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Quantifying the electronic *cis* effect of phosphine, arsine and stibine ligands by use of rhodium(I) Vaska-type complexes

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Abstract

The *cis* effects of phosphine, arsine and stibine ligands have been evaluated by measuring the IR stretching frequency in dichloromethane of the carbonyl ligand in a series of Rh(I) Vaska-type complexes, *trans*-[RhCl(CO)(L)₂]. These data were correlated with those obtained by Tolman for the electronic *trans* influences in the [Ni(L)(CO)₃] complexes. The electronic contribution, χ_{Fc} , of ferrocenyl was determined as 0.8 from these plots by evaluating PPh₂Fc as ligand. In order to accommodate arsine and stibine ligands an additional correction term, to compensate for differences in the donor atom, was added to Tolman's equation for calculation of the Tolman electronic parameter of phosphine ligands. In the resulting equation: $v(CO_{Ni}) = 2056.1 + \sum_{i=1}^{3} \chi_i + C_L$ values for C_L of $C_P = 0$, $C_{As} = -1.5$ and $C_{Sb} = -3.1$ are suggested for phosphine, arsine and stibine ligands, respectively. The crystal and molecular structures of *trans*-[RhCl(CO)(PPh₂Fc)₂] $\cdot 2C_6H_6$, *trans*-[RhCl(CO){P(NMe₂)₃}] and *trans*-[RhCl(CO)(AsPh₃)₂] are reported. The Tolman cone angles for PPh₂Fc and P(NMe₂)₃ were determined as 169° and 166°, while the effective cone angles for PPh₂Fc, P(NMe₂)₃ and AsPh₃ were determined as 171°, 168° and 147°, respectively.

Keywords: Rhodium complexes; Electronic parameters; Crystal structures

1. Introduction

In order to rationalize certain parameters, like steric bulk and electron donating capability, for ligands with no or very little data available it is important to do so in terms of other well-known ligand systems. It is also of further importance to rationalize the information obtained in such a way that all ligands employed are compared on an identical scale.

Two main aspects are involved in the coordination of tertiary phosphine ligands to transition metal atoms. Firstly, the electronic character of the M–P bond which 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 the empty 3d orbitals and σ^* orbitals of the P atom [1]. The second aspect influencing the coordination of a ligand is the steric factor associated with the specific ligand.

The diversity of tertiary phosphines in terms of their Lewis basicity and bulkiness renders them excellent candidates to tune the reactivity of square-planar complexes towards a variety of chemical processes, such as oxidative addition and substitution reactions [2]. The most widely quoted parameter to indicate Lewis basicity of tertiary phosphines is the $pK_a(H_2O)$ value thereof, which is a measure of the Brønsted basicity. In general, substituents with better electron donating capabilities will increase the Lewis basicity of the phosphine, while electron-withdrawing substituents increase the π acceptor ability.

In order to evaluate the electronic characteristics of a specific ligand one needs a probe, related to electron density in some way, that can be measured conveniently and is sensitive to changes induced in the system by the

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specific ligand. The effect of tertiary phosphine ligands with different electron donor and acceptor capabilities was illustrated by Tolman [3] by measuring, in CH₂Cl₂ medium, the CO stretching frequency of the trans carbonyl group in Ni(0) complexes of the general formula $[Ni(L)(CO)_3]$. These measurements gave a good indication of the relative "electronic trans influences" of the various phosphine ligands. Tolman also found that in this specific system the electronic measurement made was independent of the steric size of the phosphine ligands, a very important factor to keep in mind. Several additional ways of evaluating the properties of phosphine ligands are described in the literature – these include NMR measurements of first order Pt-P, P-Se or P-BH₃ coupling constants [4-6], or by measuring the CO stretching frequency of the rhodium analogues of the Vaska-type complexes in solution [7].

Vaska's compound, *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I), was first prepared by Angoletta [8] in 1959 and was later correctly formulated by Vaska [9] in 1961. The analogous Rh(I) complexes were already known at that time and investigated to some extent [10]. These complexes were soon recognized as important model compounds for studies in homogeneous catalysis [11] and are widely known and used today.

While organometallic complexes containing tertiary phosphine ligands were extensively studied, the analogous arsine and stibine complexes received very little attention. As a consequence basic parameters that are well established for phosphine ligands have not been extended to include these ligand systems. As part of our continued interest in the PPh₂Fc ligand [12–15] and also in arsine [16–21] and stibine ligands [22–24] it was of importance to quantify the electronic properties of these ligands.

The rhodium(I) Vaska-type complexes render themselves as excellent candidates for such a study and several investigations of this nature have been reported before [7]. Advantages of using this system include their ease and safety of preparation and high degree of stability. Furthermore, the CO stretching frequency is easily identifiable and gives a sensitive measure of the "electronic cis influence" of the ligands employed. An extensive range of complexes were thus prepared in order to construct a database from which a correlation could be made to gain some insight into the characteristics of the PPh₂Fc, As and Sb ligands [25]. The ligands were investigated in order to determine the electronic effect, χ , of the Fc substituent, as well as the relative contributions of As and Sb compared to P as donor atoms. The crystal structures of *trans*-[RhCl(CO) $(PPh_2Fc)_2 \cdot 2C_6H_6$ (1), trans- $[RhCl(CO){P(NMe_2)_3}_2]$ (2), and *trans*-[RhCl(CO)(AsPh₃)₂] (3), are reported to gain more information about the coordination mode of these ligands. In addition the steric demand of the ligands was calculated based on the Tolman cone angle model [3].

