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# The metal–carbon bond in vinylidene, carbonyl, isocyanide and ethylene complexes

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## Abstract

Density functional theory (DFT) calculations were carried out for *trans*-[RhX(L)(PMe<sub>3</sub>)<sub>2</sub>] (L = C=CH<sub>2</sub>, C=CHC<sub>6</sub>H<sub>5</sub>, CO, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, C<sub>2</sub>H<sub>4</sub>) which served as model compounds for the analysis of the vibrational spectra of related complexes. The characterization of the metal–carbon stretching mode allowed to study the *trans* influence of a series of ligands on the metal–carbon bond in vinylidene, carbonyl and isocyanide complexes. Furthermore, the comparison of the FT-Raman spectra of the complexes *trans*-[RhF(CO)(PiPr<sub>3</sub>)<sub>2</sub>] and *trans*-[RhF(<sup>13</sup>C=<sup>13</sup>CH<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] which possess the same reduced mass (<sup>13</sup>C=<sup>13</sup>CH<sub>2</sub> vs. CO) allowed for an evaluation of the Rh–C bond strength free of any mass effects and therefore only showing effects of electronic nature.

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## 1. Introduction

Motivated by our interest in understanding catalytic processes, we have started a spectroscopic and theoretical study of transition-metal complexes employing FT-Raman and FT-IR spectroscopy as well as DFT calculations. Because in general it is not possible to isolate intermediate species in catalytic processes, the explanation of the mechanism of such reactions is often hypothetical. However, the structural elucidation of the species involved in a catalytic process can be supported by theoretical methods [1]. It should be noted that an essential property of a good catalyst is to bind a ligand with high selectivity but not so strongly that it can be easily removed from the coordination sphere of the metal. In this context, the assignment of the fundamental metal–ligand stretching modes is particularly relevant, since it is an easily available source of

information about the bonding properties in these complexes. Moreover, the study of the influence of different ligands on the metal–ligand bond is crucial for the designing of new catalysts and for the understanding of catalytic processes.

In contrast to the abundance of electron-rich transition metal complexes containing chloride, bromide and iodide as ligands, only a small number of related compounds with covalent metal–fluorine bonds have been reported [2]. Recent studies have shown that not only the chemistry of fluorometal compounds is substantially different from that of analogous chloro-, bromo- or iodo-metal derivatives [2,3], but also that complexes containing M–F bonds can play an important role in homogeneous catalysis [2,4]. Taking these results into consideration, we have carried out spectroscopic and theoretical investigations on different square-planar rhodium(I) complexes, in the hope of gaining information about the nature of both the Rh–F and Rh–C bonds.

Additionally, the changes in the wavenumber of the  $\nu(\text{CO})$  vibrational mode are often used as an indirect

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probe to study the donor capabilities of the ligands coordinated to the metal center in transition-metal carbonyl complexes [5–10]. However, to the best of our knowledge, no such studies have been carried out using the  $\nu(\text{M}-\text{CO})$  mode, despite the fact that the metal–carbon stretching mode is expected to be sensitive to variations in the electronic density on the metal. This is true also for transition-metal carbene, carbyne, isocyanide and thioaldehyde complexes, for which only a few vibrational studies have been reported [11–23].

## 2. Results and discussion

### 2.1. Vinylidene and carbonyl complexes

The parent ligand  $\text{C}=\text{CH}_2$  is not only an isomer of acetylene but also, and perhaps more importantly, isoelectronic to  $\text{CO}$  and  $\text{CNH}$ . Since various reports seem to indicate that vinylidene [24], carbon monoxide and isocyanide ligands possess similar donor–acceptor properties, we thought it of interest to investigate this similarity by means of Raman and IR spectroscopy. Based on these studies, it was possible for the first time to assign exactly the  $\nu(\text{Rh}=\text{C})$  stretching mode in the vinylidene rhodium(I) complex  $\text{trans}-[\text{RhF}(\text{C}=\text{CH}_2)(\text{P}i\text{Pr}_3)_2]$  by using isotopic substitution, in conjunction with theoretical calculations. According to the DFT calculations, the  $\nu(\text{Rh}=\text{C})$  mode has been attributed to the strong band at  $572\text{ cm}^{-1}$  (calculated at  $575\text{ cm}^{-1}$  using the DFT5 method) in the FT-Raman spectrum of  $\text{trans}-[\text{RhF}(\text{C}=\text{CH}_2)(\text{P}i\text{Pr}_3)_2]$ . This assignment is supported by the shift of this band to lower wavenumbers ( $559\text{ cm}^{-1}$ ) in the carbon-13 labelled complex  $\text{trans}-[\text{RhF}(^{13}\text{C}=\text{CH}_2)(\text{P}i\text{Pr}_3)_2]$  [25]. Since the values obtained from the DFT calculations were in excellent agreement with the experimental data, further characteristic modes of the rhodium(I) compounds could be assigned [26].

The preparation of a series of vinylidene- and carbonyl rhodium(I) complexes containing different ligands in *trans* position to the isoelectronic vinylidene and  $\text{CO}$  ligands provided the opportunity to study the influence of the *trans*-disposed ligands on the metal–carbon bond. It was rather surprising to note that owing to the shift in the wavenumber of the  $\nu(\text{Rh}=\text{C})$  mode for the vinylidene complexes  $\text{trans}-[\text{RhX}(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2]$ , where  $\text{R} = \text{H}$  or  $\text{Ph}$ , the strength of the  $\text{Rh}=\text{C}$  bond increases along the sequence  $\text{X} = \text{C}\equiv\text{CPh} < \text{CH}_3 < \text{I} < \text{Br} < \text{Cl} < \text{F}$ . Moreover, we found that the  $\nu(\text{Rh}=\text{C})$  mode of  $\text{trans}-[\text{RhF}(\text{C}=\text{CH}_2)(\text{P}i\text{Pr}_3)_2]$  is shifted by  $7\text{ cm}^{-1}$  to higher wavenumbers compared to  $\text{trans}-[\text{RhF}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2]$ . Although this increase might indicate that substitution of  $\text{H}$  by  $\text{Ph}$  leads to a strengthening of the  $\text{Rh}=\text{C}$  bond, it could also

originate from the coupling between the  $\nu(\text{Rh}=\text{C})$  and an in-plane ring deformation mode [26].

In addition to the  $\nu(\text{Rh}=\text{C})$  stretching vibration, two further modes were of great relevance for our studies. The first is the deformation mode  $\delta(\text{RhCC})$ , which was observed in the FT-Raman spectra of the phenyl-substituted vinylidene complexes  $\text{trans}-[\text{RhX}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2]$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). This mode, which was calculated at  $472\text{ cm}^{-1}$  for the model compound  $\text{trans}-[\text{RhF}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2]$  by the DFT2 method, is assigned to the band of medium intensity at  $475\text{ cm}^{-1}$  in the FT-Raman spectrum of  $\text{trans}-[\text{RhF}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2]$ . The second is the  $\nu(\text{C}-\text{C}_{\text{ring}})$  mode for which a high Raman activity is characteristic. This mode was attributed on the basis of calculations using the DFT2 method to the strong bands in the FT-Raman spectra of  $\text{trans}-[\text{RhX}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2]$  at  $1230$  ( $\text{X} = \text{F}$ ; calc.  $1231\text{ cm}^{-1}$ ),  $1225$  ( $\text{X} = \text{Cl}$ ; calc.  $1226\text{ cm}^{-1}$ ),  $1224$  ( $\text{X} = \text{Br}$ ) and  $1220\text{ cm}^{-1}$  ( $\text{X} = \text{I}$ ), respectively (Fig. 1). It is important to note that these modes are also shifted to lower wavenumbers in the order  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ , which again reflects the *trans* influence of the halide ligand in the square-planar vinylidene complexes.

