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 ground 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 halogen 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 C₂H₄ (allene), C₂H₆, C₂H₈, C₃H₄, and C₃H₆O (furan). For PtC₃, the range is narrower, including C₂H₄ (allene), C₂H₆, and C₃H₄, 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-pwCV5Z basis set for each C atom and the aug-cc-pCV5Z-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

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 CH₄ under the conditions described in the text. Bottom: J→J′ = 6→5 transitions of each of 1⁹⁰PtC₃, 1⁹⁶PtC₃, 1⁹⁸PtC₃, and 1⁹⁵PtC₃ are displayed in the bottom-left panel, J→J′ = 7→6 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 PtC₃ (from the set of ¹⁹⁵Pt, ¹⁹⁶Pt, ¹⁹³Pt, ¹⁹⁸Pt, ¹²C, and ¹³C atoms) using samples prepared by mixing ¹³CH₄ and commercially supplied ¹³CH₃. It was also found that PtC₃ can be generated from a mixture of ¹³C₂H₆ and ¹³CH₃ precursors with the result that the spectra of ¹⁹⁵Pt¹³C₂O¹³C₃, ¹⁹⁶Pt¹³C₂O¹³C₃, and ¹⁹³Pt¹³C₂O¹³C₃ were detected with equal intensities. The observation that the ¹³C isotope does not preferentially occupy an end position of the C₃ subunit strongly implies that the C≡C bond of CH₃ cleaves during the sequence of reactions that generates PtC₃ from this set of precursors.

The present study is believed to be the first to characterize M₃C units by rotational spectroscopy. Transition-metal dicar-
bides, such as ScC₃ and YC₃, have been studied previously.¹² The dipole moments of PdC₃ and PtC₃ are calculated at the MP2 level to be 6.1 and 5.6 D, respectively. The lengths of bonds within PtC₃ were fitted to experimentally determined rotational constants using Kisiel’s STRFIT.¹³ Spectra were measured for 26 distinct isotopologues of PtC₃ where the set includes every permutation of C₃ that is possible to generate from ¹²C and ¹³C isotopes. The bond lengths thus determined are compared with those in isolated PtC, C₃ and OC₃ molecules in Table 2. The r₀ geometry of PtC₃ is in good agreement with the rₑ geometry calculated at the CCSD(T) level. The Pt–C bond in PtC₃ is longer than found in diatomic PtC¹⁰ by 0.053 Å. There are similarities between r(MC) in PtC₃ and in PdCO¹⁴ and also in changes when these molecules form from their component Pt and C₃/CO subunits. The r(MC) parameter in PtC₃ is shorter than the same quantity in PdCO by 0.031 Å. The first C≡C bond (that is contiguous with the Pt–C bond) of PtC₃ is longer than the C≡C bond in isolated C₃ by 0.022 Å. The set of isotopologues studied is less extensive for PdC₃ than for PtC₃ 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(PdC₃) is determined to be 1.784 Å, 3.588 Å, and 3.58 Å for C₃, PtC, and PdC, respectively.

Spectra were measured for isotopologues of PtC₃ and PdC₃ 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 rₑ 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 (rₑ) geometry that is linear. The ab initio calculations suggest that both molecules are linear at equilibrium. The intensities of PdC₃ transitions were found to be highly dependent on the choice of precursor, in the order C₃H₆ > C₃H₅ > CH₄. Transition intensities were lower when the population of PdC₃ was divided across many isotopic permutations and isotopically enriched allene is prohibitively expensive. These factors prevented measurement of the spectrum of any PdC₃ isotologue that contains both ¹²C and ¹³C isotopes. The intensities of PtC₃ transitions were insensitive to the choice of precursor and it was possible to

