

Binding of molecular oxygen and alkenes to coordinatively unsaturated bipyridinium metal complexes in the gas phase

Steen Brøndsted Nielsen^a, Åse Marit L. Øiestad^b, Gustav Bojesen^{c,*}, Einar Uggerud^{b,*}

^a Department of Physics and Astronomy, University of Aarhus, Ny Munkegade, DK-8000 Aarhus C, Denmark

^b Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

^c Department of Chemistry, University of Copenhagen, DK-2100 København Ø, Denmark

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Abstract

Unsaturated metal complexes have vacant sites for binding and may promote insertion reactions. Rate coefficients were determined for the formation of adduct ions in ion–molecule reactions between $M(\text{bipy})_2^{2+}$ ($M = \text{Cr}, \text{Ru}, \text{or Os}$; $\text{bipy} = \text{bipyridine}$) and dioxygen, propane, ethene, propene, and 1-butene in the cell of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Together with estimated capture rate coefficients, these lead to efficiencies for adduct formation. Efficiencies for O_2 adduct formation are small, which is indicative of a weak binding between the metal and dioxygen. The efficiency was independent of pressure, and consequently radiative emission must be responsible for cooling of the excited adducts, $M(\text{bipy})_2(\text{O}_2)^{2+*}$. The efficiency for addition of alkenes to $\text{Ru}(\text{bipy})_2^{2+}$ is higher. Reactions between $\text{Ru}(\text{bipy})_2(\text{alkene})^{2+}$ and alkene were investigated. In the case of ethene, simple addition occurred to give the $\text{Ru}(\text{bipy})_2(\text{ethene})_2^{2+}$ ion. In contrast, reactions with propene and 1-butene produced the ions $\text{Ru}(\text{bipy})_2(\text{C}_2\text{H}_3)(\text{alkene})^{2+}$ and $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_5)(\text{alkene})^{2+}$ which are indicative of alkene activation. In the ion–molecule reaction between $\text{Ru}(\text{bipy})_2^{2+}$ and propene, a small abundance of the bis(allyl) complex, $\text{Ru}(\text{bipy})(\text{allyl})_2^{2+}$, was also observed. The assignment of the products and elucidation of the detailed reaction mechanisms is based on collisional activation and supported by experiments with deuterium-labeled propene.

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1. Introduction

Molecular activation at metal centers is essential for many biological and chemical processes, e.g., for the utilization of O_2 in oxidation and insertion reactions and the polymerization of alkenes and alkynes. For example, oxygen atom insertion into $\text{C}=\text{C}$ and $\text{C}-\text{H}$ bonds and the formation of epoxides and carbonyl compounds by dioxoruthenium(VI) and dioxoosmium(VI) complexes have been reported [1]. In addition, the oxochromium(V) functionality is important for the epoxidation of alkenes [2]. However, it is often a difficult task to follow a molecular activation reaction taking

place in solution and correctly assign the short-lived intermediates. Therefore, ion–molecule reactions (IMRs) that are carried out under well-controlled conditions are helpful for an understanding of these fundamental processes [3].

The reactions of bare and singly charged transition metal ions, M^+ , or clusters, M_n^+ , with alkanes and alkenes have been investigated in detail, and much of the work has been reviewed by Eller and Schwarz [4] and Armentrout and coworkers [5]. Ion–molecule reactions of dioxygen with singly charged metal ions, monoligated metal ion complexes, and metal cluster ions, M_n^+ , have been studied in detail as well [6–8]. On the other hand, only a limited amount of data exist for bare doubly charged metal ions [9]; the first results published in 1986 by Tonkyn and Weisshaar [9]. They showed that reactions between M^{2+} and alkanes result in addition, hydride ion transfer, or electron transfer but in some cases also

* Corresponding authors.

E-mail addresses: bojesen@kiku.dk (G. Bojesen), einar.uggerud@kjemi.uio.no (E. Uggerud).

in elimination of H₂, 2H₂, CH₄, and C₂H₆ from the alkane as was observed for the reactions between singly charged metal ions and alkanes.

Even less has been published for ligated M²⁺ complexes [10]. In previous work by Molina-Svendsen et al. [10], coordinatively unsaturated bis(2,2'-bipyridine)metal complexes M(bipy)₂²⁺ were subjected to reactions in the collision cell of a triple quadrupole instrument under pressures of a few times 10⁻³ mbar. It was demonstrated that the only type of reaction that took place was adduct formation, and that this reaction depended on the metal. Thus, for M = Cr, Ru, and Os, the dioxygen adduct ion, M(bipy)₂(O₂)²⁺, was observed but not for M = Mn, Fe, Co, Ni, and Cu. With propene, addition occurred only for M = Ru and Os. Collision-induced dissociation (CID) experiments showed that Cr(bipy)₂(O₂)²⁺ and Ru(bipy)₂(O₂)²⁺ readily lost O₂ in contrast to Os(bipy)₂(O₂)²⁺, indicative of a different binding of O₂ for Os than that for Cr and Ru.

The purpose of the present work was to measure rate coefficients for adduct formation between M(bipy)₂²⁺ and O₂ under controlled conditions in the cell of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. In the case of Ru(bipy)₂²⁺, investigations were extended to include also ethene, 1-butene, and propane. IMRs were performed with both dioxygen and propene/propane in the ICR cell to test for oxygen atom insertion.

2. Experimental

Measurements were performed with a Bruker Daltonics 47e FT-ICR instrument with an external electrospray ion (ESI) source from Analytica of Branford Inc.

2.1. Ion production

Tris(2,2'-bipyridine)metal(II/III) perchlorate salts were dissolved in either acetonitrile or methanol and electrosprayed. The ESI needle was displaced off-axis relative to the capillary to reduce the amount of solvent transferred from the source to the ICR cell, in order to avoid the formation of complexes with solvent molecules in the case of acetonitrile. Even though the cell pressure increased upon electrospraying, there was no sign of binding of methanol to M(bipy)₂²⁺. Quite harsh ion source conditions were required to generate M(bipy)₂²⁺ from M(bipy)₃²⁺ by loss of a bipyridine ligand in energetic collisions with residual gas. Hence, the ions may be internally hot.

