Rhodium Complexes Containing *O*-Bonded $NH_xMe_{2-x}CHO$ ($x = 0, 1, 2$): X-Ray Structure of $[Rh(PPh_3)_3(OCHNHMe)]ClO_4$

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This paper commemorates the enormous contribution *Luigi M. Venanzi* made to inorganic coordination chemistry over many years

Displacement of norbornadiene (nbd; bicyclo[2.2.1]hepta-2,5-diene) from $[Rh(PPh_3)_2(nbd)]ClO_4$ by hydrogenation in the presence of PPh_3 and formamide or Me-substituted derivatives, results in the formation of *O*-bonded formamide complexes $[Rh(PPh_3)_3(OCHNH_xMe_{2-x})]ClO_4$ ($x = 0$, 1, 2) rather than *N*-bonded derivatives. These have been characterised by spectroscopic measurements and, in the case of $[Rh(PPh_3)_3(OCHNHMe)]ClO_4$, by X-ray crystallography. All undergo oxidative addition with H_2, and the rates of ligand exchange in the Rh^I and Rh^{III} complexes have been determined by magnetisation-transfer measurements.

Introduction. – Formamides (L), $NH_xMe_{2-x}CHO$ ($x = 0 = L'$; $x = 1 = L''$; $x = 2 = L'''$), are versatile reagents in transition-metal chemistry since they are often found to decarbonylate and also have the possibility to behave as a ligand through either *N*- or *O*-coordination. Yet, despite dimethylformamide (L′) being commonly used as a solvent, there are relatively few crystallographically reported examples of monomeric, Pt metal complexes containing L′ as a ligand and, as far as we are aware, no crystallographically characterised complexes containing L‴ and only one example containing L″; all the structurally characterised Pt metal complexes so far reported are *O*-bonded to Ru [1–7], Rh [8][9], Pd [10][11], or Pt [12–14]. Nevertheless, for formamide and other amides, $NH_2C(O)R$ (R = alkyl), bonding to transition metals has been found to occur either through the O- or N-atom *via* the hydroxy imide tautomer, NHC(OH)R. Thus, X-ray-analysis and ^{1}H-NMR confirm the presence of the *N*-bonded isomer for $[PtCl_5(NHC(OH)Me)]^-$ [15] and *trans*-$[PtCl_2(NHC(OH)^tBu)_2]$ [16]. The X-ray structure of a five-coordinate Ni^I macrocyclic complex, (*R*,*S*,*R*,*S*)-[Ni(L)(NH-C(OH)CH_3)]ClO_4, where L is 1,3,6,8,12,15-hexazatricyclo[13.3.1.1^{8,12}]icosane, also shows coordination *via* the N-atom [17], and separate bands due to $\tilde{\nu}$(NH) and $\tilde{\nu}$(OH)

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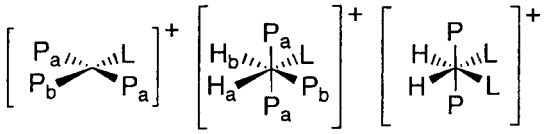
can be distinguished in the IR spectrum. The presence of equally intense ^{1}H-NMR resonances due to the NH and OH protons is also consistent with the *N*-bonded isomer for $[Co(NH_3)_5(NHC(OH)R)]^{3+}$ (R = H, Me) [18]. In the case of $[Pt(dien)(OCRNH_2)]^{2+}$ (R = H, Me), the *O*-bonded isomer is kinetically preferred but rearranges *intramolecularly* to the thermodynamically preferred *N*-bonded isomer [19], whereas, for the harder metal-ion fragments (*e.g.*, $[M(NH_3)_5]^{3+}$, M = Cr, Ru, Co), the reverse is true [19]. In this paper, we report the preparation and spectroscopic characterisation (IR and NMR) of $[Rh(PPh_3)_3L]^+$ (**1**), $[Rh(PPh_3)_3LH_2]^+$ (**2**) and $[Rh(PPh_3)_2L_2H_2]^+$ (**3**), which all contain monodentate formamides, and X-ray crystallographic studies on $[Rh(PPh_3)_3L'']ClO_4$ show that L″ is *O*-bonded; the similarity of the spectroscopic data for analogous complexes suggest L′ and L‴ are also *O*-bonded. The kinetics of ligand exchange in the above Rh^I and Rh^{III} complexes have been obtained from magnetisation-transfer measurements, and these data are compared with rates found for analogous complexes.



