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Ligand binding energy in $[(\mathrm{bipy})\mathrm{Rh}(\mathrm{P{\equiv}CH})]^+$ by collision-induced dissociation threshold measurements

Young-Min Kim, Peter Chen*

Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland

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Abstract

The complex $[(\mathrm{bipy})\mathrm{Rh}(\mathrm{P{\equiv}CH})]^+$, **1**, prepared by sequential fragmentation of electrosprayed $[(\mathrm{bipy})\mathrm{Rh}(\mathrm{PMe_3})_2(\mathrm{H})_2]^+$, has been investigated computationally and experimentally. A collision-induced dissociation threshold measurement finds a very strongly bound phosphaethyne ligand, suggesting that **1** adopts a side-on, metallophosphacyclopropene structure. The computed binding energy compares surprisingly favorably with experiment. (Int J Mass Spectrom 202 (2000) 1–7) © 2000 Elsevier Science B.V.

Keywords: Phosphaalkyne; Rhodium complexes; Ligand binding energy; Collision-induced dissociation threshold

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1. Introduction

The paucity of quantitative thermochemical data poses one of the major experimental challenges to mechanistic arguments in organometallic chemistry. While the binding of simple ligands, e.g. hydride, alkyl, CO, etc. in homoleptic complexes has been approached previously, data for even marginally more complicated complexes are rare [1]. The recent preparation of phosphaalkynes [2] and their transition-metal complexes [3,4], coupled with their use in the synthesis of novel phosphacycles [5], makes the binding energy of the phosphaalkyne ligand an attractive target for measurement.

Furthermore, as has been summarized by Bedford et al. [3], there are at least three binding modes for a phosphaalkyne moiety to a single metal center, classified as either side-on, i.e. $\eta^2(4e)$ and $\eta^2(2e)$, or end-on, i.e. a σ complex, for which the ligand binding energy might be expected to decrease in the $\eta^2(4e) > \eta^2(2e) > \sigma$ complex order. For complexes with more than one metal center, further binding modes have been documented.

We report a gas-phase measurement of the binding energy of the phosphaalkyne ligand in $[(\mathrm{bipy})\mathrm{Rh}(\mathrm{P{\equiv}CH})]^+$, **1**, of 2.02 ± 0.15 eV, or 46.5 ± 3.5 kcal/mol, for the parent phosphaethyne. Accompanying density functional theory (DFT) calculations suggest a side-on structure, and furthermore find a computed binding energy of the phosphaethyne ligand that is in good agreement with experiment even at a modest level of theory.

2. Experimental

The modified Finnigan MAT TSQ-7000 electrospray ionization tandem mass spectrometer with an

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* Corresponding author. E-mail: chen@org.chem.ethz.ch

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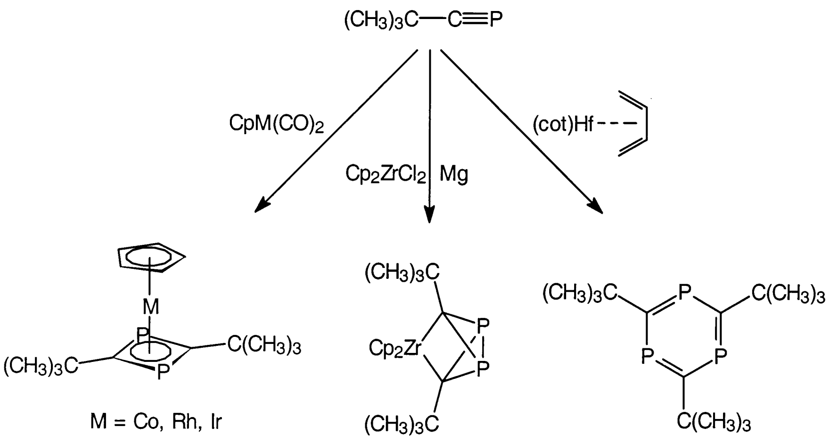
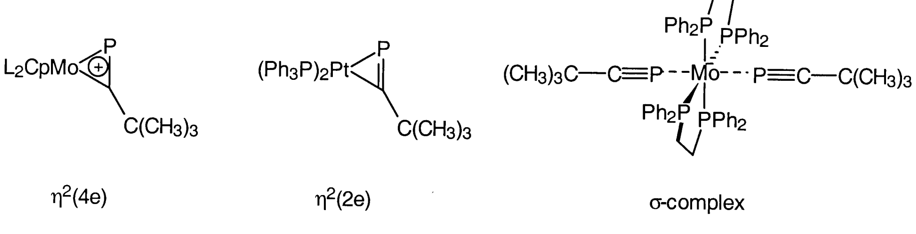