2.2. MS/MS experiments

The mixture of ions produced in the source was transferred to the ICR cell. All ions, except those of interest, were ejected from the cell using correlated sweep and clean-up shots. The sweep removed unwanted ions over a broad frequency range, but still clean-up shots at particular frequencies were nec-

essary to remove ions present in large abundances. Single isotopomers with respect to the metal were isolated unless otherwise noted. As a result of excitation of the parent ion, charge separation products, i.e., two singly charged fragment ions, were formed at high pressures in the cell. The pressure was adjusted during the experiments and kept constant within 10% variation. Collisional activation of several product ions was done, in some cases without prior ion isolation. It was difficult to isolate isotopomers of M(bipy)₂(O₂)²⁺ (M = Cr, Ru), since O₂ was lost under the separation due to excitation.

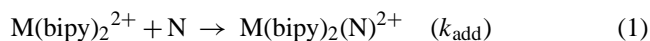
For Os(bipy)₂²⁺, there were interfering ions, assignable to [Os(bipy)₂ - xH]²⁺ (x = 1, 2, ...) by hydrogen loss from the bipyridine ligand and the formation of a carbon-bound metal-localcarbacycle [2,2'-bipyridinyl(1-)-C³,N' ligand] (oxidative-addition mechanism). [Such a reaction is well known for both Ru and Os bipyridine complexes, and deuterium exchange reactions in solution have provided evidence for acidic 3,3'-protons of the bipy ligand [11,12].] However, in an experiment with a selection of all isotopes, the peak pattern in the *m/z* range of assumed Os(bipy)₂(O₂)²⁺ is in reasonable agreement with the calculated isotope pattern of Os(bipy)₂(O₂)²⁺. Hence, [Os(bipy)₂ - xH]²⁺ did not undergo as much O₂ addition as Os(bipy)₂²⁺ on the time scale of the experiment (seconds) and our expected rate coefficient for O₂ adduct formation is a lower limit value.

2.3. Calibration of the pressure transducer

The calibration of the pressure transducer (ionization gauge) was based on the known rate coefficient for the proton transfer reaction between acetyl ions (CH₃CO⁺) (formed by electron ionization of acetone in the cell) and acetone ((CH₃)₂CO). The rate coefficient was measured to be 1.9 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, which results in a calibration factor of 1.1 by matching with the value determined by Grover et al. [13] (2.14 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹). The pressure was corrected for the relative sensitivity of the gas (calculated from the polarizability) compared to N₂ [14]. We estimate the uncertainty in the pressure to be 20%.

2.4. Evaluation of rate coefficients

The rate coefficient, *k*_{add}, for the adduct formation reaction between M(bipy)₂²⁺ and a molecule N (Eq. (1)) is given by Eq. (2):



$$\ln \left(\frac{A}{A_{\text{total}}} \right) = -k_{\text{add}}[\text{N}]t \quad (2)$$

where *A* is the abundance of M(bipy)₂²⁺, *A*_{total} is the total ion abundance, [N] is the gas concentration of N, and *t* is the reaction time. [N] is obtained from the ideal gas law assuming room temperature within the ICR cell: [N] = *P*/*RT*, where *T* = 295 K.

3. Results and discussion

3.1. Primary reactions (<30 s)

3.1.1. Adduct formation and kinetics

Addition of O₂, ethene, propene, and 1-butene to M(bipy)₂²⁺ did not occur to M = Fe or Ni. For M = Cr, adduct formation was seen with O₂ but not with alkenes, while for M = Ru, Os, both dioxygen and alkene adduct ions were formed [15]. Hence, the dependence on the metal is the same as that observed when the reactions were studied in a triple quadrupole instrument.

Electron transfer from O₂ or a hydrocarbon to M(bipy)₂²⁺ resulting in M(bipy)₂⁺ and ionized gas was not observed.

3.1.1.1. Dioxygen. Relative abundances of Cr(bipy)₂(O₂)²⁺ and Cr(bipy)₂²⁺ 40 s after ion selection are shown in Fig. 1. Half of the precursor ions have undergone adduct formation. It took approximately 15 s at a pressure of 8 × 10⁻⁸ mbar of O₂ before the abundances obeyed the logarithmic rate law given by Eq. (2) as illustrated in Fig. 2A, which indicates that the initial ions in the cell were slightly translationally excited [16] or vibrationally excited. The higher the pressure of O₂, the shorter was the cooling time: at a pressure of 2 × 10⁻⁷ mbar, the cooling time was about 8 s. The incoming reactant ions must become completely thermalized before they can undergo efficient adduct ion formation. Similar results were obtained for M = Ru, whereas the cooling time was much shorter for Os (Fig. 2B).

In order to determine whether adduct formation occurs by radiative or collisional (or both) stabilization, the following mechanism is considered:

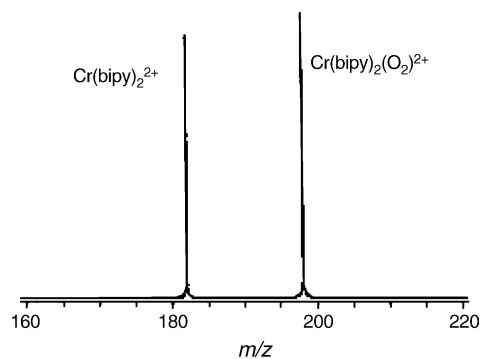
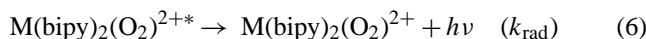
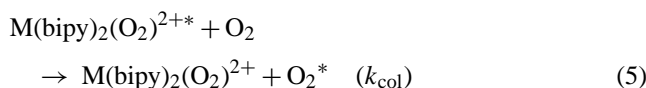
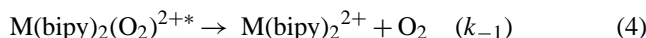
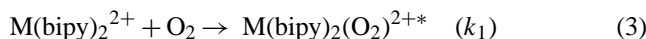


Fig. 1. Cr(bipy)₂²⁺ (*m/z* 182) + O₂ → Cr(bipy)₂(O₂)²⁺ (*m/z* 198). Reaction time: 40 s; pressure: 7.4 × 10⁻⁸ mbar.

