Structures of Square-pyramidal Acyl and Octahedral Alkyl Intermediates in the Decarbonylation of Acid Halides by Chlorotris(triphenylphosphine)-rhodium(I)

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Oxidative addition of acetyl chloride to the compound $[RhCl(PPh_3)_3]$ leads to the formation of two acetyl- and one methyl-rhodium species, all isomeric, before reductive elimination of methyl chloride occurs to give $[RhCl(CO)(PPh_3)_2]$. The structures of all the compounds have been determined using i.r. and both ^1H and ^{31}P n.m.r. spectroscopy. The effects of changing the nature of the acid halide and the tertiary phosphine have been determined as have thermodynamic parameters for the ' carbonyl-insertion ' reactions involved. The *X*-ray crystal structure of the compound $[RhCl_2(COCH_2CH_2Ph)(PPh_3)_2]$ demonstrates essentially a square pyramid with *trans*-basal chlorides, *trans*-basal phosphines, and an apical acyl group.

REVERSIBLE ' insertion ' of carbon monoxide into (carbonylation of) a metal–carbon σ bond to form an acylmetal compound is a very well known reaction in organotransition-metal chemistry, and is undoubtedly a key step in hydroformylation-type syntheses.[1,2] The reaction and its reverse, decarbonylation of an acylmetal group, have therefore been studied in great detail, and it is generally accepted that the mechanism involves a 1,2 migration of the alkyl group between a co-ordinated carbonyl group and a *cis* co-ordination site on the metal [equation (**1**)]. This mechanism is consistent with a

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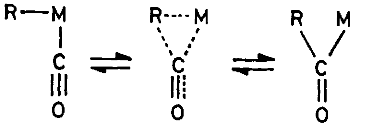
[1] A. Wojcicki, *Adv. Organometallic Chem.*, 1973, **11**, 87.
[2] R. F. Heck, ' Organotransition Metal Chemistry,' Academic Press, New York, 1974, ch. 9.

large number of kinetic studies,[1] with the observation that the reaction appears always to proceed with retention of configuration at the α-carbon atom of the R group,[3-7] and with observed stereochemical changes at


(1)

the metal in octahedral manganese complexes[8] and pseudo-tetrahedral iron complexes.[9] In contrast, there is very little in the literature pertaining to thermodynamic data for carbonylation reactions; the only such work of which we are aware is concerned with the conversion of compounds of the type $[IrCl_2(COR)(PPh_3)_2]$ into the corresponding $[IrRCl_2(CO)(PPh_3)_2]$ in the solid state.[10]

One of us has previously reported the oxidative addition of acid chlorides to chlorotris(triphenylphosphine)rhodium(I),[6,11] $[RhCl(PPh_3)_3]$, to give five-co-ordinate acylrhodium(III) compounds of the type $[RhCl_2(COR)(PPh_3)_2]$. In some cases, the latter readily isomerize to yield the six-co-ordinate alkylrhodium compounds, $[RhRCl_2(CO)(PPh_3)_2]$. We have now investigated further aspects of these oxidative additions and acyl ⇌ alkyl isomerization reactions using i.r. and both ^{31}P and

$$[RhCl(PPh_3)_2] + RCOCl \longrightarrow [RhCl_2(COR)(PPh_3)_2] \rightleftharpoons [RhRCl_2(CO)(PPh_3)_2] \longrightarrow RCl + [RhCl(CO)(PPh_3)_2] \quad (2)$$

^1H n.m.r. spectroscopy to determine the stereochemistry of the acyl and alkyl compounds in solution. In addition, we have obtained thermodynamic data for the acyl ⇌ alkyl conversion step. Some of this work has appeared as a preliminary communication.[12]

EXPERIMENTAL

The phosphines $P(C_6H_4F\text{-}p)_3$ [13] and $P(C_6H_4Me\text{-}p)_3$ [14] were prepared by standard literature methods. Triphenylphosphine was used as obtained from Aldrich Chemical Company. Rhodium compounds $[RhCl(PR_3)_3]$ [15-17] ($R = C_6H_4Me\text{-}p$, Ph, or $C_6H_4F\text{-}p$), $[RhMeCl_2(CO)(PPh_3)_2]$,[11] and $[RhMeI_2(PPh_3)_2]$ [18] were also prepared by known methods. The salt $RhCl_3\cdot 3H_2O$ was supplied by Johnson, Matthey Ltd.

