Highly Unsaturated Platinum and Palladium Carbenes PtC$_3$ and PdC$_3$ Isolated and Characterized in the Gas Phase

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Abstract: Carbenes of platinum and palladium, PtC$_3$ and PdC$_3$, 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$_3$ 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. PtC$_3$ and PdC$_3$ (each in a $^2$E 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.\[2\] 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 PtC$_3$ and PdC$_3$. For PdC$_3$, the range of effective precursors includes C$_3$H$_4$ (allene), C$_5$H$_4$, C$_6$H$_4$, C$_6$H$_8$, and C$_4$H$_6$O (furan). For PtC$_3$, the range is narrower, including C$_3$H$_4$ (allene), C$_5$H$_4$, and CH$_4$, 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. 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.\[7\] The ECP-28-MDF and ECP-60-MDF effective core potentials were used to account for scalar relativistic effects on Pd and

Figure 1. Top: The broadband rotational spectrum (showing the 9 GHz to 16.5 GHz region) averaged over 48000 free induction decays (FIDs) and recorded while vaporizing a Pt source in the presence of CH$_4$ under the conditions described in the text. Bottom: $J' - J'' = 5$ transitions of each of $^{195}$PtC$_3$, $^{197}$PtC$_3$, $^{199}$PtC$_3$, and $^{197}$PdC$_3$ are displayed in the bottom-left panel, $J' - J'' = 5$ and $J' - J'' = 8$–7 transitions of the isotopologues listed above are shown in the bottom-center and bottom-right panels, respectively.

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generate and record spectra for many isotopic permutations of PtC (from the set of $^{184}$Pt, $^{185}$Pt, $^{186}$Pt, $^{189}$Pt, $^{12}$C, and $^{13}$C atoms) using samples prepared by mixing $^{12}$CH$_4$ and commercially supplied $^{13}$CH$_4$. It was also found that PtC$_3$ can be generated from a mixture of $^{13}$C$_2$H$_2$ and $^{13}$CH$_4$ precursors with the result that the spectra of $^{189}$Pt$^{12}$C$^{12}$C$^{13}$C, $^{190}$Pt$^{12}$C$^{12}$C$^{13}$C, and $^{190}$Pt$^{13}$C$^{13}$C$^{13}$C were detected with equal intensities. The observation that the $^{12}$C isotope does not preferentially occupy an end position of the C$_3$ subunit strongly implies that the C=C bond of C$_2$H$_2$ cleaves during the sequence of reactions that generates PtC$_3$ from this set of precursors.

The present study is believed to be the first to characterize MC$_3$ units by rotational spectroscopy. Transition-metal dicarbides, such as ScC$_2$ and YC$_2$, have been studied previously.$[12]$ The dipole moments of PdC$_3$ and PtC$_3$ are calculated at the MP2 level to be 6.1 and 5.6 D, respectively. The lengths of bonds within PtC$_3$ were fitted to experimentally determined rotational constants using Kisiel's STRFIT.$[13]$ Spectra were measured for 26 distinct isotopologues of PtC$_3$ where the set includes every permutation of C$_3$ that it is possible to generate from $^{12}$C and $^{13}$C isotopes. The bond lengths thus determined are compared with those in isolated PtC$_3$ and OC$_3$ molecules in Table 2. The $r_0$ geometry of PtC$_3$ is in good agreement with the $r_e$ geometry calculated at the CCSD(T) level. The Pt–C bond in PtC$_3$ is longer than found in diatomic PtC$[10]$ by 0.053 Å. There are similarities between r(MC) in PtC$_3$ and in PtCO$[14]$ and also in changes when these molecules form from their component Pt and C/CO subunits. The r(MC) parameter in PtC$_3$ 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 PtC$_3$ is longer than the C=C bond in isolated C$_3$ by 0.022 Å. The set of isotopologues studied is less extensive for PdC$_3$ than for PtC$_3$ 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, $r$(PdC) is determined to be

