

A crystallographic and DFT study on Vaska-type *trans*-[Rh(CO)Cl(PR₃)₂] complexes containing flexible ligands: The molecular structure of *trans*-[Rh(CO)Cl{P(OC₆H₅)₃}₂]

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Abstract

An investigation into the effect of the flexibility of substituents on the disorder of the Cl–Rh–CO moiety in Vaska-type *trans*-[Rh(CO)Cl(PR₃)₂] complexes is presented. The influence of the packing of the complexes with PR₃ = P(CH₂C₆H₅)₃, P(OC₆H₅)₃, P(O-2-MeC₆H₄)₃ and P(O-2,6-Me₂C₆H₃)₃ was evaluated by comparing the X-ray structures with the results of DFT calculations on these complexes. Reasonable agreement between the calculated and molecular structures was found. A good agreement, however, was found between the calculated and crystallographic structures when comparing the coordination polyhedron around the Rh atom. The main difference between the calculated and solid state structures appeared to be in the orientation of the phenyl groups of the P-donor ligands. © 2006 Elsevier B.V. All rights reserved.

Keywords: Rhodium; X-ray structure; DFT calculation

1. Introduction

A well-known early organometallic complex, *trans*-[Ir(CO)Cl(PPh₃)₂], which was first reported by Angoletta in 1959 [1], and later correctly formulated by Vaska and DiLuzio [2], is known to exhibit catalytic activity. Interestingly enough, at that time the rhodium analogue was already known [3] and was investigated to some extent [4]. Despite this, complexes with the general formula *trans*-[M(CO)Cl(L)₂] (M = Rh(I), Ir(I); X = halide or pseudo-halide; L = neutral ligand) are still in many instances today known as analogues to Vaska's complex [5,6]. Nevertheless, the Vaska-type complexes are typical of those studied by Chatt, which enabled the application of theories that has been developed [7]. These d⁸ square-

planar systems undergo a range of reactions, such as oxidative addition, with different substrates [5] and were recognized as important model systems for studies in homogeneous catalysis. Early work by Wilkinson [8] explored several aspects regarding the steric and electronic properties in these Rh(I) analogues, but definite crystal structural confirmation of the reaction products could not be achieved.

Important aspects involved in the coordination of ligands (mainly PR₃, AsR₃ and SbR₃) to transition metal atoms are the electronic and steric parameters. Firstly, the electronic character of the M–P bond is a combined effect of the σ-bond formed by donation of the lone pair electron from the P to the M atom and by the ability of the P ligand to accept electron density from the metal by back-donation into a combination of the empty 3d-orbitals and σ*-orbitals of the P atom [9]. A second factor, known to influence the coordination of a ligand is the spatial demand, or steric size, associated with the specific ligand. In order to rationalise certain parameters, such as steric

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bulk and electron-donating capability, for ligands with no or very little data available, it is important to cross-reference to other well-known ligand systems, ensuring that all ligands employed are compared on an identical scale. The diversity of tertiary phosphines in terms of their Lewis basicity and bulkiness render them excellent candidates to tune the reactivity of square-planar complexes towards a variety of chemical processes, such as oxidative addition and substitution reactions [10]. The effect of tertiary phosphine ligands with different electron-donor and -acceptor capabilities was illustrated by Tolman [11] by measuring the CO-stretching frequency of the *trans*-carbonyl group in Ni(0) complexes of the general formula $[\text{Ni}(\text{CO})_3\text{PR}_3]$. We have evaluated the electronic parameters of an extended range of phosphines using the CO-stretching frequencies of *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2]$ [12]. The latter complexes are simple to prepare, air stable and their preparation do not pose the synthetic problems encountered with pyrophoric and volatile starting materials such as $[\text{Ni}(\text{CO})_4]$.

Calculation of the cone angles in *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2]$ were performed based on the Tolman model [11], but using the actual Rh–PR₃ bond distances and angles determined in the crystallographic studies, i.e., the effective cone angles, θ_E , in this case [13]. While evaluating the steric properties of the ligands in the *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2]$ complexes in the solid state it was observed, as illustrated by Tolman, that the cone angles of the phosphines can vary significantly, even for rigid groups such as a phenyl, simply by rotation [14]. Here we report the effect of even more flexible phosphorous containing ligands, thus having the possibility of even larger variations in their cone angle values. Normally these are ligands containing some spacer group (O, CH₂) between the phosphorous atom and the phenyl substituent. This allows for various orientations of the ligand which could influence the outcome of the packing of the molecule, possibly also resulting in the statistical disorder of the Cl–Rh–CO moiety.

Though several complexes with a *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{P}(\text{OR})_3)_2]$ molecular structure have previously been synthesized (R = Me [15], Ph [15–17], 4-MeC₆H₄ [17], 4-ClC₆H₄ [17]), none of these compounds' solid state structures, as determined by X-ray diffraction, has yet been described, although structures of related phosphine complexes have been extensively reported [12]. In this study, only aryl substituents were selected, as these are the most comparable to the other Vaska-type systems studied, containing aryl phosphines. Previous to our study, the molecular structure of only one rhodium Vaska-type compound containing P(OR)₃ with the aryl moiety was reported, namely *trans*- $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{O}-2-t\text{Bu}-\text{C}_6\text{H}_4)_3\}_2]$ [18].