Hydrogen-1, $^1H\text{-}\{^{31}P\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were recorded on a Bruker HX60 N.M.R. spectrometer for $CDCl_3$ solutions. Infrared spectra were obtained on Beckman Acculab 6 or Perkin-Elmer 180 instruments for Nujol mulls or $CHCl_3$ solutions. Molecular weights in chloroform solution were determined using a Hewlett–Packard 302B vapour-pressure osmometer. Analyses were by Microanalysis Laboratories Ltd., Toronto. As noted previously,[11] it is very difficult to free the compounds from all traces of solvent (CH_2Cl_2 or CS_2), and thus carbon analyses tend to be slightly low. Spectroscopic data, however, confirm the proposed formulations (see below).

Acetyldichlorobis(triphenylphosphine)rhodium(III).—To a stirred CH_2Cl_2 solution (3 cm³) of $[RhCl(PPh_3)_3]$ (0.5 g) was added acetyl chloride in excess (0.25 cm³). The solution was stirred for 10 min, during which time the colour changed from deep red to orange-yellow. The solvent volume was reduced *in vacuo* to half the original volume, CS_2 (*ca.* 5 cm³) was added, and the solvent volume was again reduced until a yellow product precipitated. The product was filtered off, washed with CS_2, and dried *in vacuo*, yield 75% (Found: C, 59.0, 59.4; H, 4.1, 4.5%; *M* 710. Calc. for $C_{38}H_{33}Cl_2OP_2Rh$: C, 61.6; H, 4.5%; *M* 746).

*Acetyldichlorobis[tris(*p-*fluorophenyl)phosphine]rhodium*(III).—This compound was prepared similarly, except that the solution was stirred for 15 min. A yellow product was obtained, yield 50% (Found: C, 49.5, 51.3; H, 3.2, 3.2. Calc. for $C_{38}H_{27}Cl_2F_6OP_2Rh$: C, 53.7; H, 3.2%).

*Acetyldichlorobis[tris(*p-*tolyl)phosphine]rhodium*(III).—This compound was prepared similarly except that the product was obtained by the addition of excess of light petroleum to the orange-yellow solution. The yellow product was filtered off, washed with light petroleum, and dried *in vacuo*, yield 60% (Found: C, 61.1, 64.1; H, 4.9, 6.0. Calc. for $C_{44}H_{45}Cl_2OP_2Rh$: C, 64.0; H, 5.5%).

Equilibrium Constants.—Acetyl–methyl equilibrium constants were determined from integrated ^1H and ^{31}P n.m.r. spectra. Nuclear Overhauser effects appeared to be negligible in the ^{31}P spectra of both species. The chemical shifts of the methyl protons of the acetyl compounds differed sufficiently from those of the methyl species that the area underneath each peak could be readily determined.

Thermochemical Studies.—Variable-temperature n.m.r. studies were carried out on equilibrated solutions of each acetylrhodium compound. Plots of log K_e against T^{-1} yielded straight lines with gradients of $-\Delta H/R$. From this information, values of ΔG_{298} and ΔS_{298} were calculated.

RESULTS AND DISCUSSION

Stereochemistry.—Oxidative addition of acetyl chloride to the compounds $[RhCl(PR_3)_3]$ ($R = C_6H_4Me\text{-}p$, Ph, or $C_6H_4F\text{-}p$) yielded yellow, monomeric, five-co-ordinate acetylrhodium(III) compounds $[RhCl_2(COMe)(PR_3)_2]$ (1). The latter rearrange in solution to monomeric, five-co-ordinate, orange acetyl isomers (2), and isomerize

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[3] L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, 1974, **94**, 485.

[4] K. M. Nicholas and M. Rosenblum, *J. Amer. Chem. Soc.*, 1973, **95**, 4449.

[5] P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 2814.

[6] N. A. Dunham and M. C. Baird, *J.C.S. Dalton*, 1975, 774.

[7] J. A. Labinger, D. W. Hart, W. E. Seibert, and J. Schwartz, *J. Amer. Chem. Soc.*, 1975, **97**, 3851.

[8] K. Noack and F. Calderazzo, *J. Organometallic Chem.*, 1967, **10**, 101.

[9] H. Brunner and J. Strutz, *Z. Naturforsch.*, 1974, **B29**, 446.

[10] D. M. Blake, J. de Faller, Y. L. Chung, and A. Winkelman, *J. Amer. Chem. Soc.*, 1974, **96**, 5568; D. M. Blake, A. Winkelman, and Y. L. Chung, *Inorg. Chem.*, 1975, **14**, 1326.

