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Highly Unsaturated Platinum and Palladium Carbenes PtC₃ and PdC₃ Isolated and Characterized in the Gas Phase

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Abstract: Carbenes of platinum and palladium, PtC₃ and PdC₃, 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 PtC₃ 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⁺, and Pt atoms.

The importance of industrial catalysis by platinum and palladium has prompted extensive studies of their gas-phase chemistry.[1] 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. PtC₃ and PdC₃ (each in a 1Σ 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 Pykkö et al.[2] 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 PtC₃ and PdC₃. For PdC₃, the range of effective precursors includes C₄H₄ (allene), C₅H₄, C₆H₄, C₇H₄, and C₈H₆O (furan). For PtC₃, the range is narrower, including C₄H₄ (allene), C₅H₄, and CH₄, 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 previously in detail.[3] Each spectrum was assigned and fitted to the Hamiltonian of a linear molecule using Western’s program PGOPHER.[4] The low number of J→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.[5] Structure optimizations, reaction energies, and orbital energy level diagrams were calculated using the MOLPRO package[6] at the CCSD(T) level of theory.[7] The basis set combination employed the aug-cc-pVQZ basis set for each C atom and the aug-cc-pCVQZ-PP basis set for each of Pt and Pd.[8] The ECP-28-MDF and ECP-60-MDF effective core potentials were used to account for scalar relativistic effects on Pd and
Pt, respectively,[9] with all electrons included in the correlation treatment. Electric dipole moments and centrifugal distortion
constants were calculated with the GAUSSIAN09 package[9]
at the MP2 level of theory using a basis set combination
consisting of aug-cc-pVTZ on C atoms and aug-cc-pV
tZ-PP
on Pd and Pt atoms.[9] 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 PtC2 nor PdC2 were identified
despite a careful search of the spectra. Rotational transitions of
both PtC[10] (measured previously) and PdC lie higher in
frequency than the upper limit of the spectrometer. Where
PdC2 was generated from a furan precursor, intense transitions
of PdCO[11] were detected in addition to those assigned
to PdC2.

Table 1: Spectroscopic parameters of PtC2 and PdC2.[c]

<table>
<thead>
<tr>
<th>Species</th>
<th>B0</th>
<th>D0 [MHz]</th>
<th>C0 [MHz]</th>
<th>α</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>195Pt13C12C13C</td>
<td>1592.94589(35)</td>
<td>[6.2]</td>
<td>–</td>
<td>5.0</td>
<td>3</td>
</tr>
<tr>
<td>195Pt12C13C13C</td>
<td>1486.74426(60)</td>
<td>[5.4]</td>
<td>–</td>
<td>11.1</td>
<td>4</td>
</tr>
<tr>
<td>195Pt12C13C12C</td>
<td>1522.47541(52)</td>
<td>[5.6]</td>
<td>–</td>
<td>9.1</td>
<td>3</td>
</tr>
<tr>
<td>195Pt13C12C12C</td>
<td>1560.77077(27)</td>
<td>[6.0]</td>
<td>–</td>
<td>3.4</td>
<td>2</td>
</tr>
<tr>
<td>195Pt13C13C12C</td>
<td>1585.00114(43)</td>
<td>[6.2]</td>
<td>–</td>
<td>6.1</td>
<td>3</td>
</tr>
<tr>
<td>195Pd13C13C13C</td>
<td>1702.33446(43)</td>
<td>[9.5]</td>
<td>–</td>
<td>6.3</td>
<td>4</td>
</tr>
<tr>
<td>195Pd12C13C13C</td>
<td>1705.89035(57)</td>
<td>[9.6]</td>
<td>35.88(43)</td>
<td>14.5</td>
<td>9</td>
</tr>
<tr>
<td>195Pd13C12C13C</td>
<td>1599.5465(53)</td>
<td>[8.4]</td>
<td>–</td>
<td>–</td>
<td>1</td>
</tr>
</tbody>
</table>