The aim of the present study was thus to investigate the effect of the flexibility of the substituents on the disorder of the Cl–Rh–CO moiety in *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2]$ type complexes. The influence of the packing of the complexes with PR₃ = P(CH₂C₆H₅)₃, **1** [19], P(OC₆H₅)₃, **2**, P(O-2-

MeC₆H₄)₃, **3**, [20] and P(O-2,6-Me₂C₆H₃)₃, **4**, [21] was evaluated by comparing the X-ray structures with the results from DFT calculations on these complexes. Two of these complexes do not show statistical disorder of the Cl–Rh–CO moiety in the solid state, namely **1** and **2**, while **3** and **4** show a disorder of this moiety.

2. Experimental

2.1. Reagents and general procedures

Pentane and dichloromethane were pre-dried by passage over alumina (neutral, Brockmann grade I) and subsequently distilled from the appropriate drying agent [22]. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was prepared according to the method described in the literature [23], while the substituted phosphites were prepared by reacting the appropriate phenol with PCl₃ in the presence of NEt₃ analogous to the synthesis of tris(2-butylphenyl)phosphite [24]. The compounds *trans*- $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3\}_2]$, **1**, [19], *trans*- $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{O}-2-\text{MeC}_6\text{H}_4)_3\}_2]$, **3**, [20] and *trans*- $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{O}-2,6-\text{Me}_2\text{C}_6\text{H}_3)_3\}_2]$, **4**, [21] were prepared as communicated previously. All other chemicals were obtained from Sigma–Aldrich and used as obtained.

NMR spectra were recorded on a Varian Inova 300 MHz spectrometer (¹H: 300 MHz, ¹³C: 75.5 MHz, ³¹P: 121.46 MHz) at ambient temperature, and were referenced relative to TMS (¹H and ¹³C) or 85% H₃PO₄ (³¹P), using one of the following: the residual protonated impurities in the solvent (¹H NMR: CDCl₃; δ 7.27) or external 85% H₃PO₄ (³¹P). Infrared spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer and analysed with the Bruker OPUS-NT software. Infrared data for solution spectra were collected using NaCl windows (optical path-length 0.1 mm).

2.2. Structure determination

Crystals of *trans*- $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$, **2**, were grown from CH₂Cl₂ as described below. X-Ray diffraction data for **2** were collected on a Bruker SMART CCD 1K diffractometer using MoK _{α} (0.71073 Å) and ω -scans at 293(2) K. After the collection was completed, the first 50 frames were repeated to check for decay, which was not observed. All reflections were merged and integrated using SAINT [25] and were corrected for Lorentz, polarization and absorption effects using SADABS [26]. The structures were solved by the heavy atom method and refined through full-matrix least-squares cycles using the SHELXL97 [27] software package with $\Sigma(|F_o| - |F_c|)^2$ being minimized. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites by means of a riding model. The DIAMOND [28] Visual Crystal Structure Information System software was used for the graphics. Crystal data and details of data collection and refinement are given in Table 1. (CCDC reference number CCDC620798. See <http://www.ccdc.cam.ac.uk>).

Table 1
Crystal data and structural refinement for *trans*-[Rh(CO)Cl{-P(OC₆H₅)₃]₂, **2**

<i>trans</i> -[Rh(CO)Cl{P(OC ₆ H ₅) ₃] ₂	
Empirical formula	C ₃₇ H ₃₀ ClO ₇ P ₂ Rh
Formula weight	786.91
<i>T</i> (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.039(2)
<i>b</i> (Å)	10.973(2)
<i>c</i> (Å)	16.872(3)
α (°)	98.34(3)
β (°)	97.90(3)
γ (°)	103.85(3)
<i>V</i> (Å ³)	1756.5(6)
<i>Z</i>	2
Calculated density (mg m ⁻³)	1.488
Absorption coefficient (mm ⁻¹)	0.701
<i>F</i> (000)	800
Crystal size (mm)	0.34 × 0.20 × 0.12
θ Range (°)	2.0–28.3
Index ranges	–12 ≤ <i>h</i> ≤ 13, –13 ≤ <i>k</i> ≤ 14, –22 ≤ <i>l</i> ≤ 22
Collected reflections collected	12095
Unique reflections	8416
Observed reflections	5020
<i>R</i> _{int}	0.0272
Completeness to 2 θ	96.1%
Maximum and minimum transmission	0.921–0.796
Refinement method	Full-matrix least square on <i>F</i> ²
Data/restraints/parameters	8416/0/433
Goodness-of-fit on <i>F</i> ²	0.990
Final <i>R</i> ₁ indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0514, <i>wR</i> ₂ = 0.1019
<i>R</i> ₁ (all data)	<i>R</i> ₁ = 0.1084, <i>wR</i> ₂ = 0.1214
Largest different peak and hole (e Å ⁻³)	0.512 and –0.446

2.3. Preparation of *trans*-carbonylchlorobis(triphenylphosphite)rhodium(I), **2**

A solution of P(OC₆H₅)₃ (80 mg, 0.258 mmol) in pentane (1.0 ml) was slowly added to a yellow solution of [Rh(CO)₂Cl]₂ (24.9 mg, 0.064 mmol) in pentane (3.0 ml). Gas evolution was observed immediately, the solution decolorized and a light yellow precipitate formed. The supernatant was decanted and the solids washed with pentane (3 × 2 ml) to leave the pure title compound. Crystals suitable for single crystal X-ray analysis were grown from CH₂Cl₂. Yield: 94 mg, 93%; ¹H NMR (300 MHz, CDCl₃): δ 7.37–7.14 (m, 30H); ³¹P{H} NMR (121.46 MHz, CDCl₃): δ 121.5 (d, ¹*J*_{Rh–P} = 214 Hz); IR ν (CO): 2016 cm⁻¹.

