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Chloro-carbonyl disorder determination in Vaska-type complexes

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An investigation into the effect of mixed phenyl-cyclohexyl substituted aryl tertiary phosphines on the disorder of the Cl–Rh–CO moiety in Vaska-type complexes *trans*-[M(CO)Cl($PPh_nCy_{3-n})_2$], where M = Rh(I) or Ir(I), Ph = C_6H_5, Cy = C_6H_{11} and n = 1 or 2, is presented. Single crystal X-ray analysis of four examples of the series is reported and compared with related structures which often reveal disorder of the Cl–Rh–CO moiety, governed by crystallographic symmetry. DFT geometry optimisations and energy calculations on conformers of these complexes are within reasonable agreement that the disorder is likely. An unexpected disorder between phenyl and cyclohexyl substituents of the phosphines is also discussed.

Keywords: Vaska, disorder, X-ray structure, DFT calculation

Chloro-karboniel vastetoestand-wanordebepaling in Vaska tipe komplekse: 'n Ondersoek na die effek van gemengde feniel-sikloheksiel gesubstitueerde ariel tersiêre fosfiene op die vastetoestandwanorde van die Cl–Rh–CO-groep in Vaska-tipe komplekse *trans*-[M(CO)Cl($PPh_nCy_{3-n})_2$], waar M = Rh(I) of Ir(I), Ph = C_6H_5, Cy = C_6H_{11} en n = 1 of 2, word aangebied. Enkelkristal X-straalstrukture van 4 voorbeelde van die reeks word geraporteer en vergelyk met verwante strukture wat dikwels die wanorde van die Cl–Rh–CO-groep, wat deur kristallografiese simmetrie beheer word, openbaar. Digtheids funksionele teorie (DFT) geometrie-optimalisering en energieberekenings op konformere van hierdie komplekse dui aan dat die wanorde waarskynlik is. 'n Onverwagte vastetoestandwanorde tussen feniel- en sikloheksielsubstituente van die fosfiene word ook bespreek.

Sleutelwoorde: Vaska; wanorde, X-straalstruktuur; DFT berekening

Introduction

Complexes with the general formula *trans*-[Rh(CO)$X(L)_2$] (X = halide or *pseudo*-halide; L = aryl or alkyl substituted tertiary phosphorus ligand) are in many instances referred to as Vaska-type complexes (Ohgomori and Watanabe 1990; Galding et al. 2016; Smoleński et al. 2011; Roodt et al. 2003), a name linked to the work of Vaska and DiLuzio, 1961 on the original *trans*-[Ir(CO)Cl($PPh_3)_2$] complex. The history behind the naming is somewhat controversial since Angoletta, 1959 already described the complex two years prior to the work of Vaska and DiLuzio and even at that time, the rhodium analogue had already been reported (Vallarino 1957) and investigated to some extent by Chatt and co-workers (Winterton and Leigh 2002). The trail of events that led to the fixation of the name is detailed in a 50th anniversary article of the complex (Kirss 2013); the reasons mainly ascribed to earlier, incorrect identification of the compound and the wider impact of the journal used by Vaska. Nevertheless, the Vaska-type complexes studied by Chatt enabled the application of theories that have been developed in today's textbooks.

The rhodium Vaska-type complex, *trans*-[RhCl(CO)($PPh_3)_2$], was shown to be an effective homogeneous catalyst for the hydrogenation of olefins and acetylenes in organic solvents (Osborn et al. 1966). However, the iridium Vaska-type complexes are even more reactive and readily form adducts with numerous molecules such as H_2, O_2, SO_2, CO, HCl and RX (R = organic fragment; X = halogen) (Collman and Hegedus 1980). As these complexes can partake in a series of elementary reactions that are key steps in the catalytic synthesis of organic products (Pignolet 1983), it is thus important to understand their characteristics in order to have kinetic control over the cycle. It is here that the tertiary phosphines play a vital role due to their tailoring ability, either electronically or sterically, and have proven their

importance in the role of catalysis (van Leeuwen 2004), although several advances in the area (Roodt et al. 2003; Muller et al. 2008) to understand the tailoring, steric and electronic properties of phosphines remain a challenge to identify and separate. Amongst these attempts to interpret ligand effects is the QALE (Quantitative Analysis of Ligand Effects) model (Fernandez et al. 2003). This approach makes use of the classical model of phosphorus σ-donation to the metal centre and π-back donation from the metal centre as developed by Dewar 1951 and Chatt and Duncanson 1953. It also considers the bulkiness of the ligand and incorporates a steric switching parameter to compensate when steric effects become significant.

The Vaska complexes and their analogues also lend themselves as important candidates to the evaluation of these phosphine ligands as they contain several convenient probes: a) In the case of Rh Vaska-type complexes, the $^{1}J_{Rh\text{-}P}$ coupling values in ^{31}P-NMR, b) IR ν(CO) stretching frequencies which are indirectly influenced by the σ-donating and π-back donation ability of the phosphine and c) the easy crystalising nature of Vaska complexes that lend access to single crystal X-ray crystallographic geometrical data of both M–P and M–CO distances (Roodt et al. 2003). All of these techniques are very sensitive to substituent changes on the phosphorus centre. However, an interesting crystallographic disorder phenomenon plagues Vaska complexes, *i.e.* they often crystallise with the metal on a crystallographic inversion centre. This symmetry is then also transferred to the molecule with the metal accepting a *pseudo*-inversion symmetry, and the ligands related through inversion as well. In effect, this implies that the two trans phosphine ligands must have a perfectly staggered conformation (viewed along the P–M–P bond), but more concerning is that the chlorido and carbonyl in the Cl–M–CO moiety show a packing disorder of which the distribution is exactly 50:50 on both sides of the square-planar coordination environment. (see Figure 1). This direction of the Cl–M–CO is not necessarily alternating with every adjacent unit cell and may be regarded as random. However, in this case it statistically adds up to an equal packing disorder distribution over all unit cells. This "equal" distribution results in the observed crystallographic symmetry element in the single crystal X-ray data, and it has become common practice in literature to refer to this type of Cl–M–CO packing in Vaska-type complexes as a statistical disorder due to the association with crystallographic symmetry.

