X-Ray Photoelectron Spectra of Compounds Containing Rhodium–Halogen Bonds and of Rhodium(II) Acetate and its Derivatives: Rhodium 3d and Halogen np Binding Energies

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Rhodium $3d_{3/2}$ and $3d_{5/2}$ electron binding energies have been recorded for a series of complexes containing rhodium in the formal oxidation states +3, +2, and +1. The $3d_{5/2}$ binding energies were observed to vary over a range of 2·8 eV and for the rhodium(III) complexes these were fairly sensitive to the ligand environment, but little variation was found for adducts of $Rh_2(OAc)_4$. In general, there is a decrease in the $3d$ binding energies with decrease in oxidation state provided comparisons are made within related series of complexes. The chlorine $2p$, bromine $3p$, and iodine $3d$ binding energies have also been recorded for several of these complexes.

THE exploitation of X-ray photoelectron spectroscopy (ESCA) [1] to determine the oxidation state of compounds of the heavy transition metals, has led to the investigation of the core electron binding energies of several well characterized complexes of molybdenum,[2] palladium,[3] and platinum.[4,5] Our interest in the chemistry of certain low oxidation states of the heavier transition elements, led us to explore the X-ray p.e. spectra of a variety of complexes of rhodium, silver, and rhenium. Our results on the rhodium systems are described in the present report. These latter studies resulted from our need to distinguish between diamagnetic rhodium-(III) and rhodium(II) complexes.[6] Other reports will deal with related studies on complexes of silver [7] and rhenium.[8,9]

For the rhodium complexes, the $3d$ core was the preferred level for the binding energy measurements.† Accordingly, the spin–orbit levels $3d_{3/2}$ and $3d_{5/2}$, of approximate relative intensity 2 : 3, were those whose binding energies were measured. These energies for 28 complexes of rhodium are given in Tables 1 and 2 together with some related data for the chlorine $2p_{1/2,3/2}$ levels. Representative spectra are shown in Figure 1. Binding energies (E_b) can be calculated from the expression [1]

$$E_b = E_X - E_k - \phi_s$$

where E_X is the incident X-ray energy (1486·6 eV), E_k is the kinetic energy of the emitted electron, and ϕ_s is the spectrometer work function. However, in practice the spectrometer was calibrated with reference to the following standards: Cu $2p_{1/2}$ and $2p_{3/2}$ of a copper plate, C $1s$ of graphite, and the $4f_{5/2}$ and $4f_{7/2}$ levels of metallic gold and platinum. From a knowledge of the ' spectrometer constant ' and the measured value of E_k, the appropriate binding energy could be calculated. In all instances, the E_b values of the rhodium complexes

are referenced to the carbon $1s$ peak of graphite at 284·0 eV. In addition to serving as an internal reference check, intimate grinding of the sample with graphite served to eliminate sample charging effects. This procedure involved recording the Rh $3d_{3/2}$ and $3d_{5/2}$ binding energies of the undiluted complex and then diluting the sample with increasing amounts of graphite until the binding energies achieved constant values. In many instances, this procedure indicated that the undiluted samples had not charged. The complexes chosen for this study have, with one exception, namely $RhCl_3,1·5PhSCH_2CH_2SPh$, previously been described in the literature. References to their original syntheses and characterizations are given in the Experimental section.

For the complexes listed in Tables 1 and 2, we were usually able to locate the peak maxima with the following precision: Rh $3d_{3/2}$ $\pm0·2$ and $3d_{5/2}$ $\pm0·1$ eV; Cl $2p_{1/2}$ $\pm0·2$ and $2p_{3/2}$ $\pm0·1$ eV; Br $3p_{1/2}$ $\pm0·2$ and $3p_{3/2}$ $\pm0·1$ eV; I $3d_{3/2}$ $\pm0·1$ and $3d_{5/2}$ $\pm0·1$ eV. For $[RhCl_3,PhSCH_2CH_2SPh]_n$, $RhCl_3,3PPh_3$, and $Rh(CO)Cl,2P(o\text{-tolyl})_3$, the two rhodium $3d$ components are quoted to $\pm0·2$ eV; these spectra were of decidedly poorer quality and for the latter two complexes this is attributed to their low rhodium content. For the rhodium, chlorine, and bromine binding energies, the highest energy component of each spin–orbit pair, i.e., Rh $3d_{3/2}$, Cl $2p_{1/2}$, and Br $3p_{1/2}$, had the lowest intensity and was the least precisely located. We will therefore consider chemical shifts with reference to the more intense component, i.e., Rh $3d_{5/2}$, Cl $2p_{3/2}$, etc. This is justified, since with the exception of the less well characterizable rhodium(I) complexes, the spin–orbit splittings usually remain invariant within experimental error for a particular rhodium oxidation state. The one possible exception is the rhodium(II) complex $RhCl_2,2P(o\text{-tolyl})_3$, for which