2.4. DFT calculations

To allow more insight in the geometrical conformations of complexes **1–4**, DFT calculations were performed using the GAUSSIAN03 package [29] on a pentium computer. We employed the Becke hybrid three parameter DFT method using the Lee, Yang and Parr correlation functional

(B3LYP) [30] and the LANL2DZ [31] basis set. The structures of complexes **1–4** and its isomers were optimized without constraints. Minima were verified via frequency analysis of the stationary point. The Hyperchem 7.52 package [32] was used for the overlay of solid state and calculated structures, as well as for the calculation of the root mean difference.

3. Results and discussion

3.1. Solid state structure of *trans*-[Rh(CO)Cl{P(OC₆H₅)₃]₂, **2**

A molecular diagram showing the numbering scheme of the title compound *trans*-[Rh(CO)Cl{P(OC₆H₅)₃]₂, **2**, is presented in Fig. 1, with selected bond lengths, angles and torsion angles in Table 2 and the hydrogen bonding interactions in Table 3. The compound *trans*-[Rh(CO)Cl{-P(OC₆H₅)₃]₂, **2**, crystallizes in the triclinic space group *P* $\bar{1}$ with *Z* = 2. This results in the Rh atom lying on a general position and no disorder of the Cl–Rh–CO moiety. All angles within the Rh coordination polyhedron are close to those expected for a square-planar environment (Table 2) with the Rh atom displaced 0.0080(10) Å from the coordination plane (rms error of fitted atoms = 0.0042). Each triphenylphosphite has one oxygen atom close to the coordination plane, with O–P–Rh–CO torsion angles of only –1.58(18) and –1.92(2)° (Table 2), and with the oxygens in a *gauche* conformation relative to the P–P axis giving rise to a pseudo mirror plane through the Cl–Rh–CO moiety, perpendicular to the P–Rh–P' axis.

Due to the phosphites' flexible nature, different orientations resulting in variations in cone angle sizes are observed and may not necessarily be a true reflexion of the steric properties of the phosphite in solution compared with the solid state. In the title compound, intramolecular hydrogen interactions (Table 3) are observed between some phenyl rings with the O spacers of adjacent substituents on the P atom, yielding significant differences in steric profile for the two triphenylphosphites. The cone angle values (Table 4) obtained for P1 and P2 respectively show a difference of ca. 10° mainly due to the influence of this interaction found in phosphite P1. A similar, but weaker interaction is also noted in phosphite P2 in the C42–H42...O5 interaction. Various intermolecular interactions, with Cl and O of the central Cl–Rh–CO moiety, are also noted which could be partly responsible for the observed packing.

We previously communicated the solid state structures of *trans*-[Rh(CO)Cl{P(CH₂C₆H₅)₃]₂, **1**, [19], *trans*-[Rh(CO)Cl{P(O-2-MeC₆H₄)₃]₂, **3**, [20] and *trans*-[Rh(CO)Cl{P(O-2,6-Me₂C₆H₃)₃]₂, **4**, [21]. It appears that the more flexible Group 15 ligands discussed here might play some part in the outcome of the statistical disorder of the Cl–Rh–CO moiety. This may either be due to intramolecular interactions found in the substituents of the phosphites, varying its steric size, or by the inter- and intramolecular interactions to the chloride of the Cl–Rh–CO moiety. There are