2. Experimental

2.1. Preparation of ligands and complexes

The PPh₂Fc and PPhFc₂ ligands were prepared according to the literature procedures [26] while all other ligands were obtained from commercially available sources. The Vaska-type complexes were prepared in acetone medium by reacting [Rh(CO)₂(μ -Cl)]₂ with 4.4 equivalents of the respective ligands resulting in near quantitative yields. The SbPh₃ complexes were prepared as reported previously [23].

2.2. Crystallography

Crystals of a *trans*-[RhCl(CO)(PPh₂Fc)₂] \cdot 2C₆H₆ were obtained after recrystallization from benzene, *trans*-[RhCl(CO){ $P(NMe_2)_3$ }] were obtained directly from the acetone reaction medium and *trans*-[RhCl(CO) $(AsPh_3)_2$ were recrystallized from dichloromethane. The densities of the crystals were determined experimentally by flotation in aqueous NaI. All data collections were done on a Bruker SMART CCD diffractometer using Mo K α (0.71073 A) and ω -scans at 293(2) K. After completion of the data collection the first 50 frames were repeated to check for decay of which none was observed. All reflections were merged and integrated using SAINT [27] and were corrected for Lorentz, polarization and absorption effects using SADABS [28]. The structures were solved by the heavy atom method and refined through full-matrix least squares cycles using the SHELXL97 [29] software package with $\sum (|F_o| - |F_c|)^2$ being minimized. All non-H atoms were refined with anisotropic displacement parameters while the H atoms were constrained to parent sites using a riding model (aromatic C-H = 0.93 Å; aliphatic C-H = 0.96 Å). The graphics were done with the DIAMOND [30] Visual Crystal Structure Information System software.

2.3. Cone angle calculations

The cone angles for the ligands were calculated according to Tolman's model [3]. Per definition a Rh–P bond distance of 2.28 Å was used to calculate the Tolman cone angles (θ_T) for the phosphine ligands, while the observed Rh–P/As bond distances were used to calculate the effective cone angles (θ_E) of the phosphine and arsine ligands. A van der Waals radius of hydrogen of 1.2 Å was used in all calculations. In the tables containing the geometrical parameters of the different structures the individual half angles ($\theta/2$) are reported for the cone angle calculations of each ligand. These half angles represent the largest angle towards each of the three substituents on the ligand as measured to the hydrogen atom listed in brackets.

Table 1 Crystallographic data for complexes 1, 2 and 3

	1 ^a	2 ^b	3 ^c
Empirical formula	C ₅₇ H ₅₀ ClOFe ₂ P ₂ Rh	C13H36ClN6OP2Rh	C ₃₇ H ₃₀ ClOAs ₂ Rh
Formula weight	1062.97	492.78	778.81
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\overline{1}$	$P2_1/n$	$P\overline{1}$
a (Å)	9.4583(19)	7.963(1)	9.9134(4)
b (Å)	12.954(2)	12.479(1)	10.1532(5)
c (Å)	10.466(3)	11.143(1)	18.1213(8)
a (°)	97.73(3)	90	75.393(10)
β (°)	86.67(3)	98.92(1)	75.625(10)
γ ^(°) ,	107.61(3)	90	72.398(10)
$V(\dot{A})$	1211.0(4)	1093.89(19)	1652.86(13)
Ζ	1	2	2
$D_{\rm c}~({\rm g~cm^{-3}})$	1.458	1.496	1.565
$\mu ({\rm mm^{-1}})$	1.089	1.062	2.612
$T_{\rm max}/T_{\rm min}$	0.908/0.743	0.901/0.857	0.637/0.479
F(000)	544	512	776
Crystal size (mm)	$0.29 \times 0.21 \times 0.09$	$0.15 \times 0.13 \times 0.10$	0.33 imes 0.20 imes 0.19
θ limit (°)	1.66-32.02	2.47-31.86	5.86-28.33
Index ranges	$-13 \leq h \leq 12$	$-11 \leq h \leq 11$	$-13 \leq h \leq 13$
	$-15 \leq k \leq 19$	$-18 \leqslant k \leqslant 18$	$-13 \leq k \leq 13$
	$-15 \leq l \leq 15$	$-12 \leq l \leq 16$	$-24 \leq l \leq 22$
Collected reflections	12906	11862	18 287
Independent reflections	7349	3420	8045
Observed reflections $[I > 2\sigma I]$	5294	2229	6097
R _{int}	0.0259	0.0434	0.0229
Data/restraints/parameters	7349/0/305	3420/0/131	8045/0/380
S	0.984	0.901	1.029
$R(I > 2\sigma I)^{\mathrm{d}}$	0.0352	0.0303	0.0319
wR ^e	0.0765	0.0611	0.0661
R (all data)	0.0605	0.0639	0.0513
wR	0.0835	0.0667	0.0739
$\Delta ho_{ m max}; \Delta ho_{ m min}$ (e Å ⁻³)	0.383; -0.458	0.348; -0.663	0.747; -0.810

^a trans-[RhCl(CO)(PPh₂Fc)₂] \cdot 2C₆H₆ ^b trans-[RhCl(CO){P(NMe₂)₃}₂]

^c trans-[RhCl(CO)(AsPh₃)₂]

 ${}^{d}R = \left[\left(\sum_{\nu} \Delta F \right) / \left(\sum_{\nu} F_{0} \right) \right]$

$$wR = \sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}]^{1/2}$$

2.4. Spectroscopic measurements and data fitting

All IR spectroscopic measurements were made on a Hitachi 270-50 spectrometer as dichloromethane solutions using a NaCl cell with the background spectrum of dichloromethane being corrected for, the measurements being accurate to within 1 cm⁻¹. It was imminent to determine the values of $v(CO_{Rh})$ in solution since packing effects may have a significant influence on the measured value as shown before [31]. The data were fitted to a simple quadratic function ($y = ax^2 + bx + c$) using the SCIENTIST least-squares program [32].