Table 1: Spectroscopic parameters of PdC₃ and PtC₃.¹³

| Species       | B₀ [MHz] | D × 10⁻⁶ [kHz] | X₁₀⁴(Pd) [MHz] | α [kHz] | N |
|---------------|----------|----------------|----------------|---------|---|
| ¹⁹⁵Pt¹³C₂O¹³C₃| 1592.94589(35) | 6.2 | – | 5.0 | 3 |
| ¹⁹⁵Pt¹³C₂O¹³C₃| 1486.74426(60) | 5.4 | – | 11.1 | 4 |
| ¹⁹⁵Pt¹³C₂O¹³C₃| 1522.47541(52) | 5.6 | – | 9.1 | 3 |
| ¹⁹⁵Pt¹³C₂O¹³C₃| 1560.77077(27) | 6.0 | – | 3.4 | 2 |
| ¹⁹⁵Pt¹³C₂O¹³C₃| 1585.00014(43) | 6.2 | – | 6.1 | 3 |
| ¹⁹⁵Pt¹³C₂O¹³C₃| 1702.33446(43) | 9.5 | – | 6.3 | 4 |
| ¹⁹⁵Pt¹³C₂O¹³C₃| 1705.89034(57) | 9.6 | – | 35.88(43) | 14.5 | 9 |
| ¹⁹⁵Pt¹³C₂O¹³C₃| 1599.5465(43) | 8.4 | – | – | 1 |

[a] Results of selected spectroscopic fits illustrating the dependence of rotational (B₀) and centrifugal distortion (D) constants on isotopic substitution. X₁₀⁴(Pd) denotes the nuclear quadrupole 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.

Table 2: Structural parameters of PtC₃, PdC₃, and related molecules.¹⁴

| Species       | r(MC) [Å] | r(CC) [Å] | r(CC′) [Å] |
|---------------|-----------|-----------|-----------|
| PtC₃         | 1.679     | –         | –         |
| PtC₃          | 1.150     | 1.306     | 1.254     |
| PtC₃ (rₑ)    | 1.7315(14)| 1.2993(19)| 1.2759(11)|
| PtC₃ (rₑ)    | 1.7280    | 1.2942    | 1.2836    |
| PtC₃ (rₑ)    | 1.79898(4)| [1.3009]  | [1.2789]  |
| PtC₃ (rₑ)    | 1.7962    | 1.2958    | 1.2866    |
| PdC₃ (rₑ)    | 1.7625(4) | 1.1466(6)| –         |
| PdC₃ (rₑ)    | 1.8447(1) | 1.1374(2)| –         |

[a] r(MC) denotes the bond between the metal atom (or oxygen atom in OC₃) and its coordinated carbon. r(CC′) denotes the C≡C bond nearest to the metal atom with r(CC) used to label the other. rₑ values are determined experimentally and rₑ 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 rₑ value calculated ab initio for PdC₃ for the difference between the rₑ and rₑ values determined for the equivalent parameter in PtC₃. [d] Data from Refs. [11, 14].
The detected palladium/ and CO on Pt. Within this model, the and MCCH or MC although the Ni clusters 2016 will have was generated with measured during the present did not unambiguously distin-

theion is presented in Figure S1 in the cluster ion. Some caution at transient species of an autogenic isolobal might be generated in an equivalent structural form. previously by al aser vaporization/ by Brown et al. Angew. Chem. Int. Ed. = The energy changes accompanying the M configuration is analogous to the clusters and PtC 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, but not yet PtC, have been detected. The results of the present work thus support the suggestion that platinum can be regarded 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 and CO on Pt clusters[14] and the structures of PtO, clusters[18] have been studied. Harding et al. identified a PtC 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.[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 (C,O) is known to be stable, suggesting that PtC might be generated in an equivalent structural form. An experimental study[26] of AuC and CuC revealed ion intensities in the mass spectra that are significantly stronger where n = 3 than for clusters of other sizes.[28] Some caution must be exercised in drawing conclusions about the thermo-
dynamic stability of AuC relative to other cluster sizes from these results. As in the present work, the experiment performed by Ticknor et al.[23] did not unambiguously distin-
guish between various factors that contribute to observed spectral intensities. It is likely that C was generated with a significantly higher abundance[19] than C within the expanding gas sample and this may cause the generation of AuC to be favored over the generation of clusters of other sizes, regardless of the thermodynamic stability of AuC. Indeed, during a previous study, signals for NiC and NiC were detected in mass spectra with higher intensity than units containing 1, 2, 4, or 5 carbon atoms,[27] although the Ni ion is not isoelectronic and isolobal with O. However, the reported fragmentation behavior of AuC 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[24] 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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