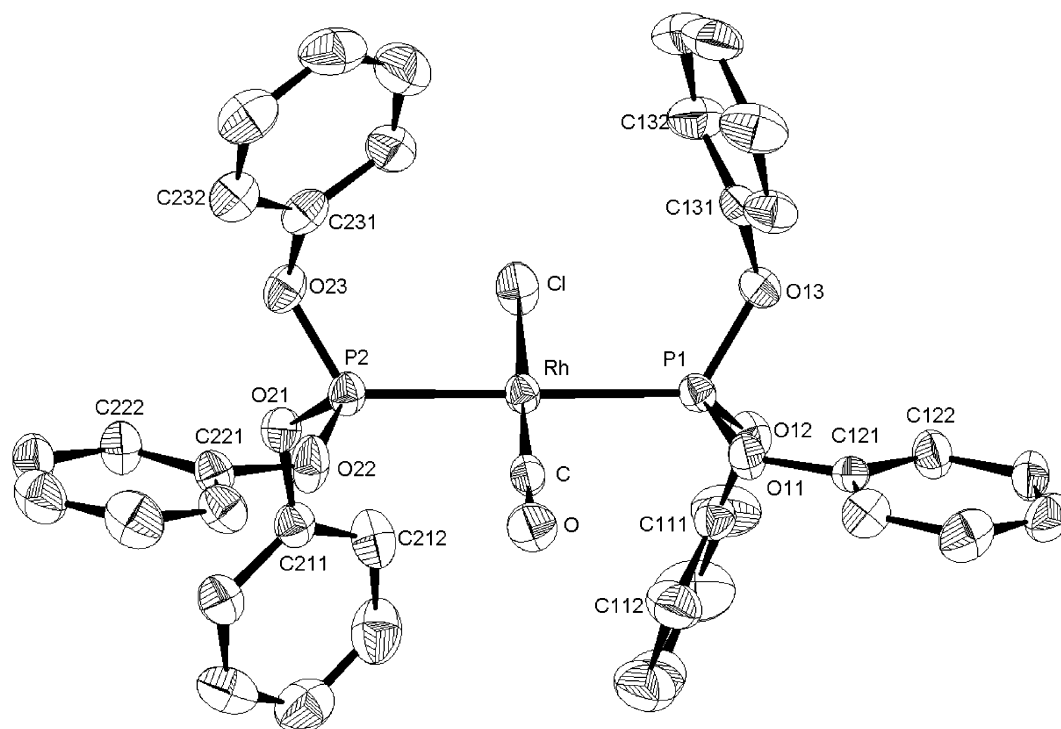


Fig. 1. Molecular structure of *trans*-[Rh(CO)Cl{P(OC₆H₅)₃]₂, **2** (30% probability). H atoms have been omitted for clarity. For the aromatic rings, the first digit refers to the P-atom, the second digit to the ring number, while the third digit indicates the number of the C atom in the ring.

Table 2
Selected interatomic bond distances (Å) and angles (°) for *trans*-[Rh(CO)Cl{P(OC₆H₅)₃]₂, **2**

Distances (Å)			
Rh–C	1.814(4)	P1–O1	1.588(3)
Rh–P1	2.2651(12)	P1–O2	1.588(3)
Rh–P2	2.2747(12)	P1–O3	1.585(3)
Rh–Cl	2.3538(12)	P2–O4	1.580(3)
C–O	1.141(4)	P2–O5	1.584(3)
		P2–O6	1.589(3)
Angles (°)			
C–Rh–P1	90.60(12)	Rh–P1–O1	110.97(10)
C–Rh–P2	90.35(12)	Rh–P1–O2	118.40(11)
P1–Rh–P2	178.89(4)	Rh–P1–O3	120.89(11)
C–Rh–Cl	179.30(13)	Rh–P2–O4	109.22(11)
O–C–Rh	179.0(4)	Rh–P2–O5	120.28(12)
P1–Rh–Cl	88.89(4)	Rh–P2–O6	120.22(12)
P2–Rh–Cl	90.16(4)		
Torsion angles (°)			
C–Rh–P1–O1	–1.61(17)	C–Rh–P2–O4	–1.82(19)
C–Rh–P1–O2	120.96(18)	C–Rh–P2–O5	–124.50(18)
C–Rh–P1–O3	–125.53(18)	C–Rh–P2–O6	121.28(18)

also the interactions from some hydrogens of the phosphine substituents with the metal centre which could influence the packing arrangement. Here we discuss more detail of the above mentioned molecular structures and specifically evaluate several similar interactions found in these. In addition, we would like to draw attention to the structure of **4** [21], which is the only complex studied in this series with two independent molecules in the asymmetric unit in the solid

Table 3
Inter- and intra-molecular hydrogen interactions (Å) and angles (°) for *trans*-[Rh(CO)Cl{P(OC₆H₅)₃]₂, **2**

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
C16–H16···O2	0.93	2.50	3.104(5)	123.2
C16–H16···O2 ⁱ	0.93	2.90	3.436(5)	118.1
C16–H16···O3 ⁱ	0.93	2.66	3.369(5)	133.6
C15–H15···Cl ⁱ	0.93	2.89	3.797(5)	166.7
C34–H34···O ⁱⁱ	0.93	2.65	3.380(6)	136.0
C43–H43···Cl ⁱⁱⁱ	0.93	2.87	3.711(6)	151.8
C42–H42···O5	0.93	2.73	3.321(5)	122.1

i = –x, 1 – y, 1 – z; ii = –1 + x, y, z; iii = –x, –y, –z.

state. The two molecules show little difference in the two orientations, possibly due to slightly different packing effects. The similarity of the two independent molecules of compound **4** is shown in a superimposed ball-and-stick drawing in Fig. 2. The calculated rms overlay error in the two structures was less than 0.1 Å.

All the Vaska-type compounds in the above series crystallize in the triclinic space group *P* $\bar{1}$. Both compounds *trans*-[Rh(CO)Cl{P(CH₂C₆H₅)₃]₂, **1** [19] and *trans*-[Rh(CO)Cl{P(O-2,6-Me₂C₆H₃)₃]₂, **4** [21] crystallize with *Z* = 2. This results in the case of compound **1**, like compound **2**, in the Rh atom lying on a general position and therefore no statistical disorder of the Cl–Rh–CO moiety was observed. In the case of compound **4**, however, both molecules lie on inversion centers, imposing a 50% statistical disorder on both Cl–Rh–CO moieties, as observed for both the molecules in **4**.

Table 4
Selected geometrical parameters (Å, °) for the compounds with general formula *trans*-[Rh(CO)Cl(PR₃)₂] (R = phenolate or benzyl)^a

Complex	M–P	M–Cl	C–M–Cl	θ_E	θ_T	Ref.
1	2.3166(10)	2.3649(10)	178.76(12)	167.6	168.5	[19]
	2.3143(11)			169.3	170.1	
				172.0	172.6	
2	2.2651(12)	2.3538(12)	179.30(13)	156.1	155.8	T.W.
	2.2747(12)			166.5	166.4	
3	2.2906(9)	2.401(4)	180.0	167.4	167.7	[20]
4	2.3102(9)	2.381(3)	180.0	182.0	182.7	[21]
	2.2996(9)	2.380(3)		182.2	182.6	
PR ₃ = O-2- <i>t</i> BuC ₆ H ₄	2.2856(7)	2.370(3)	175.85	181.2	181.3	[18]

^a Bond lengths in Å, cone angles in degrees. Only selected parameters are shown.