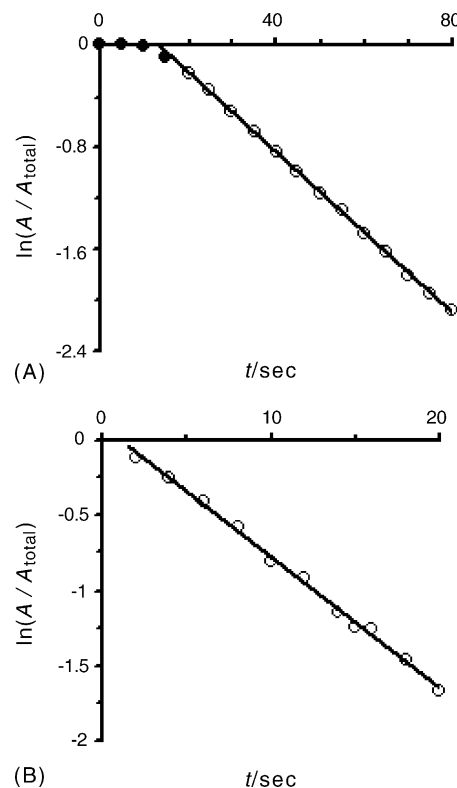


Fig. 2. (A) Cr(bipy)₂²⁺ + O₂ → Cr(bipy)₂(O₂)²⁺. ln(*A*/*A*_{total}) vs. reaction time. Pressure: 7.7 × 10⁻⁸ mbar. (B) Os(bipy)₂²⁺ + O₂ → Os(bipy)₂(O₂)²⁺. ln(*A*/*A*_{total}) vs. reaction time. Pressure: 1.0 × 10⁻⁷ mbar.

Applying a steady-state analysis where the concentration of the excited intermediate complex, M(bipy)₂(O₂)^{2+*}, is assumed constant together with the assumption that the forward rate coefficient *k*₁ equals the capture rate coefficient, *k*_{cap}, results in the following expression for the association efficiency (Eq. (7)) [16]:

$$\text{Eff.} = \frac{k_{\text{add}}}{k_{\text{cap}}} = \frac{k_{\text{rad}} + k_{\text{col}}[\text{O}_2]}{k_{-1} + k_{\text{rad}} + k_{\text{col}}[\text{O}_2]} \quad (7)$$

*k*_{col} and *k*_{rad} are the rate coefficients for collisional and radiative cooling of M(bipy)₂(O₂)^{2+*}, respectively. Since *k*_{cap} is the rate coefficient for the formation of any encounter complex between M(bipy)₂²⁺ and O₂, the efficiency is an overestimate (*k*_{cap} > *k*₁). If collisional cooling is important, the efficiency should increase with the pressure. Therefore, the observed rate of addition, *k*_{add}, was determined at different pressures (Fig. 3). Within experimental error, there is no increase in the rate coefficient with pressure.

Average values for the obtained rate coefficients were calculated (Table 1; values obtained at a pressure less than 3 × 10⁻⁷ mbar were used). Included in the table are calculated Langevin capture rate coefficients and efficiencies. The association efficiency is seen to be small (1–3%) and highest for M = Os.

3.1.1.2. Alkenes. Cooling times were less for addition of alkenes to Ru(bipy)₂²⁺ than for addition of O₂, only about

Table 1
Rate coefficients for addition of neutral molecules N to $M(\text{bipy})_2^{2+}$

M	N	α^a (\AA^3)	μ_D^a (D)	k_{cap} (Langevin)	k_{cap} (ADO)	k_{cap} (SC)	k_{add} (experimental)	Efficiency
Cr	O ₂	1.60	0	109			1.6 ± 0.1	0.015 ± 0.001
Ru	O ₂	1.60	0	109			1.5 ± 0.1	0.014 ± 0.001
Os	O ₂	1.60	0	108			3.2 ± 0.2	0.030 ± 0.002
Ru	Ethene	4.252	0	189			15 ± 2	0.079 ± 0.011
Ru	Propene	6.07	0.366	187	211	201	52 ± 4	0.26 ± 0.02^b
Ru	1-Butene	7.97, 8.52	0.34	188, 195	206, 212	199, 205	$53, 56 \pm 4$	0.27 ± 0.02^b

α : polarizability; μ_D : dipole moment; rate coefficients: $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; temperature: 295 K; ADO: average dipole orientation (see [17]); SC: Su and Chesnavich, trajectory calculation (see [18]). Capture rate coefficients were calculated with the ADOX program by D. Thölmann.

^a Values taken from [19].

^b k_{cap} (SC) used.

1–3 s, and smaller for a large alkene. The rate coefficients obtained for addition of ethene, propene, and 1-butene are shown in Table 1 together with capture rate coefficients from Langevin theory (only polarizability involved), average dipole orientation (ADO) theory [17], and a parameterization scheme due to Su and Chesnavich (SC) [18]. Experimental rate coefficients were obtained from an average of 6–10 measurements in the pressure range $0.5\text{--}3 \times 10^{-8}$ mbar. ADO often overestimates the importance of a molecule's permanent dipole moment (μ_D), and therefore SC calculations were done to calculate the reaction efficiency for propene and 1-butene. Ethene has no dipole moment (like dioxygen), and Langevin theory is applicable. The efficiency for propene and 1-butene is approximately the same and much larger than that for ethene. The efficiency for alkene adduct formation is much larger than that for dioxygen. For $\text{Os}(\text{bipy})_2^{2+}$, other products than the adduct ions, $\text{Os}(\text{bipy})_2(\text{alkene})^{2+}$, were formed. These are mainly due to H₂ elimination.