For the series of carbonyl compounds  $\text{trans}-[\text{RhX}(\text{CO})(\text{P}i\text{Pr}_3)_2]$ , where  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$  and  $\text{C}\equiv\text{CPh}$ , analogous results were obtained. These were equally compared with the wavenumbers calculated for the model compounds  $\text{trans}-[\text{RhX}(\text{CO})(\text{P}i\text{Pr}_3)_2]$ . Thus, the position of the  $\nu(\text{RhC})$  stretching mode is shifted to lower wavenumbers in the order  $\text{F} > \text{Cl} > \text{Br} > \text{I} \geq \text{C}\equiv\text{CPh}$  as it has been observed for the related vinylidene complexes. However, the DFT calculations carried out on the model compound  $\text{trans}-[\text{Rh}(\text{C}\equiv\text{CPh})(\text{CO})(\text{P}i\text{Pr}_3)_2]$  reveal that the  $\nu(\text{RhCO})$  and  $\nu(\text{Rh}-\text{C}\equiv\text{C})$  stretching modes (calculated at  $537$  and  $496\text{ cm}^{-1}$ , respectively, using the DFT2 method) are strongly

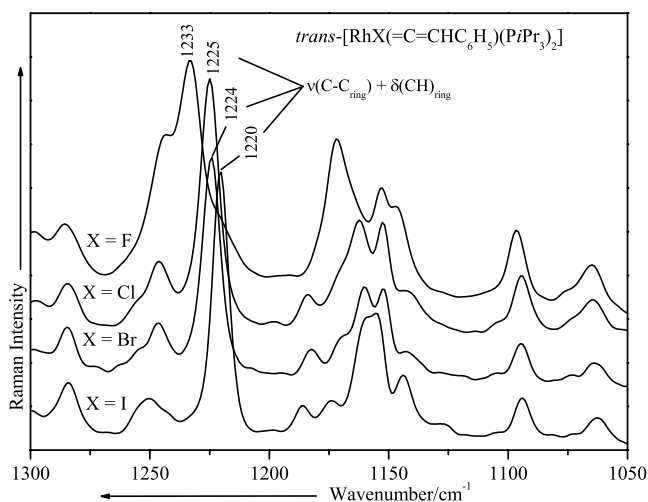


Fig. 1. The fingerprint region of the FT-Raman spectra of  $\text{trans}-[\text{RhX}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2]$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ).

mixed. These modes are assigned to the bands at 546 and 503  $\text{cm}^{-1}$  in the FT-Raman spectrum of *trans*-[Rh(C≡CPh)(CO)(PiPr<sub>3</sub>)<sub>2</sub>] (Fig. 2). Peaks at 1948 (strong) and 1941  $\text{cm}^{-1}$  (weak) were assigned to the  $\nu(\text{CO})$  mode in the FT-IR and FT-Raman spectrum of *trans*-[Rh(C≡CPh)(CO)(PiPr<sub>3</sub>)<sub>2</sub>]. The calculated wavenumber of this mode by the DFT2 method for the model complex *trans*-[Rh(C≡CPh)(CO)(PMe<sub>3</sub>)<sub>2</sub>] is 1958  $\text{cm}^{-1}$ .

Quite remarkably, also other fundamental vibrational modes are sensitive to the *trans*-disposed ligand. Thus, the very strong band at 601  $\text{cm}^{-1}$  in the IR spectrum of *trans*-[RhF(CO)(PiPr<sub>3</sub>)<sub>2</sub>], which was attributed to the  $\delta(\text{RhCO})$  mode, is shifted to lower wavenumbers in the spectrum of the corresponding chloro (582  $\text{cm}^{-1}$ ), bromo (576  $\text{cm}^{-1}$ ) and iodo (566  $\text{cm}^{-1}$ ) carbonyl compounds. In the related complexes *trans*-[RhX(CO)(PPh<sub>3</sub>)<sub>2</sub>], the  $\delta(\text{RhCO})$  deformation mode has been assigned at 596, 574, 567 and 558  $\text{cm}^{-1}$  for X = F, Cl, Br and I, respectively [27–29], which is in good agreement with our calculated wavenumbers.

The observed opposite trends of the  $\nu(\text{CO})$  (1929, 1938, 1939, 1943) and  $\delta(\text{RhCO})$  (601, 582, 576, 566) modes for *trans*-[RhX(CO)(PiPr<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br and I) are the same as found for the complexes *trans*-[RhX(CO)(PPh<sub>3</sub>)<sub>2</sub>] [27–29] and *trans*-[RhX(CO)(PCy<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br, I) [10], and have been explained in terms of an increasing  $\pi$ -donor capability of X on going up in Group 17. The surprising situation thus arises that the metal center seems to be more electron-rich if it is bonded to a more electronegative halogen. This supposition has been used to explain the variation of the half-wave reduction potentials and the equilibrium constants for the halide exchange in *trans*-[RhX(CO)(PPh<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br, I) [10,27–29] as well as in related halide complexes of Fe [6], Ru [30], Ir [7] and Pd [31]. With regard to our work, the same clue about a push–pull  $\pi$ -interaction X → Rh → C provides an explanation for why

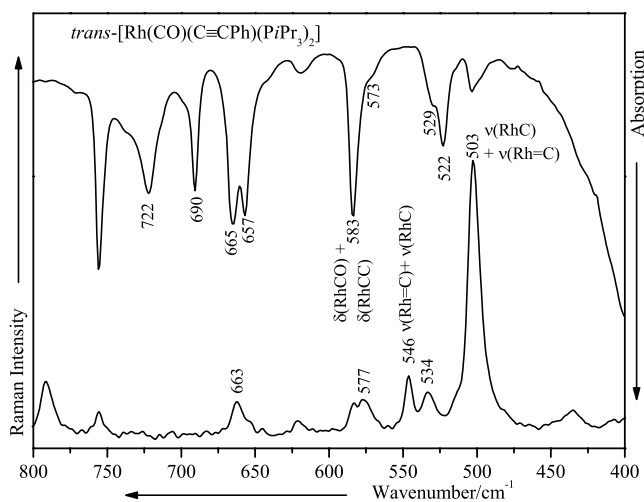


Fig. 2. The low wavenumber region of the FT-Raman (lower) and FT-IR (upper) spectra of *trans*-[Rh(CO)(C≡CPh)(PiPr<sub>3</sub>)<sub>2</sub>].

we find for both the vinylidene and the carbonyl complexes the highest Rh–C bond strength when fluoride is the *trans*-disposed ligand. However, the calculated atomic charges for the model compounds *trans*-[RhX(L)(PMe<sub>3</sub>)<sub>2</sub>], where L = C=CH<sub>2</sub> or CO and X = F, Cl, Br, I and CH<sub>3</sub>, are not in agreement with the assumption that the metal center becomes more electron-rich along the sequence F < Cl < Br < I < CH<sub>3</sub> [26]. In contrast, the NPA analysis reveals that the metal becomes more electron-rich by varying the ligand X along the sequence F < CH<sub>3</sub> < Cl < Br < I. In the case of the fluoro complexes, the considerable difference in charge between Rh and F (0.68 for L = C=CH<sub>2</sub> and 0.59 for L = CO), calculated by the DFT1 method, suggests that: (i) the Rh–F bond has a strong electrostatic component; and (ii) the small and highly negatively charged fluorine atom will cause severe electrostatic repulsions with the electron density at the metal [32]. It should be noticed that this is in agreement with the very high peak observed for the  $\nu(\text{RhF})$  stretching vibration in the FT-IR spectrum of the fluoro complexes. Furthermore, in the NMR spectra of the complexes *trans*-[RhX(L)(PiPr<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br, I; L = <sup>13</sup>C=CH<sub>2</sub>, CO), the  $\alpha$ -carbon and the phosphorus atoms resonate at higher field when the electronegativity of X increases (Table 1). The change in the chemical shift is consistent with the variation of the metal charge, since the calculated charges on the  $\alpha$ -carbon and phosphorus atoms do not vary significantly for X = F, Cl, Br or I, but the charge on Rh is positive for X = F and less negative for X = Cl, Br than for X = I.