This often creates problematic refinement of single crystal data, where restraints sometimes have to be applied, resulting in less accurate bond distances/angles, and thus rendering data unreliable for subtle changes induced by substituents on the phosphorus centre. In the case of *trans*-[IrCl(CO)(PPh_3)$_2$], the Cambridge Crystallographic Database (Groom et al. 2016) reveals two disordered polymorphs (Churchill et al. 1988; Blake et al. 1991), and eleven entries for the Rh-PPh_3 Vaska-type analogue (Del Pra et al. 1979; Ceriotti et al. 1983; Rheingold and Gieb 1987; Chen et al. 1991; Kemp et al. 1995; Mills et al. 2002; Chaloner et al. 1991; Dunbar and Haefner 1992; Sharma et al. 1988; Lorenzini et al. 2016; Ren et al. 2017). For the Rh-PPh_3 Vaska-type structures those in a monoclinic space group were reported as non-disordered, whereas the triclinic and orthorhombic examples as disordered. In some of the disordered cases, the Rh–Cl and Rh–C distances were taken from the non-disordered samples to assist the restraint refinements. A further search for Vaska-type complexes with the more bulky cyclohexyl substituent on the phosphorus atom, *i.e. trans*-[MCl(CO)(PCy_3)$_2$] (M = Rh(I) or Ir(I)), appears to be all disordered in triclinic space group Pī (Wilson et al. 2002; Kuwabara and Bau 1994; Churchill et al. 1994; Clarke et al. 2002; Grobbelaar et al. 2009). Thus, it seems that a possible source for the disorder might be the varying steric bulk on the phosphorus centre as the Tolman cone angle values (determined from CPK models) for PPh_3 and PCy_3 span over a large range of 145° to 170°. To test this postulate, Vaska-type complexes of Rh(I) and Ir(I) with phosphine ligands having steric bulk between PPh_3 and PCy_3 were prepared and the results are reported in this paper. To minimise other factors that may play a role in the disordered packing, phosphine ligands having mixtures of phenyl and cyclohexyl substituents were used. Thus, reported here are the structures of Rh(I) and Ir(I) Vaska-type complexes containing the phosphines PPh_2Cy and $PPhCy_2$ as well as an in-depth investigation in an attempt to pinpoint the origin of the Cl–M–CO disorder.

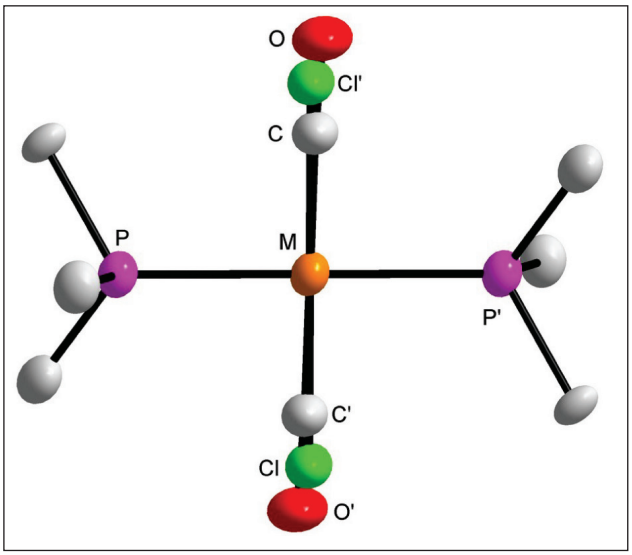


FIGURE 1: Simplified structure representation of the Cl–M–CO disorder found in X-ray structures of Vaska-type complexes. Accented lettering indicates atoms generated by crystallographic symmetry operation, in this case an inversion centre.

Materials and methods

Chemicals and instrumentation

Acetone, ethanol, methanol, dichloromethane, hexane, phosphorus pentoxide, cyclohexyldiphenyl phosphine (PPh_2Cy), dicyclohexylphenyl phosphine ($PPhCy_2$), hydroquinone, *cis,cis*-1,5 cyclooctadiene (all from Sigma-Aldrich), $RhCl_3.xH_2O$ and $H_2IrCl_6.6H_2O$ (all from Next Chimica) were used as received. NMR spectra were recorded on a Varian Inova 300 MHz spectrometer (^1H: 300 MHz, ^{31}P: 121.46 MHz) at ambient temperature and were calibrated to the residual protonated impurities in the $CDCl_3$ solvent ($CHCl_3$ = 7.24 ppm) and a sealed capillary containing 85% H_3PO_4 (at zero ppm), respectively. ^{31}P NMR spectra are proton decoupled. Infrared spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer and analysed with the Bruker OPUS-NT software. The ν(CO) IR data were recorded in $CHCl_3$ solution since packing effects induced at the M–CO bond have been shown to potentially induce a significant influence on the values (Kemp et al. 1995). This renders solid-state measurements unreliable and therefore infrared data for solution spectra were collected using NaCl windows (optical path length 0.1 mm).

Single crystal data were collected on a Bruker SMART system with a 1K CCD camera using Mo Kα λ 0.71073 Å. All data collections were done at room temperature. Data were collected using the SMART (Bruker 1998) program system with ω-scans, cell refinement and data reduction were done with SAINT-Plus and XPREP (Bruker 1999). All structures were solved using the SIR97 (Altomare et al. 1999) package while molecular graphics were prepared with DIAMOND (Brandenburg and Berndt 2001). Multi-scan absorption techniques were applied to all data using SADABS (Bruker 1998), and all data were refined using full-matrix least-squares on F^2. The aromatic, methane and methylene H atoms were placed in geometrically idealised positions (C-H = 0.97-0.98) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Disorders on the Cl–M–CO entity were refined unrestrained, while the phenyl-cyclohexyl disorders were treated by refinement of two positions for each component, with geometric restraints (SAME, FLAT, SIMU and DELU) where necessary to keep the refinement stable. Care was taken that all fractions of disordered atomic sites should add up to integer numbers. All data were checked for decay by collecting the first 50 frames again after the complete data collection, and decomposition was negligible within experimental error for all data. Online checkCIF results indicated no serious alert level A warnings for all data sets, except for *trans*-$[Rh(CO)Cl(PPh_2Cy)_2]$ which showed three alert level B warnings, possibly due to weak high angle data. These were left untreated as data proved to be adequate for the refinement of all the disorders within the molecule.

For determination of the steric demand, crystallographic cone angles were calculated with Steric (Taverner 1996). Adaptions were made from the Tolman cone angle model (Tolman 1977) where the orientation of the substituents are taken from crystallographic data (instead of a CPK model), and the M–PR_3 bond distance adjusted to 2.28 Å (to normalise any influence this variation may have on the cone size) (Müller and Mingos 1995; Otto et al. 2000). As most parts of the phosphines studied here are disordered, values were calculated for both components before averaging. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles, hydrogen coordinates and hydrogen bonding interactions are provided.

DFT calculations were performed on the Rh Vaska-type complexes of PPh_2Cy and $PPhCy_2$ using the Gaussian03 (Frisch et al. 2004) package to allow more insight in the geometrical conformations of the prepared Vaska-type complexes. Several starting structures were identified due to the disorders present and, in each case, were carefully examined to avoid duplicates of input geometries. These were optimised without constraints at a B3LYP/LanL2DZ level of theory. Minima were verified *via* frequency analysis of the stationary point. Topological analysis of the wave functions for the free phosphine series $PPh_{3-n}Cy_n$, n = 0 to 3, utilising Gaussian03 was conducted to generate an electrostatic potential cube file from the optimised geometry (B3LYP/6–31G(d,p)), Vesta (Momma and Izumi 2011) to visualise the potential surface from the cube file to obtain a rough representation of the negative potential surface and Univis 2000 (Limaye and Gadre 2001) to select two coordinates from this surface. These surface coordinates were then inserted into Gaussian03 to compute the optimised values for the molecular electrostatic potential minimum value (V_{min}).