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† For a discussion of the effect of angular momentum quantum number on the cross-section for photoelectron interaction, see C. D. Wagner, *Analyt. Chem.*, 1972, **44**, 1050.

[1] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, ' ESCA; Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy,' Almquist and Wiksells, Uppsala, 1967.

[2] W. E. Swartz, jun., and D. M. Hercules, *Analyt. Chem.*, 1971, **43**, 1774.

[3] C. Kumar, J. R. Blackburn, R. G. Albridge, W. E. Moddeman, and M. M. Jones, *Inorg. Chem.*, 1972, **11**, 296.

[4] D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Comm.*, 1971, 602.

[5] C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 1972, **93**, 1904.

[6] R. W. Matthews, A. D. Hamer, D. L. Hoof, D. G. Tisley, and R. A. Walton, *J.C.S. Dalton*, submitted for publication.

[7] D. P. Murtha and R. A. Walton, *Inorg. Chem.*, 1973, **12**, in the press.

[8] D. G. Tisley and R. A. Walton, *Inorg. Chem.*, 1973, **12**, in the press.

[9] D. G. Tisley and R. A. Walton, *J. Mol. Structure*, submitted for publication.

this spin–orbit difference is perhaps marginally smaller than that of rhodium(II) acetate and its derivatives (Table 2).

With the exception of Wilkinson's compound RhCl,3PPh$_3$, the rhodium $3d_{5/2}$ and chlorine $2p_{3/2}$ binding energy half-widths (FWHM) * occurred in the range

(o-tolyl)$_3$, were we believe not located because of their low elemental content (less than 8%) in the complexes concerned. This trend was also apparent for Rh(CO)-Cl,2PPh$_3$ (5·3% chlorine), for which the chlorine $2p$ binding energies were ill defined (Table 2). The only system for which we have no explanation of our failure

TABLE 1

Rhodium $3d$ and halogen binding energies (in eV) for rhodium(III) halide complexes

Complex [a,b]		Rh		Cl			Other B.E.'s
		$3d_{3/2}$	$3d_{5/2}$	$2p_{1/2}$		$2p_{3/2}$	
trans-[RhCl$_2$(py)$_4$]Cl,2H$_2$O	I	315·1	310·6	199·6	198·2	196·5	N 1s, 400·7
cis-[RhCl$_2$(bipy)$_2$]Cl,2H$_2$O	II	315·0	310·3	199·6	197·9	196·9	N 1s, 400·9
trans-[RhCl$_2$(dth)$_2$]Cl	III	314·9	310·3	199·5	197·9	196·5	
trans-[RhCl$_2$(dth)$_2$]PF$_6$	IV	314·3	309·8	199·6		197·9	
trans-[RhCl$_2$(dth)$_2$]ClO$_4$	V	314·2	309·6	199·1		197·7 [c]	
trans-[RhBr$_2$(dth)$_2$]ClO$_4$	VI	314·1	309·6	c		c	
phenH[RhCl$_4$(phen)]	VII	313·6	309·0	198·7		197·1	
cis-RhCl$_3$,3MeCN	VIII	314·7	310·0	198·9		197·4	N 1s, 400·4
RhCl$_3$3pic	IX	314·0	309·6	198·9		197·3	
cis-RhCl$_3$,3(thiox)	X	314·0	309·3	199·0		197·5	
cis-RhBr$_3$,3(thiox)	XI	313·7	309·0				Br $3p_{1/2,3/2}$, 182·0, 175·5
RhI$_3$,3(thiox)	XII	313·0	308·5				I $3d_{3/2,5/2}$, 629·6, 618·2
[RhCl$_3$,PhSCH$_2$CH$_2$SPh]$_n$	XIII	313·6	309·3	d		d	
RhCl$_3$,(dth),PPh$_3$	XIV	313·4	309·0	198·9		197·2	
trans-RhCl$_3$,3PMe$_2$Ph	XV	313·9	309·1	ca. 199·0 [e]		197·4	
RhClIMe,2PPh$_3$,MeI	XVI	313·0	308·4	d		d	I $3d_{3/2,5/2}$, 630·9, 619·5
RhCl$_3$,1·5bipy	XVII	314·3	309·7	198·9		197·5	
RhBr$_3$,1·5bipy	XVIII	314·0	309·3				Br $3p_{1/2,3/2}$, 181·9, 175·3
RhCl$_3$,1·5PhSCH$_2$CH$_2$SPh	XIX	313·6	309·0	198·8		197·4	