Thus, the coordination of fluoride has two effects on the Rh–C bond. On one hand, the higher positive charge on the metal leads to an increase in the  $\sigma$ -donation from carbon to rhodium, while on the other hand the repulsion between the  $p_\pi$  electrons of fluoride and the  $d_\pi$  electrons of rhodium favors a  $\pi$ -back donation from the metal to the empty  $p_\pi$  orbitals of the vinylidene ligand. In addition to these two effects, the electrostatic behavior of rhodium may also play a role in the observed variation of the  $\nu(\text{CO})$  mode, since it has been shown that the electrostatic influence of a positively charged atom bonded to CO initiates a shift of the CO stretching vibration to lower wavenumbers [33].

The DFT calculations carried out on the model compounds *trans*-[RhF(=C=CH<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>] and *trans*-[RhF(=CH<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>] together with the vibrational spectra of the corresponding PiPr<sub>3</sub> complexes clearly indicate that the  $\nu(\text{RhC})$  and  $\nu(\text{RhF})$  modes are weakly coupled [25,26]. This can be also observed for the fluoro(carbonyl) complex. Indeed, the wavenumbers difference between the  $\Delta\delta(\text{RhCO})$  (F → Cl) and  $\Delta\nu(\text{RhC})$  (F → Cl) modes is 5  $\text{cm}^{-1}$ , while between the chloro and bromo and the bromo and iodo complexes it is only about 1–2  $\text{cm}^{-1}$ .

The assignment of the  $\nu(\text{RhC})$  stretching mode in the carbonylrhodium(I) complex *trans*-[RhF(CO)(PiPr<sub>3</sub>)<sub>2</sub>]

Table 1

Selected chemical shifts  $\delta$  (in ppm) and coupling constants  $J$  (in Hz) for the square-planar rhodium(I) complexes  $trans$ -[RhX(L)(PiPr<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br, I; L = <sup>13</sup>C=<sup>13</sup>CH<sub>2</sub>, CO, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC) in C<sub>6</sub>D<sub>6</sub>

Complex	$\delta$ (Rh–C)	$J$ (RhC)	$J$ (CC)	$\delta$ (P)	$J$ (RhP)
$trans$ -[RhF( <sup>13</sup> C= <sup>13</sup> CH <sub>2</sub> )(PiPr <sub>3</sub> ) <sub>2</sub> ]	297.1	51.1	92.7	45.4	145.0
$trans$ -[RhCl( <sup>13</sup> C= <sup>13</sup> CH <sub>2</sub> )(PiPr <sub>3</sub> ) <sub>2</sub> ]	290.6	56.6	113.2	42.2	134.9
$trans$ -[RhBr( <sup>13</sup> C= <sup>13</sup> CH <sub>2</sub> )(PiPr <sub>3</sub> ) <sub>2</sub> ]	287.8	58.6	115.3	40.9	133.9
$trans$ -[RhI( <sup>13</sup> C= <sup>13</sup> CH <sub>2</sub> )(PiPr <sub>3</sub> ) <sub>2</sub> ]	283.4	60.7	116.3	40.2	132.2
$trans$ -[RhF(CO)(PiPr <sub>3</sub> ) <sub>2</sub> ]	192.9	68.1	–	51.8	130.6
$trans$ -[RhCl(CO)(PiPr <sub>3</sub> ) <sub>2</sub> ]	–	–	–	49.9	119.5
$trans$ -[RhBr(CO)(PiPr <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	188.5	75.8	–	47.7	117.0
$trans$ -[RhI(CO)(PiPr <sub>3</sub> ) <sub>2</sub> ]	187.5	75.0	–	47.6	117.0
$trans$ -[RhF(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC)(PiPr <sub>3</sub> ) <sub>2</sub> ]	–	–	–	50.3	137.1
$trans$ -[RhCl(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC)(PiPr <sub>3</sub> ) <sub>2</sub> ]	–	–	–	47.6	127.0
$trans$ -[RhBr(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC)(PiPr <sub>3</sub> ) <sub>2</sub> ]	–	–	–	46.8	124.8
$trans$ -[RhI(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC)(PiPr <sub>3</sub> ) <sub>2</sub> ]	–	–	–	46.2	122.8

<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub>

provides an essential information. By comparing the  $\nu$ (RhC) wavenumbers of the compounds  $trans$ -[RhF(<sup>13</sup>C=<sup>13</sup>CH<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] and  $trans$ -[RhF(CO)(PiPr<sub>3</sub>)<sub>2</sub>] (Fig. 3), in which the isoelectronic ligands <sup>13</sup>C=<sup>13</sup>CH<sub>2</sub> and CO have the same reduced mass, it is obvious that the RhC bond is stronger in the carbonyl than in the vinylidene complex. This result, which is free of any mass effects, is therefore electronic in nature. Moreover, the  $\nu$ (RhF) stretching mode, which has been observed at higher wavenumbers in the FT-Raman and FT-IR spectra of  $trans$ -[RhF(CO)(PiPr<sub>3</sub>)<sub>2</sub>] compared with  $trans$ -[RhF(<sup>13</sup>C=<sup>13</sup>CH<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>], showed that the carbonyl ligand is a better  $\pi$ -acceptor and a less effective  $\sigma$ -donor than the vinylidene group.

## 2.2. Isocyanide complexes

In the course of our investigations, it was also possible to characterize most of the fundamental metal–ligand

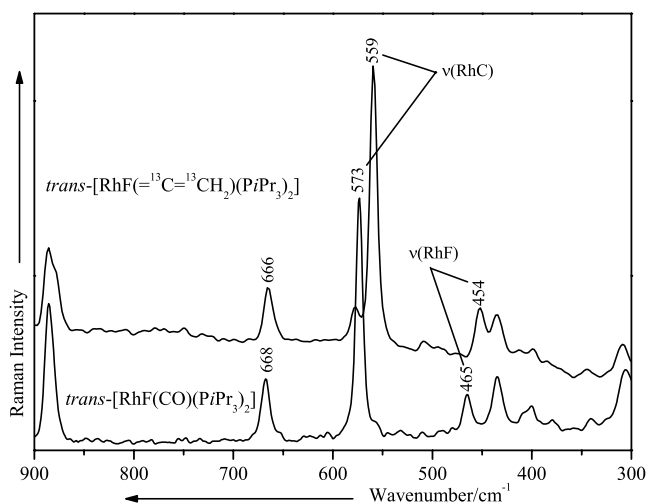


Fig. 3. The low wavenumber region of the FT-Raman spectra of  $trans$ -[RhF(<sup>13</sup>C=<sup>13</sup>CH<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] and  $trans$ -[RhF(CO)(PiPr<sub>3</sub>)<sub>2</sub>].