General synthesis

Various synthetic routes for Vaska-type complexes of Rh(I) and Ir(I) exist. For rhodium the method preferred here was sublimation of the $[Rh(Cl)(CO)_2]_2$ dimer from the $RhCl_3.xH_2O$ salt under a carbon monoxide atmosphere (McCleverty et al. 1990). The $[Rh(Cl)(CO)_2]_2$ dimer is relatively stable and can be stored for a few years with only a small amount of sublimation occurring. The Vaska-type complexes can be readily produced from it by simple stoichiometric addition of the phosphine at room temperature in a suitable solvent. For the iridium Vaska complexes, virtually any chloride salt of iridium can be heated with a phosphine and a carbon monoxide source. For the current study the $[Ir(Cl)(cod)_2]_2$ dimer was first prepared from the $H_2IrCl_6.xH_2O$ salt (Bezman et al. 1980). This dimer is also stable and allows for synthesis of the iridium Vaska-type compounds at room temperature. The procedure for preparing Ir(I) Vaska-type analogous compounds from the dimer is somewhat different compared to that of the Rh analogue; here the steric size of the phosphine ligand is first taken into account. As described by Burk and Crabtree 1986: if the phosphine ligand has a small Tolman cone angle, bubbling CO gas through a solution containing the dimer will replace the cod ligands. This is then followed by

adding the phosphine ligand giving the desired product. For more bulky phosphines, this sequence is reversed, *i.e.* the phosphine ligand is added first and then followed by bubbling of CO gas. In our case the latter provided the best results for the Ir(I) Vaska complexes. For both Rh and Ir Vaska-type complexes crystals suitable for single crystal X-ray data collection were obtained directly from the reaction mixture. Detailed experimental procedures and analytical data of the precursors and products are provided in the supplementary material.

Results and discussion

Crystal data, details of the data collection and refinement parameters for *trans*-[MCl(CO)(PPh_2Cy)$_2$] (M=Rh (**1**), Ir (**3**)) en [MCl(CO)($PPhCy_2$)$_2$] (M=Rh (**2**), Ir (**4**)) are summarised in Table 1. As the molecular diagrams for **1** and **3** are very similar, and those of **2** and **4** as well, only **1** and **2** are shown in Figure 2. For structural comparison with literature, the data of the isomorphous *trans*-[MCl(CO)(PX_3)$_2$] (M=Rh, Ir; X = Ph, Cy) from Chen et al. 1991 and Wilson et al. 2002 (for Rh-PPh_3/PCy_3 samples), and Churchill et al. 1994 and Kuwabara and Bau 1994 (for Ir-PPh_3/PCy_3 samples) were used in order to eliminate possible packing effects from different space group arrangements. It should also be noted that all data collections, here and reported, are at room temperature, and should also eliminate any temperature effects.[1] The decision for room temperature X-ray data collections for **1** to **4** was also supported by the fact that all the disorders encountered could be clearly elucidated with relative ease. Additionally, it was anticipated that the increase in geometrical accuracy obtained from lower temperature data collections would reveal similar trends as already observed for the room temperature data sets. Moreover, the possibility of polymorphs crystalising at low temperatures was also eliminated.

The crystal structures of **1** to **4** show that molecules are situated on a crystallographic inversion centre of symmetry imposing a 50% statistical disorder on the Cl–Rh–CO moiety. An initial observation would be that neither the electronic effect nor the steric size induced on the phosphine ligands have any effect on the outcome of the Cl–M–CO disorder. However, closer investigation of the complexes reveals several aspects that may be indicative of why this occurs.

The initial refinement of the structures shows phenyl rings deviate from planarity and cyclohexyl rings are not completely adopting a chair conformation. Thermal ellipsoids for some the carbon atoms in these rings also appear to be larger than usual and are indicative of disorder (see Figure 3 as example). In the case of the PPh_2Cy samples one of the phenyl rings appears to be less distorted, *i.e.* < 5°

TABLE 1: Crystallographic data collection and refinement parameters for complexes *trans*-[MCl(CO)(PPh_nCy_{3-n})$_2$] (M=Ir, Rh; n=1,2).*

Identification code[a]	$RhPh_2Cy$ (**1**)	$RhPhCy_2$ (**2**)	$IrPh_2Cy$ (**3**)	$IrPhCy_2$ (**4**)
Empirical formula	$C_{37}H_{42}ClOP_2Rh$	$C_{37}H_{54}ClOP_2Rh$	$C_{37}H_{42}ClIrOP_2$	$C_{37}H_{54}ClIrOP_2$
Formula weight	703.01	715.10	792.30	804.39
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions:				
a(Å)	9.469(13)	9.4969(19)	9.4689(19)	9.5126(19)
b(Å)	10.129(19)	10.211(2)	10.062(2)	10.241(2)
c(Å)	10.826(13)	10.886(2)	10.878(2)	10.904(2)
α(°)	116.25(2)	113.69(3)	116.58(3)	113.82(3)
β(°)	105.83(2)	107.27(3)	105.98(3)	107.33(3)
γ(°)	92.66(3)	91.41(3)	92.49(3)	91.43(3)
Volume (Å^3)	879(2)	910.5(3)	874.2(3)	914.7(3)
Z	1	1	1	1
Calculated density (Mg/m^3)	1.328	1.304	1.505	1.46
Absoption coefficient (mm^{-1})	0.680	0.657	4.013	3.836
F(000)	364	376	396	408
Crystal size (mm)	0.40x0.25x0.10	0.26x0.14x0.13	0.13x0.10x0.08	0.20x0.13x0.10
θ range / completenes foor collection (°)	2.2 - 28.0/99.7%	2.2 - 27.5/97.7%	2.2 - 28.0/99.7%	2.2 - 27.5/99.5%
Limiting indices	-12≤h≤12 -13≤k≤12 -14≤l≤14	-12≤h≤12 -12≤k≤13 -14≤l≤9	-6≤h≤12 -13≤k≤13 -14≤l≤14	-12≤h≤11 -13≤k≤12 -14≤l≤14
Reflections collected / unique / observed (I>2σ(I))	7511/4229/3361 R(int) = 0.1829	6016/4085/3613 R(int) = 0.0177	7600/4214/3509 R(int) = 0.0394	7466/4185/4116 R(int) = 0.0282
Max. and min. transmission	0.9352 - 0.7727	0.9195 - 0.8478	0.7396 - 0.6235	0.7003 - 0.5142
Data / restraints / parameters	4229 / 343 / 315	4085 / 314 / 314	4214 / 383 / 314	4185 / 329 / 314
Goodness-of-fit on F²	1.149	1.06	1.026	1.039
Finale R indekse (I>2σ(I))	R1 = 0.0505, wR2 = 0.1177	R1 = 0.0305, wR2 = 0.0664	R1 = 0.0452, wR2 = 0.0872	R1 = 0.0290, wR2 = 0.0584
indices (all data)	R1 = 0.0754, wR2 = 0.1567	R1 = 0.0382, wR2 = 0.0696	R1 = 0.0631, wR2 = 0.0950	R1 = 0.0301, wR2 = 0.0590
Extinction coefficient	0.015(3)	-	-	-
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e.Å^{-3})	1.230 and -1.450	0.282 and -0.329	1.623 and -0.545	0.797 and -0.457

* The data for the four crystal structures have been deposited in the Cambridge Crystallographic Structural Database with Reference Numbers: 1949313 -1949316, and are available for free on request.