[11] M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1347.

[12] D. Egglestone and M. C. Baird, *J. Organometallic Chem.*, 1976, **113**, C25.

[13] A. W. Johnson and H. L. Jones, *J. Amer. Chem. Soc.*, 1968, **90**, 5232.

[14] F. G. Mann and E. Chaplin, *J. Chem. Soc.*, 1937, 530.

[15] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[16] S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 1054.

[17] M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 1969, **91**, 6266.

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

further to six-co-ordinate methylrhodium compounds $[RhMeCl_2(CO)(PR_3)_2]$. Subsequent reductive elimination of methyl chloride leads to the formation of $[RhCl(CO)(PR_3)_2]$ [equation (2)]. These conclusions are largely in agreement with those reached in earlier work [11] on the triphenylphosphine system, based on i.r. [in the carbonyl (1 600—2 100 cm^{-1}) and rhodium–chloride (240—360 cm^{-1}) stretching regions] and ^1H n.m.r. spectroscopy.

TABLE 1

Infrared data (Nujol mulls, cm^{-1}) for the compounds $[RhCl_2(COMe)(PR_3)_2]$, (1) and (2), $[RhMeCl_2(CO)(PR_3)_2]$, and $[RhCl(CO)(PR_3)_2]$

Tertiary phosphine	(1)		(2)		$[RhMeCl_2(CO)(PR_3)_2]$		$[RhCl(CO)(PR_3)_2]$	
	ν(C=O)	ν(RhCl)	ν(C=O)	ν(RhCl)	ν(C=O)	ν(RhCl)	ν(C=O)	ν(RhCl)
PPh_3	1 700	314, 273	1 700	357, 328	2 045	304, 248	1 957	309
$P(C_6H_4F\text{-}p)_3$	1 704	316, 281	1 704	354, 326	2 070	302, 256	1 985	306
$P(C_6H_4Me\text{-}p)_3$	1 693	311, 280	1 693	358, 322	2 060	298, 250	1 960	308

TABLE 2

Pertinent ^1H and ^{31}P n.m.r. data for the compounds $[RhCl_2(COMe)(PR_3)_2]$, (1) and (2), $[RhMeCl_2(CO)(PR_3)_2]$, and $[RhCl(CO)(PR_3)_2]$ in $CDCl_3$

	^1H Chemical shifts (τ)			^{31}P Chemical shifts [c]			
PR_3	(1)	(2) [a]	$[RhMeCl_2(CO)(PR_3)_2]$ [b]	(1)	(2)	$[RhMeCl_2(CO)(PR_3)_2]$	$[RhCl(CO)(PR_3)_2]$
PPh_3	6.63	7.51 (1)	9.16 (5.2, 2.0)	29.8 (145)	23.6 (108)	18.7 (90)	29.1 (127)
$P(C_6H_4Me\text{-}p)_3$	6.65	7.52 (1)	9.20 (5.2, 2.0)	28.6 (146)	22.4 (107)	17.8 (89)	27.0 (126)
$P(C_6H_4F\text{-}p)_3$	6.67	7.52 (1)	9.18 (5.2, 2.0)	28.1 (146)	21.7 (108)	16.9 (91)	27.0 (128)

[a] Collapses to a singlet on phosphorus decoupling; *J*(PH) given in parentheses. [b] Collapses to a doublet on phosphorus decoupling; *J*(PH), *J*(RhH) given in parentheses. [c] In p.p.m. downfield from external H_3PO_4; *J*(RhP) given in parentheses.

Our i.r. and ^1H n.m.r. data (Tables 1 and 2, respectively) and their interpretation are reasonably consistent with the earlier work [11] with few exceptions. Some of the far-i.r. data have been reinterpreted in the light of the larger number of data now available, and the ^1H n.m.r. data should be more accurate. In addition, a rather broad band in the n.m.r. spectra at *ca.* τ 8.4, attributed previously [11] to a second methylrhodium compound, was found to occur irregularly, did not contribute to the ^{31}P n.m.r. spectra (see below), and disappeared when exchanged with D_2O. Thus it must be reassigned to the presence of some hydroxylic impurity.