stretching vibrations for  $trans$ -[ $\{\text{RhX}(\text{PiPr}_3)_2\}_2\{\mu\text{-}1,3\text{-}(\text{CN})_2\text{C}_6\text{H}_4\}$ ] (X = Cl, I) by taking the  $trans$  influence of the halide ligand on the metal–isocyanide bonds into consideration. The band of high intensity at 1583 (for X = Cl) and 1577 cm<sup>-1</sup> (for X = I) was assigned to the  $\nu$ (C=C) mode; it is slightly shifted to lower wavenumbers due to the stronger  $trans$  influence of iodine. The medium or strong peaks at 1149 and 1268 cm<sup>-1</sup> (for X = Cl) and at 1144 and 1263 cm<sup>-1</sup> (for X = I) were assigned to the  $\nu_{\text{as}}(\text{N-C}_{\text{ring}})$  and  $\nu_{\text{s}}(\text{N-C}_{\text{ring}})$  stretching modes, respectively. Regarding the  $\nu_{\text{s}}(\text{N-C}_{\text{ring}})$  vibration, there is a remarkable analogy between the rhodium isocyanides  $trans$ -[ $\{\text{RhX}(\text{PiPr}_3)_2\}_2\{\mu\text{-}1,3\text{-}(\text{CN})_2\text{C}_6\text{H}_4\}$ ] (X = Cl, I) and the corresponding vinylidene complexes  $trans$ -[RhX(=C=CHPh)(PiPr<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br, I). In both cases, the  $trans$  influence of the halide ligand is quite obvious.

The vibrational modes for the dinuclear model compound  $trans$ -[ $\{\text{RhF}(\text{PMe}_3)_2\}_2\{\mu\text{-}1,3\text{-}(\text{CN})_2\text{C}_6\text{H}_4\}$ ] were also calculated [34]. However, the size of this molecule limits the use of a large basis set and therefore the calculations were performed only with the small basis set LANL2DZ (DFT1). The FT-Raman spectrum of  $trans$ -[ $\{\text{RhCl}(\text{PiPr}_3)_2\}_2\{\mu\text{-}1,3\text{-}(\text{CN})_2\text{C}_6\text{H}_4\}$ ] displays two medium to weak bands at 784 and 770 cm<sup>-1</sup>, which are shifted by 13 and 10 cm<sup>-1</sup> to higher and lower wavenumbers in the spectrum of  $trans$ -[ $\{\text{RhI}(\text{PiPr}_3)_2\}_2\{\mu\text{-}1,3\text{-}(\text{CN})_2\text{C}_6\text{H}_4\}$ ]. According to the DFT calculations for the model compound  $trans$ -[ $\{\text{RhF}(\text{PMe}_3)_2\}_2\{\mu\text{-}1,3\text{-}(\text{CN})_2\text{C}_6\text{H}_4\}$ ], the peak at higher wavenumbers (calc. 786 cm<sup>-1</sup>) should be attributed to a  $\delta$ (CH) vibration and that at lower wavenumbers (calc. 764 cm<sup>-1</sup>) to a symmetric ring bending vibration mixed with the  $\nu$ (RhC) stretching mode. The positions of the two  $\nu$ (RhC) modes (symmetric and antisymmetric) anticipated for the model compound  $trans$ -[ $\{\text{RhF}(\text{PMe}_3)_2\}_2\{\mu\text{-}1,3\text{-}(\text{CN})_2\text{C}_6\text{H}_4\}$ ] have been calculated at 598 and 587 cm<sup>-1</sup>, respectively. This result allows to assign the



Table 2

Selected calculated and experimental wavenumbers ( $\text{cm}^{-1}$ ) for the fundamental vibrations of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC together with their tentative assignment

BPW91/6-311+G(d)	BPW91/6-31+G(d)	$I_{\text{Ra}}$ ( $\text{\AA}^4/\text{amu}$ )	Experimental	$I_{\text{Ra}}$	Assignment
2096	2108	461.4	2122	vs	$\nu(\text{CN})$
1591	1597	74.1	1603	m	$\nu(\text{C}=\text{C})$ (8a)
1583	1588	7.4	1592	vs	$\nu(\text{C}=\text{C})$ (8b)
1480	1485	6.1	1474	m	$\nu(\text{CCC})$ (19b) + $\delta(\text{CH}_3)$
1476	1482	14.8	1468	m	$\nu(\text{CCC})$ (18a) + $\delta(\text{CH}_3)$
1457	1464	19.9	1474	sh	$\delta(\text{CH}_3)$
1413	1421	14.3	1442	mbr	$\nu(\text{CCC})$ (19a) + $\nu(\text{CN}-\text{C}_{\text{ring}})$ + $\delta(\text{CH}_3)$
			1428	mw	
1386	1398	19.8	1386	s	i. phase $\delta_s(\text{CH}_3)$
1384	1396	16.4			o.o. phase $\delta_s(\text{CH}_3)$
1326	1340	5.4	1377	m	$\nu(\text{CCC})$ (14) + $\delta(\text{CH}_3)$
1255	1259	59.9	1269	s	$\nu(\text{NC}_{\text{ring}})$ + $\nu(\text{C}-\text{CH}_3)$
1251	1254	0.1	1259	s	$\delta(\text{CH})$
1171	1174	17.9	1175	vs	$\nu(\text{CN}-\text{C}_{\text{ring}})$ + i.p. $\delta(\text{CCC})$
1168	1172	5.6			
1085	1089	27.3	1097	m	$\delta(\text{CH})$
			1082	s	
633	635	30.1	641	vs	Ring breathing
563	563	2.2	570	m	$\delta(\text{C}-\text{N}-\text{ring})$
537	553	0.5	547	mw	$\delta(\text{CCCC})$ (16b)
500	509	0.01	510	mw	$\delta(\text{CCCC})$ (16a)
491	491	3.5	497	ms	$\delta(\text{C}-\text{N}-\text{ring})$ + $\delta(\text{CCCC})$
452	451	5.0	463	ms	$\delta(\text{CCCC})$ (6a)
357	370	2.5	366	ms	$\delta(\text{CNC})$ (16b)
	358	0.9			$\delta(\text{CNC})$ + $\rho(\text{CH}_3-\text{ring})$
	272	1.1	291		
	222	2.2	245		
	138	5.8	166	vs	$\delta(\text{CNC})$ (10b)

bands observed at 595 and 574  $\text{cm}^{-1}$  for *trans*-[ $\{\text{RhCl}(\text{PiPr}_3)_2\}_2\{\mu-1,3-(\text{CN})_2\text{C}_6\text{H}_4\}$ ] and at 589 and 571  $\text{cm}^{-1}$  for *trans*-[ $\{\text{RhI}(\text{PiPr}_3)_2\}_2\{\mu-1,3-(\text{CN})_2\text{C}_6\text{H}_4\}$ ] to these rhodium–carbon stretching modes. Similarly as for the vinylidene complexes, the shift of the  $\nu(\text{RhC})$  vibrations reflects the *trans* influence of the halide ligand in the order  $\text{I} > \text{Cl}$ .