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Experimental. – *Safety Note. Caution!* Although no problems were encountered in the preparation of the complexes as perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds, and only small amounts of material should be prepared.

Instrumentation. IR Spectra of CH_2Cl_2 solns. were recorded on a *Perkin-Elmer 1720-X Fourier*-transform spectrometer with CaF_2 cells. NMR Spectra were recorded on *Bruker WM-200*, *WM-250* or *AMX-400* spectrometers. ^{31}P Chemical shifts are referenced to external H_3PO_4 (85% in D_2O), and ^{15}N shifts to $MeNO_2$.

Starting Materials. Solvents were dried by standard techniques and stored under a N_2 atmosphere. Substituted formamides (*B. D. H.*) and formamide (*Hopkins-Simpson*) were all distilled under reduced pressure before use. $[Rh(PPh_3)_2(nbd)]ClO_4$ was prepared as described in [20].

Synthesis of [Rh(PPh$_3$)$_3$L]ClO$_4$. H_2 was bubbled through a soln. containing $[Rh(PPh_3)_2(nbd)]ClO_4$ (100 mg, 0.12 mmol) and PPh_3 (32 mg, 0.12 mmol) in CH_2Cl_2 (2 ml) until it turned a very intense brown-red. N_2 was then bubbled through the soln. to remove the excess H_2. 1 mol-equiv. of L (4.8 µl NH_2CHO, 7.1 µl NHMeCHO, 9.5 µl NMe_2CHO) was added, and the product precipitated on addition of petroleum ether 40 : 60 (10 ml). The yellow precipitate was filtered off, washed with petroleum ether and dried under vacuum, except for the formamide compound, which was dried by blowing N_2 through the glass scinter. In all cases, yields were *ca.* 90% and the products were characterised by ^{31}P- and, in some cases, by ^{15}N-NMR measurements.

Synthesis of [Rh(PPh$_3$)$_3$LH$_2$]$^+$. The appropriate Rh^I compound from above was dissolved in CH_2Cl_2 (2 ml). H_2 was then bubbled through the soln. until the colour changed from red to light yellow. Multinuclear NMR measurements were used to characterise the complexes.

Synthesis of [Rh(PPh$_3$)$_2$L$_2$H$_2$]$^+$. H_2 was bubbled through a soln. of $[Rh(PPh_3)_2(nbd)]ClO_4$ (100 mg, 0.12 mmol) in CH_2Cl_2 (2 ml), and 2 equiv. of L (9.6 µl NH_2CHO, 14.2 µl NHMeCHO, 19.0 µl NMe_2CHO) were then added. The complexes were not isolated, but were characterised by multinuclear NMR *in situ*.

Preparation of Crystals of [Rh(PPh$_3$)$_3$(OCHNHMe)]ClO$_4$ for X-Ray Analysis. $AgClO_4$ (0.71 g, 3.4 mmol) was added to a MeOH soln. (15 ml) of $RhCl_3 \cdot 3\,H_2O$ (0.30 g, 1.1 mmol) and stirred for 3 h under protection from light. The MeOH soln. of $Rh(ClO_4)_3$ was then decanted from the prepicitated AgCl and added to a boiling soln. of PPh_3 (1.6 g, 6.1 mmol) in MeOH (90 ml). The soln. was allowed to cool, and then NHMeCHO (67.2 µl, 1.1 mmol) was added. After 3 weeks, orange crystals of the product were obtained.

Crystal-Structure Determinations. An orange crystal of dimensions $0.30 \times 0.15 \times 0.40$ mm was mounted on a glass fibre and covered in Nujol oil. X-Ray data were collected on a *Rigaku AFC6S* diffractometer with the ω-scan technique with scan width of $1.29 + 0.30 \tan\theta$, scan speed 4° min^{-1} with graphite-monochromated MoK_α