The changes which occurred in the ^1H n.m.r. spectra were duplicated by changes in the proton-decoupled ^{31}P n.m.r. spectra (Figure 1). The resonance of each compound appeared as a simple doublet due to coupling with ^{103}Rh, and thus the two phosphorus atoms in each of the acetyl isomers as well as in the methylrhodium compound must be magnetically equivalent. Chemical-shift and coupling-constant data are presented in Table 2. As can be seen, there is a shift to higher field and a decrease of the rhodium–phosphorus coupling constants on going from (1) to (2) to the methylrhodium compound for the compounds of all the three phosphines. Data for the rhodium(I) compounds are also given, as they were the products of irreversible reductive elimination of methyl chloride in each case.

Consideration of the ^1H and ^{31}P n.m.r. data leads to the conclusion that the corresponding acyl and methyl species have the same structures for all the three phosphines. Although we initially [12] favoured a square-pyramidal to a trigonal-bipyramidal structure for the five-co-ordinate acyl species on the basis of the reported crystal structures of $[RhMeI_2(PPh_3)_2]$ [19] and $[RhIL(COEt)(mdt)]^-$ (L = CO or PPh_3; mdt = maleonitriledithiolate),[20] we have now determined the structure of $[RhCl_2(COCH_2CH_2Ph)(PPh_3)_2]$ [6] as well (see below). This orange compound was expected to have the same structure as (2), which is also orange, an assumption verified by the great similarities in its ^{31}P n.m.r. para-

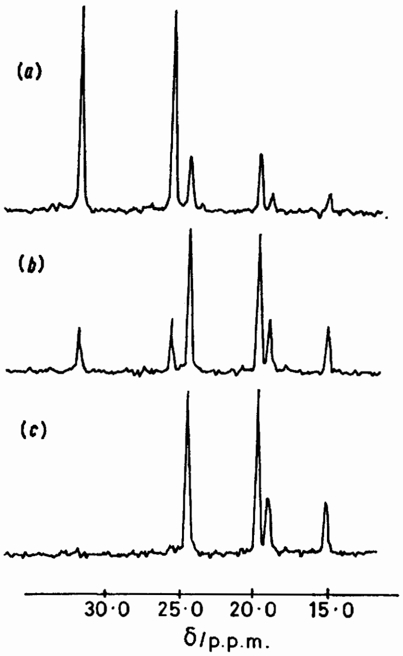

FIGURE 1 Phosphorus-31 n.m.r. spectrum of $[RhCl_2(COMe)\{P(C_6H_4F\text{-}p)_3\}_2]$ in $CDCl_3$ after (*a*) 3, (*b*) 14, and (*c*) 35 min

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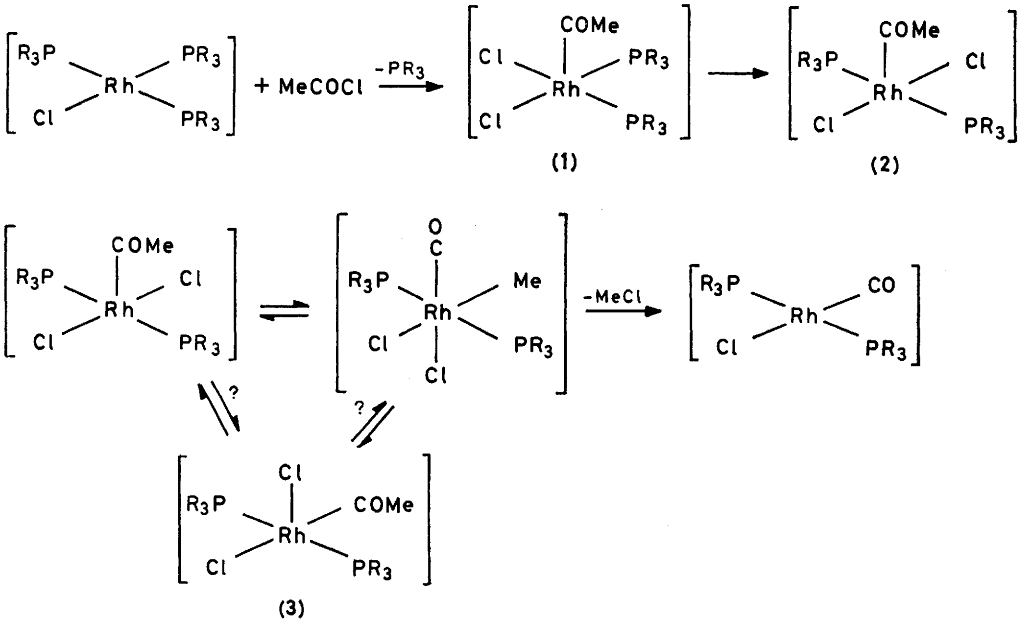
[19] P. G. H. Troughton and A. C. Skapski, *Chem. Comm.*, 1968, 575.