Scheme 1.

octopole, quadrupole, octopole, quadrupole (O1/Q1/O2/Q2) configuration behind a conventional electrospray source, was operated as described earlier [6]. For the threshold measurements, the phosphaethyne complex **1** was synthesized by an electrospray of a 10^{-4} M dichloromethane solution of $[(bipy)Rh(PMe_3)_2(H)_2]PF_6$ with the tube lens potential set to 95 V. A high tube lens potential corresponds to hard desolvation and/or collisional activation conditions in the source region. The first octopole was fitted with an open cylindrical sheath around the rods into which nitrogen was introduced as thermalization gas at pressures ~10 mTorr. Thermalization to the vacuum manifold temperature of 40 °C was judged to be complete because, with the 10 mTorr N_2 in O1, there was no observed dependence of the threshold curves on the temperature of the heated capillary in the electrospray source itself. The first quadrupole was operated in RFD mode (radio-frequency only) as a high-pass filter instead of in the alternative daughter-ion mode because of the narrower ion kinetic energy distribution, 0.4–0.5 eV full width half maximum (FWHM) (lab frame) versus 0.8–1.0 eV. Selected ions were subjected to collision-induced dissociation (CID) with xenon in the second octopole under single-collision conditions, and then mass-analyzed in the second quadrupole. Xenon was chosen for the quantitative CID threshold measurements because of its better kinematics.

Because the phosphaethyne complex **1** cannot be selected exclusively in RFD mode, spectra were recorded pairwise, with the cutoff mass just above and just below $m/z = 303$. The spectra were normalized against a prominent peak present in both spectra which did not change in intensity, and subtracted, giving a difference spectrum of acceptable quality. It should be noted that the spectral subtraction is legitimate only if the conditions during acquisition remain



Scheme 2.

stable. We found that sufficiently stable conditions could be achieved by careful alignment of the spray capillary through which the sample solution was pumped.

The CID threshold data were fitted, along with the expected kinetic shift, using Armentrout's CRUNCH program [7]. Our procedures were checked by reproducing published CID thresholds from the Kebarle [8] and Armentrout [9] groups. The geometries and frequencies of the complexes for this deconvolution were obtained by quantum chemical calculations on DEC Alpha AXP 8400 5/300 workstations with the Gaussian 94 package of programs [10]. Calculations at the B3LYP/LANL2DZ level were done as a compromise between accuracy and computational time; this level of theory had proven sufficient for the $[CpIr(PMe_3)(CH_3)]^+$ experiment reported previously by this group.

$[(bipy)Rh(PMe_3)(H)_2]PF_6$ was synthesized from $[(bipy)Rh(cod)]PF_6$, prepared from the (1,5-cyclooctadiene)Rh^ICl dimer by the procedure of Cocevar et al. [11], starting from 50 mg (0.1 mmol) $[(bipy)Rh(cod)]PF_6$ in 12 mL of a 5:1 mixture of methanol and dichloromethane. After degassing by multiple freeze–pump–thaw cycles, the solution was treated with 0.2 mL of a 1 M THF solution of $P(CH_3)_3$. The solution was then placed under 4 bar H_2 and stirred overnight at room temperature. The product was not isolated, but rather introduced directly into the mass spectrometer after diluting to 10^{-4} M with dichloromethane. The corresponding complex with $P(CD_3)_3$ was prepared in the same fashion.