radiation. The data were collected at a temp. of $-120\pm1°$. 9672 reflections measured ($2.5\leq\theta\leq25°$), giving 4384 unique with $I>3\sigma(I)$. The intensities of three representative reflections, which were measured after every 150 reflections remained constant throughout data collection. An empirical absorption correction based on azimuthal scans was used. Structure analysis and refinement were by direct methods, followed by normal heavy-atom procedures. Full-matrix least-squares refinement was used with all non-H-atoms anisotropic except for the perchlorate O-atoms and with H-atoms in calculated positions. The methylformamide ligand was disordered. Attempts to model this on the basis of two sites for the carbonyl C-atom (C(55)) and the N-atom (N(1)) with site occupancy factors of 0.7 and 0.3, resp., were only partially successful, and are not included. The perchlorate O-atoms were also disordered. Two arrangements were modelled, with site occupancy factors of 0.6 and 0.4. The weighting scheme $w=1/\sigma^2(F)$ gave satisfactory agreement analyses. Programs, computers, and sources of scattering factor data have been described previously [21]. Crystallographic data are summarised in *Table 1*, and selected bond lengths and angles are collected in *Table 2*.

Magnetisation-Transfer Experiments. These were carried out and evaluated as outlined in [22].

Table 1. *Crystal and Data-Collection Parameters for [Rh(PPh$_3$)$_3$(OCHNHMe)]ClO$_4$·0.5 MeOH*

Formula	$C_{56}H_{50}ClNO_5P_3Rh\cdot0.5\ CH_3OH$
M_r	1064.3
Crystal system	orthorhombic
Space group	P_{bca} (No. 61)
a [Å]	25.14(2)
b [Å]	21.55(1)
c [Å]	18.67(2)
V [Å^3]	10118
Z	8
D_c [g cm^{-3}]	1.397
$F(000)$	4392
$\mu(\mathrm{Mo}K_\alpha)$ [cm^{-1}]	5.25
T [°C]	−120
λ [Å]	0.71073
$2\theta_{max}$	50°
No. observations ($I>3.0\sigma(I)$)	4384
No. variables	626
R [a])	0.066
Rw [b])	0.064
max. negative peak in final diff. map	−0.67 e/Å^3
max. positive peak in final diff. map	0.78 e/Å^3

[a]) $R=\Sigma\,\|\,|F_o|-|F_c|\,\|/\Sigma|F_o|$. [b]) $R_w=[(\Sigma w|F_o|-|F_c|^2/\Sigma wF_o^2)]^{1/2}$.

Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *for [Rh(PPh$_3$)$_3$(OCHNHMe)]ClO$_4$·0.5 MeOH*

Bond lengths			
Rh(1)–P(1)	2.309(3)	O(1)–C(55)	1.48(2)
Rh(1)–P(2)	2.218(3)	N(1)–C(55)	1.17(2)
Rh(1)–P(3)	2.358(3)	N(1)–C(56)	1.54(2)
Rh(1)–O(1)	2.161(7)		
Bond Angles			
P(1)–Rh(1)–P(2)	95.0(1)	P(3)–Rh(1)–O(1)	82.3(2)
P(2)–Rh(1)–P(3)	94.2(1)	Rh(1)–O(1)–C(55)	114.8(9)
P(1)–Rh(1)–P(3)	170.8(1)	O(1)–C(55)–N(1)	112(2)
P(1)–Rh(1)–O(1)	88.5(2)	C(55)–N(1)–C(56)	109(2)
P(2)–Rh(1)–O(1)	175.1(2)		

Results and Discussion. – *The Structure of [Rh(PPh$_3$)$_3$L″]ClO$_4$ and Related Complexes Containing either L′ or L‴.* The most convenient method of preparation of [Rh(PPh$_3$)$_3$L]ClO$_4$ is according to *Eqn. 1*, but [Rh(PPh$_3$)$_3$L″]ClO$_4$ could also be prepared by the reaction of a MeOH solution of Rh(ClO$_4$)$_3$ with PPh$_3$ (5.5 mol) and L″ (1 mol). It should be noted that ^{31}P-NMR measurements show that the reaction shown in *Eqn. 1* proceeds very cleanly, and the multinuclear NMR data of [Rh(PPh$_3$)$_3$L″]ClO$_4$ from the above preparations are identical and entirely consistent with the proposed formulation.

$$[Rh(PPh_3)_2(nbd)]ClO_4 \xrightarrow[ii)+N_2+1\,L]{i)+1\,PPh_3+H_2} [Rh(PPh_3)_3L]ClO_4 \qquad (1)$$

The NMR data for all the Rh^I complexes containing formamides are very similar and are summarised in *Table 3*. It should be noted that, for [Rh(PPh$_3$)$_3$L′]$^+$, there is little change in the appearance of the ^{1}H-NMR spectrum from 298 to 193 K, and the presence of two, sharp, equally intense Me resonances (2.6 and 2.8 ppm), which are at lower field than the Me resonances of the free ligand (2.9 and 3.0 ppm), is consistent with the presence of the *O*-bonded isomer (*vide infra*) and the lack (over this temperature range) of Rh–L′ inter-exchange on the NMR time scale.