3. Results and discussion

3.1. Crystallography

Details of the data collections and the refinement parameters are given in Table 1 and selected geometrical parameters are summarized in Tables 2–4, respectively. The molecular structures with thermal ellipsoids and numbering schemes for 1, 2 and 3 are shown in Figs. 1, 2 and 3, respectively.

3.1.1. Crystal structure of trans-[RhCl(CO) ($PPh_2 Fc$)₂] · 2 C_6H_6 (1)

As part of a preliminary study [25] crystals of *trans*- $[RhCl(CO)(PPh_2Fc)_2] \cdot CH_2Cl_2$ were isolated and the structure was determined.² Since severe disorders were

²*trans*-[RhCl(CO)(PPh₂Fc)₂] · $\frac{1}{2}$ CH₂Cl₂; Enraf Nonius CAD 4; Mo *K*α = 0.71073 Å; empirical formula, C_{45.5}H₃₉Cl₂OP₂Fe₂Rh; FW, 944.20; crystal system, triclinic; space group, *P*Ī; *a*, 9.4680(10) Å; *b*, 12.995(2) Å; *c*, 18.085(3) Å; *a*, 107.93(2)°; β, 96.31(2)°; γ, 95.19(2)°; V, 2086.0(5) Å³; *Z*, 2; *D_c*, 1.500 g cm⁻³; *D_m*, 1.454 g cm⁻³; *μ*, 1.315 mm⁻¹; *T_{max}/T_{min}*, 0.737/ 0.668; *F*(000), 954; crystal size, 0.45 × 0.30 × 0.28 mm; 1.71 ≤ θ ≤ 24.97°; index ranges, 0 ≤ *h* ≤ 11, -15 ≤ *k* ≤ 15, -21*l* ≤ 21; collected reflections, 5411; independent reflections, 5071; *R_{int}*, 0.0154; observed reflections, *I* > 2*σI* 5396; data/restraints/parameters, 5396/72/545; *S*, 1.156; *R/wR(I* > 2*σI*), 0.0382/ 0.1223; *R/wR* (all data), 0.0382/0.1223; $\Delta\rho_{max}/\Delta\rho_{min}$, 1.142/-0.796 e Å⁻³.

Table 2		
Bond lengths (Å), bond-,	torsion- and steric angles (°) for tran	$s-[RhCl(CO)(PPh_2Fc)_2] \cdot 2C_6H_6$

Rh–P	2.3346(9)	Rh–Cl	2.3670(18)
Rh–C(0)	1.787(6)	O–C(0)	1.138(6)
C(0)–Cl′	0.581(5)	O–Cl′	0.559(3)
P–C(11)	1.831(2)	P–C(21)	1.822(2)
P–C(31)	1.807(2)	Fe–Cp(3) _{avg}	2.038(2)
Fe-Cp(4) _{avg}	2.036(3)		
C(0)–Rh–P	87.8(2)	C(0)'-Rh-P	92.2(2)
C(0)–Rh–Cl	179.2(3)	C(0)'-Rh-Cl	0.8(3)
P-Rh-Cl	92.51(5)	P'-Rh-Cl	87.49(5)
C(11)–P–C(21)	103.10(10)	C(11)–P–C(31)	102.25(10)
C(21)–P–C(31)	102.92(9)	C(11)–P–Rh	118.50(7)
C(21)–P–Rh	112.26(7)	C(31)–P–Rh	115.87(7)
O–C(0)–Rh	179.1(8)		
Cl-Rh-P-C(11)	-12.39(9)	Cl-Rh-P-C(21)	-132.44(9)
Cl-Rh-P-C(31)	109.72(9)	Rh–P–C(31)–C(41)	-46.72(8)
$(\theta/2)_{\rm E}$ (H12)	67.3	$(\theta/_2)_{\rm T}$ (H12)	68.2
$(\theta/2)_{\rm E}$ (H26)	81.9	$(\theta/2)_{\rm T}$ (H26)	82.9
$(\theta/2)_{\rm E}$ (H42)	105.0	$(\theta/2)_{\rm T}$ (H41)	105.8
$ heta_{ m E}$	169	θ_{T}	171

Table 3

Selected bond lengths (Å), bond, torsion and steric angles (°) for *trans*-[RhCl(CO){P(NMe₂)₃}]