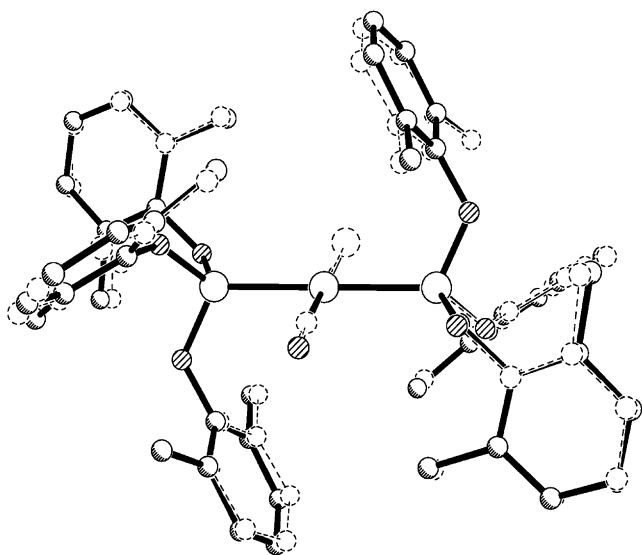


Fig. 2. Superimposed ball-and-stick drawing of the two independent molecules of *trans*-[Rh(CO)Cl{P(O-2,6-Me₂C₆H₃)₂]₂, **4**.

Compound *trans*-[Rh(CO)Cl{P(O-2-MeC₆H₄)₃]₂, **3** [20], is the only compound in the current study to crystallize in the triclinic space group $P\bar{1}$ with $Z = 1$. This results in the molecule lying on an inversion centre, imposing a 50% statistical disorder on the Cl–Rh–CO moiety.

All bond lengths and angles for compounds **1**, **3** and **4** are within normal ranges for this type of compound. All angles within the Rh coordination sphere are close to those expected for a square-planar environment, the Rh atom being typically displaced slightly from the coordination plane. The Rh atom is displaced 0.0148(13) Å from the coordination plane (rms error of fitted atoms = 0.0089) for *trans*-[Rh(CO)Cl{P(CH₂C₆H₅)₃]₂, **1**. A displacement of 0.009(5) Å from the coordination plane (rms error of fitted atoms = 0.0088) is observed for *trans*-[Rh(CO)Cl{P(O-2-MeC₆H₄)₃]₂, **3**. Finally Rh1 and Rh2 atoms are displaced –0.004(5) and 0.015(5) Å from the coordination planes (rms deviation of fitted atoms = 0.0043 and 0.0154 respectively) for *trans*-[Rh(CO)Cl{P(O-2,6-Me₂C₆H₃)₂]₂, **4**.

In compound **1**, only one tribenzylphosphine has one substituent close to the coordination plane, i.e. C4 while the other phosphine shows a –30.21(18)° torsion angle

with the coordination plane. This results in an orientation of the two phosphines showing a pseudo inversion centre similar to that found in the complexes with statistical disorders. It should also be noted that a similar interaction with the metal centre is present in the other structures containing the 50% statistical disorder.

Torsion angles C–Rh–P–O show one substituent close to the coordination plane on each side of the Cl–Rh–CO moiety for both compounds **3** and **4**. Several intra- and intermolecular interactions were also observed for both compounds, though some of these should be regarded with some skepticism. On the other hand, some of these interactions are similar to the intra molecular interactions found in *trans*-[Rh(CO)Cl{P(OC₆H₅)₃]₂, **2**. An agostic interaction [33] between rhodium and a phenyl ring H atom, affording a pseudo octahedral coordination environment for the metal centre, is also observed. The latter interaction could also be regarded as a factor contributing to the orientation for a crystallographic inversion centre as this is also not observed for *trans*-[Rh(CO)Cl{P(OC₆H₅)₃]₂, **2**, which did not contain the statistical disorder of the Cl–Rh–CO moiety.

In addition, an agostic interaction between the rhodium centre and a methyl group H atom on a phenyl ring, giving rise to a pseudo octahedral coordination environment around the metal centre, is also observed for compound **4**. This supports the argument that these interactions could have some influence on the disorder of the Cl–Rh–CO moiety.

Some of the most important geometrical parameters are summarized in Table 4 along with the data of other relevant structures.

Important to note is the increase (thus the weakening) of the Rh–P bond distance as methyl groups are introduced on the phenyl rings of the phosphites. This is most probably a steric effect, as it is clear that the cone-angle of the phosphites increases with increasing number of methyl groups [$\theta_E = 156, 166$ (**1**), 167 (**3**) and 182 (**4**)]. The electronic effect of Group 15 ligands in Vaska-type compounds was discussed earlier [12]. The electronic effect is reflected in the CO stretching frequency, which decreases only slightly for the three phosphite complexes [$\nu_{CO} = 2016$ (**2**), 2011 (**3**) and 2004 cm^{–1} (**4**)]. As expected, the *trans*-

[Rh(CO)Cl{P(CH₂C₆H₅)₃}₂] (**1**, $\nu_{\text{CO}} = 1968 \text{ cm}^{-1}$) complex, having a different electronic nature due to the lack of electron withdrawing oxygen atoms, is at the bottom of this range.

