74426(60)	[5.4]	–	11.1	4
<sup>194</sup> Pt <sup>12</sup> C <sup>12</sup> C <sup>13</sup> C	1522.47541(52)	[5.6]	–	9.1	3
<sup>194</sup> Pt <sup>12</sup> C <sup>13</sup> C <sup>12</sup> C	1560.77071(27)	[6.0]	–	3.4	2
<sup>194</sup> Pt <sup>13</sup> C <sup>12</sup> C <sup>12</sup> C	1585.00114(43)	[6.2]	–	6.1	3
<sup>106</sup> Pd <sup>12</sup> C <sup>12</sup> C <sup>12</sup> C	1702.33446(43)	[9.5]	–	6.3	4
<sup>105</sup> Pd <sup>12</sup> C <sup>12</sup> C <sup>12</sup> C	1705.89034(57)	[9.6]	35.88(43)	14.5	9
<sup>106</sup> Pd <sup>13</sup> C <sup>13</sup> C <sup>13</sup> C	1599.5465 <sup>[c]</sup>	[8.4]	–	–	1

[a] Results of selected spectroscopic fits illustrating the dependence of rotational ( $B_0$ ) and centrifugal distortion ( $D_j$ ) constants on isotopic substitution.  $\chi_{aa}^{(105\text{Pd})}$  denotes the nuclear quadrupole coupling constant of the <sup>105</sup>Pd atom.  $N$  and  $\sigma$  are the number of fitted transitions and the standard deviation of the fit, respectively. Further results are presented in Table S1 in the Supporting Information. [b] Centrifugal distortion constants are fixed to results calculated ab initio at the MP2/AVTZ level. [c] Result calculated from a single transition frequency.

Spectra were measured for isotopologues of PtC<sub>3</sub> and PdC<sub>3</sub> that contain the <sup>13</sup>C isotope to ensure assignment of the correct molecular carriers and allow precise determination of the molecular geometries. Experimental data are available only for the ground vibrational state of each molecule allowing an effective  $r_0$  geometry to be fitted in each case. The experimental results are consistent with two possibilities for each molecule: 1) a geometry that is slightly bent at equilibrium but quasilinear in the  $\nu=0$  state, and 2) an equilibrium ( $r_e$ ) geometry that is linear. The ab initio calculations suggest that both molecules are linear at equilibrium. The intensities of PdC<sub>3</sub> transitions were found to be highly dependent on the choice of precursor, in the order C<sub>3</sub>H<sub>4</sub> > C<sub>2</sub>H<sub>4</sub> > CH<sub>4</sub>. Transition intensities were lower when the population of PdC<sub>3</sub> was divided across many isotopic permutations and isotopically enriched allene is prohibitively expensive. These factors prevented measurement of the spectrum of any PdC<sub>3</sub> isotopologue that contains both <sup>12</sup>C and <sup>13</sup>C isotopes. The intensities of PtC<sub>3</sub> transitions were insensitive to the choice of precursor and it was possible to

generate and record spectra for many isotopic permutations of PtC<sub>3</sub> (from the set of <sup>194</sup>Pt, <sup>195</sup>Pt, <sup>196</sup>Pt, <sup>198</sup>Pt, <sup>12</sup>C, and <sup>13</sup>C atoms) using samples prepared by mixing <sup>12</sup>CH<sub>4</sub> and commercially supplied <sup>13</sup>CH<sub>4</sub>. It was also found that PtC<sub>3</sub> can be generated from a mixture of <sup>12</sup>C<sub>2</sub>H<sub>2</sub> and <sup>13</sup>CH<sub>4</sub> precursors with the result that the spectra of <sup>194</sup>Pt<sup>12</sup>C<sup>12</sup>C<sup>13</sup>C, <sup>194</sup>Pt<sup>12</sup>C<sup>13</sup>C<sup>12</sup>C, and <sup>194</sup>Pt<sup>13</sup>C<sup>12</sup>C<sup>12</sup>C were detected with equal intensities. The observation that the <sup>13</sup>C isotope does not preferentially occupy an end position of the C<sub>3</sub> subunit strongly implies that the C≡C bond of C<sub>2</sub>H<sub>2</sub> cleaves during the sequence of reactions that generates PtC<sub>3</sub> from this set of precursors.