Rh–P	2.3416(6)	Rh–Cl	2.447(4)
Rh–C(0)	1.723(6)	C(0)–O	1.145(9)
C1-C(0)'	0.724(6)	Cl–O'	0.425(10)
P-N(1)	1.6932(18)	P–N(3)	1.6637(17)
P-N(2)	1.6691(19)		
N(1)–C(11)	1.465(3)	N(1)–C(12)	1.464(3)
N(2)-C(21)	1.449(3)	N(3)-C(31)	1.446(3)
N(2)–C(22)	1.459(3)	N(3)-C(32)	1.459(3)
P-Rh-P'	180.0	C(0)–Rh–Cl	179.5(2)
C(0)–Rh–P	89.1(2)	P-Rh-Cl	90.9(2)
C(0)-Rh-Cl'	0.5(2)	O–C(0)–Rh	177.1(11)
N(2)-P-N(1)	101.60(9)	N(1)–P–Rh	120.94(7)
N(3)–P–N(1)	99.12(9)	N(2)–P–Rh	110.38(7)
N(3)–P–N(2)	111.07(10)	N(3)–P–Rh	112.78(7)
C(11)–N(1)–P	116.03(15)	C(12)–N(1)–P	119.71(16)
C(21)–N(2)–P	122.50(16)	C(22)–N(2)–P	122.90(16)
C(31)–N(3)–P	122.10(16)	C(32)–N(3)–P	124.24(16)
C(12)–N(1)–C(11)	112.96(18)	C(21)–N(2)–C(22)	113.07(19)
C(31)-N(3)-C(32)	112.78(18)		
Cl-Rh-P-N(1)	-4.86(14)	Cl-Rh-P-N(2)	-123.08(14)
Cl-Rh-P-N(3)	112.03(15)		
$(\theta/2)_{\rm E}$ (H11C)	70.5	$(\theta/2)_{\rm T}$ (H11C)	71.4
$(\theta/2)_{\rm E}$ (H21A)	90.2	$(\theta/2)_{\rm T}$ (H21A)	91.6
$(\theta/2)_{\rm E}$ (H31B)	88.2	$(\theta/2)_{\rm T}$ (H31B)	89.6
$ heta_{ m E}$	166	$ heta_{ m T}$	168

encountered in both the rhodium co-ordination compound and the solvent of crystallization the current structure determination was selected for a detailed report in this paper. Compound 1, *trans*-[RhCl(CO) (PPh₂Fc)₂]. $2C_6H_6$, crystallize isomorphous to the previously reported *trans*-[PtCl₂(PPh₂Fc)₂]. $2C_6H_6$ [12] and *trans*- $[PdClMe(PPh_2Fc)_2] \cdot 2C_6H_6$ [14] complexes in $P\overline{1}$ with the metal atom situated on an inversion centre resulting in a 50% statistical disorder in the CO and Cl positions. Each Rh moiety co-crystallized with two benzene solvent molecules in the unit cell. It is clearly the bulky nature of the PPh_2Fc ligand that predominantly determines the

Table 4 Selected bond lengths (Å), bond, torsion and steric angles (°) for *trans*-[RhCl(CO)(AsPh₃)₂]

Rh–As(1)	2.4226(4)	Rh–As(2)	2.4217(4)
Rh–C(1)	2.015(7)	Rh–Cl	2.3599(12)
As(1)–C(111)	1.944(3)	As(2)–C(211)	1.951(3)
As(1)–C(121)	1.943(3)	As(2)–C(221)	1.946(3)
As(1)–C(131)	1.945(3)	As(2)–C(231)	1.943(3)
C(0)–O	0.707(8)		
As(1)–Rh–As(2)	176.020(15)	C(0)-Rh-Cl	179.01(17)
C(0)-Rh-As(1)	88.61(16)	Cl–Rh–As(1)	92.28(3)
C(0)-Rh-As(2)	91.48(16)	Cl-Rh-As(2)	87.59(3)
O–C(0)–Rh	175.7(11)		
C(111)–As(1)–Rh	112.43(8)	C(211)–As(2)–Rh	120.79(9)
C(121)–As(1)–Rh	114.15(8)	C(221)–As(2)–Rh	114.67(8)
C(131)–As(1)–Rh	121.50(8)	C(231)–As(2)–Rh	110.31(9)
[C-As(1)-C] _{avg}	102.07(12)	[C-As(2)-C] _{avg}	103.03(13)
Cl-Rh-As(1)-C(111)	-147.50(10)	Cl-Rh-As(2)-C(111)	-156.09(12)
Cl-Rh-As(1)-C(121)	97.78(10)	Cl-Rh-As(2)-C(121)	-31.21(10)
Cl-Rh-As(1)-C(131)	-26.87(11)	Cl-Rh-As(2)-C(131)	84.92(10)
$(\theta/2)_{\rm E}$ (H116)	77.2	$(\theta/2)_{\rm E}$ (H216)	65.7
$(\theta/2)_{\rm E}$ (H126)	74.6	$\left(\theta/2\right)_{\rm E}$ (H226)	71.6
$(\theta/2)_{\rm E}$ (H132)	66.4	$(\theta/2)_{\rm E}$ (H236)	85.4
$ heta_{\mathrm{E}(1)}$	145	$ heta_{\mathrm{E}(2)}$	148



Fig. 1. Molecular diagram showing the numbering scheme and displacement ellipsoids (30% probability) in *trans*-[RhCl(CO) (PPh₂Fc)₂] \cdot 2C₆H₆. Hydrogen atoms and the benzene solvent molecules were omitted for clarity. In the numbering scheme of the Ph and Cp rings the first digit refers to the number of the ring, 1 and 2 for Ph and 3 and 4 for Cp, the second digit refers to the number of the C atom in the rings.

mode of packing when a relatively small metal core is present. Except for a fairly short Rh–Cl bond distance of 2.3670(18) Å all the other bonds were within expected limits. The O–C–Rh moiety is close to linear with an angle of 179.1(8)°. The P–C bond of 1.807(2) Å towards the ferrocenyl is significantly shorter than those to the phenyl substituents that averages 1.826(2) Å, and is comparable with that found in previously reported crystallographic studies containing the PPh₂Fc ligand [12–15].

From previous studies it was found that the steric demand of the PPh₂Fc ligand is very sensitive to the

orientation of the ferrocenyl moiety [14]. In this regard the Rh–P–C(31)–C(41) solid state torsion angle of -46.72(8)° results in effective- and Tolman cone angles of $\theta_{\rm E} = 169^{\circ}$ and $\theta_{\rm T} = 171^{\circ}$.