[a] The particular isomer studied is indicated when known. [b] Ligand abbreviations are as follows: py = pyridine; pic = γ-picoline; thiox = 1,4-thioxan; bipy = 2,2'-bipyridyl; phen = 1 : 10-phenanthroline; dth = 2,5-dithiahexane (MeSCH$_2$CH$_2$SMe). [c] Chlorine $2p$ binding energies of ClO$_4^-$ were not located (see text). [d] Chlorine binding energies poorly defined and accordingly are not given (see text). [e] Not well resolved from the more intense $2p_{3/2}$ component.

TABLE 2

Rhodium $3d$ binding energies (in eV) for complexes of rhodium(II) and rhodium(I)

Complex [a]		Rh		Other B.E.'s
		$3d_{3/2}$	$3d_{5/2}$	
Rh$_2$(OAc)$_4$ [b]	XX	313·3	308·2	O1s, 531·9
Rh$_2$(OAc)$_4$,2PPh$_3$	XXI	312·9	308·0	O1s, 531·5
Rh$_2$(OAc)$_4$,2tu	XXII	313·2	308·4	
Rh$_2$(OAc)$_4$,2DMSO	XXIII	313·4	308·5	O1s, 532·3
Rh$_2$(OAc)$_4$,2py	XXIV	313·3	308·5	N1s, 399·9; O1s, 532·4
trans-RhCl$_2$,2[P(o-tolyl)$_3$]	XXV	313·0	308·6	Cl2$p_{1/2,3/2}$, 199·5 and 198·1
Rh(CO)Cl,2[P(o-tolyl)$_3$]	XXVI	312·2	307·9	
RhCl,3PPh$_3$ [c]	XXVII	312·5	307·8	
trans-Rh(CO)Cl,2PPh$_3$	XXVIII	312·7	307·9	Cl2p, ca. 198 (vbr)

[a] Ligand abbreviations are as follows: py = pyridine; tu = thiourea; DMSO = dimethyl sulphoxide. [b] The adducts Rh$_2$(OAc)$_4$,2MeCN and Rh$_2$(OAc)$_4$, 2THF (THF = tetrahydrofuran) lost their co-ordinated ligand molecules, under the high vacuum conditions of the ESCA experiment, to form the anhydrous acetate. [c] Charging effects with the undiluted complex were significant, but unfortunately a satisfactory spectrum of the graphite-diluted sample could not be obtained. Consequently, the experimentally observed carbon 1s spectrum of the undiluted complex, with a binding energy of 281·8 eV, was corrected to 284·0 eV, and a corresponding correction of +2·2 eV applied to the rhodium $3d$ binding energies to give the values quoted in the Table.

1·2—1·8 eV. For RhCl,3PPh$_3$, which did not give a satisfactory spectrum when diluted with graphite, the rhodium $3d_{5/2}$ peak had FWHM ca. 3·4 eV, a consequence of surface charging.

Before considering binding energy ‘ chemical shifts ’, it is pertinent to mention our failure to locate chlorine binding energies in certain of the complexes. Per-chlorate chlorine in trans-[RhX$_2$(dth)$_2$]ClO$_4$, and chlorine in RhClIMe,2PPh$_3$,MeI, RhCl,3PPh$_3$, and Rh(CO)Cl,2P-

* Full width at half maximum.

[10] R. A. Walton, *J. Chem. Soc. (A)*, 1967, 1852.