[a]Identification codes for single crystal structures: $RhPh_2Cy$ = *trans*-[RhCl(CO)(PPh_2Cy)$_2$], $RhPhCy_2$ = *trans*-[RhCl(CO)($PPhCy_2$)$_2$], $IrPh_2Cy$ = *trans*-[IrCl(CO)(PPh_2Cy)$_2$], $IrPhCy_2$ = *trans*-[IrCl(CO)($PPhCy_2$)$_2$]

1. *Cf.* Ir–Cl distances in *trans*-[IrCl(CO)(PPh_3)$_2$] at 2.382(3) Å *vs.* 2.306(8) Å for the monoclinic (Blake et al. 1991) and triclinic (Churchill et al. 1988) polymorphs. Similarly, *cf.* the small variation in Ir–C distances in *trans*-[IrCl(CO)(PCy_3)$_2$] at 1.127(10) Å *vs*. 1.10(2) Å for data collected at room temperature (Kuwabara and Bau 1994) and 100 K (Grobbelaar et al. 2009), respectively.

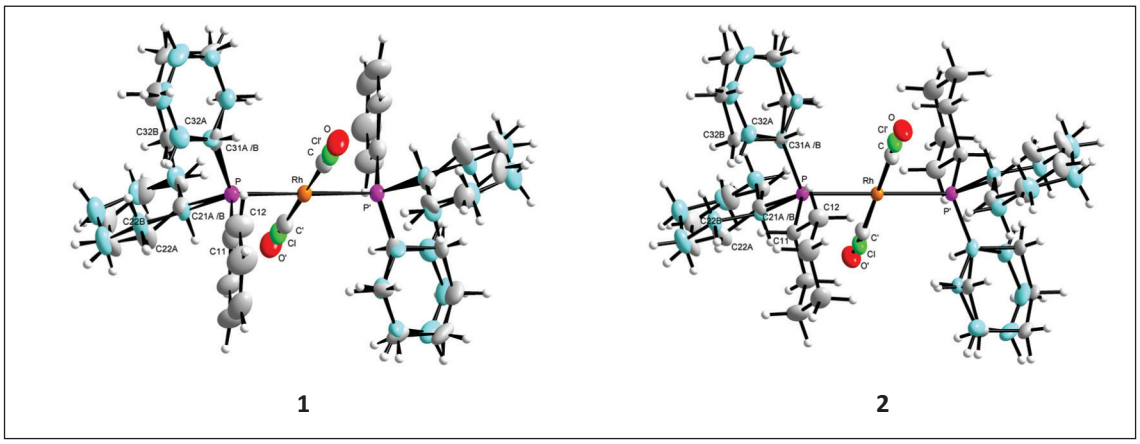


FIGURE 2: Molecular diagram showing the numbering scheme and displacement ellipsoids (30% probability) for **1** and **2**. Numbering scheme of the C-rings: first digit indicates ring number; second digit indicates number of the atom in the ring; A/B indicates disordered phenyl or cyclohexyl respectively. Disordered parts belonging together are coloured cyan or grey for clarity. Accented lettering indicates atoms generated by symmetry operation (1-x,1-y,1-z).

deviation from planarity, and in the case of the $PPhCy_2$ samples the same observation could be made for one of the cyclohexyl rings, *i.e.* < 5° deviation from the ideal 60° torsion angles observed for a chair conformation. As additional proof of the disorder of these rings, analytic data confirmed the composition of each phosphine, indicating that samples are pure. It was decided that the single crystal data of these need to be treated to disorder refinement on the phosphine ligands as well.

Attempts to refine a disorder model over all three substituents of the phosphine proved to be unstable, and the decision was made to continue with a refinement model where the disorder is addressed with one set of phenyl and cyclohexyl rings superimposed on one another. The remaining phenyl in PPh_2Cy and the cyclohexyl in $PPhCy_2$ were left untreated. This resulted in an acceptable and stable refinement of the phosphine ligands as shown in the example illustrated in Figure 4.

This type of phenyl-cyclohexyl disorder over two of the substituents is rare and only found in a handful of reported examples from the Cambridge Crystallographic Database (Groom et al. 2016).[2] This disorder is indicative of partial freedom for complete rotation at the M–P bond and although it appears that the space taken up by a phenyl to be comparable to that of a cyclohexyl, it is not entirely the case. Given that the crystal structures in the series *trans*-$[MCl(CO)(L)_2]$ (M = Rh, Ir; L = PPh_3, PPh_2Cy, $PPhCy_2$, PCy_3) are isomorphous (see unit cell dimensions in Table 1), a comparison of unit cell volumes in Table 2 shows a steady increase in unit cell volume (*ca.* 40 Å^3 for each phenyl substituted with a cyclohexyl) in the series. This clearly illustrate the size factor of cyclohexyl as it is incorporated stepwise in the series. Moreover, interesting to note is that the occupancy distribution between phenyl and cyclohexyl disorder is not equal, with the Ir(I) Vaska-type structures having the most skewed distribution of

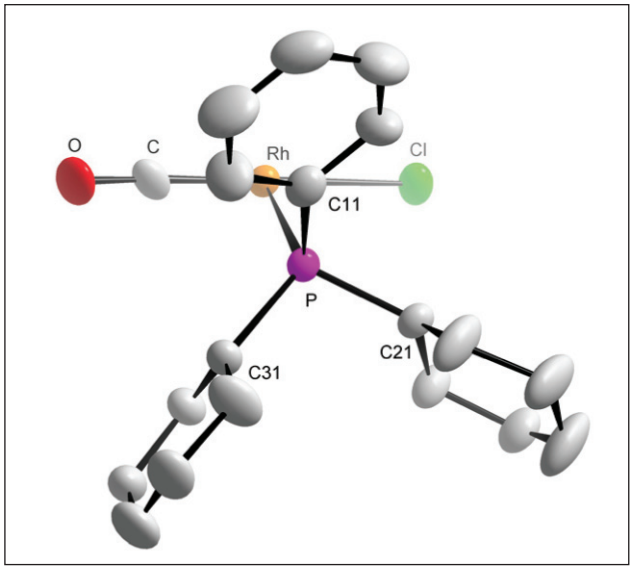


FIGURE 3: Partial molecular diagram showing differing ellipsoid sizes (30% probability) for carbon atoms of the PPh_2Cy phosphine ligand during the initial refinement of **1**.