We also found that the  $\nu(\text{C}=\text{C})$  stretching mode of the ring is sensitive to the type of ligand *trans*-disposed to the CNR unit and is shifted to lower wavenumbers for *trans*-[ $\{\text{RhI}(\text{PiPr}_3)_2\}_2\{\mu-1,3-(\text{CN})_2\text{C}_6\text{H}_4\}$ ] compared to *trans*-[ $\{\text{RhCl}(\text{PiPr}_3)_2\}_2\{\mu-1,3-(\text{CN})_2\text{C}_6\text{H}_4\}$ ] ( $\Delta\nu = 6 \text{ cm}^{-1}$ ). The fact that the  $\nu(\text{RhC})$  stretching mode is also shifted to lower wavenumbers ( $\Delta\nu = 6 \text{ cm}^{-1}$ ) by replacing the chloride for iodide indicates that both modes are coupled. Although it is curious that the  $\nu(\text{RhC})$  stretching mode appears at the same wavenumber for the analogous isocyanide and the vinylidene compounds, a direct comparison of this mode for both *trans*-[ $\{\text{RhCl}(\text{PiPr}_3)_2\}_2\{\mu-1,3-(\text{CN})_2\text{C}_6\text{H}_4\}$ ] and *trans*-[ $\{\text{RhCl}(\text{C}=\text{CHPh})(\text{PiPr}_3)_2\}$ ] is unreasonable due to its coupling with a ring vibration.

Although the IR and Raman spectra of liquid C<sub>6</sub>H<sub>5</sub>NC and C<sub>6</sub>D<sub>5</sub>NC have been investigated [35], we also measured the FT-Raman spectrum of the isocya-

nide 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC and performed DFT calculations to assign its characteristic vibrational modes (Table 2). In the high wavenumber region of the FT-Raman spectrum of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, the very strong band at 2122  $\text{cm}^{-1}$ , corresponding to the  $\nu(\text{C}\equiv\text{N})$  stretching mode, has been calculated at 2108  $\text{cm}^{-1}$  using BPW91/6-31+G(d). The  $\nu(\text{C}=\text{C})$  vibrational modes can be assigned to the bands observed at 1603 and 1592  $\text{cm}^{-1}$ .

The very intense band appearing at 1175  $\text{cm}^{-1}$  in the FT-Raman spectrum of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC corresponds to the  $\nu(\text{CN}-\text{C}_{\text{ring}})$  mode and has been calculated at 1174  $\text{cm}^{-1}$  using the BPW91/6-31+G(d) method. This mode is found at 1185  $\text{cm}^{-1}$  in the Raman spectrum of phenylisocyanide [35]. The strong band observed at 641  $\text{cm}^{-1}$  (calc. 635  $\text{cm}^{-1}$ ) for 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC is attributed to the ring breathing vibration. In agreement with the DFT calculations, the peaks observed at 570, 547, 510 and 497  $\text{cm}^{-1}$  can be attributed to the CNC deformation modes.

In contrast to the dinuclear complexes *trans*-[ $\{\text{RhX}(\text{PiPr}_3)_2\}_2\{\mu-1,3-(\text{CN})_2\text{C}_6\text{H}_4\}$ ] (X = Cl, I), where the  $\nu(\text{C}=\text{C})$  stretching mode is sensitive to the halide in *trans* disposition, this mode is observed at 1589  $\text{cm}^{-1}$  (calc. 1580 and 1600  $\text{cm}^{-1}$  for X = F (DFT1); 1581 and 1600  $\text{cm}^{-1}$  for X = Cl (DFT1); 1582 and 1600  $\text{cm}^{-1}$  for

Table 3

Comparison of selected bond lengths (pm) and angles ( $^{\circ}$ ) for the complexes  $trans$ -[RhCl(CNR)(PiPr<sub>3</sub>)<sub>2</sub>] (R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, CH<sub>2</sub>CMe<sub>3</sub>) and the model compounds  $trans$ -[RhX(CNR)(PMe<sub>3</sub>)<sub>2</sub>] (X = F, Cl; R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, *t*Bu)

	$trans$ -[RhF(CNR)(PMe <sub>3</sub> ) <sub>2</sub> ]				$trans$ -[RhCl(CNR)(PMe <sub>3</sub> ) <sub>2</sub> ]			$trans$ -[RhCl(CNR)(PiPr <sub>3</sub> ) <sub>2</sub> ]	
	R = 2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC		R = <i>t</i> Bu		R = 2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC			R = 2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC	R = CH <sub>2</sub> CMe <sub>3</sub>
	DFT1	DFT5	DFT1	DFT2	DFT1	DFT2	DFT5	Experimental <sup>a</sup>	
<b>Bond lengths (pm)</b>									
Rh–X	206.8	204.8	207.5	207.7	247.5	244.6	242.2	239.5(1)	238.9(2)
Rh–P1	237.7	232.1	237.2	232.7	238.7	234.4	233.0	233.4(1)	232.3(1)
Rh–P2	237.7	232.1	237.2	232.7	238.7	234.4	233.0	233.4(1)	232.1(3)
Rh–C1	184.8	182.7	185.4	184.6	185.2	184.9	183.7	183.0(5)	183.4(4)
C1–N	122.0	121.8	122.1	121.4	121.8	121.0	121.4	117.7(6)	115.9(5)
N–C2	138.4	138.4	146.0	145.2	138.7	137.9	138.4	139.5(6)	143.4(6)
<b>Bond angles (<math>^{\circ}</math>)</b>									
P1–Rh–P2	164.4	167.4	164.2	166.1	170.9	171.8	172.2	178.21(5)	175.88(4)
F–Rh–C1	179.7	179.2	179.9	179.8	178.8	179.0	179.4	<sup>b</sup>	
P1–Rh–F	82.2	83.7	82.1	83.3	85.5	86.0	86.2	89.11(3)	90.76(5)
P1–Rh–C1	97.7	96.3	97.9	96.8	94.5	94.0	93.8	90.89(3)	88.7(1)
Rh–C1–N	180.0	174.7	176.3	175.6	180.0	178.5	176.2	180.0	178.4(4)
C1–N–C2	179.1	155.2	157.9	152.0	175.2	168.9	157.7	180.0	166.8(4)

<sup>a</sup> Ref. [36].

<sup>b</sup> Value is not given.

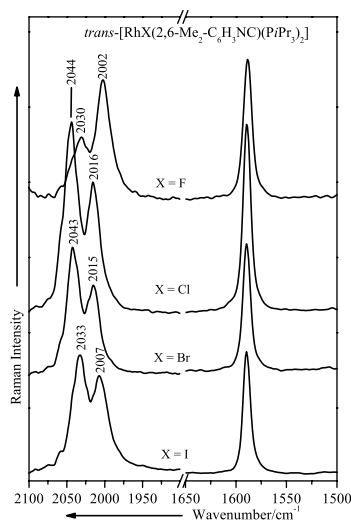


Fig. 4. The high wavenumber region of the FT-Raman spectra of  $trans$ -[RhX(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)(PiPr<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br, I).

X = I (DFT1)) in the FT-Raman spectrum of  $trans$ -[RhX(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>NC)(PiPr<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br, I). The  $\nu$ (CN) stretching mode for these complexes is shifted to higher wavenumbers in the order F < I < Cl  $\approx$  Br (Fig. 4). This order is slightly different to that of the analogous carbonyl complexes where the  $\nu$ (CO) stretching mode increases along F < Cl < Br < I. The calculated CN bond lengths are similar for X = F or Cl in the model compounds  $trans$ -[RhX(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)(PMe<sub>3</sub>)<sub>2</sub>] (Table 3), while the  $\nu$ (CN) stretching mode is calculated at 1991 for X = F and 2009 cm<sup>-1</sup> for X = Cl using the method DFT5.