3.1.2. Crystal structure of trans- $[RhCl(CO){P(NMe_2)_3}_2]$ (2)

The molecular structure of **2**, *trans*-[RhCl(CO) {P(NMe₂)₃}₂], shows the coordination complex to exhibit a square planar geometry with angles deviating only slightly from the expected 90°. As in **1** the Rh atom is situated on a special position in the monoclinic space group $P2_1/n$ resulting in a 50% statistical disorder between the CO and Cl positions. Some of the most noteworthy observations made from the structure include an exceptionally long Rh–Cl bond of 2.443(7) Å as well as a relatively long Rh–P bond distance of 2.3426(7) Å.

As encountered with other phosphine ligands in the case of the P–C bond distances one of the P–N bond distances is considerably longer than the other two with P-N(1) = 1.695(2) compared to P-N(2) = 1.668(2) and P-N(3) = 1.661(2), respectively. The O–C–Rh angle is 175.8(14)° and deviates significantly from linearity.

The effective (θ_E) and Tolman (θ_T) cone angles of the P(NMe₂)₃ ligand were determined as $\theta_E = 166^\circ$ and $\theta_T = 168^\circ$, respectively.

3.1.3. Crystal structure of trans-[RhCl(CO)(AsPh₃)₂] (3)

Although several structures of rhodium complexes containing bidentate arsine ligands are reported in the literature [33], the monodentate tertiary arsine complexes are far less studied. Several polymorphs of the



Fig. 2. Molecular diagram showing the numbering scheme and displacement ellipsoids (30% probability) in *trans*-[RhCl(CO){P(NMe₂)₃}]. Hydrogen atoms (thermal ellipsoids of arbitrary size) were included to give an indication of the size of the P(NMe₂)₃ ligand.



Fig. 3. Molecular diagram showing the numbering scheme and displacement ellipsoids (30% probability) in *trans*-[RhCl(CO)(AsPh₃)₂]. The first digit in the phenyl rings refers to the number of the As ligand (1 or 2), the second digit to the number of the ring (1–3) and the third digit to the number of the C atom in the ring (1–6). Hydrogen atoms were omitted for clarity.

analogous PPh₃ complex have been reported to date [31], but surprisingly this structure is not isomorphous to any of these. The structure of **3**, *trans*-[RhCl(CO)(AsPh₃)₂], shows the coordination complex to exhibit a slightly distorted square planar geometry, with the bulky arsine ligands in a *trans* orientation as expected. The As(1)–Rh(1)–As(2) angle of 175.97(15)° deviates slightly from linearity and is a probable reason why the molecule crystallizes on a general position in $P\overline{1}$ rather than on an inversion centre.

The Rh–Cl bond distance of 2.3538(14) A is slightly shorter than that generally encountered while the average Rh–As bond length of 2.4225(4) Å is almost 0.1 Å longer than that normally found for Rh–P bonds in similar complexes. Contrary to the P-C bonds in phosphine ligands, it was found that all the As-C bonds are comparable in length, an effect probably induced by the longer As-C bonds compared to P-C bonds resulting in less steric strain in the As ligand system. It was found, however, that one of the C-As-Rh tetrahedral angles on each ligand deviates quite significantly, $120.50(10)^{\circ}$ and $120.74(10)^{\circ}$ for C(131)-As(1)-Rh and C(211)-As(2)-Rh, respectively, from the other two, as well as from the normal 109°. An O-C-Rh angle of 175.0(12)°, deviating from linearity, was also observed while the C-O bond refined to a slightly obscure value of 0.717(7) A, an effect probably caused by the long Rh-C bond of 2.017(7) A. The structure was checked for a random disorder in the CO and Cl positions, but no exclusive evidence for such an effect was observed. Similar effects have been observed before and are well documented in the literature [34,35].

The effective (θ_E) cone angles of the AsPh₃ ligands were determined as $\theta_{E(1)} = 145^{\circ}$ and $\theta_{E(2)} = 148^{\circ}$ for As(1) and As(2), respectively.

3.1.4. Solid state comparisons

The Rh–Cl bond distances for the complexes listed in Table 5 average 2.371(7) Å and range from 2.315(3) to 2.443(7) Å for the bis-SbPh₃ and the P(NMe₂)₃ complexes, respectively. It was also found that the Rh–Cl bond distance decreased from 2.382(1) to 2.3538(14) to 2.315(3) Å for the PPh₃ to AsPh₃ to SbPh₃ complexes; indicative of a decrease in the *cis* effect when descending in group 15. This can most probably be attributed to a combination of the formation of more electrophilic metal centres combined with a decrease in the steric crowding experienced in the molecules in that order [22,23,36–41].

Table 5 Comparison of *trans*-[RhCl(CO)(L)₂] complexes

L	Rh-L ^a (Å)	Rh–Cl (Å)	Rh–C (Å)	C–O (Å)	L-Pt-L (°)	Reference
PPh ₃	2.322(1)	2.382(1)	1.77(1)	1.140(2)	180.0(1)	[36]
PPh ₂ Me	2.317(2)	2.363(2)	1.795(7)	1.142(8)	178.2(1)	[37]
PPhMe ₂	2.314(2)	2.357(2)	1.800(6)	1.154(8)	174.11(6)	[38]
PBz ₃	2.3160(16)	2.3654(15)	1.783(6)	1.162(6)	177.67(6)	[39]
PPh_2Fc	2.3344(14)	2.415(7)	1.814(14)	1.056(14)	180	TW
$P(NMe_2)_3$	2.3426(7)	2.443(7)	1.731(9)	1.15(2)	180	TW
$P(p-Tol)_3$	2.3325(11)	2.3581(12)	1.798(5)	1.139(6)	175.67(4)	[40]
$P(p-F-Ph)_3$	2.322(2)	2.381(2)	1.800(2)	1.150(7)	178.7(2)	[41]
As(p-Tol) ₃	2.4120(10)	2.347(2)	1.788(10)	1.139(10)	175.69(4)	[22]
AsPh ₃	2.4222(4)	2.3599(12)	2.015(7)	0.707(8)	176.020(15)	TW
SbPh ₃	2.5655(2)	2.315(3)	1.797(13)	1.175(13)	180	[23]

^a Average of unequivalent bonds where applicable.