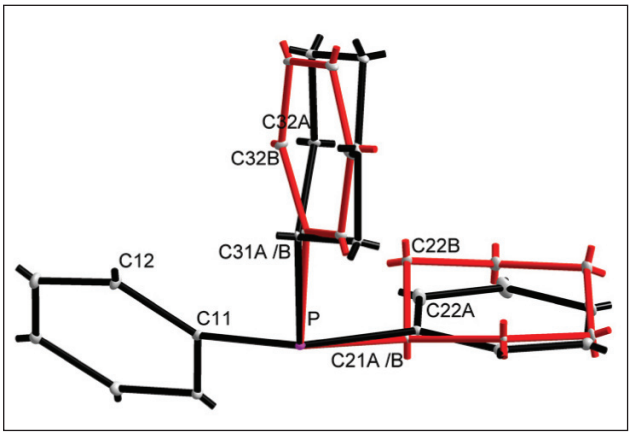


FIGURE 4: Partial wire frame diagram of **1** (phosphine only) showing the disorder present between a phenyl and cyclohexyl. The second component of the disorder is illustrated in red for clarity.

2. A search in the database for PPh_2Cy reveals 55 structures with 2 showing disorder similar to that discussed here. For $PPhCy_2$ there are 48 hits with 6 having this disorder.

60:40; an observation that could possibly be linked to the slightly larger size and reactivity of the latter metal.

TABLE 2: Unit cell volumes of Vaska-type complexes with formula *trans*-[MCl(CO)(L)$_2$] (M = Rh, Ir; L = PPh_3, PPh_2Cy, $PPhCy_2$, PCy_3).

(L)	Rh	Ir
PPh_3	815.721[a]	824.174[b]
PPh_2Cy	879(2)	874.2(3)
$PPhCy_2$	910.5(3)	914.7(3)
PCy_3	935.549[c]	935.983[d]

[a] Chen et al. 1991; [b] Wilson et al. 2002; [c] Wilson et al. 2002; [d] Kuwabara and Bau 1994

When investigating the geometrical data of the metal coordination sphere, a convenient method for comparison between the coordination environments of **1 – 4** is to calculate the displacement of the metal from the plane formed by the coordinating atoms. In the current study the metal is displaced 0.012(5), 0.001(3), -0.045(8) and -0.002(5) Å above or below a plane formed by the four donor atoms in **1** to **4** respectively. Similar observations can be made for the PPh_3 and PCy_3 analogues of Rh(I) and Ir(I) Vaska-type systems. Additionally, moderate distortions are detected in geometrical angles (P–M–P, Cl–M–C and C/Cl–M–P) at the metal coordination environment (almost all angles deviate less than 3° from ideal geometries). It is concluded that distortions at the metal centre are minor.

Alkyl substituted phosphines, *e.g.* PCy_3, are regarded as strong bases and thus good σ-donor ligands. However, they are also weak π-acidic in nature and bonding is therefore not significantly strengthened by back-donation into the σ* orbital of phosphorus. In the present case, where phenyl is replaced stepwise by cyclohexyl, it is expected that M–P bonds will be gradually elongated. Literature examples to support the above statement include work done on Taft and Hammet parameters that correlate to calculated pK_a values of PPh_3 *vs.* PCy_3 (Allman and Goel 1982), kinetic measurements that showed an increase in the rate of oxidative addition of KSeCN to phosphines containing an increasing number of cyclohexyl substituents (Muller et al. 2008), as well as an analogue R = Ph/Cy system, *i.e.* SeP(p-NMe_2-C_6H_4)R_2 (Davis and Muller 2012; Phasha et al. 2012). Additionally, the CO bond, even though *cis* with respect to M–P, will be weakened gradually due to increased π-back donation (π*→d) at the M–C bond. Values for bond distances in Table 3 are indicative of this, but discrepancy for the PPh_2Cy ligand across the Rh series, with the Ir complexes showing this a little less, is noted.

Also, interesting to note is that crystallographic cone angles calculated show a discrepancy for this particular ligand: the value for both Rh(I) and Ir(I) PPh_2Cy Vaska-type complexes is substantially smaller than that of PPh_3! It is expected that the cone angle will increase with subsequent replacing of phenyl with cyclohexyl as is the case with the Tolman cone angles from the idealised CPK model (145°, 153°, 161°, 170° for PPh_3, PPh_2Cy, $PPhCy_2$ and PCy_3, respectively). However, the use of crystallographic cone angles considers real phosphine ligand environments and as a result is a better indication of ligand steric behaviour. Even though the above are solid state measurements, behaviour in the solution state is also not well behaved: phosphorus NMR coupling constants and IR carbonyl stretching frequencies are virtually similar ($^1J_{Rh\text{-}P}$ = 123 *vs.* 124 Hz and ν(CO) = 1964 *vs.* 1966 cm^{-1}) for these two Rh Vaska-type complexes of PPh_2Cy and $PPhCy_2$ respectively. A possible explanation for these observations can be found in investigating the M–P–C_{ipso} bond angles. For Rh(I) and Ir(I) Vaska-type complexes of PPh_3, $PPhCy_2$ and PCy_3, these angles are at least 110° or above. However, in the case of the Rh(I) and Ir(I) Vaska-type complexes of PPh_2Cy specifically, a smaller than 110° is observed for the non-disordered phenyl substituent. A possible reason for this discrepancy is firstly that the disordered phenyl and cyclohexyl substituent combinations are twisted along the C–M–P–C_{ipso} in order for cyclohexyl and phenyl to mimic each other's space occupied (see Figure 4). This is evident in the semi-angle calculated for the non-disordered phenyl substituent which is at least 6° lower than any of the other calculated semi-angles. Secondly, the C_{ipso}–H of non-disordered cyclohexyl also shows a C–H···Cl intramolecular interaction (see supplementary material) which is absent in the PPh_2Cy complexes. It could be speculated that both these observations cause the PPh_2Cy ligand to have a different than expected crystallographic cone angle as well as an orbital overlap at the C_{ipso}–P bond causing unexpected discrepancies in both steric and electronic parameters.

In support of the above observations, $SePPh_2Cy$ and $SePPhCy_2$ from Muller et al. 2008, show a phosphorus environment that is less restricted for PPh_2Cy since crystallographic cone

TABLE 3: Selected geometrical parameters (Å, °) for the compounds with general formula *trans*-[MCl(CO)(L)$_2$].