The present study is believed to be the first to characterize MC<sub>3</sub> units by rotational spectroscopy. Transition-metal dicarbides, such as ScC<sub>2</sub> and YC<sub>2</sub>, have been studied previously.<sup>[12]</sup> The dipole moments of PdC<sub>3</sub> and PtC<sub>3</sub> are calculated at the MP2 level to be 6.1 and 5.6 D, respectively. The lengths of bonds within PtC<sub>3</sub> were fitted to experimentally determined rotational constants using Kisiel's STRFIT.<sup>[13]</sup> Spectra were measured for 26 distinct isotopologues of PtC<sub>3</sub> where the set includes every permutation of C<sub>3</sub> that it is possible to generate from <sup>12</sup>C and <sup>13</sup>C isotopes. The bond lengths thus determined are compared with those in isolated PtC, C<sub>3</sub> and OC<sub>3</sub> molecules in Table 2. The  $r_0$  geometry of PtC<sub>3</sub> is in good agreement with the  $r_e$  geometry calculated at the CCSD(T) level. The Pt–C bond in PtC<sub>3</sub> is longer than found in diatomic PtC<sup>[10]</sup> by 0.053 Å. There are similarities between  $r(\text{MC})$  in PtC<sub>3</sub> and in PtCO,<sup>[14]</sup> and also in changes when these molecules form from their component Pt and C<sub>3</sub>/CO subunits. The  $r(\text{MC})$  parameter in PtC<sub>3</sub> is shorter than the same quantity in PtCO by 0.031 Å. The first C=C bond (that which is contiguous with the Pt–C bond) of PtC<sub>3</sub> is longer than the C=C bond in isolated C<sub>3</sub> by 0.022 Å. The set of isotopologues studied is less extensive for PdC<sub>3</sub> than for PtC<sub>3</sub> and does not permit determination of all bond lengths from the experimental data. If the lengths of C=C bonds within the molecule are fixed as shown in Table 2,  $r(\text{PdC})$  is determined to be

**Table 2:** Structural parameters of PtC<sub>3</sub>, PdC<sub>3</sub>, and related molecules.<sup>[a]</sup>

Species <sup>[a]</sup>	$r(\text{MC})$ [Å]	$r(\text{CC1})$ [Å]	$r(\text{CC2})$ [Å]
PtC <sup>[b]</sup>	1.679	–	–
C <sub>3</sub> ( $r_0$ ) <sup>[b]</sup>	–	1.277247(2)	1.277247(2)
OC <sub>3</sub> ( $r_0$ ) <sup>[b]</sup>	1.150	1.306	1.254
PtC <sub>3</sub> ( $r_0$ )	1.7315(14)	1.2993(19)	1.2759(11)
PtC <sub>3</sub> ( $r_e$ )	1.7280	1.2942	1.2836
PdC <sub>3</sub> ( $r_0$ )	1.79898(4)	[1.3009] <sup>[c]</sup>	[1.2789] <sup>[c]</sup>
PdC <sub>3</sub> ( $r_e$ )	1.7962	1.2958	1.2866
	$r(\text{MC})$ [Å]	$r(\text{CO})$ [Å]	
CO	–	1.128	
PtCO ( $r_0$ ) <sup>[d]</sup>	1.7625(4)	1.1466(6)	
PdCO ( $r_0$ ) <sup>[d]</sup>	1.8447(1)	1.1374(2)	

[a]  $r(\text{MC})$  denotes the bond between the metal atom (or oxygen atom in OC<sub>3</sub>) and its coordinated carbon.  $r(\text{CC1})$  denotes the C=C bond nearest to the metal atom with  $r(\text{CC2})$  used to label the other.  $r_0$  values are determined experimentally and  $r_e$  values are calculated ab initio. [b] Data from Refs. [10, 19, 22]. [c] Each number in square brackets is fixed to the result obtained by correcting the  $r_e$  value calculated ab initio for PdC<sub>3</sub> for the difference between the  $r_0$  and  $r_e$  values determined for the equivalent parameter in PtC<sub>3</sub>. [d] Data from Refs. [11, 14].

1.79898(4) Å. Values of vibrational wavenumbers calculated ab initio are provided in the Supporting Information.