Unfortunately, only two Rh–Cl bond distances are available for complexes containing arsine ligands, but they do seem to be slightly shorter than in the analogous phosphine complexes. The Rh–C and C–O bond lengths average 1.82(2) and 1.09(3) Å, respectively, but there are usually such large s.u.'s associated with these values that it may be a risk to make conclusions based purely thereupon.

An increase in the Rh–L bond lengths is observed when descending periodically from PPh₃ to AsPh₃ to SbPh₃ as ligands as illustrated by the values of 2.322(1), 2.4226(4) and 2.5655(2) Å, respectively. The general L– C bond distances for the P, As and Sb ligands increase from ca. 1.8 to 1.9 to 2.1 Å while the C–L–C tetrahedral angles for the triphenyl derivatives of group 15 elements were reported [42] to decrease from N to P to As to Sb to Bi in the sequence 116°, 109°, 102°, 97°, and 94°. These changes in bond length and tetrahedral angles are in accordance with the increase in the covalent radii of the ligands going from N(0.70) to P(1.10) to As(1.21) to Sb(1.41) to Bi(1.47) Å.

In the PPh₂Fc ligand all bond distances and angles of the coordination polyhedron were within normal limits indicating its behaviour to be similar to most other phosphine ligands investigated. Investigating the Vaska complex thereof did, however, make it possible to get an additional value for the cone angle, as well as an estimation of its electron donating capability.

3.2. Spectroscopic measurements

The synthesized complexes and the corresponding IR data collected are listed in Table 6, and these $v(CO_{Rh})$ values were plotted against the $v(CO_{Ni})$ data reported by Tolman. A good fit of the data, within the region of interest, was obtained by fitting a simple quadratic function, $y = ax^2 + bx + c$, through the points with values of $a = (7.2 \pm 1.1) \times 10^{-3}$, $b = -28 \pm 4$ and $c = (29 \pm 4) \times 10^3$ being obtained. This mathematical equation is in no means implicated to give a fundamental quantum mechanical relationship between the

values, but is purely intended as representative of the experimental points within the region described by the data. Even though the equation could in principle be used to calculate the $v(CO_{Ni})$ value with fair accuracy for any ligand if the corresponding $v(CO_{Rh})$ value is known, no physical meaning is attached to any of the constants. Tolman rationalized the measurements on the [NiL(CO)₃] complexes in terms of Eq. (1) that can now

Table 6 IR (CH₂Cl₂), data for the $[Ni(L)(CO)_3]$ and *trans*- $[RhCl(CO)(L)_2]$ complexes

	L	$v(CO_{Ni})^a (cm^{-1})$	$v(CO_{Rh}) (cm^{-1})$
1	PCy ₃	2056.4	1943
2	P ⁱ Pr ₃	2059.2	1950
3	AsEt ₃	2059.6 ^b	1954
4	$P^n Bu_3$	2060.3	1955
5	PPhFc ₂	2060.5 ^b	1957°
6	PEt ₃	2061.7	1958
7	$P(NMe_2)_3$	2061.9	1964
8	PPhEt ₂	2063.7	1964
9	PPhCy ₂	2060.6	1964
10	PPh ₂ Cy	2064.8	1966
11	PPh_2Me	2067.0	1968
12	PBz ₃	2066.4	1970
13	PPh_2Fc	2065.5 ^b	1970
14	SbPh ₃	2065.8 ^b	1971
15	PPh ₂ Et	2066.7	1973
16	$As(p-Tol)_3$	2066.8 ^b	1973
17	$P(o-Tol)_3$	2066.6	1974
18	AsPh ₃	2067.9 ^b	1975
19	$P(p-OMe-Ph)_3$	2066.1	1975
20	$P(p-Tol)_3$	2066.7	1976
21	PPh ₂ (p-Tol)	2068.2	1977
22	PPh ₃	2068.9	1979
23	$PPh_2(C_6F_5)$	2075.9	1983
24	$P(p-F-Ph)_3$	2071.3	1983
25	$P(p-Cl-Ph)_3$	2072.8	1983
26	PPh ₂ Cl	2080.7	1993
27	$PPh(C_6F_5)_2$	2082.8	1996
28	$P(C_6F_{53})$	2090.9	2005

^a Ref. [3].

^bObtained from Fig. 4.

^c Measurement in KBr.