[20] C. H. Cheng, B. Spivack, and R. Eisenberg, *Abs. INOR* 125, Centennial Amer. Chem. Soc. Meeting, New York, April 1976.

meters [δ 23.2 p.p.m., J(RhP) 108 Hz] to those of the species (2). The ^{31}P n.m.r. spectrum of [$RhMeI_2(PPh_3)_2$] [19] [δ 21.1 p.p.m., J(RhP) 100 Hz] is also consistent with its structure. As discussed below, the benzylacetyl compound assumes a square-pyramidal structure similar to the above compounds in that the σ-bonded carbon donor is in the apical position; thus the i.r. and n.m.r. data are best rationalized as in Scheme 1.



Scheme 1

Compounds of the type [$RhCl(PR_3)_3$] have been shown to have planar structures [21,22] on the basis of ^{31}P n.m.r. data, although the kinetics of the oxidative addition of hydrogen to such species have shown that the reactive species is actually the three-co-ordinate [$RhCl(PR_3)_2$].[22,23] It seems highly likely that the more sterically demanding acid chlorides should also be more reactive with [$RhCl(PR_3)_2$], and since, on the basis of relative *trans* effects, it is probable that the latter forms by dissociation of one of the mutually *trans* phosphines, then (1) is the expected product of *cis* oxidative addition. Certainly the species (1) are predominant in the initially precipitated products, although minor amounts of (2) and methyl compounds are always present in solution by the time i.r. and n.m.r. spectra can be obtained. However, by following the slow oxidative addition to [$RhCl(PPh_3)_3$] at 270 °C it was possible to show that the doublet of (1) was the only product formed as the AB_2X [21] multiplet of the rhodium(I) compound disappeared.

The structure of (1), which is monomeric in chloroform solution, can be inferred from its ^{31}P n.m.r. and far-i.r. spectra. As already mentioned, the two phosphines must be in magnetically equivalent positions. Conclusions concerning the nature of the structural change during the (1) $\longrightarrow$ (2) conversion are based on previous work,[22,24,25] which has shown that ^1J(RhP) values for phosphines *trans* to chloride are much greater than ^1J(RhP) for mutually *trans* phosphines. Phosphines *trans* to chloride also resonate at lower field than do mutually *trans* phosphines. Thus the data in Table 2 are clearly consistent with the formulations of (1) and (2) illustrated in Scheme 1. [The ratio ^1J(RhP, *trans* Cl): ^1J(RhP, *trans* P) is 0.745, quite consistent with an average literature value [24] of 0.754.] No other structure, in fact, is possible for (1), although a second is possible in solution for (2) (see below) on the basis of the n.m.r. data, and was indeed favoured in the preliminary communication.[12]

Although rate studies were not carried out on the (2) $\longrightarrow$ (1) conversions, the relative rates appeared to decrease in the order $P(C_6H_4F\text{-}p)_3 \approx PPh_3$ ($t_{\frac{1}{2}} \approx 6$ min) $\gg P(C_6H_4Me\text{-}p)_3$ ($t_{\frac{1}{2}} \approx 40$ min). Added phosphine had no effect on either the ^{31}P n.m.r. spectra of any of the species in solution or on the rates of isomerization.

The far-i.r. spectra (Table 1) of the acyl complexes are also consistent with the formulations. Nujol-mull spectra of (1) and (2) ($PR_3 = PPh_3$) exhibit bands at 314s and 273s cm^{-1}, and 356vs and 328w cm^{-1}, respectively. Although there are few precedents in the literature for i.r. spectra of such five-co-ordinate compounds,[26-29] assignment of the bands at 314 and 273 cm^{-1}

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[21] P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94**, 3240.

[22] C. A. Tolman, P. Meakin, D. L. Lindner, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 2762.

[23] J. Halpern and C. S. Wong, *J.C.S. Chem. Comm.*, 1973, 629.

[24] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

[25] S. O. Grim and R. A. Ference, *Inorg. Chim. Acta*, 1970, **4**, 277.

[26] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597.