The described results confirm that the heavier elements of Group 10 can form linear arrangements similar to that previously identified for Ni<sub>2</sub>C<sub>3</sub>.<sup>[15]</sup> The detected palladium/platinum carbenes are amongst the smallest to be structurally characterized.<sup>[16]</sup> There is a correspondence between the linear geometries of the MC<sub>3</sub> units identified herein and the linear carbon chains that are interceded by Pt/Pd atoms which are a feature of many synthetic coordination polymers.<sup>[17]</sup> The results are also interesting in the context of the wider chemistry of metal atoms in hydrocarbon plasmas. Early transition metals are known to react with hydrocarbon precursors to generate metallocarbohydrides (met-cars).<sup>[18]</sup> Late transition metals show no general tendency to form such extended structures. The present experiment does not unambiguously distinguish the reaction sequences (or networks of competing reactions) that generate PdC<sub>3</sub> and PtC<sub>3</sub>. It is possible that a fraction of the population of each forms through gas-phase association of individual metal atoms with intact C<sub>3</sub> or other units generated independently of any metal atom.<sup>[19]</sup> The energy changes accompanying the M + C<sub>3</sub> → MC<sub>3</sub> association reactions to yield linear MC<sub>3</sub> units are calculated to be −295 kJ mol<sup>−1</sup> and −417 kJ mol<sup>−1</sup> when M = Pd and M = Pt, respectively (detailed calculations are shown in the Supporting Information). However, it is also possible that the metals themselves initiate the sequence of chemical reactions that leads to dehydrogenation of the precursor. There is extensive evidence from previous studies that both Pt and Pd atoms undergo bond-insertion and cleavage reactions with hydrocarbons.<sup>[1a,20]</sup> MCH<sub>2</sub> and MCCH<sub>2</sub> have both been generated<sup>[1a,b,21]</sup> previously by a laser vaporization/supersonic expansion method, characterized by matrix isolation spectroscopy, and are also likely to be generated under the present experimental conditions. Transition frequencies of MCH<sub>2</sub> are expected to be above the upper frequency limit of the spectrometer and both MCH<sub>2</sub> and MCCH<sub>2</sub> will have comparatively low dipole moments which significantly decrease the intensity of their rotational transitions relative to those of MC<sub>3</sub>.

An empirical model proposed by Pyykkö et al.<sup>[2a]</sup> provides a chemical rationalization for an enhanced stability of MC<sub>3</sub> relative to MC<sub>2</sub> or MC<sub>4</sub>. Calculations of the geometries of CAu<sup>2+</sup>, CAu<sup>3+</sup>, Pt<sub>2</sub>C, Pt<sub>2</sub>C<sub>3</sub>, and Au<sub>2</sub>C<sub>2</sub> revealed analogies between the behavior of each of Au<sup>+</sup> and Pt and a chalcogen atom such as O.<sup>[2a]</sup> Within this model, the σ hole on platinum arising from the 5d<sup>10</sup>6s<sup>0</sup> configuration is analogous to the 2pσ<sup>0</sup> hole on oxygen, and the 5dπ orbitals of platinum participate in π-bonding interactions analogous to those involving the 2pπ orbital of oxygen. The existence of a family of stable molecules was thus predicted. An orbital energy level diagram for PtC<sub>3</sub> is presented in Figure S1 in the Supporting Information. There are striking similarities between the geometries of MC<sub>3</sub> measured during the present work and that reported earlier for OC<sub>3</sub> by Brown et al.<sup>[22]</sup> Applying the model of Pyykkö et al., PtCO, PtC, and Pt<sub>2</sub>C<sub>3</sub> are analogues of the well-known, stable oxocarbons carbon dioxide, monoxide, and suboxide, respectively, each of which have been known since the 19th century. Similarly, PtSi<sup>[23]</sup> can

be regarded as an analogue of SiO. The oxocarbon analogue of Pt<sub>2</sub>C<sub>2</sub> would be ethylene dione,<sup>[24]</sup> a transient species characterized, only through spectroscopy, for the first time in 2015. This model can thus explain why PtCO, PtC, and PtC<sub>3</sub>, but not yet PtC<sub>2</sub>, have been detected. The results of the present work thus support the suggestion that platinum can be regarded an isoelectronic, isolobal counterpart of oxygen. The proposal can be further assessed with reference to previous works.