The fact that the  $\nu$ (CN) stretching mode appears at lower wavenumbers for the iodo complex than for the chloro analogue could be due either to crystal packing effects or to steric hindrance between the isopropyl groups at phosphorus and the methyl groups of the 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC ligand. This steric hindrance should be stronger for the iodo complex, since the P–Rh–P angle increases from the fluoro to the iodo complex with the consequence that the triisopropylphosphine ligands are pushed toward the 2,6-xylenyl unit.

Two vibrations corresponding to the  $\nu$ (RhC) stretching mode have been calculated for the model compounds  $trans$ -[RhX(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)(PMe<sub>3</sub>)<sub>2</sub>] at 525 and 690 cm<sup>-1</sup> for X = F (DFT5) and at 523 and 687 cm<sup>-1</sup> for X = Cl (DFT5). However, both modes mix strongly with a ring bending vibration. Therefore, the medium to strong band at 688 cm<sup>-1</sup> in the FT-Raman spectrum of  $trans$ -[RhF(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)(PiPr<sub>3</sub>)<sub>2</sub>], being shifted to lower wavenumbers in  $trans$ -[RhX(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)(PiPr<sub>3</sub>)<sub>2</sub>] (X = Cl, Br, I), can be assigned to the  $\delta$ (CCC)<sub>ring</sub> and  $\nu$ (RhC) vibrational modes. Similarly to the vinylidene and carbonyl complexes, the shift of these modes to lower wavenumbers in the order F > Cl  $\geq$  Br > I (Fig. 5) reflects the  $trans$  influence of the halide ligand in the order I > Br > Cl > F. The assignment of the second  $\nu$ (RhC) vibrational mode is more complicated due to the presence of several broad peaks in the 510–540 cm<sup>-1</sup> spectral region of the FT-Raman and FT-IR spectra of  $trans$ -[RhX(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)(PiPr<sub>3</sub>)<sub>2</sub>] (X = F, Cl, Br, I) (Figs. 5 and 6). The medium band at 580 cm<sup>-1</sup> in the FT-Raman spectrum of  $trans$ -[RhF(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)(PiPr<sub>3</sub>)<sub>2</sub>] is



Table 4

Selected calculated and experimental vibrational wavenumbers ( $\text{cm}^{-1}$ ) for the complexes  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$  and  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  together with their tentative assignment

$\text{trans-}[\text{RhX}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$							Assignment
R = <i>i</i> Pr, X = F		R = Me, X = F				R = Me, X = Cl	
R	IR	DFT1	DFT2	DFT3	DFT5	DFT5	
1501w	1505m	1495	1501	1480	1510	1516	$\nu(\text{C}=\text{C}) + \delta(\text{CH}_2)$
1438m	1438br	1436	1419	1424	1439	1440	$\delta(\text{CH}_2)$
1197s	1197s	1188	1187	1198	1197	1198	$\delta(\text{CH}_2) + \nu(\text{C}=\text{C})$
1183w	1183w	1180	1168	1164	1184	1184	$\tau(\text{CH}_2)$
885vs	882s						$\nu(\text{CCC})_{\text{PiPr}_3}$
	801m	791	782		712		$\rho(\text{CH}_2)$
	665vs						$\nu(\text{PC}_3)$
656m	659vs	620	642	646	642	642	
648m	650vs	615	636	639	635	636	
576s	576mw						
514m	514mw	470	477	492	494	485	$\nu_{\text{as}}(\text{Rh}-\text{C}_2\text{H}_4)$
471m	471m	456	448	466	468		$\nu_{\text{s}}(\text{Rh}-\text{C}_2\text{H}_4) + \nu(\text{RhF})$
						436	$\nu_{\text{s}}(\text{Rh}-\text{C}_2\text{H}_4)$
425vs	425vs	409	404	419	423		$\nu(\text{RhF}) + \nu_{\text{s}}(\text{Rh}-\text{C}_2\text{H}_4)$
349w		320	330	337	337	337	$\nu(\text{RhP})$
306m		319	312	311	316	318	$\nu(\text{RhP})$
						284	$\nu(\text{RhCl})$

the spectrum of  $\text{trans-}[\text{RhCl}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})(\text{PiPr}_3)_2]$ . Therefore, these bands are good candidates for assigning the ring deformation modes of the 2,6-xylylisocyanide ligand, whereas the band at  $752 \text{ cm}^{-1}$  in the FT-Raman spectrum of  $\text{trans-}[\text{RhCl}(\text{CN}t\text{Bu})(\text{PiPr}_3)_2]$  should be attributed to the  $\nu(\text{CC}_3)$  mode of the *t*Bu group. This mode is calculated at  $744 \text{ cm}^{-1}$  (DFT2) for the model compound  $\text{trans-}[\text{RhF}(\text{CN}t\text{Bu})(\text{PMe}_3)_2]$  and is mixed with the  $\nu(\text{RhC})$  vibrational mode. Furthermore, a vibrational mode with  $\nu(\text{RhC})$  and  $\delta(\text{CNC})$  components is found at  $520 \text{ cm}^{-1}$  and is assigned to the medium band at  $531 \text{ cm}^{-1}$  in the FT-Raman spectrum of  $\text{trans-}[\text{RhCl}(\text{CN}t\text{Bu})(\text{PiPr}_3)_2]$ .

### 2.3. Ethylene complexes

As an extension of our studies of the vinylidene complexes  $\text{trans-}[\text{RhX}(\text{C}=\text{CH}_2)(\text{PiPr}_3)_2]$ , we recently became also interested to investigate the bonding characteristics of the corresponding ethylene rhodium(I) derivative  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$ . The calculated geometries using the DFT3 and DFT5 methods for the model compound  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$  were in excellent agreement with the experimental data found for  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  [2c]. There is a minor difference between the Rh–C bond lengths of  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  (209.6(5) and 210.3(5) pm) and of the analogous chloro complex  $\text{trans-}[\text{RhCl}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  (211.6(2) and 212.8(2) pm) [37], which indicate that in the fluoro derivative the bond between ethene and the metal is somewhat stronger. For the bis(tri-

methylphosphine) complex  $\text{trans-}[\text{RhCl}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$ , the Rh–C bond lengths were calculated as 212.2 and 212.9 pm, respectively.

A larger difference exists between the C1–C2 distance of the ethene ligand in  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  (138.0(8) pm) and in the chloro counterpart (131.9(4) pm) resulting from a higher degree of back bonding from rhodium to the olefin in  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$ . As the electron density on the metal increases, the back donation is enhanced and the double bond character of the ethene ligand is reduced. This is reflected in a longer (and weaker C–C) bond and a bending back of the substituents on the carbon atoms. As expected, the fluoro ligand shows a lower *trans* influence than the chloro ligand and permits a stronger push–pull effect to the  $\pi^*$ -orbital of ethene.

The bonding in alkene complexes can be described by two models, the synergistic ligand-to-metal  $\sigma$ -donation and metal-to-ligand  $\pi$ -back-donation of Dewar, Chatt and Duncanson [38,39], and the model where there are two metal–carbon  $\sigma$ -bonds forming a metallacyclopropane ring. In molecules described by the first method only one metal–carbon stretching band is expected, while in metallacyclopropane-type compounds two bands, one symmetrical and one antisymmetrical, should be observed [5,40,41].