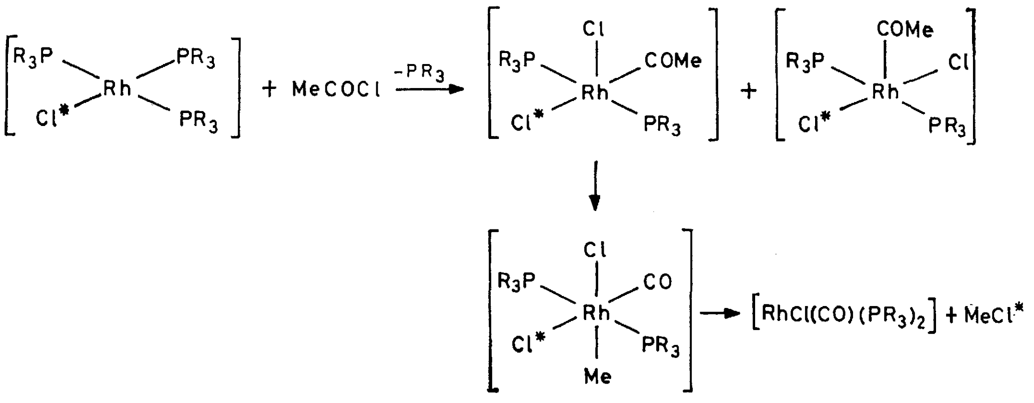
[27] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1647.

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

[29] J. K. Stille and M. T. Regan, *J. Amer. Chem. Soc.*, 1974, **96**, 1508.

as ν_{asym}(RhCl) and ν_{sym}(RhCl) (Cl *trans* to PR_3) of (1) is quite reasonable. Since the ClRhCl moiety of (2) is not quite linear, ν_{asym}(RhCl) would be much more intense than ν_{sym}(RhCl), also consistent with the observed spectrum. Precedents in this case may be found in the i.r. spectra of planar gold(III) compounds, $[AuCl_3L]$,[30] and in the i.r. and Raman spectra of mercury(II) chloride in weakly co-ordinating solvents.[31] The conversion of (1) into (2) in solution could be readily followed in the far-i.r. spectrum using polyethylene solution cells.

Conversion of (2) into the methyl compound was more rapid than the (1) ⟶ (2) isomerization, and thus (2) and methyl compounds were always present together in solution. Similarly, equilibration of the two compounds on dissolution of pure methyl compound also appeared to be very rapid. The proposed structure of the methyl compound is consistent with both the i.r. and the ^1H and ^{31}P n.m.r. spectra. A structure with *cis* chlorides is consistent with the presence in the far-i.r. spectrum of two ν(RhCl) bands at 304s (*trans* CO) and 248vs cm^{-1} (*trans* Me).[26-29] We also note that the decrease by 5/6 in ^1J(RhP) on going from (2) to the methyl compound is exactly that expected for a change from five- to six-co-ordination.[23]



SCHEME 2

Assuming that the isomerization of (2) to the methyl compound proceeds by methyl migration to a *cis* site (the structures of these two compounds argue against migration to a *trans* site), then the migration must either be preceded by or accompanied by migration of a chloride to the site *trans* to CO. Although no evidence for a third, possibly intermediate, acyl isomer exists in the n.m.r. spectra, there is such evidence in the i.r. spectra. As mentioned before,[12] the high-resolution i.r. spectrum of an equilibrated chloroform solution of $[RhCl_2(COMe)(PPh_3)_2]$ containing no (1) exhibits a shoulder on the carbonyl-stretching band. This was previously taken as evidence for the presence of rotational isomers in a structure of (2) having non-equivalent chlorides.[12] As the now known structure of (2) cannot exhibit rotational isomerism, the extra band must indicate geometrical isomerism. The far-i.r. spectrum also contains evidence of further species in solution, as a rather broad band centred at *ca.* 280 cm^{-1} is always present in solution and often present in precipitated solids. Interconversion between the hypothetical species, which we formulate as (3) in Scheme 1, and either or both (2) and methyl compound must be rapid on the n.m.r. time scale, and no evidence for a new species is present in the ^{31}P n.m.r. spectrum down to 258 K. If a species such as (3) were in equilibrium with either (2) or methyl compound, however, the position of equilibrium and thus the observed, time-averaged, chemical shifts might be expected to be temperature dependent. In fact, both doublets change slightly, diverging by *ca.* 0.6 p.p.m. on cooling from 298 to 258 K. The suggested structure for (3) has a vacant site *cis* to the acetyl group; interconversion between it and the methyl compound would thus require no rearrangement of ligands except for methyl migration, which would then be rapid on the n.m.r. time scale.