3.1.1.3. *Propane*. To test whether a high efficiency is correlated with the polarizability and permanent dipole moment of the gas only, the same experiment was performed with propane in the cell, but no adduct ions were observed even though the polarizability of propane (6.29, 6.37 \AA^3) [19] is higher than those of dioxygen, ethene, and propene (cf. Table 1), and propane has a small permanent dipole moment (0.084 D) [19] in contrast to dioxygen and ethene. Hence, the

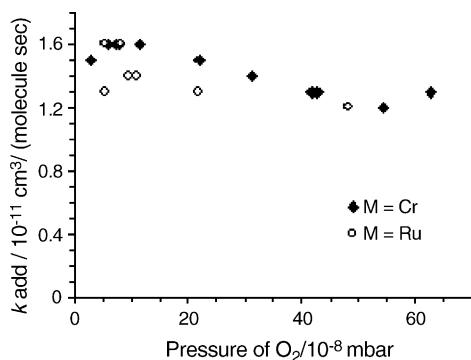


Fig. 3. Rate coefficients for $M(\text{bipy})_2^{2+} + \text{O}_2 \rightarrow M(\text{bipy})_2(\text{O}_2)^{2+}$ obtained at different O₂ pressures.

O₂ and alkene adduct ions are not simple ion-induced dipole complexes, which is also in accordance with the fact that adduct formation depends on the type of metal (no adduct ions were observed for M = Fe, Ni).

3.1.1.4. *Dioxygen and propene*. When $M(\text{bipy})_2^{2+}$ was allowed to react with both dioxygen and an alkene in the ICR cell, no new products were detected, except for the adduct ion $M(\text{bipy})_2(\text{O}_2)(\text{C}_3\text{H}_6)^{2+}$ for M = Cr, Os.

3.1.1.5. *Dioxygen and propane*. When $M(\text{bipy})_2^{2+}$ was allowed to react with both dioxygen and propane in the ICR cell, only dioxygen adduct ions were observed.

3.1.2. Binding motifs

In contrast to propane, dioxygen and alkenes can form a π -complex with the metal center, which could account for the ease of addition of these molecules to some of the metals. A qualitative model of a metal–alkene bond has been developed by Dewar and coworkers [20]. Binding occurs by the formation of two donor–acceptor bonds: a σ -bond by electron donation from the $2p\pi$ alkene orbital to an empty metal orbital and a bond by back-donation from a filled metal orbital to the empty $2p\pi^*$ alkene orbital.

Dioxygen can bind in more than one way to a metal, and the possible structural formulations are summarized in Fig. 4. The low efficiencies for the association reactions indicate that the binding is rather weak [21]. This is in line with recent density functional theory calculations on the binding of O₂ to $\text{Cr}(\text{bipy})_2^{2+}$ done by Howe et al. [22]. Their calculations indicate that the O₂ molecule is initially trapped as a η^2 -bound superoxide ion but that a *cis*-dioxo Cr(VI) complex is significantly more stable. The conversion is, however, hindered by a large barrier and associated with a spin change.

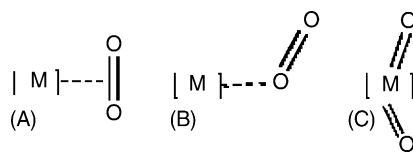


Fig. 4. Binding of dioxygen to a metal ion: (A) *side-on* η^2 -complex (peroxide); (B) *end-on* η^1 -complex (superoxide); (C) dioxide. [M] = $M(\text{bipy})_2^{2+}$.

Table 2
Mass to charge ratios of the different ruthenium complexes involved

m/z	Assignment
207	[Ru]
220.5	[Ru](C ₂ H ₃)
221	[Ru](C ₂ H ₄)
227.5	[Ru](C ₃ H ₅)
228	[Ru](C ₃ H ₆)
234	[Ru](C ₄ H ₆)
235	[Ru](C ₂ H ₄) ₂
235	[Ru](C ₄ H ₈)
241.5	[Ru](C ₂ H ₃)(C ₃ H ₆)
248	[Ru](C ₃ H ₅) ₂
248.5	[Ru](C ₃ H ₅)(C ₃ H ₆)
248.5	[Ru](C ₂ H ₃)(C ₄ H ₈)
255.5	[Ru](C ₃ H ₅)(C ₄ H ₈)

[Ru] = ¹⁰²Ru(bipy)₂²⁺.

M(IV)-peroxo and M(III)-superoxide complex ions are particularly relevant for chromium [23].

In the case of Os, a high collision energy is required to loose O₂ from Os(bipy)₂(O₂)²⁺. Moreover, the efficiency for adduct formation is at least a factor of two higher than that for M=Cr and Ru. An interpretation based on the formation of a dioxo Os(VI) complex (Fig. 4C) was earlier proposed by Molina-Svendsen et al. [10] based on CID experiments, which agrees with the known solution and solid-state properties of osmium compounds. Actually, the [Os^{VI}(bipy)₂(O)₂]²⁺ cation is known from X-ray crystallography of the complex [Os(bipy)₂(O)₂](ClO₄)₂ [24].

3.2. Secondary reactions (>30 s and pressure of about 10⁻⁷ mbar)

3.2.1. Spectral data

After approximately 30 s, only the adduct ions were present in the ICR cell in any significant amount with none of the precursor ions left. These adducts were allowed to react further with the alkene molecules present in the cell. Mass to charge ratios of product ions described in the following are summarized in Table 2.

3.2.1.1. Ru(bipy)₂(ethene)₂²⁺ + ethene. Spectra for the reaction between ¹⁰²Ru(bipy)₂(ethene)₂²⁺ (m/z 221) and C₂H₄ (mass 28) are shown in Fig. 5A. The complex containing two ethene molecules was formed, Ru(bipy)₂(ethene)₂²⁺ (m/z 235). Collisional activation of this complex resulted in loss of one or two ethene molecules (Fig. 5B), and hence the two ethene ligands are likely bound as intact molecules. There are small peaks below m/z 235 that correspond to ions that have lost hydrogens.