Table 3. *Multinuclear NMR Data of Rh^I Complexes Containing NH$_x$Me$_{2-x}$CHO* (L′, $x=0$; L″, $x=1$; L‴, $x=2$) *in CH$_2$Cl$_2$ solution*

Complex	*T*/K	$\delta(P_a)$ [a] [ppm]	$\delta(P_b)$ [b] [ppm]	$\delta(^{15}N)$ [ppm]	$^1J(Rh,P_a)$ [Hz]	$^1J(Rh,P_b)$ [Hz]	$^2J(P_a,P_b)$ [Hz]
[Rh(PPh$_3$)$_3$L′]$^+$	243	34.2	52.0		144	188	40
[Rh(PPh$_3$)$_3$L″]$^+$	193	33.5	51.6	−272.3	144	188	41
[Rh(PPh$_3$)$_3$L‴]$^+$	223	33.8	51.4		143	188	40

[a]) *trans* to PPh$_3$. [b]) *trans* to L.

IR Solution spectra of [Rh(PPh$_3$)$_3$L]ClO$_4$ show that, in all cases, there is a decrease in $\tilde{\nu}$(CO) of *ca.* 37 cm^{-1} compared to the free ligand; this is consistent with coordination of L to Rh, but, in order to be sure whether L is *O*- or *N*-bonded, it was necessary to obtain crystals for X-ray analysis and/or ^{15}N-NMR spectra. It proved possible to obtain X-ray-quality crystals of [Rh(PPh$_3$)$_3$L″]ClO$_4$ from the preparation involving Rh(ClO$_4$)$_3$, and the structure shows that L″ is *O*-bonded (*vide infra*). Consistent with this formulation, the low-temperature ^{15}N-NMR spectrum of [Rh(PPh$_3$)$_3$L″]$^+$ consists of a sharp *singlet* at −272.3 ppm, which is well-removed from the resonance of the free ligand in the same solvent at the same temperature (−260.6 ppm).

The structure of [Rh(PPh$_3$)$_3$L″]ClO$_4$ is shown in the *Figure*, and selected bond lengths and angles in *Table 2*. In the cation, the Rh^I is essentially square-planar. The Rh–P bond lengths for phosphine *trans* to phosphine (Rh(1)–P(1) 2.309(3), Rh(1)–P(3) 2.358(3) Å) are significantly longer than the Rh–P bond length for phosphine *trans* to oxygen (Rh(1)–P(2) 2.218(3) Å), but it is surprising that the values of Rh(1)–P(1) and Rh(1)–P(3) are so different.

The methylformamide ligand is clearly *O*-bonded, but there is disorder in the ligand chain. Attempts to model this by refining two sites for the central C-atom (C(55)) and for the N-atom (N(1)) with site occupancy factors of 0.7 and 0.3, respectively, were