[a] Results of selected spectroscopic fits illustrating the dependence of rotational (B0) and centrifugal distortion (D0) constants on isotopic substitution. C0(2Pd) denotes the nuclear quadruple coupling constant of the 195Pd atom. N and α 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 PtC2 and
PdC2 that contain the 13C 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 r0 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 v = 0 state, and 2) an
equilibrium (r0) geometry that is linear. The ab initio calculations
suggest that both molecules are linear at equilibrium.
The intensities of PdC2 transitions were found to be highly
dependent on the choice of precursor, in the order C3H3 >
C3H2 > CH4. Transition intensities were lower when the
population of PdC2 was divided across many isotopic permu-
tations and isotopically enriched allene is prohibitively
expensive. These factors prevented measurement of the
spectrum of any PdC2 isotopologue that contains both 12C
and 13C isotopes. The intensities of PtC2 transitions were
insensitive to the choice of precursor and it was possible to
generate and record spectra for many isotopic permutations of
PtC2 (from the set of 194Pt, 195Pt, 196Pt, 198Pt, 12C, and
13C atoms) using samples prepared by mixing 13CH4 and
commercially supplied 13CH3. It was also found that PtC2 can
be generated from a mixture of 13CH3 and 13CH4 precursors
with the result that the spectra of 195Pt13C12C13C,
195Pt12C13C13C, and 195Pt13C13C13C were detected with equal
intensities. The observation that the 13C isotope does not
preferentially occupy an end position of the C2 subunit
strongly implies that the C=C bond of CH3 cleaves during
the sequence of reactions that generates PtC2 from this set of
precursors.

The present study is believed to be the first to characterize
MC2 units by rotational spectroscopy. Transition-metal dicar-
bides, such as ScC2 and YC2, have been studied previously.[12]
The dipole moments of PdC2 and PtC2 are calculated at the
MP2 level to be 6.1 and 5.6 D, respectively. The lengths of
bonds within PtC2 were fitted to experimentally determined
rotational constants using Kisieli's STRFIT.[13] Spectra were
measured for 26 distinct isotopologues of PtC2 where the set
includes every permutation of C1 that it is possible to generate
from 12C and 13C isotopes. The bond lengths thus determined
are compared with those in isolated PtC2, C2, and OC2
molecules in Table 2. The r0 geometry of PtC2 is in good
agreement with the r0 geometry calculated at the CCSD(T)
level. The Pb–C bond in PtC2 is longer than found in diatomic
PtC2[10] by 0.053 Å. There are similarities between r(MC) in
PtC2 and in PtCO,[14] and also in changes when these molecules
form from their component Pt and C2/CO subunits.
The r(MC) parameter in PtC2 is shorter than the same
quantity in PtCO by 0.031 Å. The first C=C bond (that is
contiguous with the Pt–C bond) of PtC2 is longer than the
C=C bond in isolated C2 by 0.022 Å. The set of isotopologues
studied is less extensive for PdC2 than for PtC2 and does not
permit determination of all bond lengths from the experi-
mental data. If the lengths of C=C bonds within the molecule
are fixed as shown in Table 2, r(PdC2) is determined to be

Table 2: Structural parameters of PtC2, PdC2, and related molecules.[c]

<table>
<thead>
<tr>
<th>Species</th>
<th>r(MC) [Å]</th>
<th>r(CC1) [Å]</th>
<th>r(CC2) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtC2[c]</td>
<td>1.679</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C2 (r0)[c]</td>
<td>1.150</td>
<td>1.27274(2)</td>
<td>1.27274(2)</td>
</tr>
<tr>
<td>OC2 (r0)[c]</td>
<td>1.306</td>
<td>1.2939(19)</td>
<td>1.2759(11)</td>
</tr>
<tr>
<td>PtC2 (r0)</td>
<td>1.7315(14)</td>
<td>1.2942(1)</td>
<td>1.2836</td>
</tr>
<tr>
<td>PdC2 (r0)</td>
<td>1.7280</td>
<td>1.2958</td>
<td>1.2866</td>
</tr>
<tr>
<td>PdCO (r0)[c]</td>
<td>1.79898(4)</td>
<td>[1.3009][c]</td>
<td>1.2789(4)</td>
</tr>
<tr>
<td>195Pt13C12C13C</td>
<td>1.7962</td>
<td>1.2958</td>
<td>1.2866</td>
</tr>
</tbody>
</table>