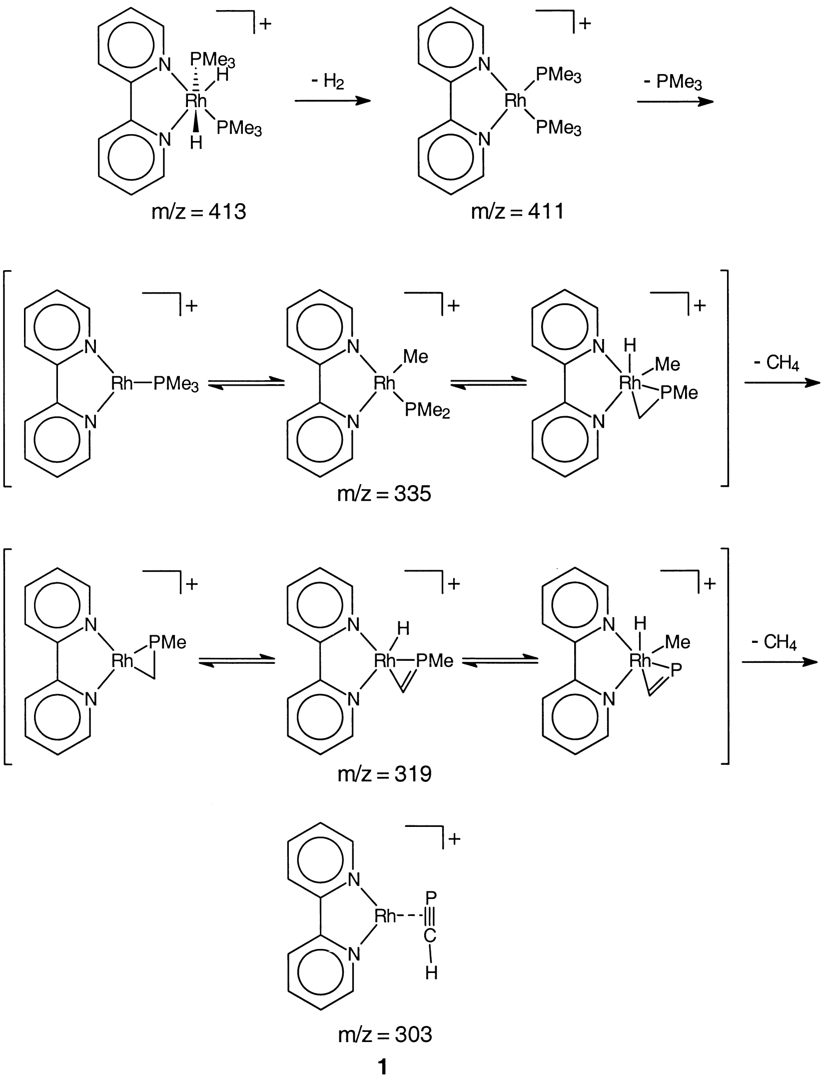
3. Results

Reduction of the experimentally observed threshold to meaningful chemical information requires two determinations: the structure of the initial ion needs to be determined, and the binding energy needs to be extracted from the experimental threshold. The former can be fortunately claimed unambiguously on the basis of the observed intermediate ions in the gas-phase preparation of **1**. The latter is done by conventional methods which, nevertheless, present a significant challenge because of the size of the molecule.

Complex **1**, $m/z = 303$, was prepared by sequential loss of methane units from the cationic complex $[(bipy)Rh(PMe_3)_2(H)_2]^+$, which was readily prepared and electrosprayed. Under very mild desolvation conditions in the source region, a clean mass spectrum of $[(bipy)Rh(PMe_3)]^+$, $m/z = 411$, is obtained. As the tube lens potential is raised from 50 to 90 V up to three successive fragmentation products, the first at 76 mass units lower and the next two spaced at 16 mass units (mu), appear in the mass spectrum. If perdeuterated trimethylphosphine is used in the preparation of the original complex, then the same pattern of fragments appears, but with spacings of 85, 20, and 20 mu, indicating that there is no direct involvement of the bipyridyl ligand in the fragmentation, e.g. *ortho*-metalation on the arene with subsequent reductive elimination can be ruled out. If the intermediate ions at $m/z = 335$ or 319 are selected individually in the first quadrupole, and then subjected to collision-induced dissociation (with argon, nominal pressure, and collision energy: 1.2 mTorr, 15 eV lab frame) in the second octopole, clean loss of methane is observed, confirming that a sequential fragmentation mechanism is operative.

In our previous mass spectrometric studies on rhodium phosphine complexes [6], we observed facile, reversible cyclometalations on the trimethylphosphine ligands, with the concomitant possibility of subsequent reductive elimination of methane. The cyclometalation reactions were ascertained by specific isotopic labelling. The present results are fully rationalized by the same reactions, with the proposed sequence of structures shown in Scheme 3.

The very clean collision-induced dissociation reactions, exclusion of direct participation by the bipyridine ligand, and the precedent from our previous work provide an unambiguous assignment of **1** as a complex formally built from a $[(bipy)Rh]^+$ fragment and P≡CH. Accordingly, the ion **1**, with $m/z = 303$, prepared directly by subjecting **2** to "hard" desolvation conditions in electrospray source, is assigned as $[(bipy)Rh(P{\equiv}CH)]^+$ with binding mode of the phosphaethyne ligand left undetermined.