3.2.1.2. Ru(bipy)₂(propene)₂²⁺ + propene. When ¹⁰²Ru(bipy)₂(propene)₂²⁺ (m/z 228) was allowed to react with propene (mass 42), the addition product containing two propenes was not formed (Fig. 6) in contrast to the ethene case. Instead, two other peaks at m/z 241.5 and

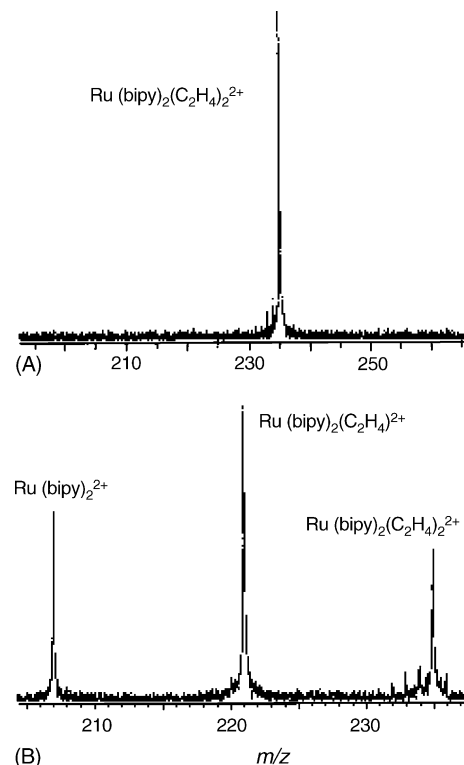


Fig. 5. Reactions between Ru(bipy)₂²⁺ and C₂H₄ (pressure: 3.4 × 10⁻⁷ mbar). (A) Reaction time: 100 s. (B) Collisional activation of Ru(bipy)₂(C₂H₄)₂²⁺ formed after 100 s without prior ion selection.

248.6 are seen. By conducting the experiment with two other isotopomers of the original reagent ion [⁹⁶Ru(bipy)₂²⁺ and ¹⁰⁴Ru(bipy)₂²⁺], these peaks can quite confidently be assigned to Ru-containing complexes. Collisional activation of the two ions resulted in a new peak corresponding to the loss of propene, and at higher collision energies Ru(bipy)₂²⁺ was recovered, corresponding to mass losses of 27 and 41, respectively (Fig. 7). The collisional activation may also lead to Ru(bipy)₂(propene)₂²⁺ but this cannot be concluded with certainty, since the desired parent ions

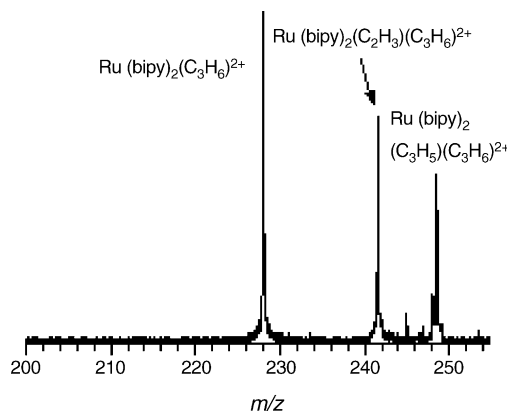


Fig. 6. Reactions between Ru(bipy)₂²⁺ and C₃H₆ (pressure: 1.7 × 10⁻⁷ mbar). Reaction time: 120 s.

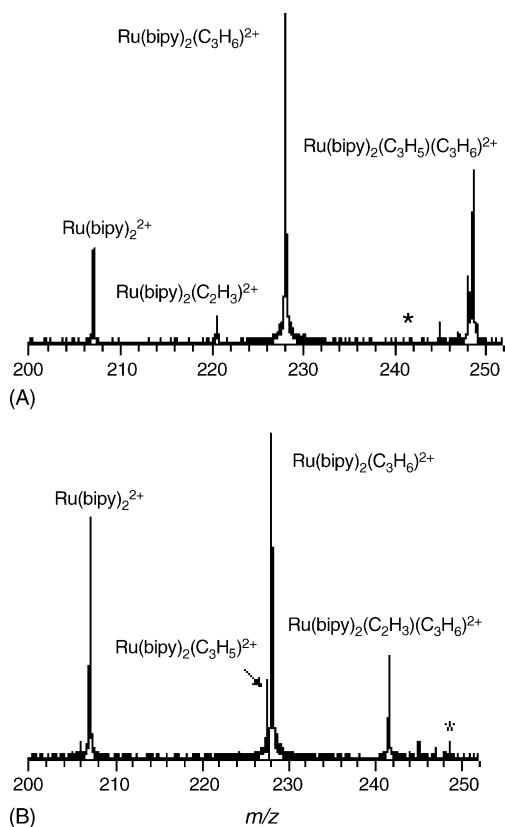


Fig. 7. Reaction between $\text{Ru}(\text{bipy})_2^{2+}$ and C_3H_6 (pressure: 1.7×10^{-7} mbar; reaction time: 120 s) followed by collisional activation of $\text{Ru}(\text{bipy})_2(\text{C}_2\text{H}_3)(\text{C}_3\text{H}_6)^{2+}$ (A) and $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_5)(\text{C}_3\text{H}_6)^{2+}$ (B) without prior ion selection (major ion present is $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_6)^{2+}$). The activated ions are indicated by an asterisk.

were not isolated prior to collisional activation. The ions were too fragile to be isolated. Both m/z 241.5 and 248.6 ions were observed when electrospraying complexes in either acetonitrile or methanol, and their formation was established in two sets of experiments performed 1 year apart but quantification was prevented by considerable variations in their relative intensities from day to day. The collisional activation data lead to a formulation of the products as vinylic and allylic, $\text{Ru}(\text{bipy})_2(\text{vinyl})(\text{propene})^{2+}$ and $\text{Ru}(\text{bipy})_2(\text{allyl})(\text{propene})^{2+}$ with the vinyl, allyl, and propene bound as intact ligands. The formation of vinylic and allylic products implies concomitant formation of methyl and hydrogen radicals, respectively. A small peak at m/z 248 was also observed in some of the spectra which may correspond to the bis(allyl) complex, $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_5)_2^{2+}$ likely formed by prompt loss of H_2 from $\text{Ru}(\text{bipy})_2(\text{propene})_2^{2+}$. Accurate mass measurement is difficult due to the high pressure in the ICR cell (order of 10^{-7} mbar), which is necessary in order to observe these products on a reasonable time scale (minutes). The deviation in m/z is in the range 10–70 ppm.