[11] D. N. Lawson, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1733.

to locate well defined chlorine binding energies was the polymeric compound [RhCl$_3$,PhSCH$_2$CH$_2$SPh]$_n$.[10]

Rhodium $3d_{5/2}$ *Binding Energies.*—An inspection of the data in Tables 1 and 2, shows that these binding energies generally decrease in the order Rh^{III} > Rh^{II} > Rh^I, the trend which is expected from a simple point charge model. However, this interpretation does not take account of changes in co-ordination number and ligands, and in fact the rhodium(III) complex RhClIMe,2PPh$_3$,MeI, obtained by the oxidative addition of methyl iodide to RhCl,3PPh$_3$,[11] has a similar rhodium $3d_{5/2}$ binding energy (308·4 eV) to that of dimeric rhodium(II) acetate and its derivatives (308·0—308·5 eV). Thus, unless

comparisons are made between structurally related species in similar ligand environments, an unambiguous correlation between binding energies and formal oxidation state should not necessarily be expected.

The *trans*-planar rhodium(II) complex $RhCl_2,2P$-(o-tolyl)$_3$,[12] has a higher binding energy (308·6 eV) than the distorted planar rhodium(I) complex $RhCl,$-$3PPh_3$,[13] and planar *trans*-$Rh(CO)Cl,2PPh_3$[14] and $Rh(CO)Cl,2P(o$-tolyl)$_3$ (presumably the *trans*-isomer?)[12] (307·8 or 307·9 eV), the expected result in view of the structural similarity and not too dissimilar ligand environments. Furthermore, it is interesting that the two carbonyl derivatives fit so well into this trend, since $Cr(CO)_6$ [formally chromium(0)] has higher chromium $2p$ and $3s$ binding energies than does Cr-(π-C_5H_5)$_2$, a chromium(II) derivative,[15] a reflection on the overall electron transfer from the metal to the CO ligands, with consequent increase in chromium binding
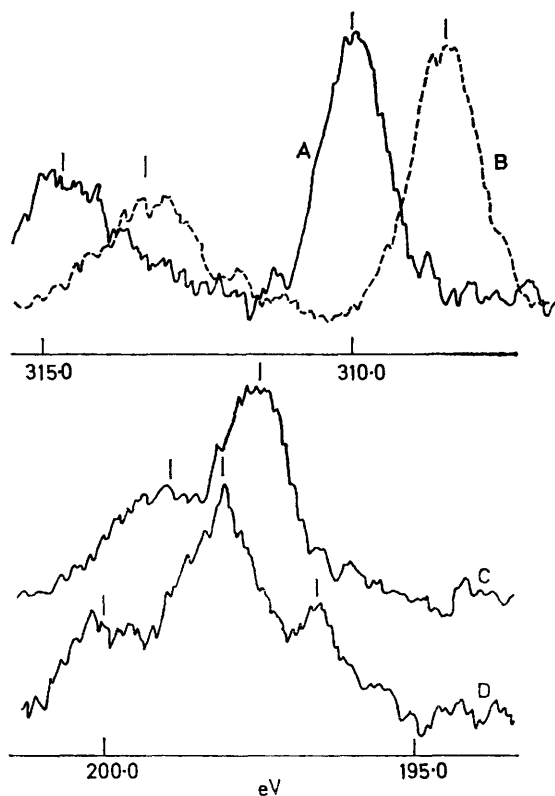

FIGURE 1 Rhodium $3d_{3/2}$ and $3d_{5/2}$ binding energies of A, $RhCl_3$, 3MeCN and B, $Rh_2(OAc)_4,2DMSO$ and chlorine $2p_{1/2}$ and $2p_{3/2}$ binding energies of C, $RhCl_3,3thiox$ and D, [$RhCl_2(dth)_2$]Cl. For these four complexes, signal-background ratios, which are fairly typical for the rhodium and chlorine binding energies of complexes of these types, were as follows: A, Rh $3d_{5/2}$, 1·75; B, Rh $3d_{5/2}$, 3·5; C, Cl $2p_{3/2}$ 0·8; D, Cl $2p_{3/2}$, 0·8

energies. In the case of $Rh(CO)Cl,2L$, such an electron drift involving a single CO ligand does not apparently

[12] M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 1969, **91**, 6266.
[13] R. Mason, P. B. Hitchock, and M. McPartlin, *Chem. Comm.*, 1969, 1367.
[14] W. P. Griffith, 'The Chemistry of the Rarer Platinum Metals,' Interscience, 1967, p. 388.

compensate for the reduction in formal positive charge from rhodium(II) to rhodium(I).