)

be used to calculate the electronic parameter $v(CO_{Ni})$ for phosphine ligands containing common substituents

$$v(\text{CO}_{\text{Ni}}) \text{ for } PX_1X_2X_3: \ v(\text{CO}_{\text{Ni}}) = 2056.1 + \sum_{i=1}^{3} \chi_i.$$
(1)

In Eq. (1) each substituent has a value for χ (*t*-Bu = 0; Cy = 0.1; Et = 1.8; Ph = 4.3, etc.) that has to be known to calculate the value of $v(CO_{Ni})$. This equation implies that P(^{*i*}Bu)₃ has the highest electronic *trans* influence (strongest electron donor) and on replacing the ^{*i*}Bu groups with other groups, a correction must be applied since a decrease in the *trans* influence results in an increase in the CO stretching frequency. This observation is best explained in terms of a decrease in electron density on the metal centre giving rise to poorer back donation from the metal into the anti-bonding orbital on the C atom. The decrease in the back donation results in a weaker Rh–C bond and thus a stronger CO bond that in turn results in an increase in the CO stretching frequency.

The $v(CO_{Ni})$ versus $v(CO_{Rh})$ data from Table 6 were fitted to the curve shown in Fig. 4. It is clear that the $v(CO_{Rh})$ values cover almost twice the range than the $v(CO_{Ni})$ values with $\Delta v(CO_{Rh}) = 62$ cm⁻¹ and $\Delta v(CO_{Ni}) = 34.5$ cm⁻¹. From this graph the corresponding $v(CO_{Ni})$ values for the PPh₂Fc, As and Sb ligands were obtained and are reported in Table 6. Substituting the $v(CO_{Ni})$ value for PPh₂Fc (2065.5 cm⁻¹) obtained from Fig. 4 into Eq. (1) and solving $(\chi_{Ph} = 4.3)$ gives: $2065.5 = 2056.1 + 2(4.3) + \chi_{Fc}$; thus $\chi_{Fc} = 0.8$. This value of 0.8 for χ_{Fc} indicates it to be a good electron-donating group, comparable to *o*-OMe– Ph ($\chi = 0.9$). In an attempt to obtain an additional value for χ_{Fc} the Vaska complex of PPhFc₂ was also prepared. The solubility of this complex was, however, so limited in all common organic solvents evaluated (even acetonitrile and DMF) that no solution measurements could be made. A solid state stretching frequency of 1955 cm⁻¹ was obtained in KBr discs resulting in a $v(CO_{Ni})$ value of 2060.5 and a χ_{Fc} value of only 0.05. This value is unfortunately not consistent with what one would expect, most probable due to the solid state-solution state extrapolation, and will hence not be used in any discussions further on.

In order to determine the contributions of As and Sb relative to P an additional term correcting for the donor atom (C_L; L=P, As or Sb) was added to Eq. (1) thus giving Eq. (2):

$$v(\text{CO}_{\text{Ni}}) = 2056.1 + \sum_{i=1}^{3} \chi_i + C_{\text{L}}.$$
 (2)

According to definition the phosphine ligands have $C_{\rm P} = 0$. Substituting the $v({\rm CO}_{\rm Ni})$ values for AsEt₃ (2059.6), AsPh₃ (2067.9), As(*p*-Tol)₃ (2066.8) and SbPh₃ (2065.8) obtained from Fig. 4 into Eq. (2) and solving gave the following values for $C_{\rm As} = -1.9$ (AsEt₃), -1.1 (AsPh₃) and +0.2 (As(*p*-Tol)₃) and $C_{\rm Sb} = -3.1$ (SbPh₃). From these results the C_{As} value of +0.2 obtained for As(*p*-Tol)₃ seems a bit strange compared to the negative values obtained for the other As ligands. Direct subtraction of the $v({\rm CO}_{\rm Rh})$ values of As(*p*-Tol)₃ and P(*p*-Tol)₃ gives 1973-1976 = -3 cm⁻¹ and dividing by 2 to convert to the smaller range for $v({\rm CO}_{\rm Ni})$ suggests a value of -1.0 to -1.5 cm⁻¹. Based on these arguments an average value of 1.5 is proposed for $C_{\rm As}$ and the values of -3.1 is retained for $C_{\rm Sb}$.



Fig. 4. Non-linear fit of $v(CO_{Rh})$ vs. $v(CO_{Rh})$ for all known complexes (\blacksquare) in Table 6, fitted values for new complexes (*) were obtained from the least-squares calculations.

At first though it might seem like the $v(CO_{Rh})$ values for both the As and the Sb complexes suggest that the Rh metal centre should be more electron rich (lower $v(CO_{Rh})$ values). However, it is clear that the Rh–Cl bond distance for these complexes significantly shortens, see Table 5 (2.382(1), 2.354(2) and 2.315(3) Å) for the PPh₃, AsPh₃ and SbPh₃ complexes, respectively. Thus it seems as if the electron density on the Rh metal centre decreases significantly from PPh₃ to AsPh₃ to SbPh₃. However, it cannot be excluded that this observation might be due to steric effects.

It is thus suggested that the decrease in electron density on the metal centres is a combined result of the longer Rh–L bond distances and the corresponding smaller steric demands of the SbPh₃ versus AsPh₃ versus PPh₃ ligands, which is in fact manifested by stronger M– Cl bonds. The increased apparent higher electron density of the complexes, based on the $v(CO_{Rh})$ values, is thus in the order PPh₃ > AsPh₃ > SbPh₃. The importance of the smaller steric demand is further manifested in the fact that five-coordinate complexes for the Sb system form with relative ease [23]. As in all experimental measurements it has to be remembered that, as illustrated, many factors may influence the $v(CO_{Rh})$ values and appropriate caution needs to be exercised when conclusions are made.