As mentioned previously, only one other single crystal structure of an aryl phosphite containing rhodium Vaska-type complex existed in the literature [18] prior to our studies. The value of the Rh–P bond distance for this complex also fits nicely into the range of studied complexes (Table 4). Furthermore, a steady increase in steric profile, as expressed by the Tolman (θ_{T}) and the effective (θ_{E}) cone angles, is noted in going from P(OC₆H₅)₃ to P(O-2,6-Me₂C₆H₃)₃. It also seems that the phosphite P(O-2-*t*BuC₆H₄) has the same steric bulk as that of P(O-2,6-Me₂C₆H₃)₃, as expressed in the Tolman cone angles (θ_{T}) of 182° for P(O-2,6-Me₂C₆H₃)₃ and 181° for P(O-2-*t*BuC₆H₄) respectively. Like compound **4**, the Vaska-type compound containing the P(O-2-*t*BuC₆H₄) phosphite ligand was reported to be disordered around the Cl–Rh–CO moiety [18].

The use of flexible aryl phosphine and phosphite ligands gives mixed results for the statistical disorder on Vaska-type complexes of rhodium. However, several aspects are noted which could have an influence on the disorder. It appears that substituents at *ortho* positions of the phenyl rings tend to yield structures containing the statistical disorder. These substituents appear to ‘shield’ the Cl–Rh–CO moiety from neighboring molecules, allowing the molecules to pack in a disordered fashion and preventing intermolecular interactions.

Furthermore, the conformation of the substituents on the phosphorous atom should also be taken into account. In all the studied cases two substituents are bent towards the metal centre while the other one is pointing away. This is the crystallographically most observed conformation for phosphite ligands in metal complexes [34]. Complexes where all three OR groups are bent towards the metal, such as in the P(OC₆H₅)₃ cobalt complex [35] or where all three groups are bent away, appear to be quite rare [34]. The substituents bent towards the metal centre also allows for H···Rh interactions, which surprisingly seems not to affect the disordered packing as this appear in both disordered and non-disordered structures, e.g. **1** vs. **3**.

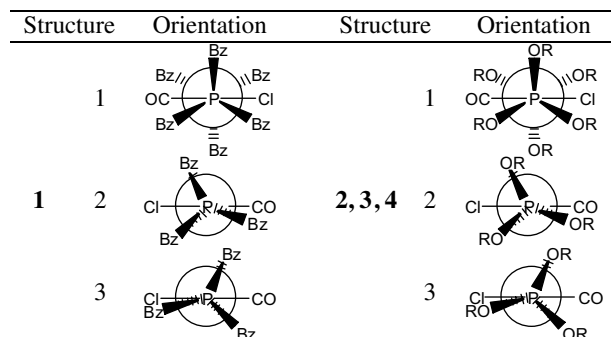


Fig. 3. Various optimized conformations of the complexes **1–4**.

Table 5

Conformation	P(OC ₆ H ₅) ₃			P(O-2-MeC ₆ H ₄) ₃			P(O-2,6-Me ₂ C ₆ H ₃) ₃		
	Experiment ^f	Calculated		Experiment ^c	Calculated		Experiment ^f	Calculated	
<i>Lengths</i>									
Rh–Cl	2.480	2.478	2.469	2.437	2.438	2.439	2.434	2.436	2.435
Rh–P	2.463	2.365	2.469	2.437	2.438	2.439	2.434	2.436	2.435
Rh–P	2.396	2.316	2.435	2.381	2.375	2.382	2.380	2.389	2.423
Rh–C	1.871	1.857	1.827	1.866	1.865	1.863	1.862	1.861	1.865
C–O	1.183	1.188	1.192	1.177	1.177	1.178	1.178	1.170	1.180
<i>Angles</i>									
Cl–Rh–P	85.3	86.2	87.7	88.2	87.1	85.6	87.7	87.8	87.5
C–Rh–P	94.7	93.9	92.4	91.8	92.9	94.4	92.3	93.3	92.5
Rh–C	–	175.6	179.4	177.0	179.1	179.8	179.2	179.8	178.4
P–Rh–P	170.6	171.8	174.9	175.8	174.1	171.1	175.4	171.5	175.0
Ox–Rh–P–O ^g	–	–30.2/–1.6	–14.6/32.6	–27.5/2.7	–1.1/–0.7	0.9/5.8	–1.7/11.8	–3.5/–10.5	–4.5/–59.8
O–P–P–O ^h	–	–12.3	41.5	–25.4	–1.9	7.0	10.2	–14.4	–64.1

^a Bond lengths in Å, bond angles in degrees. Computationally determined structures using LANL2DZ basis set and B3LYP DFT model.

^b C_{2v} symmetry, from reference 32.

^c Ref. [19].

^d This work.

^e Ref. [20].

^f Ref. [21].

^g Torsion angle between carbonyl oxygen (Ox) and C/O substituent on P atom closest to Rh–C=O moiety.

^h Torsion angle denoting relative staggered/eclipsed (ideal = 60 / 0 deg) stereochemistry between two C/O substituents on different P atoms closest to Rh–C=O moiety.

Though the structures of **1** and **2** appear to be similar, they show significant differences in their orientations of phosphorous substituents. This is clearly observed by comparing the torsion angles.