To confirm the assignments, we performed the experiment with propene-(3,3,3)- d_3 (+98%, Cambridge Isotope Laboratories). Indeed, peaks were observed that can be assigned to $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_3\text{D}_3)^{2+}$ (m/z 229.6),

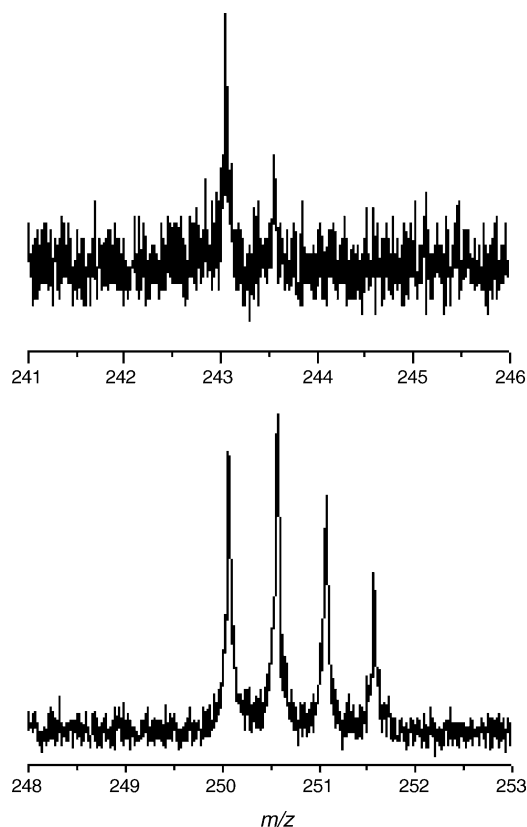


Fig. 8. Reactions between $\text{Ru}(\text{bipy})_2^{2+}$ and $\text{C}_3\text{H}_3\text{D}_3$ (pressure: 9×10^{-8} mbar). Reaction time: 300 s.

$\text{Ru}(\text{bipy})_2(\text{C}_2\text{H}_3)(\text{C}_3\text{H}_3\text{D}_3)^{2+}$ (m/z 243.1, CD_3 elimination), $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_3\text{D}_2)^{2+}$ (m/z 250.1, D_2 elimination), $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_3\text{D}_2)(\text{C}_3\text{H}_2\text{D}_3)^{2+}$ (m/z 250.6, HD elimination), $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_2\text{D}_3)^{2+}$ (m/z 251.1, H_2 elimination) or/and $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_3\text{D}_3)(\text{C}_3\text{H}_3\text{D}_2)^{2+}$ (m/z 251.1, D elimination), and $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_3\text{D}_3)(\text{C}_3\text{H}_2\text{D}_3)^{2+}$ (m/z 251.6, H elimination). Regions around the vinyl and allyl products are shown in Fig. 8. Compared to C_3H_6 , more dihydrogen elimination occurred to give the bis(allyl) complex when the reaction was carried out with $\text{C}_3\text{H}_3\text{D}_3$. However, again the relative intensities varied somewhat from day to day. While several allylic products were formed, the dominant vinylic product observed was $\text{Ru}(\text{bipy})_2(\text{C}_2\text{H}_3)(\text{C}_3\text{H}_3\text{D}_3)^{2+}$ from loss of CD_3 . There seems to be a minor peak due to loss of CD_2H but clearly the hydrogens are not statistically scrambled prior to methyl loss. This indicates different pathways for formation of the two complexes (vide infra).

A peak at m/z 234.0 is observed (data not shown) that is assigned to $\text{Ru}(\text{bipy})_2(\text{C}_4\text{H}_6)^{2+}$ due to a butadiene impurity in the propene- d_3 . The presence of butadiene was verified by electron ionization of the gas in the cell and from a GC–MS analysis of a gas sample.

3.2.1.3. $\text{Ru}(\text{bipy})_2(\text{butene})^{2+} + \text{butene}$. The results for 1-butene are similar to those obtained for propene.

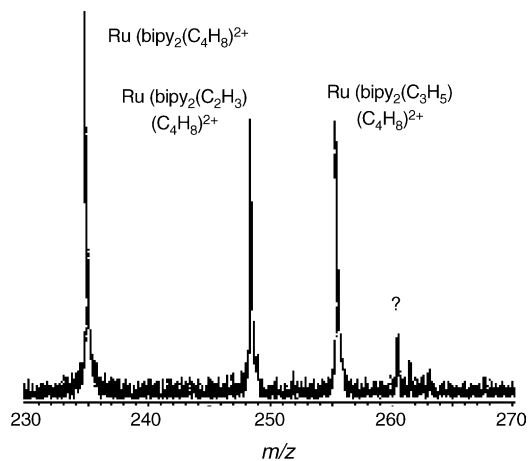


Fig. 9. Reactions between $\text{Ru}(\text{bipy})_2^{2+}$ and C_4H_8 (pressure: 2×10^{-7} mbar). Reaction time: 200 s. The peaks at the question mark are unassigned.

Thus, in the reaction between $^{102}\text{Ru}(\text{bipy})_2(\text{C}_4\text{H}_8)^{2+}$ (m/z 235) and C_4H_8 (mass 56), peaks can be assigned to $\text{Ru}(\text{bipy})_2(\text{C}_2\text{H}_3)(\text{butene})^{2+}$ (m/z 248.6) and $\text{Ru}(\text{bipy})_2(\text{C}_3\text{H}_5)(\text{butene})^{2+}$ (m/z 255.6) (Fig. 9). Selection of two other Ru-isotopomers gave the expected m/z shift of the product ions. Furthermore, the characterization of the complexes as vinylic and allylic is based on the loss of 1-butene at low collision energies and the formation of $\text{Ru}(\text{bipy})_2^{2+}$ at high collision energies. It is also possible that C_2H_3 or C_3H_5 , respectively, are lost to give $\text{Ru}(\text{bipy})_2(\text{butene})^{2+}$. Again we did not select the ions prior to collisional activation. In addition, the measured m/z ratios are in fair agreement with the calculated values (deviation in m/z of 10–40 ppm). Both the vinylic and allylic product ions were observed when the experiment was repeated after a 1-year interval.