Within the series of rhodium(III) complexes several trends are apparent. One of the problems of relating binding energies between ionic and non-ionic species is the unknown variations in Madelung-type potential. For this reason we have chosen to reference internally the rhodium $3d_{5/2}$ binding energies of the chloro-complexes with respect to the related chlorine $2p_{3/2}$ binding energies, and to consider the energy difference E_b[Rh-($3d_{5/2}$) — Cl($2p_{3/2}$)] (Table 3) as a measure of binding energy changes occurring at the metal core. From the data in Table 3, it can be seen that, with the exception of anionic [$RhCl_4(phen)$]$^-$, there is a clear distinction

TABLE 3

Selected values of the binding energy difference
E_b[Rh($3d_{5/2}$) — Cl($2p_{3/2}$)]

Complex	E_b[Rh($3d_{5/2}$) — Cl($2p_{3/2}$)]
[$RhCl_2py_4$]Cl,2H$_2$O ^{a}	112·4
[$RhCl_2(bipy)_2$]Cl,2H$_2$O ^{a}	112·4
$RhCl_3,1\cdot5bipy$	112·2
$RhCl_3,3MeCN$	112·6
$RhCl_3,3pic$	112·3
phenH[$RhCl_4(phen)$]	111·9
[$RhCl_2(dth)_2$]ClO$_4$	111·9
[$RhCl_2(dth)_2$]PF$_6$	111·9
$RhCl_3,1\cdot5PhSCH_2CH_2SPh$	111·6
$RhCl_3,3thiox$	111·8
$RhCl_3,(dth),PPh_3$	111·8
$RhCl_3,3PMe_2Ph$	111·7
$RhCl_2,2P(o$-tolyl)$_3$	110·5

^{a} For these complexes, the overlap of the $2p_{3/2}$ component of chlorine bound to rhodium, and the $2p_{1/2}$ component of ionic chlorine complicates the spectrum (see text). For the purpose of the calculation of the desired energy difference, the chlorine $2p_{3/2}$ binding energy was accordingly taken as the middle of the three component spectrum. The internal consistency of the results supports this assumption.

between the nitrogen donor complexes and those with sulphur and/or phosphorus donors. The former exhibit higher rhodium $3d_{5/2}$ binding energies, and the trend N > P $\approx$ S is in keeping with the polarizability differences between the N, P, and S donor atoms. A related trend in binding energies with change in ligand polarizability is also seen within the series of complexes $RhX_3,3thiox$ (Table 1), the rhodium $3d_{5/2}$ binding energies following the sequence Cl > Br > I. The complex $RhClIMe,2PPh_3,MeI$ which contains the strong —Me σ-donor in addition to iodine and phosphorus donors, as expected has the lowest $3d_{5/2}$ binding energy of the rhodium(III) complexes.

For the 2,2'-bipyridyl complexes of stoicheiometry $RhX_3,1\cdot5bipy$ (X = Cl or Br), there is now good spectroscopic evidence for their formulation as ionic [RhX_2-(bipy)$_2$][$RhX_4(bipy)$].[16] However, their X-ray p.e. spectra do not provide any clear evidence for the two types of rhodium-containing species. The same is

[15] D. T. Clark and D. B. Adams, *Chem. Phys. Letters*, 1971, **10**, 121.
[16] I. I. Bhayat and W. R. McWhinnie, *Spectrochim. Acta*, 1972, **28A**, 743.