The calculated fundamental modes for the model compound  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$  are summarized in Table 4 together with their tentative assignment and with the experimental values measured for  $\text{trans-}[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  (Table 4).



A vibration which is mainly a  $\nu(\text{Rh}-\text{F})$  stretching mode in character was calculated at  $409\text{ cm}^{-1}$ . The band observed in the FT-IR and FT-Raman spectra of *trans*- $[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  at  $514\text{ cm}^{-1}$  was tentatively assigned to the antisymmetric  $\text{Rh}-\text{C}_2\text{H}_4$  stretching vibration. The intense and medium bands at  $425$  and  $471\text{ cm}^{-1}$ , respectively, could be due to the  $\text{Rh}-\text{F}$  and the symmetric  $\text{Rh}-\text{C}_2\text{H}_4$  stretching modes. We note that these bands lie in the same region as those of the fluororhodium complexes *trans*- $[\text{RhF}(\text{C}_2\text{H}_2)(\text{PCy}_3)_2]$  and *trans*- $[\text{RhF}(\text{PhC}\equiv\text{CPh})(\text{PCy}_3)_2]$  ( $421$  and  $462\text{ cm}^{-1}$ , respectively) which were assigned to the  $\nu(\text{RhF})$  stretching mode [10]. The  $\nu(\text{C}=\text{C})$  vibrational mode for complex *trans*- $[\text{RhF}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  was observed at  $1505\text{ cm}^{-1}$  in the IR- and FT-Raman spectra. This value is close to the calculated one ( $1495\text{ cm}^{-1}$ , DFT1) for the model compound *trans*- $[\text{RhF}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$ . The wavenumber of the  $\nu(\text{C}=\text{C})$  mode is  $118\text{ cm}^{-1}$  smaller than that of gaseous ethylene ( $1623\text{ cm}^{-1}$ ) [42] and also slightly smaller than that of *trans*- $[\text{RhCl}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  ( $1510\text{ cm}^{-1}$ ) [37]. It should be noted that the value of the  $\nu(\text{C}=\text{C})$  stretching mode which is calculated at  $1516\text{ cm}^{-1}$  (DFT5) for the model complex *trans*- $[\text{RhCl}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$  is in good agreement with the experimental result and is consistent with the observed  $\text{C}=\text{C}$  bond distances:  $131.9(4)\text{ pm}$  for the chloro complex [37] and  $138.0(8)\text{ pm}$  for the fluoro complex [2c].

Nevertheless, only the decrease in the  $\nu(\text{C}=\text{C})$  wavenumber alone cannot be used as a measure of the  $\text{M}-\text{C}_2\text{H}_4$  bond strength, since the calculations carried out on  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$  [40],  $[\text{PdCl}_3(\text{C}_2\text{H}_4)]^-$  [41] and our model complex *trans*- $[\text{RhF}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$  show that the  $\nu(\text{C}=\text{C})$  stretching vibration is strongly coupled with the in-plane  $\text{CH}_2$  scissoring mode. The band at  $1197\text{ cm}^{-1}$ , which does not appear in the FT-Raman spectrum of *trans*- $[\text{RhF}(\text{C}=\text{CH}_2)(\text{PiPr}_3)_2]$ , was attributed to the  $\delta(\text{CH}_2)$  mode of the ethylene ligand. For the model complexes *trans*- $[\text{RhX}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$ , this band was calculated at  $1188$  ( $\text{X} = \text{F}$ ) and  $1198\text{ cm}^{-1}$  ( $\text{X} = \text{Cl}$ ), and it is also strongly coupled with the  $\nu(\text{C}=\text{C})$  mode. Moreover, for the compound *trans*- $[\text{RhCl}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$  the  $\nu_s(\text{Rh}-\text{C}_2\text{H}_4)$  and  $\nu_{as}(\text{Rh}-\text{C}_2\text{H}_4)$  stretching modes are predicted at  $436$  and  $485\text{ cm}^{-1}$  using DFT5, respectively, which is in agreement with the previous results. We finally note that the *trans* influence of the halide ligand in *trans*- $[\text{RhX}(\text{C}_2\text{H}_4)(\text{PCy}_3)_2]$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) has already been studied by van Gaal and van den Bekerom [10] using IR and NMR spectroscopy, but the assignment made was restricted to the  $\nu(\text{C}=\text{C})$  and  $\delta(\text{CH}_2)$  vibrational modes being shifted to higher wavenumbers in the order  $\text{I} < \text{Br} < \text{Cl} < \text{F}$ .

In summary, the confirmed sensitivity of the  $\nu(\text{MC})$ ,  $\nu(\text{CC})$ ,  $\nu(\text{CO})$  and  $\nu(\text{CN})$  vibrational modes to the electronic modifications occurring in the vinylidene, carbonyl, ethylene and isocyanide complexes, should

allow in the future also to examine the donor–acceptor properties of ligands of other types.

### 3. Computational and experimental details

The DFT calculations were performed using Gaussian 98 [43] and Becke's 1988 exchange functional [44] in combination with the Perdew-Wang 91 gradient-corrected correlation functional (BPW91) [45]. The Los Alamos effective core potential plus double zeta (LANL2DZ) [46,47] was employed for rhodium, whereas the Dunning/Huzinaga full double zeta basis set with or without polarization and diffuse function (D95, D95+(d) and D95+(3df,2p)) for P, C, H, F, Cl and O atoms (DFT1-3) or 6-31+G(d) for P, C, H, and O, 6-311+G(d) for Br and 3-21G(d) for I (DFT4) was used. In addition, the quasi relativistic energy-adjusted effective core potential (ECP) for the 28 core electrons of rhodium in conjunction with a contracted 6s5p3d basis (311111/22111/411) for the valence orbitals [48] and the 6-31+G(d) Pople basis set for the other atoms was employed for the calculation of the model compounds *trans*- $[\text{RhF}(\text{L})(\text{PMe}_3)_2]$  ( $\text{L} = \text{C}=\text{CH}_2, \text{CO}, \text{C}_2\text{H}_4, 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ ) and was denoted DFT5. The isopropyl groups of the existing complexes have been substituted with methyl groups in order to reduce the time for computation.

The NMR spectra were obtained at room temperature on Bruker AC 200 and Bruker AMX 400 instruments. The FT-Raman spectra were recorded at room temperature using a Bruker IFS 120-HR spectrometer with an integrated FRA 106 Raman module (resolution =  $3\text{ cm}^{-1}$ ). Radiation with  $1064\text{ nm}$  from a Nd-YAG laser was employed for excitation of crystalline samples contained in NMR tubes under argon. The infrared spectra were recorded with a Bruker IFS 25 spectrometer using Nujol suspensions between KBr plates. The synthesis and the complete spectral data for the reported compounds have been previously reported [25,26,34].

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### References

- [1] S. Niu, M.B. Hall, Chem. Rev. 100 (2000) 353.