3.2. Theoretical calculations

Previous data on calculated structures for the model Vaska complexes $trans\text{-}[\text{Rh}(\text{CO})\text{X}(\text{PY}_3)_2]$ ($\text{X} = \text{NCO}$, NCS , $\text{Y} = \text{H}$, Me) demonstrate that structural and vibrational trends of these complexes can be reliably predicted using the B3LYP DFT model [36]. The bond distances and angles from crystal structures were in agreement with the values predicted theoretically [36]. Similarly, theoretical calculations on $trans\text{-}[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ predicted small energy differences between the staggered and eclipsed conformations, with the eclipsed conformation more stable [37].

The determination of geometrical conformation for all four complexes was performed using the molecular structure determined by X-ray crystallography as the starting point for DFT calculations. In order to find the global minimum for the structural conformations of the four compounds, various starting geometries were selected from the crystal structures. These were: (i) Optimization of the crystal structure geometry. (ii) Optimization of the crystal structure geometry with both ligands rotated 180° . (iii) Optimization of the crystal structure geometry with one of the ligands rotated 180° . The resulting optimized conformations, with a view down the P–Rh–P axis, are illustrated in Fig. 3. The energy differences between these optimized structures were expected to give an indication which parameters influence the statistical disorder in some of the studied complexes. Data obtained from the various geometrical optimizations are summarized in Table 5 as well as the appropriate geometrical parameters from the

crystallographic data. For comparison the data on previously calculated structures of $trans\text{-}[\text{Rh}(\text{CO})\text{Cl}(\text{PY}_3)_2]$ ($\text{Y} = \text{H}$, Me) [37] are also included in Table 5.

The calculations gave mixed results as to the lowest energy conformation of the optimized structures. For complexes **1** and **2**, the calculated lowest energy conformation agrees with the conformation of the solid state structure. However, for complexes **3** and **4**, the calculated lowest energy conformation seems to be a different conformation from the crystallized one. It must be kept in mind, though, that the calculated conformations reflect a gas-state without polarity or diffuse functions, rather than a solid state conformation. There might, therefore, be an indication that packing effects are dominant in the structures of **3** and **4**. In addition, compounds **1** and **2** are non-disordered around the Cl–Rh–CO moiety, and compounds **3** and **4** are disordered around that moiety.

There is a fair agreement between the calculated and the solid state structures. In Fig. 4, the superimposed calculated and solid state structures are presented. The optimized bond distances agree well with the experimental ones. All calculated bond distances are approximately 10% longer than the corresponding bond distances in the solid state structures, which is typical for DFT calculations, see Table 5.

The differences between the calculated and solid state structures are mostly in the orientation of the phenyl-rings in the structures. The overall rms overlay differences of the various structures are: 1.504 Å for **1**, 1.518 Å for **2**, 1.478 Å for **3** and 1.523 Å for **4**, which are quite large. The rms overlay difference of the coordination polyhedron, however, are small. For an overlap of the Rh, Cl, C (of the CO) and the 2P atoms, an error of 0.122 (**1**), 0.090 (**2**), 0.088 (**3**) and 0.094 Å (**4**) was calculated. No obvious differences between disordered and non-disordered structure can

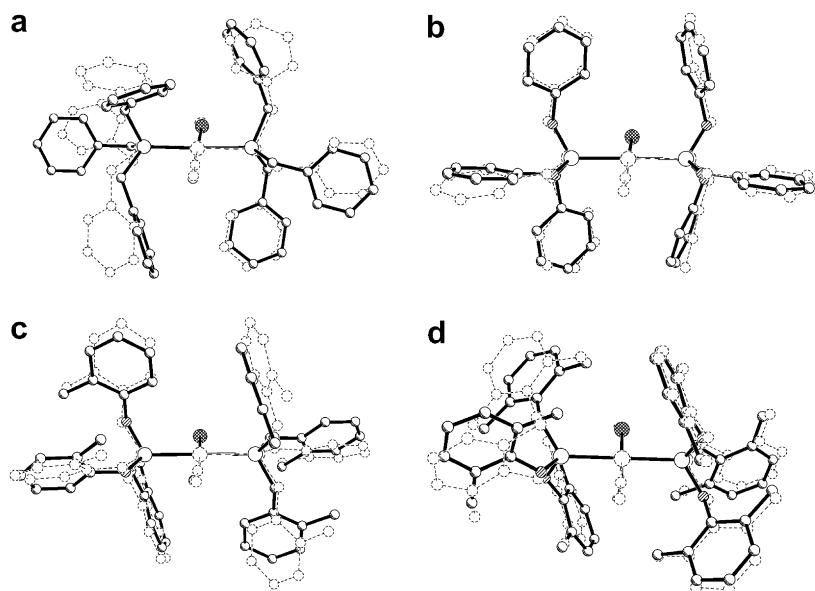


Fig. 4. Superimposed drawings of molecular (solid) and calculated (dashed, See Table 5 for conformers used) structures of (a) $trans\text{-}[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{CH}_2\text{Ph})_3\}_2]$, **1**; (b) $trans\text{-}[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$, **2**; (c) $trans\text{-}[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{O}-2\text{-MeC}_6\text{H}_4)_3\}_2]$, **3** and (d) $trans\text{-}[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\}_2]$, **4**.

be observed and the differences between the calculated (at least at the level of theory used in this study) and solid state structures can be assumed due to packing effects.