Indirect evidence for a species such as (3) has been reported in the literature. Stille and his co-workers[32,33] reported that decarbonylation (under unstated conditions) of a variety of acid halides by ^{36}Cl-labelled $[RhCl(PPh_3)_3]$ yielded $[RhCl(CO)(PPh_3)_2]$ containing about one third of the original amount of ^{36}Cl. Since the chlorides clearly become equivalent in the reaction path shown in Scheme 1, which would lead to complete scrambling and an expected loss of one half of ^{36}Cl, an alternate route must be available. A possible alternate path, involving loss of the unique phosphine from the starting rhodium(I) compound on oxidative addition, could result in the direct formation of both (2) and (3); the latter contains non-equivalent chlorides, and if its rates of isomerization to the methyl compound and concomitant reductive elimination were rapid under certain conditions relative to its rate of isomerization to (2) then labelled chloride would be lost preferentially (see Scheme 2), as is observed.[32,33]

Equilibrium Constants for the Acyl $\rightleftharpoons$ *Alkyl Isomeriz-*

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[30] D. R. Williamson and M. C. Baird, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3393.

[31] G. Allen and E. Warhurst, *Trans. Faraday Soc.*, 1958, **54**, 1786.

[32] J. K. Stille, M. T. Regan, R. W. Fries, F. Huang, and T. McCarley, *Adv. Chem. Ser.*, 1974, **132**, 181.

[33] F. Huang, *Diss. Abs. Internat.*, 1975, **B35**, 3246.

ations.—Equilibrium-constant data at 298 K for the methyl compounds studied here are presented in Table 3 in conjunction with data from the literature. Clearly the acyl species are preferred for all the three methyl systems, although there is no apparent correlation between the position of equilibrium and the nature of the *para* substituent.

TABLE 3

Equilibrium constants at 298 K for the reactions
$[\mathrm{RhCl_2(COR)(PR'_3)_2}] \rightleftharpoons [\mathrm{RhRCl_2(CO)(PR'_3)_2}]$

R	PPh_3	$P(C_6H_4F\text{-}p)_3$	$P(C_6H_4Me\text{-}p)_3$
Me	0.29 ± 0.02	0.35 ± 0.01	0.38 ± 0.02
Ph	>20		
$R''CH_2CH_2$	<0.1		
$p\text{-}ClC_6H_4CH_2$	13.7		
CH_2Cl	>20		

The greater stability of the phenyl, *p*-chlorobenzyl, and chloromethyl six-co-ordinate species may be explicable on the basis of bond-strength arguments.[34,35] Phenyl–metal bond strengths are generally believed to be greater than methyl–metal bond strengths. Similarly, substitution of hydrogen by more electronegative aryl- or chloro-substituents would also be expected to increase the strength of a metal–carbon σ bond. The monochloroacetyl compound was obtained by the addition of chloroacetyl chloride to $[\mathrm{RhCl(PPh_3)_3}]$. Although no effort was made to purify and properly characterize it, its spectroscopic properties leave little doubt as to its identity and it is included in Table 3 for purposes of comparison.

The apparently very small equilibrium constants for primary alkyl derivatives seem rather puzzling, although they may be a result of the expectedly lower metal–carbon bond strengths.[34,35] Steric factors may also play a role, as six-co-ordinate compounds of the type $[\mathrm{RhRCl_2(CO)(PPh_3)_2}]$ (R = primary alkyl) would undoubtedly be more crowded than would $[\mathrm{RhMeCl_2(CO)(PPh_3)_2}]$ or compounds of the type $[\mathrm{RhCl_2(COR)(PPh_3)_2}]$. No data are available in the literature on the magnitudes of equilibrium constants for such systems because the compounds $[\mathrm{RhRCl_2(CO)(PPh_3)_2}]$ have never been detected at room temperature;[6,11,12] it seems to have been generally believed that they do not exist. However, their apparent ' non-existence ' may only be a result of their slow formation in solution from the readily obtained acyl derivatives. Isomerization of the above chloroacetyl compound to the chloromethyl analogue takes >2 h, although the latter is thermodynamically more stable. Similarly, and rather serendipitously, we found that an aged (25 min) solution of $[\mathrm{RhCl_2(COCH_2CH_2Ph)(PPh_3)_2}]$ had changed such that a new upfield doublet appeared in the ^{31}P n.m.r. spectrum. The chemical shift and rhodium–phosphorus coupling constant of this new species [δ 15.9 p.p.m., *J*(RhP) 89 Hz] leave little doubt that it is, in fact, $[\mathrm{RhCl_2(CH_2CH_2Ph)(CO)(PPh_3)_2}]$, suggesting that other aliphatic acyl compounds may also isomerize similarly. Current reinvestigations of such compounds [11,29,35] will be reported separately.