(M)(L)	M-P	M-Cl	M-C	C-M-Cl	θ_E	Ref
(Rh)(PPh_3)	2.3279(7)	2.380(2)	1.759(7)	179.7(3)	156	Chen et al, 1991
(Rh)(PPh_2Cy)	2.308(2)	2.369(5)	1.741(15)	178.3(5)	150	**1**
(Rh)($PPhCy_2$)	2.3376(11)	2.379(2)	1.749(7)	178.2(3)	159	**2**
(Rh)(PCy_3)	2.3508(3)	2.3880(13)	1.745(5)	178.57(11)	160	Wilson et al, 2002
(Ir)(PPh_3)	2.330(l)	2.382(3)[3]	1.791(13)	178.1(4)	157	Churchill et al, 1994
(Ir)(PPh_2Cy)	2.3327(16)	2.330(6)	1.65(2)	174.8(9)	149	**3**
(Ir)($PPhCy_2$)	2.3378(12)	2.383(3)	1.788(11)	178.4(4)	159	**4**
(Ir)(PCy_3)	2.345 (2)	2.398 (7)	1.78 (2)	176.1 (7)	161	Kuwabara and Bau, 1994

3. As stated in the Cambridge Structural Database entry, the coordinates of chloride ligand was not retained. However, in the original article it states that the Cl-Ir-CO disorder could be clearly defined and geometrical data relating to this reported.

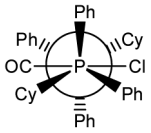
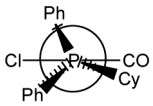
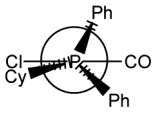
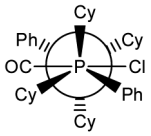
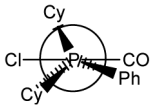
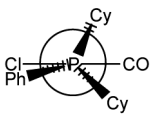
angle values of these two compounds are very similar due to all C_{ipso}–P–Se angles being comparable (175° *vs.* 176°). Here it also seems that the orbital overlap of C_{ipso}–P is more reliable as the $^{1}J_{Se-P}$ coupling constants in $^{31}P\{^{1}H\}$ NMR also show significant differences (724 *vs.* 701 ppm).

Furthermore, *computational chemistry* can also be employed to show that these two phosphines are indeed different electronically. The method developed by Suresh and Koga 2002, shows that the calculation of the molecular electrostatic potential minimum (V_{min}) can be used as direct quantitative measure for electron donating power of phosphines as opposed to the indirect methods such as ν(CO) in metal-phosphine complexes where other ligands in the coordination sphere may also influence this parameter. Calculation of V_{min} values for the free phosphine series $PPh_{3-n}Cy_n$, n = 0 to 3, resulted in progressively negative values (indicative of more electron donating power) of -34.81, -38.15, -41.63 and -45.24, respectively. Thus, this shows a more progressive trend for this series of compounds as opposed to those in the Vaska systems studied here.

In essence, the above discussion on the series of Rh/Ir $PPh_{3-n}Cy_n$, n = 0 to 3, Vaska-type complexes shows that the behaviour of the phenyl and cyclohexyl substituents is to seemingly attempt to "adapt" to the available space allowed at the metal coordination environment, causing discrepancies to steric and electronic parameters of the phosphines utilised. It also seems to have no effect on the Cl–M–CO moiety adopting a statistical disorder governed by crystallographic symmetry.

Computational chemistry was further explored in an attempt to predict the disorder of the Cl–M–CO moiety. From the Cambridge Structural Database (Groom et al. 2016) it is noticed that the Cl–M–CO disorder appears to be related to different conformations of the phosphines as well as their relative orientation to the Cl–M–CO moiety. If the phosphine substituents along the P–M–P axis are staggered, usually disorder of the Cl–M–CO moiety is observed, and when the substituents are eclipsed, a non-disordered Cl–M–CO moiety is usually the result. Additionally, non-disordered systems appear to have one substituent from each phosphine almost in line with M–CO bond, whereas the disordered system shows none of the substituents in line with the square planar coordination environment. By using the above observations, it should be possible to calculate relative energy differences between

TABLE 4: Data extracted from theoretical optimisations of the various orientations for **1** and **2**.

Orientation	ΔE (kJ.mol^{-1})	M-P[a], M-Cl, M-C (Å)	P-M-P, Cl-M-C (°)	Tors1, Tors2 (°)[c]
	0	2.4374(2.308)[b] 2.4696(2.369) 1.8280(1.741)	173.67(180.0) 178.77(178.3)	-167.16(-136.63) -37.56(-43.37)
	9	2.4380 2.4557 1.8281	177.93 173.05	-168.03 168.03
	-5	2.437 2.479 1.830	173.54 173.74	33.52 -33.52
	0	2.4508(2.338) 2.4624(2.379) 1.8278(1.749)	176.90(180.0) 178.86(178.2)	-40.05(-24.8) -151.33(-155.2)
	-8	2.4467 2.4755 1.829	175.83 174.11	-151.9 156.3
	9	2.4539 2.4525 1.826	176.48 178.16	-43.14 41.97

a = average of the two M-P bond distances; b = values in parentheses are taken from single crystal X-ray data; c = Tors1, Tors2 = torsion angles of odd phosphine substituent(s) of each ligand C_{ipso}–P–Rh–Cl.

these conformations that could provide insight into the disorder at the Cl–M–CO moiety. However, it should also be noted that since the Cl–M–CO moiety can disorder, it implies that the option where the M–Cl eclipses with one of the substituents from both phosphines should also be considered. Based on these considerations, a preliminary computational study was undertaken with **1** and **2** only at a relatively low basis set. Conformations were optimised and energies compared; the result of which is summarised in Table 4.

At the current level of theory used for the optimisations, the results show little variation in the relative energy difference between staggered and eclipsed conformations, and will not be reliable to predict the experimental outcome of conformations. However, if both eclipsed conformations (to M–CO and M–Cl) are taken into account for each phosphine, the difference between them might be regarded as significant not to adopt this conformation (*cf*. 14 kJ/mol for PPh_2Cy and 17 kJ/mol for $PPhCy_2$), but rather the staggered conformation; the latter associated with the disorder of the Cl–M–CO moiety that is observed experimentally in these systems. This postulation will require further investigation before being adopted as a means to determine the disorder of the Cl–M–CO moeity. In addition, comparison of geometrical values between optimised and those from the experimental crystal data show that conformations are somewhat different, and may indicate that additional packing effects play a part in the final conformation that is observed in the solid state.

Conclusion

Vaska-type systems of the general form *trans*-[M(CO)$Cl(PPh_{3-n}Cy_n)_2$], where M=Rh, Ir and n=0 to 3 show that the step-wise replacement of phenyl with more bulky and nucleophilic cyclohexyl does not impact on the statistical Cl–M–CO disorder observed in the single crystal X-ray crystallographic structures of these complexes. More insight was gained into the nature of the steric and electronic properties of PPh_2Cy and $PPhCy_2$ and shows that these are easily manipulated depending on their environments, especially in the case of PPh_2Cy.