4. Conclusions

The results of structural analysis using X-ray crystallography and DFT calculations on four related complexes of the type *trans*-[Rh(CO)Cl(PR₃)₂] are presented. Two of these structures show statistical disorder in the solid state around the Cl–Rh–CO moiety, while the other two are non-disordered. The solid state structures of all four compounds show similar structural features. DFT calculations show reasonable agreement with the structures found in X-ray crystallography as shown by an rms overlay error of ~1.5 Å for the complete structures, and ~0.10 Å for the coordination polyhedron. The calculations did not provide more insight into the reasons why some of these structures show statistical disorder around the Cl–Rh–CO moiety.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.09.025](https://doi.org/10.1016/j.jorganchem.2006.09.025).

References

- [1] M. Angoletta, *Gazz. Chim. Ital.* 89 (1959) 2359.
- [2] L. Vaska, J.W. DiLuzio, *J. Am. Chem. Soc.* 83 (1961) 2784.
- [3] L. Vallarino, *J. Chem. Soc.* (1957) 2287.
- [4] J. Chatt, B. Shaw, *Chem. Ind.* (1961) 290.
- [5] See for example H.A. Zahalka, H. Alper, *Organometallics* 5 (1986) 2597.
- [6] See for example M. Selke, W.L. Karney, S.I. Kahn, C.S. Foote, *Inorg. Chem.* 34 (1995) 5715, and references cited therein.
- [7] J. Chatt, L.A. Duncanson, *J. Chem. Soc.* (1953) 2939.
- [8] (a) M.C. Baird, G. Wilkinson, *J. Chem. Soc., Chem. Commun.* (1966) 267;
(b) M.J. Mays, G. Wilkinson, *J. Chem. Soc.* (1965) 6629;
(c) I.C. Douek, G. Wilkinson, *J. Chem. Soc. A* (1969) 2604.
- [9] G.O. Spessard, G.L. Miessler, *Organometallic Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1997.
- [10] W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1995.
- [11] C.A. Tolman, *Chem. Rev.* 77 (1977) 313.
- [12] A. Roodt, S. Otto, G. Steyl, *Coord. Chem. Rev.* 245 (2003) 121.
- [13] (a) S. Otto, A. Roodt, J. Smith, *Inorg. Chim. Acta* 303 (2000) 295;
(b) S. Otto, *Acta Cryst. C* 57 (2001) 793.
- [14] A.J. Muller, Ph.D. Thesis, University of Johannesburg, 2005.
- [15] M. Liwu, M.J. Desmond, R.S. Drago, *Inorg. Chem.* 18 (1979) 679.
- [16] L.S. Gracheva, E. N Yurchenko, A.D. Triotskaya, *Koord. Khim.* 3 (1977) 1718.
- [17] L. Vallarino, *J. Chem. Soc.* (1957) 2473.
- [18] E. Fernandez, A. Ruiz, C. Claver, S. Castillon, A. Polo, J.F. Piniella, A. Alvarez-Larena, *Organometallics* 17 (1998) 2857.
- [19] A. Muller, A. Roodt, S. Otto, Å. Oskarsson, S. Yong, *Acta Cryst. E* 58 (2002) m715.
- [20] R. Meijboom, A. Muller, A. Roodt, *Acta Cryst. E* 60 (2004) m1071.
- [21] R. Meijboom, A. Muller, A. Roodt, *Acta Cryst. E* 60 (2004) m455.
- [22] D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1988.
- [23] J.A. McCleverty, G. Wilkinson, *Inorg. Synth.* 28 (1990) 84.
- [24] P.W.N.M. van Leeuwen, C.F. Robeek, *J. Organomet. Chem.* 258 (1983) 343.
- [25] SAINT, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1995.
- [26] Bruker SAINT-plus, Version 6.02 (including XRPEP). Bruker AXS, Inc., Madison, Wisconsin, USA, 1999.
- [27] G.M. Sheldrick, SHELXL97, Program for solving crystal structures, University of Göttingen, Göttingen, Germany, 1997.
- [28] K. Brandenburg, M. Berndt, DIAMOND, 1999, Version 2.1c. Crystal Impact GbR, Bonn, Germany.
- [29] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.01, Gaussian, Inc., Pittsburgh, PA, 2003.
- [30] (a) A.D. Becke, *Phys. Rev. A* 38 (1988) 3098;
(b) A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648;
(c) C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [31] (a) T.H. Dunning Jr., P.J. Hay, in: H.F. Schaefer III (Ed.), *Modern Theoretical Chemistry*, 3, Plenum, New York, 1976, pp. 1–28;
(b) P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 270;
(c) W.R. Wadt, P.J. Hay, *J. Chem. Phys.* 82 (1985) 284;
(d) P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [32] Hyperchem Molecular Modeling System, Version 7.52. Hypercube, 2002.
- [33] Various intra- and intermolecular interactions have been observed in the past. See [12] and references cited therein.
- [34] K.A. Bunten, L. Chen, A.L. Fernandez, A.J. Poë, *Coord. Chem. Rev.* 233–234 (2002) 41.
- [35] M. Haumann, R. Meijboom, J.R. Moss, A. Roodt, *Dalton Trans.* (2004) 1679.
- [36] E.A. Salter, A. Wierzbicki, *J. Mol. Struct. (THEOCHEM)* 425 (1998) 101.
- [37] A. Wierzbicki, E.A. Salter, N.W. Hoffman, E.D. Stevens, L.V. Do, M.S. VanLoock, J.D. Madura, *J. Phys. Chem.* 100 (1996) 11250.