![Table 1: Spectroscopic parameters of PtC$_3$ and PdC$_3$.](image)

| Species | $B_0$ | $\Delta \times 10^6$ | $\chi_{0a}(^{10}$Pd) | $\sigma$ | $N$ |
|---------|-------|----------------|-----------------|-------|-----|
| $^{184}$Pt$^{12}$C$^{12}$C | 1592.94589(35) | 6.2 | 5.0 | 3 |
| $^{184}$Pt$^{13}$C$^{12}$C | 1486.74426(60) | 5.4 | 11.1 | 4 |
| $^{184}$Pt$^{12}$C$^{13}$C | 1522.74541(52) | 5.6 | 9.1 | 3 |
| $^{184}$Pt$^{13}$C$^{13}$C | 1560.77077(27) | 6.0 | 3.4 | 2 |
| $^{184}$Pt$^{12}$C$^{12}$C | 1585.00114(43) | 6.2 | 6.1 | 3 |
| $^{184}$Pd$^{12}$C$^{12}$C | 1702.33446(43) | 9.5 | 6.3 | 4 |
| $^{184}$Pd$^{13}$C$^{12}$C | 1705.89034(57) | 9.6 | 35.88(43) | 14.5 | 9 |
| $^{184}$Pd$^{12}$C$^{13}$C | 1599.54654(6) | 8.4 | – | 1 |

[a] Results of selected spectroscopic fits illustrating the dependence of rotational ($B_0$) and centrifugal distortion ($\Delta$) constants on isotopic substitution. $\chi_{0a}(^{10}$Pd) denotes the nuclear quadrupole coupling constant of the $^{10}$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$_3$ and PdC$_3$ that contain the $^{13}$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$_3$ transitions were found to be highly dependent on the choice of precursor, in the order C$_3$H$_3$ > C$_3$H$_2$ > CH$_4$. Transition intensities were lower when the population of PdC$_3$ was divided across many isotopic permutations and isotopically enriched allene is prohibitively expensive. These factors prevented measurement of the spectrum of any PdC$_3$ isotopologue that contains both $^{12}$C and $^{13}$C isotopes. The intensities of PtC$_3$ transitions were insensitive to the choice of precursor and it was possible to

![Table 2: Structural parameters of PtC$_3$, PdC$_3$, and related molecules.](image)

| Species | r(MC) [Å] | r(CC1) [Å] | r(CC2) [Å] |
|---------|----------|------------|------------|
| PtC$_3$ | 1.679 | – | – |
| C$_3$ (r$_0$) | 1.150 | 1.306 | 1.254 |
| OC$_3$ (r$_0$) | 1.7315(14) | 1.293(19) | 1.2759(11) |
| PtC$_3$ (r$_0$) | 1.7280 | 1.294(2) | 1.2836 |
| PdC$_3$ (r$_0$) | 1.79898(4) | 1.3009(6) | 1.2789(6) |
| PdC$_3$ (r$_0$) | 1.7962 | 1.2958 | 1.2866 |
| r(MC) [Å] | r(CO) [Å] |
| CO | – | 1.128 |
| PtCO (r$_0$) | 1.7625(4) | 1.1466(6) |
| PtCO (r$_0$) | 1.8447(1) | 1.1374(2) |

[a] r(MC) denotes the bond between the metal atom (or oxygen atom in OC$_3$) and its coordinated carbon. r(CC1) denotes the C=C bond nearest to the metal atom with r(CC2) used to label the other. r$_0$ values are determined experimentally and $r_0$ 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 $r_0$ value calculated ab initio for PdC$_3$ for the difference between the $r_0$ and $r_e$ values determined for the equivalent parameter in PtC$_3$. [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 \( \text{Ni}_2\text{C}_3 \).[15] The detected palladium/platinum carbones are amongst the smallest to be structurally characterized.[14] There is a correspondence between the linear geometries of the \( \text{MC}_3 \) 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 metalcarbohedrynes (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 \( \text{PdC}_3 \) and \( \text{PtC}_3 \). It is possible that a fraction of the population of each forms through gas-phase association of individual metal atoms with intact \( \text{C}_n \) or other units generated independently of any metal atom.[19] The energy changes accompanying the \( \text{M} + \text{C}_n \rightarrow \text{MC}_n \) association reactions to yield linear \( \text{MC}_n \) units are calculated to be \(-295 \text{ kJ mol}^{-1}\) and \(-417 \text{ kJ mol}^{-1}\) when \( \text{M} = \text{Pd} \) and \( \text{M} = \text{Pt} \) 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] \( \text{MCH}_3 \) and \( \text{MCCH}_3 \) have both been generated[1a,b,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 \( \text{MCH}_3 \) are expected to be above the upper frequency limit of the spectrometer and both \( \text{MCH}_2 \) and \( \text{MCCH}_2 \) will have comparatively low dipole moments which significantly decrease the intensity of their rotational transitions relative to those of \( \text{MC}_3 \).