There are a few unassigned peaks in the spectrum indicated by the question mark. They may be due to impurities in the butene gas.

3.2.2. Reaction mechanisms for alkene insertion

Homolytic cleavages of propene to give either C_2H_3 and CH_3 or C_3H_5 and H are thermochemically demanding reactions that require 4.4 and 3.8 eV, respectively [25]. In the case

of 1-butene, it takes 3.3 eV for dissociation into C_3H_5 and CH_3 and 4.3 eV for dissociation into C_2H_3 and C_2H_5 [25]. Our results clearly show that the energy cost is considerably reduced when the reactions take place on a ligated Ru^{2+} complex. Since the $\text{Ru}(\text{bipy})_2^{2+}$ parent ion is recovered after collisional activation of $\text{Ru}(\text{bipy})_2(\text{alkene})(\text{vinyl/allyl})^{2+}$, the cycle could be repeated with breakup of new alkene molecules. Possible mechanisms that explain the allylic and vinylic products are presented in the following. The mechanisms are expected to be similar for propene and 1-butene, and we limit our discussion to propene.

An important observation is the formation of a dominant vinylic product in reactions with propene-(3,3,3)- d_3 , $\text{Ru}(\text{bipy})_2(\text{C}_2\text{H}_3)(\text{propene})^{2+}$, whereas several allylic products were formed, which implies different reactant complexes, or at least lifetimes.

First, consider the allylic products. We suggest that initially a π - or η^2 -complex, $\text{Ru}(\text{bipy})_2(\text{propene})^{2+}$, is formed that is in equilibrium with an allyl-hydrido complex, $\text{Ru}(\text{bipy})_2(\text{allyl})(\text{H})^{2+}$, thereby scrambling the terminal hydrogens (Fig. 10, route a). This insertion reaction may be driven by the formation of an 18 valence electron complex [$6(\text{Ru}) + 4 \times 2(\text{N}) + 3(\text{allyl}) + 1(\text{H})$, electrons] that is favourable for most organometallic compounds of group 6, 7, or 8 metals. The existence of such equilibria is well known [26], e.g., Byrd and Freiser [26] have shown that $\text{Rh}(\text{propene})^+$ is in equilibrium with $\text{Rh}(\text{allyl})(\text{H})^+$, since $\text{Rh}(\text{propene})^+$ underwent five H/D-exchanges in reactions with D_2 . We propose that $\text{Ru}(\text{bipy})_2(\text{allyl})(\text{propene})^{2+}$ (19 valence electrons) is formed after substitution of hydrogen with a new incoming propene molecule. It is possible that the allyl ligand is η^1 instead of η^3 to lower the steric crowding in the complex. Hydrogen is most likely more weakly bound than allyl. In Ru^+-H at 0 K, the binding energy is only 1.62 eV [27]. Dihydrogen elimination and the formation of a bis(allyl) complex is a competing reaction channel.

Next, a mechanism for the formation of $\text{Ru}(\text{bipy})_2(\text{vinyl})(\text{propene})^{2+}$ is considered. Even though the signal-to-noise ratio is poor in our experiments, several spectra indicate that the dominant vinylic product that is formed in reactions with $\text{C}_3\text{H}_3\text{D}_3$ is $\text{Ru}(\text{bipy})_2(\text{C}_2\text{H}_3)(\text{C}_3\text{H}_3\text{D}_3)^{2+}$, and hence $\text{Ru}(\text{bipy})_2(\text{vinyl})(\text{CH}_3)^{2+}$ cannot be formed from

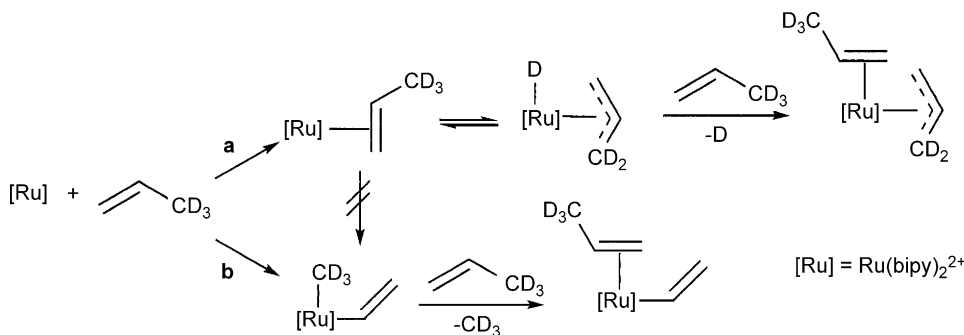


Fig. 10. Possible mechanism for insertion into alkenes.

the π -complex precursor. Instead, we suggest that direct insertion into C–C occurs to give a vinyl methyl complex, $\text{Ru}(\text{bipy})_2(\text{vinyl})(\text{CH}_3)^{2+}$ (Fig. 10, route b). Substitution of methyl by a new incoming propene molecule then provides the product. Armentrout and Chen [27] reported the binding energy of $\text{Ru}^+-\text{C}_2\text{H}_3$ at 0 K to be 3.03 eV, which is larger than that of Ru^+-CH_3 (1.66 eV). Likewise, $\text{Ru}-\text{C}_2\text{H}_3$ is ca. 0.26 eV more strongly bound than $\text{Ru}-\text{CH}_3$ according to calculations by Siegbahn et al. [28]. Assuming a similar trend for binding to $\text{Ru}(\text{bipy})_2^{2+}$, thermodynamics supports that CH_3 and not C_2H_3 in $\text{Ru}(\text{bipy})_2(\text{CH}_3)(\text{CH}_3)^{2+}$ is displaced by propene. The binding energy of propene to Ru^+ has been estimated to be larger than 1.22 eV [27], whereas the Ru^+-H and Ru^+-CH_3 binding energies are 1.62 and 1.66 eV, respectively, as mentioned earlier. Owing to the steric bulk in the ligated complex it seems likely that the exchanges of H for C_3H_6 in $\text{Ru}(\text{bipy})_2(\text{H})(\text{C}_3\text{H}_5)^+$ and CH_3 for C_3H_6 in $\text{Ru}(\text{bipy})_2(\text{CH}_3)(\text{C}_2\text{H}_3)^{2+}$ are both endothermic.