[a] r(MC) denotes the bond between the metal atom (or oxygen atom in
OC2) and its coordinated carbon. r(CC1) denotes the C=C bond nearest
to the metal atom with r(CC2) used to label the other. r0 values are
determined experimentally and r0 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 r0 value calculated ab initio for PdC2,
for the difference between the r0 and r0 values determined for the equivalent
parameter in PtC2. [d] Data from Refs. [11, 14].
The described results confirm that the heavier elements of Group 10 can form linear arrangements similar to that previously identified for Ni$_3$C$_3$[15]. The detected palladium/platinum carbides are amongst the smallest to be structurally characterized. [16] There is a correspondence between the linear geometries of the MC$_3$ units identified herein and the linear carbon chains that are interceded by Pt/Pd atoms which are a feature of many synthetic coordination polymers.[17] 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 metallocarbohydrenes (met-cars).[18] 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$_3$ and PtC$_3$. It is possible that a fraction of the population of each forms through gas-phase association of individual metal atoms with intact C$_3$ or other units generated independently of any metal atom.[19] The energy changes accompanying the M + C$_3$ → MC$_3$ association reactions to yield linear MC$_3$ units are calculated to be $-295 \text{ kJ mol}^{-1}$ and $-417 \text{ kJ mol}^{-1}$ when $M = \text{Pd}$ and $M = \text{Pt}$ 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.[1a,20] MCH$_2$ and MCCCH$_3$ have both been generated[1a,21] 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$_2$ are expected to be above the upper frequency limit of the spectrometer and both MCH$_2$ and MCCCH$_3$ will have comparatively low dipole moments which significantly decrease the intensity of their rotational transitions relative to those of MC$_3$.

An empirical model proposed by Pyykkö et al.[22] provides a chemical rationalization for an enhanced stability of MC$_3$ relative to MC$_2$ or MC$_4$. Calculations of the geometries of CAu$^+$, CAu$^{2+}$, Pt$_2$C, Pt$_2$C$_3$, and Au$_4$C$_2$ revealed analogies between the behavior of each of Au$^+$ and Pt and a chalcogen atom such as O.[24] Within this model, the $\sigma$ hole on platinum arising from the 5d$^{10}$s$^1$ configuration is analogous to the 2po$^0$ hole on oxygen, and the 5dx orbitals of platinum participate in $\pi$-bonding interactions analogous to those involving the 2px orbital of oxygen. The existence of a family of stable molecules was thus predicted. An orbital energy level diagram for PtC$_3$ is presented in Figure S1 in the Supporting Information. There are striking similarities between the geometries of MC$_3$ measured during the present work and that reported earlier for OC$_3$ by Brown et al.[25] Applying the model of Pyykkö et al., PtCO, PtC, and Pt$_2$C$_3$ 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, Pts$^{2+}$[23] can be regarded as an analogue of SiO. The oxocarbon analogue of Pt$_2$C$_3$ would be ethylene dione,[24] a transient species characterized, only through spectroscopy, for the first time in 2015. This model can thus explain why PtCO, PtC, and PtC$_3$, but not yet PtC$_2$, have been detected. The results of the present work thus support the suggestion that platinum can be regarded as an 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$_4$ and CO on Pt$_n$ clusters[24] and the structures of Pt$_n$O$_m$ clusters[1a] have been studied. Harding et al. identified a Pt$_3$C$^+$_cluster ion[25] for which the geometry is analogous to a carbonate ion and hence consistent with the prediction of the model provided by Pyykkö et al.[22] 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$_3$O$_4$) is known to be stable, suggesting that Pt$_6$C$_6$ might be generated in an equivalent structural form. An experimental study[20] of AuC$_2$$^+$ and CuC$_2$$^+$ revealed ion intensities in the mass spectra that are significantly stronger where $n = 3$ than for clusters of other sizes.[20] Some caution must be exercised in drawing conclusions about the thermodynamic stability of AuC$_2$$^+$ relative to other cluster sizes from these results. As in the present work, the experiment performed by Ticknor et al.[20] did not unambiguously distinguish between various factors that contribute to observed spectral intensities. It is likely that C$_5$ was generated with a significantly higher abundance[19] than C$_3$ within the expanding gas sample and this may cause the generation of AuC$_3$$^+$ to be favored over the generation of clusters of other sizes, regardless of the thermodynamic stability of AuC$_3$$^+$. Indeed, during a previous study, signals for NiC$_3$$^+$ and NiC$_4$$^+$ were detected in mass spectra with higher intensity than units containing 1, 2, 4, or 5 carbon atoms,[25] although the Ni$^+$ ion is not isoelectronic and isolobal with O. However, the reported fragmentation behavior of AuC$_3$$^+$ 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[22] of an autogenic isolobal relationship of Pt and Au$^+$ centers with the O atom is powerful and useful with respect to structural trends in gas-phase clusters that contain Pt, Pd, Au$^+$, and C centers.

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