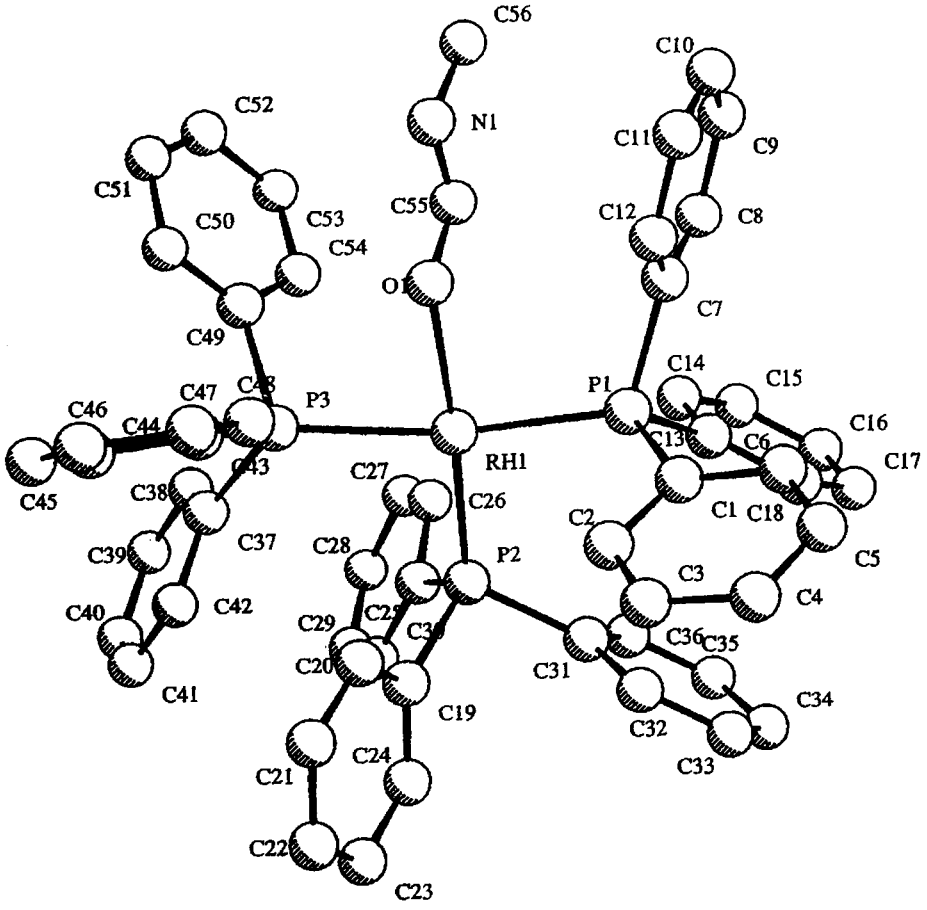
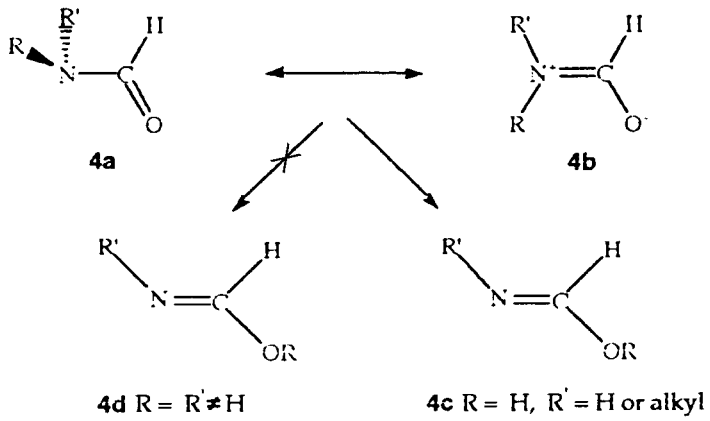


Figure. *Crystal structure of the cation of the square-planar complex [Rh(PPh$_3$)$_3$(OCHNHMe)]ClO$_4$ · 0.5 MeOH*

made. This gave satisfactory bond lengths and angles for the major component, but the C- and N-atoms of the minor component could not be located accurately. Therefore, the structure was refined on the basis of the major component only. The refinement was also hampered by a disordered perchlorate ion. Nevertheless, consistent with NMR studies, L″ is clearly *O*-bonded in $[Rh(PPh_3)_3L'']^+$, and it is worthwhile commenting upon this structure and those of other Pt-group metal complexes containing L that have so far been reported [1 – 14]. For Pt metals, it is rather surprising to have *O*- rather than *N*-coordination, but, for formamides, resonance structures (**4a** and **4b**, R = H or Me) are possible, and the involvement of **4b** significantly enhances *O*-coordination (*Scheme*).

This is supported through the following structural data of the above complexes: *a*) the formamide ligands are approximately planar, *b*) there is a slight lengthening of *d*(C–O) and a shortening of *d*(C–N) on complexation, compared to the values found for free L′ [23].