Stoutland and Bergman [29] have shown that when $(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}(\text{PMe}_3)$ reacts with ethene in solution both a π -complex (or η^2 -complex) and a hydrido vinyl complex can be formed, and that the π -complex is not an intermediate for the C–H insertion product. Hence, there are two independent transition states leading to $\text{H}-\text{Ir}-\text{CH}=\text{CH}_2$ and $\text{Ir}-(\text{CH}_2=\text{CH}_2)$. Only at high temperatures, the hydrido vinyl complex is transformed to the π -complex. Similar observations were made by Baker and Field [30] who investigated the reaction between a coordinatively unsaturated iron-complex, $\text{Fe}(\text{DEPE})_2$ [DEPE = 1,2-bis(diethylphosphino)ethane], and ethene taking place in solution. For comparison, the work described here indicates that insertion in alkene C–C does not occur via the π -complex, and the mechanism may be parallel to *insertion* in ethylenic C–H.

Buckner and Freiser [31] observed substitution reactions that involved hydrogen and methyl radicals. Thus, $\text{M}(\text{NH}_3)(c\text{-C}_5\text{H}_5)^+$ ($\text{M} = \text{Fe}, \text{Co}$) and H were formed in reactions between NH_3 and $\text{M}(c\text{-C}_5\text{H}_5)(\text{H})^+$ [in equilibrium with $\text{M}(c\text{-C}_5\text{H}_6)^+$], or *insertion* in the N–H bond occurred and subsequent loss of dihydrogen. In the reaction between $\text{Co}(\text{CH}_3)^+$ and B ($\text{B} = \text{CH}_3\text{CN}$ or NH_3), $\text{Co}(\text{B})^+$ and CH_3 were formed. These results lend some support to the proposed mechanisms where H or CH_3 is substituted for propene, or *insertion* in the second propene molecule occurs with loss of H_2 . However, the examples involve similar binding in the reactants and the products, e.g., a σ -bond between Co^+ and CH_3 and between Co^+ and NH_3 , whereas substitution of CH_3 for propene involves the formation of a π -complex and the rupture of a σ -bond and as a result a large change in the electronic structure of the ruthenium.

The formation of alkene C–H and C–C insertion products may result from a barrier for the formation of the π -complex in line with an earlier suggestion by Siegbahn et al. [28]. According to these workers, the only reason for the formation of vinyl-hydride products is the presence of a barrier

for π -coordination of ethylene, and that the barrier is due to sterically demanding ligands. For the smallest alkene in our experiment, the main product is $\text{Ru}(\text{bipy})_2(\text{C}_2\text{H}_4)_2^{2+}$, but crowding around the metal may prevent efficient binding of two propene or 1-butene molecules, and other reaction channels are instead being probed. Even though the π -complex probably is the thermodynamically most stable product, the insertion product can be the kinetically most favourable product [29,30,32]. Furthermore, calculations performed by Blomberg et al. [32] indicate that the enthalpy change for insertion of Rh(I) in methane depends considerably on whether a ligand is bound to Rh^+ or not, and what position the ligand has relative to the RhCH plane.

There are of course other plausible mechanisms than those we have presented here. One other possibility is that metal insertion first occurs when the second alkene molecule binds, and that a hydrogen or methyl is expelled concomitantly. To shed more light on the actual mechanisms at play clearly more data are needed.

4. Conclusions

Simple addition of alkenes and O_2 to $\text{M}(\text{bipy})_2^{2+}$ ($\text{M} = \text{Cr}, \text{Ru},$ or Os) occurred within 30 s of reaction time, whereas alkene activation took place at longer time scales. Adduct formation depended on both the metal and on the neutral. Hence, the electronic structure of the metal is very important for the reactivity, and the products are not simple ion-induced dipole complexes. Results obtained under single-collision conditions in a FT-ICR cell are in qualitative agreement with results obtained under different conditions in the collision cell of a triple quadrupole instrument where multiple collisions occur.

In contrast to the ethene case, two intact propene or 1-butene molecules do not bind to $\text{Ru}(\text{bipy})_2^{2+}$ under multiple collision conditions (i.e., long reaction time), likely this is prevented because of steric crowding. Instead, metal insertion into CH and CC bonds occurs to produce $\text{Ru}(\text{bipy})_2(\text{vinyl})(\text{propene})^{2+}$, $\text{Ru}(\text{bipy})_2(\text{allyl})(\text{propene})^{2+}$, $\text{Ru}(\text{bipy})_2(\text{vinyl})(\text{butene})^{2+}$, and $\text{Ru}(\text{bipy})_2(\text{allyl})(\text{butene})^{2+}$ along with alkyl or hydrogen radicals. Moreover, experiments with propene-(3,3,3)- d_3 indicate that two different insertion mechanisms are operative. We have presented preliminary mechanisms that involve competitive π -complexation and C–C bond insertion. The π -complex is in equilibrium with an allyl-hydrido complex. These reactions are followed by substitution of the less strongly bound ligand being either hydrogen or an alkyl. In the presence of O_2 , no *O-insertion* in alkenes or propane was observed to occur.

The reactions of ligated ruthenium ions with alkenes are very different from those of bare metal ions which involve dihydrogen elimination, and, to our knowledge, this work shows the first example of the formation of methyl, ethyl, and hydrogen radicals in IMRs between gaseous metal ion complexes and alkenes.

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