Scheme 3.

Extraction of thermochemical data from a quantitative collision-induced dissociation threshold measurement has been extensively documented by Armentrout and co-workers [9]. There are two principal difficulties in the present experiment. A meaningful reaction enthalpy can be extracted from the threshold only when the initial kinetic energy distribution of ions **1** is narrow. A narrow kinetic energy distribution in the present instrument is achievable when the first quadrupole is operated in RFD mode. In daughter mode, the distribution in the laboratory frame is approximately twice as wide. The distribution in RFD mode is, furthermore, nearly Gaussian. With careful normalization, the difference spectrum, with the RFD cutoff *m/z* ratio set just above and just below the target mass, gives reliable, reproducible threshold curves. A representative curve and fit are shown in Fig. 1.

The second problem in applying the CRUNCH program from Armentrout is the need to compute vibrational frequencies for the calculation of the

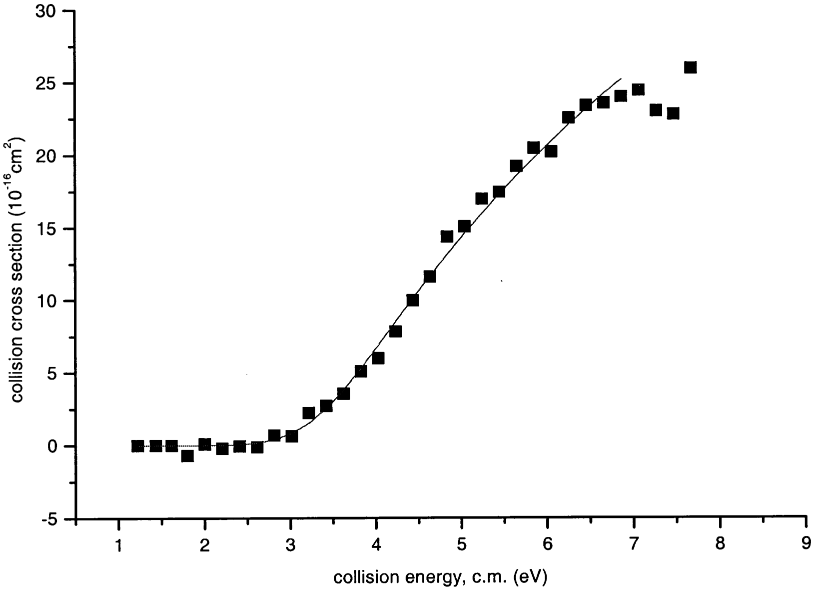


Fig. 1. Collision-induced dissociation threshold curve for the loss of $P{\equiv}CH$ from **1**, showing the fit using the parameters, $E_0 = 2.02 \pm 0.15$ eV, $\sigma = 34.5 \pm 2.6$ Å^2, and $n = 1.16 \pm 0.17$ for the points between 1.2 and 6.8 eV (center-of-mass).

kinetic shift. This effect becomes larger as the number of normal modes increases, making it non-negligible for the relatively large complexes in this study. The equilibrium geometries and vibrational frequencies for the various species in this study are needed for the CRUNCH program. They were obtained from quantum chemical calculations at the B3LYP/LANL2DZ level using Gaussian 94. Key structural parameters for isomeric structures of **1** are shown in Fig. 2.

Values for transition-state frequencies were assumed following the arguments by Armentrout [12] and Squires [13]. For an endothermic dissociation of a gas-phase ion, a loose transition state can be assumed. Accordingly, the product frequencies are used where available. Five further frequencies are needed for the transition state, which in the limit of the products, would correspond to relative rotations and translations of the two fragments. These are obtained by taking the appropriate normal modes in the starting ion, chosen by inspection of the displace-