Variable-temperature ^1H and ^{31}P n.m.r. studies made possible the determination of the temperature dependence of the acetyl (2) $\rightleftharpoons$ methyl equilibrium constants. Routine treatment of the information furnished the thermodynamic data in Table 4. The acetyl $\rightleftharpoons$ methyl conversion is slightly exothermic in all cases; the differences are probably not significant, however, so that again no correlation with the *para* substituent can be inferred. The enthalpy changes are much less exothermic than those reported previously for isomerization of a very similar acyliridium series of compounds,[10] possibly reflecting in part a weaker rhodium–carbon bond energy. The entropy changes in Table 4 are small and negative; their sign may reflect increased crowding accompanied by decreased internal rotational motion in the octahedral compounds.

TABLE 4

Thermodynamic data * for the reactions
$[\mathrm{RhCl_2(COMe)(PR_3)_2}] \rightleftharpoons [\mathrm{RhMeCl_2(CO)(PR_3)_2}]$

	PPh_3	$P(C_6H_4F\text{-}p)_3$	$P(C_6H_4Me\text{-}p)_3$
ΔH/kcal mol^{-1}	-1.7 ± 0.2	-2.0 ± 0.2	-1.3 ± 0.6
ΔS/cal K^{-1} mol^{-1}	-8.2 ± 1	-8.0 ± 1	-7.0 ± 3

* 1 cal = 4.184 J.

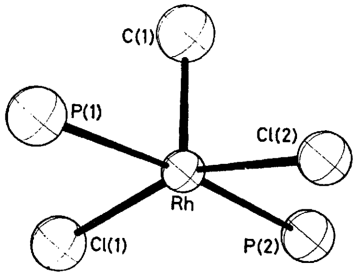

FIGURE 2 Structure of the inner co-ordination sphere of $[\mathrm{RhCl_2(COCH_2CH_2Ph)(PPh_3)_2}]$

TABLE 5

Selected interatomic distances and angles

(*a*) Distances (Å)

Rh–P(1)	2.36(2)	Rh–P(2)	2.36(2)
Rh–Cl(1)	2.33(2)	Rh–Cl(2)	2.34(2)
Rh–C(1)	1.93(7)		

(*b*) Angles (°)

C(1)–Rh–Cl(1)	100(3)	C(1)–Rh–Cl(2)	102(2)
C(1)–Rh–P(1)	91(3)	C(1)–Rh–P(2)	95(3)
Cl(1)–Rh–Cl(2)	168.7(5)	P(1)–Rh–P(2)	174.5(5)
P(1)–Rh–Cl(1)	88.1(7)	P(2)–Rh–Cl(1)	89.7(7)
P(1)–Rh–Cl(2)	91.9(6)	P(2)–Rh–Cl(2)	88.3(6)

Crystal Structure of $[\mathrm{RhCl_2(COCH_2CH_2Ph)(PPh_3)_2}]$.—Preliminary structural results * from an *X*-ray study of $[\mathrm{RhCl_2(COCH_2CH_2Ph)(PPh_3)_2}]$, carried out to determine the basic disposition of the ligands about the metal atom, show that the co-ordination about rhodium is a distorted square pyramid as shown in Figure 2. Selected bond

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* The crystal was triclinic, $P\bar{1}$, $a = 12.102$ (2), $b = 9.705$ (2), $c = 17.467$ (4) Å, $\alpha = 84.1(1)$, $\beta = 93.3(1)$, $\gamma = 74.23(1)°$, at 22 °C ($\lambda = 0.710\ 69$ Å, Mo-K_α). Intensities were measured with Mo-K_α radiation on a Syntex $P\bar{1}$ diffractometer; 1 524 independent reflections of which 1 274 were observed. Present $R = 0.177\ 1$ with 37 non-hydrogen atoms (out of 49) located.

[34] M. C. Baird, *J. Organometallic Chem.*, 1974, **64**, 289.

[35] P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, 1976, **76**, 219.

[35] K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, 1968, **90**, 99.

distances and angles around the rhodium atom are given in Table 5. The errors are still large at this stage because all the atoms in the phenyl rings have not yet been located, but the essential features of the structure are not changing as atoms are added.

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