- [2] (a) N.M. Doherty, N.W. Hoffman, *Chem. Rev.* 91 (1991) 553;  
(b) E.F. Murphy, R. Murugavel, H.W. Roesky, *Chem. Rev.* 97 (1997) 3425;  
(c) J. Gil-Rubio, B. Weberndörfer, H. Werner, *J. Chem. Soc. Dalton Trans.* (1999) 1437.
- [3] (a) N.M. Doherty, S.C. Critchlow, *J. Am. Chem. Soc.* 109 (1987) 7906;  
(b) J.E. Veltheer, P. Burger, R.G. Bergman, *J. Am. Chem. Soc.* 117 (1995) 12478;  
(c) D. Huang, K.G. Caulton, *J. Am. Chem. Soc.* 119 (1997) 3185;  
(d) K. Fagnou, M. Lautens, *Angew. Chem.* 114 (2002) 26;  
(e) K. Fagnou, M. Lautens, *Angew. Chem. Int. Ed. Engl.* 31 (2002) 26.
- [4] J. Krüger, E.M. Carreira, *J. Am. Chem. Soc.* 120 (1998) 837.
- [5] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
- [6] M. Tilst, J.-R. Hamon, P. Hamon, *Chem. Commun.* (1998) 765.
- [7] F. Abu-Hasanayn, A.S. Goldman, K. Krogh-Jespersen, *Inorg. Chem.* 33 (1994) 5122.
- [8] A.W. Ehlers, S. Dapprich, S.F. Vyboishchikov, G. Frenking, *Organometallics* 15 (1996) 105.
- [9] L. Vaska, J. Peone, *J. Chem. Soc. Chem. Commun.* (1971) 418.
- [10] H.L.M. van Gaal, F.L.A. van den Bekerom, *J. Organomet. Chem.* 134 (1977) 237.
- [11] S.-C. Chang, R.H. Hauge, Z.H. Kafafi, J.L. Margrave, W.E. Billups, *J. Am. Chem. Soc.* 110 (1988) 7975.
- [12] E. Diana, O. Gambino, R. Rossetti, P.L. Stanghellini, T. Albiez, W. Bernhardt, H. Vahrenkamp, *Spectrochim. Acta Sect. A* 49 (1993) 1247.
- [13] C.E. Anson, N. Sheppard, D.B. Powell, J.R. Norton, W. Fischer, R.L. Keiter, B.F.G. Johnson, J. Lewis, A.K. Bhattacharya, S.A.R. Knox, M.L. Turner, *J. Am. Chem. Soc.* 116 (1994) 3058.
- [14] (a) E.O. Fischer, N.Q. Dao, W.R. Wagner, *Angew. Chem.* 90 (1978) 51;  
(b) E.O. Fischer, N.Q. Dao, W.R. Wagner, *Angew. Chem. Int. Ed. Engl.* 17 (1978) 50.
- [15] G.R. Clark, K. Marsden, W.R. Roper, L.J. Wright, *J. Am. Chem. Soc.* 102 (1980) 6570.
- [16] N.Q. Dao, E.O. Fischer, T.L. Lindner, *J. Organomet. Chem.* 209 (1981) 323.
- [17] N.Q. Dao, H. Fevrier, M. Jouan, E.O. Fischer, W. Röhl, *J. Organomet. Chem.* 275 (1984) 191.
- [18] J.K. Manna, R.J. Kuk, R.F. Dallinger, M.D. Hopkins, *J. Am. Chem. Soc.* 116 (1994) 9793.
- [19] M. Barnes, D.A. Gillet, A.J. Merer, G.F. Metha, *J. Chem. Phys.* 105 (1996) 6168.
- [20] R.M. Sosa, P. Gardiol, G. Beltrame, *Int. J. Quantum Chem.* 69 (1998) 371.
- [21] P.D. Harvey, I.S. Butler, G.W. Harris, N.J. Coville, *Inorg. Chem.* 25 (1986) 3608.
- [22] P.M. Boorman, P.J. Craig, T.W. Swaddle, *Can. J. Chem.* 48 (1970) 838.
- [23] M.P. Guy, J.T. Guy, D.W. Bennett, *Organometallics* 5 (1986) 1696.
- [24] (a) M.I. Bruce, A.G. Swincer, *Adv. Organomet. Chem.* 22 (1983) 59;  
(b) M.I. Bruce, *Chem. Rev.* 91 (1991) 197.
- [25] D. Moigno, W. Kiefer, J. Gil-Rubio, H. Werner, *J. Organomet. Chem.* 612 (2000) 125.
- [26] D. Moigno, W. Kiefer, B. Callejas-Gaspar, J. Gil-Rubio, H. Werner, *New J. Chem.* 25 (2001) 1389.
- [27] Yu.S. Varshavskii, M.M. Singh, N.A. Buzina, *Zh. Neorg. Khim.* 16 (1971) 1372.
- [28] G. Schiavon, S. Zecch, G. Pilloni, M. Martelli, *J. Inorg. Nucl. Chem.* 39 (1977) 115.
- [29] (a) F. Araghizadeh, D.M. Branan, N.W. Hoffman, J.H. Jones, E.A. McElroy, N.C. Miller, D.L. Ramage, A. Battaglia Salazar, S.H. Young, *Inorg. Chem.* 27 (1988) 3752;  
(b) D.M. Branan, N.W. Hoffman, E.A. McElroy, N.C. Miller, D.L. Ramage, A.F. Schott, S.H. Young, *Inorg. Chem.* 26 (1987) 2915.
- [30] J.T. Poulton, M.P. Sigalas, K. Foltz, W.E. Streib, O. Eisenstein, K.G. Caulton, *Inorg. Chem.* 33 (1994) 1476.
- [31] J.P. Flemming, M.C. Pilon, O.Ya. Borbulevitch, M.Yu. Antipin, V.V. Grushin, *Inorg. Chim. Acta* 280 (1998) 87.
- [32] K.G. Caulton, *New J. Chem.* 18 (1994) 25.
- [33] G. Frenking, N. Fröhlich, *Chem. Rev.* 100 (2000) 717.
- [34] D. Moigno, B. Callejas-Gaspar, J. Gil-Rubio, C.D. Brandt, H. Werner, W. Kiefer, *Inorg. Chim. Acta* 334 (2002) 355.
- [35] R.A. Nalepa, J.D. Laposa, *J. Mol. Spectrosc.* 50 (1974) 106.
- [36] W.D. Jones, E.T. Hessell, *Organometallics* 9 (1990) 718.
- [37] C. Bussetto, A. D'Alfonso, F. Maspero, G. Perego, A. Zazzetta, *J. Chem. Soc. Dalton Trans.* (1977) 1828.
- [38] M.J.S. Dewar, *Bull. Soc. Chim. Fr. Sect. C* 79 (1951) 18.
- [39] J. Chatt, L.A. Duncanson, *J. Chem. Soc.* (1953) 2929.
- [40] M.J. Grogan, K. Nakamoto, *J. Am. Chem. Soc.* 88 (1966) 5454.
- [41] É. Bencze, I. Pápai, J. Mink, P.L. Goggin, *J. Organomet. Chem.* 584 (1999) 118.
- [42] (a) J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsspektroskopie*, 2nd ed., Thieme, Stuttgart, 1988;  
(b) F.R. Dollish, W.G. Fateley, F.F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, Wiley, New York, 1974;  
(c) D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, New York, 1991;  
(d) N.B. Colthup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed., Academic Press, New York, 1990.
- [43] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M. Gill, W.B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Ciolowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomberts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, *Gaussian 98*, Revision A7, Gaussian Inc., Pittsburg PA, 1998.
- [44] A.D. Becke, *Phys. Rev. Sect. A* 38 (1988) 3098.
- [45] J.P. Perdew, Y. Wang, *Phys. Rev. Sect. B* 45 (1992) 13244.
- [46] W.R. Wadt, P.J. Hay, *J. Chem. Phys.* 82 (1985) 284.
- [47] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [48] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* 77 (1990) 123.