4. Conclusions

A clear trend was illustrated between the stretching frequencies of the Rh and Ni complexes. The rhodium Vaska-type complexes were then used in a similar fashion as the $[NiL(CO)_3]$ complexes to establish the electronic parameters of various ligands, as an example the electronic parameters were determined for the ferrocenyl moiety. A correction term was added to Tolman's original equation to account for ligands containing different donor atoms of group 15 in the periodic table, i.e., phosphorous, arsenic and antimony. The rhodium Vaska-type system has the added benefits that the complexes are easily accessible and safe to work with and it covers almost twice the range than the $[NiL(CO)_3]$ complexes making more significant measurements feasible.

In addition to the Tolman cone angle model the implementation of the effective cone angle principle was extended which takes the real metal ligand bond distance into account when the cone angle is calculated. This principle is especially applicable in calculating the cone angles for the arsine and stibine ligands since no default bond distance has been established for these ligands.

5. Supplementary material

Complete crystallographic data in CIF format.

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References

- F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1988.
- [2] G.O. Spessard, G.L. Miessler, Organometallic Chemistry, Prentice-Hall, New Jersey, 1997.
- [3] C.A. Tolman, Chem. Rev. 77 (1997) 313.
- [4] D.W. Allen, B.F. Taylor, J. Chem. Soc., Dalton Trans. (1982) 51.
- [5] A.H. Cowley, M.C. Damasco, J. Am. Chem. Soc. 93 (1971) 6815.
- [6] R.W. Rudolph, C.W. Schultz, J. Am. Chem. Soc. 93 (1971) 6821.
- [7] K.G. Moloy, J.L. Petersen, J. Am. Chem. Soc. 117 (1995) 7696.
- [8] M. Angoletta, Gazz. Chim. Ital. 89 (1959) 2359.
- [9] L. Vaska, J.W. DiLuzio, J. Am. Chem. Soc. 83 (1961) 2784.
- [10] J. Chatt, B.L. Shaw, Chem. Ind. (1961) 290.
- [11] A. Roodt, S. Otto, G.J. Steyl, Coord. Chem. Rev. (2003) (in press).
- [12] S. Otto, A. Roodt, Acta Cryst. C53 (1997) 1414.
- [13] S. Otto, A. Roodt, J.J.C. Erasmus, J.C. Swarts, Polyhedron 17 (1998) 2447.
- [14] S. Otto, A. Roodt, J. Smith, Inorg. Chim. Acta 303 (2000) 295.
- [15] G. Steyl, S. Otto, A. Roodt, Acta Cryst. E57 (2001) m352.
- [16] A. Roodt, S. Otto, Acta Cryst. C51 (1995) 1105.
- [17] S. Otto, A. Roodt, Acta Cryst. C52 (1996) 1636.
- [18] S. Otto, A. Roodt, Acta Cryst. C53 (1997) 280.
- [19] M.H. Johansson, S. Otto, A. Roodt, A. Oskarsson, Acta Cryst. B56 (2000) 226.
- [20] S. Otto, A.J. Muller, Acta Cryst. C57 (2001) 1405.
- [21] S. Otto, M.H. Johansson, Inorg. Chim. Acta 329 (2002) 135.
- [22] S. Otto, S.N. Mzamane, A. Roodt, in: G.J. Leigh, N. Winterton (Eds.), Modern Coordination Chemistry, The Legacy of Joseph Chatt, Royal Society of Chemistry, Oxford, UK, 2002, p. 328.
- [23] S. Otto, A. Roodt, Inorg. Chim. Acta 331 (2002) 199.
- [24] S. Otto, A. Roodt, Acta Cryst. C58 (2002) m565.
- [25] S. Otto, Ph.D. Dissertation, University of the Free State, South Africa, 1999.
- [26] G.P. Sollot, H.E. Mertway, S. Portnoy, J.L. Snead, J. Org. Chem. 28 (1963) 1090.
- [27] SAINT, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1995.
- [28] G.M. Sheldrick, SADABS, University of Göttingen, Germany.
- [29] G.M. Sheldrick, SHELXL97, University of Göttingen, Germany.
- [30] K. Brandenburg, M. Brendt, DIAMOND, Release 2.1c, Crystal Impact GbR, Postfach 1251, D-53002, Bonn, Germany, 2000.
- [31] G. Kemp, A. Roodt, W. Purcell, Rhodium Expr. 12 (1995) 21.
- [32] SCIENTIST for Windows: Program for Least-squares Parameter Estimation, Release 4.00, Micromath Inc., Utah, 1990.
- [33] M. Cowie, S.K. Dwight, Inorg. Chem. 20 (1981) 1534.
- [34] R.L. Harlow, S.A. Westcott, D.L. Thorn, R.T. Baker, Inorg. Chem. 31 (1992) 323.
- [35] A.L. Del Pra, G. Zanotti, P. Segala, Cryst. Struct. Commun. 8 (1979) 959.
- [36] K.R. Dunbar, S.C. Haefner, Inorg. Chem. 31 (1992) 3676.

- [37] F. Dahan, R. Choukroun, Acta Cryst. C41 (1985) 704.
- [38] H. Schumann, S. Jurgis, M. Eisen, J. Blum, Inorg. Chim. Acta 172 (1990) 191.
- [39] A.J. Muller, A. Roodt, S. Otto, Å. Oskarsson, S. Yong, Acta Cryst. E58 (2002) m715.
- [40] S. Otto, S.N. Mzamane, A. Roodt, Acta Cryst. C55 (1999) 67.
- [41] A. Monge, E. Gutiérrez-Puebla, J.V. Heras, E. Pinilla, Acta Cryst. C39 (1983) 446.
- [42] A.N. Sobolev, I.P. Romm, V.K. Belsky, E.N. Guryanova, J. Organomet. Chem. 179 (1979) 153.