An empirical model proposed by Pyynkkö et al.[24] provides a chemical rationalization for an enhanced stability of \( \text{MC}_3 \) relative to \( \text{MC}_2 \) or \( \text{MC}_4 \). Calculations of the geometries of \( \text{CaC}^+ \), \( \text{CaCu}^+ \), \( \text{PtCu} \), \( \text{PtC}_2 \), and \( \text{AuC}_2 \) revealed analogies between the behavior of each of \( \text{Au}^+ \) and Pt and a chalcogen atom such as \( \text{O}^+ \).[24] Within this model, the \( \sigma \) hole on platinum arising from the 5d\(^{10}\)9s\(^{2}\) configuration is analogous to the 2p\(^6\)\(\sigma\) hole on oxygen, and the 5d\(^x\) orbitals of platinum participate in \( \pi \)-bonding interactions analogous to those involving the 2p\(\sigma\) orbital of oxygen. The existence of a family of stable molecules was thus predicted. An orbital energy level diagram for \( \text{PtC}_3 \) is presented in Figure S1 in the Supporting Information. There are striking similarities between the geometries of \( \text{MC}_3 \) measured during the present work and that reported earlier for \( \text{OC}_3 \) by Brown et al.[25] Applying the model of Pyynkkö et al., \( \text{PtCO} \), \( \text{PtC} \), and \( \text{PtC}_2 \) 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, \( \text{PtS}_2 \)[26] can be regarded as an analogue of SiO. The oxocarbon analogue of \( \text{Pt}_2\text{C}_2 \) would be ethylene dione.[26] a transient species characterized, only through spectroscopy, for the first time in 2015. This model can thus explain why \( \text{PtCO} \), \( \text{PtC} \), and \( \text{PtC}_2 \), but not yet \( \text{PtC}_3 \), 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, \( \text{CH}_4 \) and \( \text{CO} \) on \( \text{Pt} \) and \( \text{Pd} \) have been studied. Harding et al. identified a \( \text{Pl}_{3}\text{C}^+ \) cluster ion[25] for which the geometry is analogous to a carbonate ion and hence consistent with the prediction of the model provided by Pyynkkö et al.[2] 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 (\( \text{C}_4\text{O}_3 \)) is known to be stable, suggesting that \( \text{PtC}_2\text{C}_2 \) might be generated in an equivalent structural form. An experimental study[20] of \( \text{AuC}^+ \) and \( \text{CuC}^+ \) 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 \( \text{AuC}_3^+ \) 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 \( \text{C}_3 \) was generated with a significantly higher abundance[19] than \( \text{C}_4 \) within the expanding gas sample and this may cause the generation of \( \text{AuC}_3^+ \) to be favored over the generation of clusters of other sizes, regardless of the thermodynamic stability of \( \text{AuC}_3^+ \). Indeed, during a previous study, signals for \( \text{NiC}_2^+ \) and \( \text{NiC}_4^+ \) were detected in mass spectra with higher intensity than units containing 1, 2, 4, or 5 carbon atoms,[25] although the \( \text{Ni}^+ \) ion is not isoelectronic and isolobal with \( \text{O} \). However, the reported fragmentation behavior of \( \text{AuC}_n^+ \) 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 Pyynkkö et al. The perspective thus emerging from the collected results of spectroscopic experiments is that the proposal[24] of an autogenic isolobal relationship of \( \text{Pt} \) and \( \text{Au}^+ \) centers with the \( \text{O} \) 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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