Reports of clusters containing multiple carbon and platinum or palladium atoms are scarce. The adsorption of, and reactions of, CH<sub>4</sub> and CO on Pt<sub>n</sub> clusters<sup>[1e]</sup> and the structures of Pt<sub>n</sub>O<sub>m</sub> clusters<sup>[1d]</sup> have been studied. Harding et al. identified a Pt<sub>3</sub>C<sup>+</sup> cluster ion<sup>[25]</sup> for which the geometry is analogous to a carbonate ion and hence consistent with the prediction of the model provided by Pyykkö et al.<sup>[2]</sup> The geometries of other platinum/carbon clusters, which have not yet been observed or characterized, may perhaps be predicted by analogy with other oxocarbons. For example, mellitic anhydride (C<sub>12</sub>O<sub>9</sub>) is known to be stable, suggesting that Pt<sub>9</sub>C<sub>12</sub> might be generated in an equivalent structural form. An experimental study<sup>[26]</sup> of AuC<sub>n</sub><sup>+</sup> and CuC<sub>n</sub><sup>+</sup> revealed ion intensities in the mass spectra that are significantly stronger where *n* = 3 than for clusters of other sizes.<sup>[26]</sup> Some caution must be exercised in drawing conclusions about the thermodynamic stability of AuC<sub>3</sub><sup>+</sup> relative to other cluster sizes from these results. As in the present work, the experiment performed by Ticknor et al.<sup>[26]</sup> did not unambiguously distinguish between various factors that contribute to observed spectral intensities. It is likely that C<sub>3</sub> was generated with a significantly higher abundance<sup>[19]</sup> than C<sub>2</sub> within the expanding gas sample and this may cause the generation of AuC<sub>3</sub><sup>+</sup> to be favored over the generation of clusters of other sizes, regardless of the thermodynamic stability of AuC<sub>3</sub><sup>+</sup>. Indeed, during a previous study, signals for NiC<sub>3</sub><sup>+</sup> and NiC<sub>6</sub><sup>+</sup> were detected in mass spectra with higher intensity than units containing 1, 2, 4, or 5 carbon atoms,<sup>[27]</sup> although the Ni<sup>+</sup> ion is not isoelectronic and isolobal with O. However, the reported fragmentation behavior of AuC<sub>n</sub><sup>+</sup> is also notable. Clusters where *n* is odd lose only the metal atom on photodissociation whereas those with an even value of *n* display an additional loss channel corresponding to the loss of an odd number of carbon atoms. The overall result is that chains (either isolated or attached to the metal ion) containing an odd number of carbon atoms tend to be formed during photofragmentation, consistent with the proposal of Pyykkö et al. The perspective thus emerging from the collected results of spectroscopic experiments is that the proposal<sup>[2a]</sup> of an autogenic isolobal relationship of Pt and Au<sup>+</sup> centers with the O atom is powerful and useful with respect to structural trends in gas-phase clusters that contain Pt, Pd, Au<sup>+</sup>, and C centers.

## Acknowledgements

The authors thank the European Research Council (CPFTMW-307000) for project funding, the Engineering and Physical Sciences Research Council (U.K.) for the award of a DTA studentship (EPK5028931) to D.M.B., and

the EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London. A.C.L. thanks the University of Bristol for a Senior Research Fellowship. D.P.Z. thanks Newcastle University for the award of a Faculty of SAgE Research Fellowship. D.P.T. thanks the Royal Society for a University Research Fellowship.