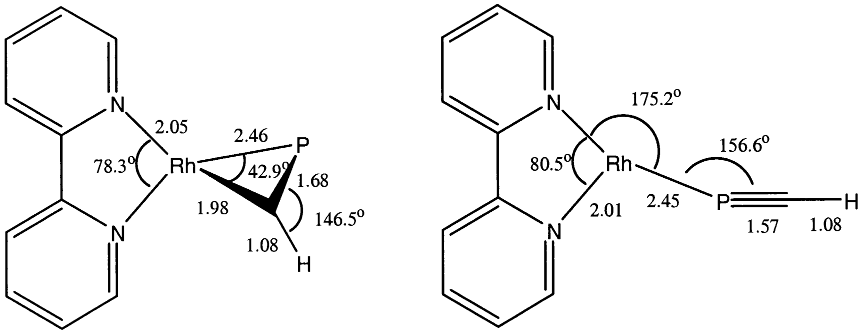


Fig. 2. Geometries for two possible structures for **1**, computed using B3LYP/LANL2DZ. Both structures represent bound minima, but the cyclic isomer was found to be 25 kcal/mol lower in energy.

ment vectors of the normal modes, and reducing the frequencies by a factor of 2. Squires argued explicitly that this builds in the needed degree of looseness; the simple procedure gives similar results to the more explicit estimates used by Armentrout. Using these values, the threshold was fitted to yield $E_0 = 2.02 \pm 0.15$ eV, $\sigma = 34.5 \pm 2.6$ Å^2, and $n = 1.16 \pm 0.17$ for the points between 1.2 and 6.8 eV (center-of-mass).

4. Discussion

A single previous gas-phase study of the R–C≡P/Fe$^+$ system has been reported in which a rich chemistry was observed [14]. No thermochemistry, however, was determined in that work. Several monocationic complexes of acetylene, however, with bare Al, Zr, and Nb ions have been experimentally studied. While the Al$^+$ complex is relatively weakly bound [15], i.e. 14 kcal/mol, the two transition metal cation complexes [16] are bound by almost 60 kcal/mol. The gas-phase preparation of **1**, by way of sequential fragmentation, gives an unambiguous identification of the present ion as the complex formed from a [(bipy)Rh]$^+$ fragment and P≡CH. The binding mode, however, cannot be extracted from the mass and chemical arguments alone. On the other hand, the very strongly bound phosphaethyne ligand indicates that the side-on, rather than the end-on, binding mode is likely. End-on binding should give a weaker metal–ligand bond, e.g. the Rh–P bond in $HRh(CO)(PPh_3)_3$ was measured to be 20 kcal/mol by dynamic nuclear magnetic resonance (NMR) [17]. The side-on mode, which can be regarded as formation of a metallaphosphacyclopropene, would be expected to give a stronger bond, closer to the value found in the present work. One could speculate as to the role of the very large binding energy in the chemistry of phosphaalkyne complexes. Release of over 40 kcal/mol in the binding act can facilitate or even drive the rich chemistry observed for these complexes.

The B3LYP/LANL2DZ calculations for the side-on complex, the end-on complex, the two fragments (the [(bipy)Rh]$^+$ fragment and P≡CH) at large separation, and the two fragments individually find that the side-on complex is lower in energy than the end-on complex by a substantial margin, i.e. 25 kcal/mol. Moreover, the side-on complex is computed to lie below the separated fragments by 43 kcal/mol. The computed structures appear reasonable—no comparison to experiment can be made for these complexes, but the geometries themselves are unsurprising—and the computed binding energy of 43 kcal/mol is not too far from the experimental value of 46.5 ± 3.5 kcal/mol reported in this work. Given that the deconvolution of the CID threshold measurement itself required a quantum chemical calculation of the geometry and frequencies for both **1** and the products, [(bipy)Rh]$^+$ and P≡CH, one could rightly ask whether or not the general procedure of using computed frequencies to deconvolute the experimental threshold represents circular logic. More generally, while there have been publications citing uncertainty bounds of only a few kcal/mol for computed energy differences in transition metal complexes, the experience in previous studies seems to indicate that, while geometries and frequencies seem to be well-modelled by DFT methods, the accuracy of these particular computational methods for the prediction of energy differences is still variable, and in many cases, poor. The general success of DFT methods in predicting equilibrium geometries of organometallic compounds indicates that the local features of a potential surface in the immediate vicinity of a minimum are well treated. This would mean that the frequencies are probably reliable, and that a deconvolution scheme that relies on the frequencies should be sound. The relative energies of two widely separated minima, however, may not be equally well described. In this light, the use of those more reliable aspects of a computation to deconvolute experimental data that pertain to less reliable aspects of the same computation is legitimate. In the particular case of **1**, the difference in energy between **1** and the separated fragments is surprisingly well modeled by the decidedly modest DFT calculation. Measurements of this kind should serve as benchmarks for the evaluation of the level of theory needed to obtain accurate thermochemistry for organometallic complexes.

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