true for the new complex RhCl$_3$,1·5PhSCH$_2$CH$_2$SPh, which is also probably of this structure type (Table 2). Although we did not have the anion [RhCl$_4$(bipy)]$^-$ available for study, a comparison of the data for [RhCl$_2$-(bipy)$_2$]$^+$ and [RhCl$_4$(phen)]$^-$ (Table 3) shows that $E_b[$Rh$(3d_{5/2}) -$ Cl$(2p_{3/2})]$ for these two species differ by only 0·5 eV, so that it is unlikely that we will see a clear distinction between the two sets of rhodium 3$d_{5/2}$ and chlorine 2$p_{3/2}$ binding energies of two such species in the mixed salt [RhCl$_2$(bipy)$_2$][RhCl$_4$(bipy)]. Accordingly, with our current limits on instrumental resolution, the best we can perhaps hope for is a distinct broadening of these binding energies, and for RhCl$_3$,1·5bipy and RhBr$_3$,1·5bipy, the chlorine 2$p_{3/2}$ and rhodium 3$d_{5/2}$ peaks, respectively, are certainly among the broadest observed for the complexes listed in Table 1, with FWHM values of ca. 1·7 and ca. 1·9 eV, respectively.

One of our reasons for investigating the X-ray p.e. spectra of rhodium(II) acetate and its derivatives, was to establish whether rhodium core binding energies would reflect the different donor strengths of the ligands triphenylphosphine, thiourea, dimethyl sulphoxide, and pyridine. The relative insensitivity of the rhodium 3$d_{5/2}$ binding energy to these ligand changes precluded any such ranking of donor properties, and probably reflects their weak interaction with the Lewis acid rhodium(II) acetate.

Chlorine 2p *Binding Energies.*—With the exception of the complexes I—III (Table 1), the rhodium(III) chloro-complexes and RhCl$_2$,2P(o-tolyl)$_3$ exhibit characteristic two component chlorine 2p binding energy spectra. With *trans*-RhCl$_3$,3PMe$_2$Ph, the less intense 2$p_{1/2}$ component was not clearly resolved from the 2$p_{3/2}$ peak, and the latter was unusually broad (FWHM ca. 1·8 eV). We attribute this broadening effect to the presence of two different Rh–Cl bond lengths, the longer Rh–Cl bond being *trans* to phosphorus. Such structural features have been found for the series *trans*-MCl$_3$,3PMe$_2$Ph (M = Re, Os, and Ir).[17] The three peak chlorine 2p spectra of complexes I—III, arise from two overlapping doublets due to the two different types of chlorine atoms. With overlap such that the 2$p_{3/2}$ component of the cationic chlorines coincides with the 2$p_{1/2}$ component of chloride ion, we would predict a three peak pattern of relative intensity 1 : 2·5 : 1. This is observed for the above three complexes (Table 1).

Correlation Between Rhodium 3d$_{5/2}$ *Binding Energies and Rhodium–Chlorine Stretching Frequencies.*—It is now well established[18] that for a particular stereochemistry, metal–halogen vibrational stretching frequencies generally increase with increase in oxidation state. Since metal core binding energies reflect the charge distribution at a metal centre, it is reasonable

to expect a correlation between these binding energies and the appropriate metal–ligand stretching vibrations. Using data from the literature for the highest frequency
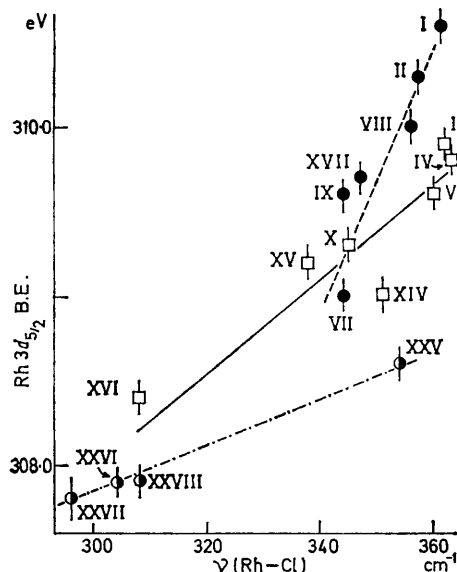