Results show that the phosphine ligands will attempt to adapt to their environment and essentially strive towards a common steric size. Whether steric size of the phosphine ligand will influence the disorder if large enough, is debatable as the single crystal X-ray structure of *trans*-[Rh(CO)Cl{P(o-tolyl)$_3$}$_2$] (Warsink et al. 2011), with a substantial Tolman cone angle of 194°, still shows disorder of the Cl–Rh–CO moiety as the crystallographic cone angle is measured at 169°. It seems therefore difficult to pinpoint the Cl–M–CO moiety disorder to steric bulk of the phosphine ligand only.

The use of computational chemistry to predict this disorder does show some promise, but this postulation will require a more expanded study at higher levels of theory before drawing any further conclusions.

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References

Bruker SMART-NT Version 5.050. (1998). *Bruker AXS Inc. Area-Detector Software Package*. Madison, WI, USA,.

Allman, T., Goel, R.G. (1982). The basicity of phosphines. *Canadian Journal of Chemistry*, 60(6), 716-722.

Altomare, A., Burla, M.C., Camalli, M., Cascarano, G.L., Giacovazzo, C., Guagliardi, A., Moliterni, A.G., Polidori, G., Spagna, R. (1999). SIR97: a new tool for crystal structure determination and refinement. *Journal of Applied Crystallography*, 32(1), pp.115-119.

Angoletta, M. (1959). Derivati carbonilici dell'iridio.-Nota III. Alogenuri di dicarbonilamminoiridio (I). *Gazzetta Chimica Italiana*, 89, 2359-2370.

Bezman, S.A., Bird, P.H., Fraser, A.R., Osborn, J.A. (1980). Metallacyclic complexes of iridium. *Inorganic Chemistry*, 19(12), 3755-3763.

Blake, A.J., Ebsworth, E.A., Murdoch, H.M., Yellowlees, L.J. (1991). Vaska's compound–dichloromethane solvate (1/2). *Acta Crystallographica Section C: Crystal Structure Communications,* 47(3), 657-659.

Brandenburg, K., Berndt, M. (2001). DIAMOND. Visual Crystal Structure Information System, Crystal Impact, Version 2.1 e.

Bruker SADABS Version 2004/1. (1998). *Bruker AXS Inc. Area Detector Absorption Correction Software*. Madison, WI, USA.

Bruker SAINT-Plus Version 6.02 (including XPREP) (1999). *Bruker AXS Inc. Area-Detector Integration Software*. Madison, WI, USA.

Burk, M.J., Crabtree, R.H. (1986). A convenient general synthesis of trans-[IrCl(CO)$(PR_3)_2$]. *Inorganic Chemistry*, 25(7), 931-932.

Ceriotti, A., Ciani, G.T., Sironi, A. (1983). The crystal and molecular structure of trans-chlorocarbonylbis (triphenylphosphine) rhodium(I) in its monoclinic form. *Journal of Organometallic Chemistry*, 247(3), 345-350.

Chaloner, P.A., Claver, C., Hitchcock, P.B., Masdeu, A.M., Ruiz, A. (1991). Orthorhombic crystal form of trans-carbonylchlorobis (triphenylphosphine) rhodium (I) dichloromethane solvate. *Acta Crystallographica Section C: Crystal Structure Communications*, 47(6), 1307-1308.

Chatt, J., Duncanson, L.A. (1953). Olefin co-ordination compounds. Part III. Infra-red spectra and structure: attempted preparation of acetylene complexes. *Journal of the Chemical Society*, 2939-2947.

Chen, Y.J., Wang, J.C., Wang, Y. (1991). Structure of trans-[Rh(CO)Cl{$P(C_6H_5)_3$}$_2$]: a centrosymmetric triclinic phase. *Acta Crystallographica Section C: Crystal Structure Communications*, 47(11), 2441-2442.

Churchill, M.R., Fettinger, J.C., Buttrey, L.A., Barkan, M.D., Thompson, J.S. (1988). An accurate X-ray diffraction study of Vaska's compound, *trans*-IrCl(CO)$(PPh_3)_2$, including resolution of the carbonyl/chloride disorder problem. *Journal of Organometallic Chemistry,* 340(2), 257-266.

Churchill, M.R., Lake, C.H., Miller, C.A., Atwood, J.D. (1994). Crystal structure oftrans-carbonylchlorobis-(tricyclohexylphosphine) iridium (I), trans-Ir(CO)Cl-$[P(cyclo\text{-}C_6H_{11})_3]_2$, a disordered species. *Journal of Chemical Crystallography*, 24(8), 557-560.

Clarke, M.L., Holliday, G.L., Slawin, A.M., Woollins, J.D. (2002). Highly electron rich alkyl-and dialkyl-N-pyrrolidinyl phosphines: an evaluation of their electronic and structural properties. *Journal of the Chemical Society, Dalton Transactions*, (6), 1093-1103.

Collman, J.P., Hegedus, L.S. (1980). *Principles and Application of Organotransition Metal Chemistry.* Mill Valley, California: University Science Books.

Davis, W.L., Muller, A. (2012). [4-(Dimethylamino) phenyl] diphenylphosphine selenide. *Acta Crystallographica Section E: Structure Reports Online*, 68(11), o3153-o3154.

Del Pra, A., Zanotti, G., Segala, P. (1979). Trans-Carbonylbis (Triphenylphosphine) Rhodium (I) Chloride, $C_{37}H_{30}ClOP_2Rh$. *Crystal Structure Communications*, 8(4), 959-964.

Dewar, M. J. (1951). A review of the pi-complex theory. *Bulletin de la Société Chimique de France, 18*, C71-C79.

Dunbar, K.R., Haefner, S.C. (1992). Crystallographic disorder in the orthorhombic form of carbonyl(chlorobis(triphenylphosphine)rhodium: relevance to the reported structure of the paramagnetic impurity in Wilkinson's catalyst. *Inorganic Chemistry*, 31 (17), 3676–3679.

Fernandez, A.L., Prock, A., Giering, W.P. (2003). *The QALE* Web Site*. Retrieved from http://www.bu.edu/qale/

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R. *et al.* (2004). Gaussian03, Revision C.02.

Galding, M.R., Virovets, A.V., Kazakov, I.V., Scheer, M., Smirnov, S.N., Timoshkin, A.Y. (2016). Diminished electron density in the Vaska-type rhodium(I) complex trans-[$Rh(NCBH_3)(CO)(PPh_3)_2$]. *Acta Crystallographica C Structural Chemistry*, 72(7), 514-517.