Scheme



There is also the possibility of *N*-coordination of formamides through the hydroxyimide-like tautomer, **4c**, but as this cannot occur for L′, **4d**, coordination of L′ appears to be always *O*-bonded with the structure resulting from a preponderance of the canonical form **4b**; for L″ and L‴, there still remains the possibility of *N*-coordination through **4a** or **4c.**

The structure of the Rh^{III} Complexes. The reactions described in *Eqns. 2* and *3* have been used to obtain the Rh^{III} derivatives $[Rh(PPh_3)_3LH_2]^+$ and $[Rh(PPh_3)_2L_2H_2]^+$, respectively.

$$[Rh(PPh_3)_2(nbd)]ClO_4 \xrightarrow[+H_2]{1\ PPh_3+1\ L} [Rh(PPh_3)_3LH_2]^+ \quad (2)$$

$$[Rh(PPh_3)_2(nbd)]ClO_4 \xrightarrow[+H_2]{2\ L} [Rh(PPh_3)_2L_2\ H_2]^+ \quad (3)$$

Their low-temperature NMR spectroscopic data, which show the presence of only one isomer, are summarised in *Table 4* and are entirely consistent with the proposed formulations. The similarity of the data in *Table 4* suggests the presence of the same

Table 4. *Multinuclear NMR Data of Rh^{III} Complexes Containing $NH_xMe_{2-x}CHO$* (L′, $x=0$; L″, $x=1$; L‴, $x=2$) *in CH_2Cl_2 solution*

Complex	*T*/K	$\delta(P_a)$ [a] [ppm]	$\delta(P_b)$ [b] [ppm]	$\delta(H_a)$ [c] [ppm]	$\delta(H_b)$ [d] [ppm]	$^1J(Rh,P_a)$ [Hz]	$^1J(Rh,P_b)$ [Hz]	$^2J(P_a,P_b)$ [Hz]
$[Rh(PPh_3)_3L'H_2]^+$	223	43.7	25.0	−20.6	−10.2	113	95	20
$[Rh(PPh_3)_3L''H_2]^+$	223	42.1	24.0	−20.5	−10.4	112	94	19
$[Rh(PPh_3)_3L'''H_2]^+$	223	41.3	22.5	−20.5	−10.3	112	94	20
$[Rh(PPh_3)_2L'_2H_2]^+$	273	45.5		−21.3		120		
$[Rh(PPh_3)_2L''_2H_2]^+$	273	44.8		−21.2		119		
$[Rh(PPh_3)_2L'''_2H_2]^+$	273	44.2		−21.2		118		

[a]) *trans* to PPh_3. [b]) *trans* to H_b. [c]) *trans* to L. [d]) *trans* to P_b.

isomer for all these derivatives, and the $^{15}N\{^1H\}$-NMR spectrum of $[Rh(PPh_3)_3L''H_2]^+$ in CH_2Cl_2 consists of a sharp *singlet* (-263.4 ppm) at 223 K, consistent with the presence of the *O*-bonded isomer. The hydride resonances of all the formamide complexes of the type $[Rh(PPh_3)_3LH_2]^+$ and $[Rh(PPh_3)_2L_2H_2]^+$ at low temperature are not well-resolved and, therefore, values of $^2J(P,H)$ could not be obtained. However, it should be noted that, in the ^1H-NMR spectrum, two, equally intense, sharp Me resonances (3.1 and 3.2 ppm) are observed for $[Rh(PPh_3)_3L'H_2]^+$ at 193 K but they broaden and coalesce, due to the onset of Rh–L′ inter-exchange at room temperature.

Kinetic Studies. The Rh^I complexes $[Rh(PPh_3)_3L]^+$, **1**, exhibit chemical exchange between the two different kinds of coordinated PPh_3, P_a and P_b. The rate is approximately the same, within experimental error, for all three complexes (*Table 5*) with a mean value of $0.6\ s^{-1}$ at 253 K. This is slightly lower than for the analogous nitrato complex, $[Rh(PPh_3)_3(ONO_2)]$, which, at 233 K, has a $k_{iso} = 0.8\ s^{-1}$ [22]. Since the rate constants of the formamide complexes differ so little, it was decided to do a full kinetic investigation of only one of the complexes, $[Rh(PPh_3)_3L'']^+$.