FIGURE 2   Correlation between the rhodium 3$d_{5/2}$ binding energy and the highest i.r.-active ν(Rh–Cl) mode of a series of rhodium(III) chloro-complexes. Numerals adjacent to points on this plot identify the particular complex, as listed in Tables 1 or 2. Sources of the i.r. spectral data are as follows: I, III, IV, V, X, XIV (ref. 10); XXV, XXVI (ref. 12); II, VII, IX, XVII (ref. 16); XV (ref. 19); XXVII, XXVIII (ref. 20); VIII (ref. 21). Since there does not appear to be a report of the low frequency i.r. spectrum of RhClIMe,2PPh$_3$,MeI we used the value 308 cm^{-1} for ν(Rh–Cl), being that found (ref. 20) for the related complex Rh(CO)ClI$_2$,2PPh$_3$. Also, for the ionic derivative [RhCl$_2$(bipy)$_2$][RhCl$_4$(bipy)] (complex XIX) ν(Rh–Cl) was taken as the average of the highest ν(Rh–Cl) mode of the cation (357 cm^{-1}) and anion (336 cm^{-1}). Symbols used in the plot are as follows: ● nitrogen donor complexes of rhodium(III); □ phosphorus and sulphur donor complexes of rhodium(III); ◐ complexes of rhodium(I) and rhodium(II). A line is arbitrarily drawn through the points which belong to each of the above three series of complexes to emphasize the trends discussed in the text.

i.r.-active ν(Rh–Cl) modes of the rhodium chloride complexes, we find that such a correlation exists (Figure 2). Increase in rhodium 3$d_{5/2}$ binding energies parallel an increase in ν(Rh–Cl). As Figure 2 shows, these correlations depend upon the co-ordination number [four for the complexes of rhodium(I) and (II), and six for the rhodium(III) species] and, in the case of the rhodium(III) complexes, upon the nature of the ligand atoms.

EXPERIMENTAL

Preparation of Complexes.—Samples of the complexes *cis*-RhX$_3$,3thiox (X = Cl or Br), *trans*-[RhCl$_2$(dth)$_2$]X (X = Cl, ClO$_4$, or PF$_6$), *trans*-[RhBr$_2$(dth)$_2$]ClO$_4$, RhCl$_3$,-(dth),PPh$_3$, [RhCl$_3$·PhSCH$_2$CH$_2$SPh]$_n$, [RhCl$_2$py$_4$]Cl,2H$_2$O, and *cis*-[RhCl$_2$(bipy)$_2$]Cl,2H$_2$O were available from an earlier

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[18] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Arnold, London, 1967, p. 48.

[19] P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1079.

[20] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1647.

[21] B. D. Catsikis and M. L. Good, *Inorg. Chem.*, 1969, **8**, 1095.

study.[10] The complexes cis-RhCl$_3$,3MeCN [21,22] RhClIMe,-2PPh$_3$,MeI,[11] RhI$_3$,3thiox,[10] RhCl,3PPh$_3$,[23] trans-Rh(CO)-Cl,2PPh$_3$,[24] trans-RhCl$_3$,3PMe$_2$Ph,[25] phenH[RhCl$_4$(phen)],[26] RhX$_3$,1·5bipy,[16] RhCl$_3$,3pic,[16] and Rh$_2$(OAc)$_4$ and its derivatives [27-29] were prepared by standard literature methods. They were characterized by low frequency i.r. spectroscopy and/or microanalyses.

The blue-green rhodium(II) complex RhCl$_2$,2P(o-tolyl)$_3$ was isolated using the procedure of Bennett and Long-staff [12] (Found: C, 63·3; H, 5·6. C$_{42}$H$_{42}$Cl$_2$P$_2$Rh requires C, 63·9; H, 5·4%). Addition of 37% formaldehyde solution to the above reaction filtrate afforded yellow crystals of the carbonyl complex Rh(CO)Cl,2P(o-tolyl)$_3$, identified by its i.r. spectrum (4000—200 cm^{-1}).[12]

The new orange complex of stoicheiometry RhCl$_3$,-1·5PhSCH$_2$CH$_2$SPh crystallized from the reaction filtrate of the [RhCl$_3$,PhSCH$_2$CH$_2$SPh]$_n$ preparation (Found: C, 43·7; H, 3·5; S, 16·7. C$_{21}$H$_{21}$Cl$_3$RhS$_3$ requires C, 43·6; H, 3·7; S, 16·6%).

Physical Measurements.—The X-ray p.e. spectra were recorded using a Hewlett–Packard 5950A ESCA spectrometer. The aluminium $K_{\alpha 1,2}$ line (1486·6 eV) was used as the X-ray excitation source and the powdered samples were dispersed on a gold-plated copper surface.

I.r. spectra were recorded as Nujol mulls on a Beckman IR 12 spectrophotometer.

[22] B. F. G. Johnson and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1901.

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