Grobbelaar, E., Lötter, S., Visser, H.G., Conradie, J., Purcell, W. (2009). Investigation of the electron density of iridium (I) Vaska-type complexes using DFT calculations and structural results: Structure of trans-carbonyl-chloro-bis (tricyclohexylphosphine)-iridium(I). *Inorganica Chimica Acta*, 362(11), 3949-3954.

Groom, C.R., Bruno, I.J., Lightfoot, M.P., Ward, S.C. (2016). The Cambridge structural database. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials*, 72(2), 171-179.

Kemp, G., Roodt, A., Purcell, W. (1995). A New Crystalline Form of the Rhodium (I) Analog of Vaska Complex- Crystal Structure of *Trans*-Chlorocarbonylbis (Triphenylphosphine) Rhodium(I). *Rhodium Express*, (12), 21-26.

Kirss, R. (2013). Fifty Years of Vaska's Compound (1). *Bulletin for the History of Chemistry*, 52-60.

Kuwabara, E., Bau, R. (1994). trans-Carbonylchlorobis (tricyclohexylphosphine) iridium (I). *Acta Crystallographica Section C: Crystal Structure Communications*, 50(9), 1409-1411.

Limaye, A.C., Gadre, S.R. (2001). UNIVIS-2000: an indigenously developed comprehensive visualization package. *Current Science (India)*, 80, 1296-1300.

Lorenzini, F., Qian, S., Blake, A.J., Marchetti, F., Saunders, G C., Marr, A.C. (2016). *Private communication*.

McCleverty, J.A., Wilkinson, G., Lipson, L.G., Maddox, M.L., Kaesz, H.D. (1990). Tetracarbonyldichlorodirhodium. *Inorganic Syntheses: Reagents for Transition Metal Complex and Organometallic Syntheses*, 28, 84-86.

Mills, A.M., van der Vlugt, J.I., Vogt, D., Spek, A. (2002). *Private Communication*.

Momma, K., Izumi, F. (2011). VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, 44(6), 1272-1276.

Muller, A.J., Otto, S., Roodt, A. (2008). Rapid phosphorus(III) ligand evaluation utilising potassium selenocyanate. *Dalton Transactions*, 650-657.

Müller, T.E., Mingos, D.M. (1995). Determination of the Tolman cone angle from crystallographic parameters and a statistical analysis using the crystallographic data base. *Transition Metal Chemistry*, 20(6), 533-539.

Ohgomori, Y., Watanabe, Y. (1990). The Vaska-type rhodium complexes, *trans*-$RhX(CO)L_2$. *Inorganic Syntheses, Vol 27*, 290-293.

Osborn, J.A., Jardine, F.H., Young, J.F., Wilkinson, G. (1966). The preparation and properties of tris(triphenylphosphine)halogenorhodium(I) and some reactions thereof including catalytic homogeneous hydrogenation of olefins and acetylenes and their derivatives. *Journal of the Chemical Society (A)*, 1711-1732.

Otto, S., Roodt, A., Smith, J. (2000). Steric effects induced by ferrocenyl in tertiary organophosphines: crystal structure of trans-chloromethylbis (ferrocenyldiphenylphosphine) palladium (II) benzene disolvate. *Inorganica Chimica Acta*, 303(2), 295-299.

Phasha, Z.H., Makhoba, S., Muller, A. (2012). Dicyclohexyl [4-(dimethylamino) phenyl] phosphine selenide. *Acta Crystallographica Section E: Structure Reports Online*, 68(1), o243-o243.

Pignolet, L.M. (1983). *Homogeneous Catalysis with Metal Phosphine Complexes.* New York: Plenum press.

Ren, X., Zheng, Z., Zhang, L., Wang, Z., Xia, C., Ding, K. (2017). Rhodium Complex Catalyzed Hydroformylation of Olefins with CO_2 and Hydrosilane. *Angewandte Chemie International Edition*, 56(1), 310-313.

Rheingold, A.L., Geib, S.J. (1987). trans-Carbonylchlorobis (triphenylphosphine) rhodium (I), a new polymorph. *Acta Crystallographica Section C: Crystal Structure Communications*, 43(4), 784-786.

Roodt, A., Otto, S., Steyl, G. (2003). Structure and solution behaviour of rhodium(I) Vaska-type complexes for correlation of steric and electronic properties of tertiary phosphine ligands. *Coordination Chemistry Reviews, 245*, 121-137.

Sharma, P., Cabrera, A., Le Lagadec, R., Manzo, R.L., Espinosa, G., Sharma, M., Arias, J.L. (1988). *Acta Ciencia Indica, Series Chemistry*, 24, 137.

Smoleński, P., Kirillov, A.M., Guedes da Silva, M.F., Pombeiro, A.J. (2011). Transformations of the Vaska-type complex trans-[$RhCl(CO)(PTA)_2$] (PTA = 1,3,5-triaza-7-phosphaadamantane) during stepwise addition of HCl: Synthesis, characterization and crystal structure of trans-[$RhCl_2(PTA)(PTAH)$]. *Inorganica Chimica Acta*, 378, 342-346.

Suresh, C.H., Koga, N. (2002). Quantifying the electronic effect of substituted phosphine ligands via molecular electrostatic potential. *Inorganic Chemistry*, 41(6), 1573-1578.

Taverner, B.C. (1996). Improved algorithm for accurate computation of molecular solid angles. *Journal of Computational Chemistry*, 17(14), 1612-1623.

Tolman, C.A. (1977). Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis. *Chemical Reviews*, 77(3), 313-348.

Vallarino, L. (1957). Carbonyl complexes of rhodium. Part I. Complexes with triarylphosphines, triarylarsines, and triarylstibines. *Journal of the Chemical Society*, 2287-2292.

van Leeuwen, P.W. (2004). *Homogeneous Catalysis, Understanding the Art.* The Netherlands: Kluwer Academic Publishers.

Vaska, L., DiLuzio, J.W. (1961). Carbonyl and Hydrido-Carbonyl Complexes of Iridium by Reaction with Alcohols Hydrido Complexes by Reaction with Acid. *Journal of the American Chemical Society*, 83, 2784-2785.

Warsink, S., Koen, R., Roodt, A. (2011). trans-Carbonylchloridobis (tri-o-tolylphosphine-κP) rhodium (I). *Acta Crystallographica Section E: Structure Reports Online*, 67(12), m1666-m1666.

Wilson, M.R., Prock, A., Giering, W.P., Fernandez, A.L., Haar, C.M., Nolan, S.P. (2002). Wilson, M.R., Prock, A., Giering, W.P., Fernandez, A.L., Haar, C.M., Nolan, S.P.π Effects Involving Rh− PZ3 Compounds. The Quantitative Analysis of Ligand Effects (QALE). *Organometallics*, 21(13), 2758-2763.

Winterton, N., Leigh, J. (2002). *Modern Coordination Chemistry: The Legacy of Joseph Chatt*. Springer Verlag.