**Keywords:** ab initio calculations · carbenes · palladium · platinum · rotational spectroscopy

**How to cite:** *Angew. Chem. Int. Ed.* **2016**, *55*, 3768–3771  
*Angew. Chem.* **2016**, *128*, 3832–3835

- [1] a) H.-G. Cho, L. Andrews, *J. Phys. Chem. A* **2004**, *108*, 6272–6278; b) J. J. Carroll, J. C. Weisshaar, P. E. M. Siegbahn, C. A. M. Wittborn, M. R. A. Blomberg, *J. Phys. Chem.* **1995**, *99*, 14388–14396; c) X.-G. Zhang, R. Liyanage, P. B. Armentrout, *J. Am. Chem. Soc.* **2001**, *123*, 5563–5575; d) D. J. Harding, A. Fielicke, *Chem. Eur. J.* **2014**, *20*, 3258–3267; e) D. J. Harding, C. Kerpál, G. Meijer, A. Fielicke, *Angew. Chem. Int. Ed.* **2012**, *51*, 817–819; *Angew. Chem.* **2012**, *124*, 842–845.
- [2] a) P. Pyykkö, M. Patzschke, J. Suurpere, *Chem. Phys. Lett.* **2003**, *381*, 45–52; b) L. G. M. de Macedo, P. Pyykkö, *Chem. Phys. Lett.* **2008**, *462*, 138–143.
- [3] D. P. Zaleski, S. L. Stephens, N. R. Walker, *Phys. Chem. Chem. Phys.* **2014**, *16*, 25221–25228.
- [4] PGOPHER, a Program for Simulating Rotational, Vibrational, and Electronic Structure, C. M. Western, University of Bristol, <http://pgopher.chm.bris.ac.uk>.
- [5] D. P. Zaleski, S. L. Stephens, D. P. Tew, D. M. Bittner, N. R. Walker, A. C. Legon, *Phys. Chem. Chem. Phys.* **2015**, *17*, 19230–19237.
- [6] Molpro: a general-purpose quantum chemistry program package: H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, *WIREs Comput. Mol. Sci.* **2012**, *2*, 242–253.
- [7] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479–483.
- [8] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurmooorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052.
- [9] Gaussian 09, Revision D.01, M. J. Frisch et al., Gaussian, Inc., Wallingford, CT, USA, **2009**.
- [10] a) T. C. Steimle, K. Y. Jung, B. Z. Li, *J. Chem. Phys.* **1995**, *102*, 5937–5941; b) C. Qin, R. Zhang, F. Wang, T. C. Steimle, *Chem. Phys. Lett.* **2012**, *535*, 40–43.
- [11] N. R. Walker, J. K. H. Hui, M. C. L. Gerry, *J. Phys. Chem. A* **2002**, *106*, 5803–5808.
- [12] a) J. Min, D. T. Halfen, L. M. Ziurys, *Chem. Phys. Lett.* **2014**, *609*, 70–75; b) D. T. Halfen, J. Min, L. M. Ziurys, *Chem. Phys. Lett.* **2013**, *555*, 31–37.
- [13] Z. Kisiel, *J. Mol. Spectrosc.* **2003**, *218*, 58–67.
- [14] C. J. Evans, M. C. L. Gerry, *J. Phys. Chem. A* **2001**, *105*, 9659–9663.
- [15] R. E. Kinzer, C. M. L. Rittby, W. R. M. Graham, *J. Chem. Phys.* **2008**, *128*, 064312.
- [16] C. C. Womack, K. N. Crabtree, L. McCaslin, O. Martinez, R. W. Field, J. F. Stanton, M. C. McCarthy, *Angew. Chem. Int. Ed.* **2014**, *53*, 4089–4092; *Angew. Chem.* **2014**, *126*, 4173–4176.
- [17] a) H. F. Wittmann, R. H. Friend, M. S. Khan, J. Lewis, *J. Chem. Phys.* **1994**, *101*, 2693–2698; b) C. R. Horn, J. A. Gladysz, *Eur. J. Inorg. Chem.* **2003**, 2211–2218.
- [18] a) L.-S. Wang, X. Li, *J. Chem. Phys.* **2000**, *112*, 3602–3608; b) R. E. Kinzer, C. M. L. Rittby, W. R. M. Graham, *J. Chem. Phys.* **2006**, *125*, 074513.
- [19] A. Van Orden, R. J. Saykally, *Chem. Rev.* **1998**, *98*, 2313–2358.
- [20] H.-G. Cho, L. Andrews, *Organometallics* **2009**, *28*, 1358–1368.
- [21] V. J. F. Lapoutre, B. Redlich, A. F. G. van der Meer, J. Oomens, J. M. Bakker, A. Sweeney, A. Mookherjee, P. B. Armentrout, *J. Phys. Chem. A* **2013**, *117*, 4115–4126.
- [22] R. D. Brown, P. D. Godfrey, P. S. Elmes, M. Rodler, L. M. Tack, *J. Am. Chem. Soc.* **1985**, *107*, 4112–4115.
- [23] S. A. Cooke, M. C. L. Gerry, D. J. Brugh, R. D. Suenram, *J. Mol. Spectrosc.* **2004**, *223*, 185–194.
- [24] A. R. Dixon, T. Xue, A. Sanov, *Angew. Chem. Int. Ed.* **2015**, *54*, 8764–8767; *Angew. Chem.* **2015**, *127*, 8888–8891.
- [25] D. J. Harding, C. Kerpál, G. Meijer, A. Fielicke, *J. Phys. Chem. Lett.* **2013**, *4*, 892–896.
- [26] B. W. Ticknor, B. Bandyopadhyay, M. A. Duncan, *J. Phys. Chem. A* **2008**, *112*, 12355–12366.
- [27] J. E. Reddic, M. A. Duncan, *Chem. Phys. Lett.* **1997**, *264*, 157–162.

Received: December 15, 2015

Published online: February 15, 2016