Table 5. *Phosphine-Isomerisation Rate Constants at 253 K in 25 mM CH_2Cl_2 Solutions*

	$[Rh(PPh_3)_3L']^+$	$[Rh(PPh_3)_3L'']^+$	$[Rh(PPh_3)_3L''']^+$
k [s^{-1}]	0.4	0.8	0.5

Exchange also takes place between free and coordinated PPh_3. However, since there is rapid isomerisation between P_a and P_b, separate exchange rate constants for the two sites cannot be obtained; only the overall rate constant, k_{diss}, can be determined. When PPh_3 (2 equiv.) is added to a solution of $[Rh(PPh_3)_3L'']^+$ (25 mM), $k_{diss} = 2.0\ s^{-1}$ at 253 K. The corresponding value for $[Rh(PPh_3)_3(ONO_2)]$ is $0.5\ s^{-1}$ at 233 K [22]. Assuming a twofold increase in k_{diss} for every 10° temperature rise would give an estimated $k_{diss} = 2.0\ s^{-1}$ at 253 K for the nitrato complex, approximately equal to $[Rh(PPh_3)_3L'']^+$.

When H_2 is bubbled through a solution of $[Rh(PPh_3)_3L'']^+$, H_2 adds to the complex, forming $[Rh(PPh_3)_3L''H_2]^+$. This Rh^{III} complex is also fluxional, although less so than the corresponding Rh^I complex, and, for this complex, three different processes can be observed: in the ^1H-NMR spectra, exchange occurs between the two different kinds of hydrides, H_a (*trans* to L) and H_b (*trans* to PPh_3), even at low temperature[3]); in the ^{31}P-NMR spectra, intramolecular exchange occurs between P_a and P_b, and, finally, there is intermolecular exchange between free and coordinated phosphine. This is in marked contrast to the previously studied nitrato, chloro, and ammine complexes, where no intramolecular phosphine exchange could be observed [22]. At 298 K, the hydride isomerisation rate constant $k_{iso} = 44\ s^{-1}$, compared to $120\ s^{-1}$ at 303 K for $[Rh(PPh_3)_3(ONO_2)H_2]$. The phosphine isomerisation rate constant at 298 K for $[Rh(PPh_3)_3L''H_2]^+$ is $45\ s^{-1}$, but is not observable for the analogous nitrato complex; in the presence of PPh_3 (2 equiv.), the overall phosphine dissociation rate constant at 298 K is $7\ s^{-1}$. For $[Rh(PPh_3)_3L''H_2]^+$, the rate of phosphine isomerisation is faster than

[3]) It should be noted that at higher temperature $[Rh(PPh_3)_3L'H_2]^+$ undergoes Rh–L′ inter-exchange, and it is probable that Rh–L″ inter-exchange is also very significant in $[Rh(PPh_3)_3L''H_2]^+$.

the rate of phosphine dissociation, making it impossible to obtain separate dissociation rate constants for P_a and P_b, as found for the Rh^I complexes reported here and in [22]. Thus, only an overall dissociation rate constant for P_a/P_b could be obtained. The values of k_{diss} reported previously for $[Rh(PPh_3)_3(ONO_2)H_2]$ at 303 K are 2.5 s^{-1} and 96 s^{-1} for P_a and P_b, respectively[4]).

Conclusions. – In summary, these kinetic results deserve two comments: first, although the dynamics of the tris-phosphine/Rh^I complexes containing various X ligands are similar, the dynamics of the corresponding Rh^{III}/dihydride complexes differ markedly in their rates of intramolecular phosphine isomerisation. Whereas the formamide complexes exhibit fast intramolecular phosphine isomerisation, the corresponding chloro, nitrato, and ammine complexes do not. That the rate constants of both hydride and phosphine isomerisation agree within experimental error suggest that the isomerisation observed for the formamide complex can be attributed to X-ligand dissociation, which was absent in the previously investigated Rh^{III} complexes; this is supported by the coalescence of the Me resonances of L′ in $[RhH_2(PPh_3)_3L']^+$ at room temperature. An intramolecular rearrangement *via* a trigonal prismatic transition state is for energetic reasons less likely. Second, in contrast to the analogous chloro, nitrato, and ammine complexes of Rh^{III}, the phosphine dissociation of the formamide complex is not obviously coupled to the hydride isomerisation. If any such correlation exists for the formamide complex, it is effectively masked by the fast intramolecular rearrangements.

Crystallographic data for the structure reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre*, CCDC No. 163807. Copies of this information may be obtained, free of charge, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://ccdc.cam.ac.uk).

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[4]) It is important to note that direct comparison of rate constants for different complexes is only possible for intramolecular processes because the rate constants for intermolecular processes are dependent on reagent concentrations in an unknown way.

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