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Preliminary communication

A STEREOCHEMICAL AND THERMOCHEMICAL STUDY OF 1,2 ALKYL SHIFTS FROM A CARBONYL GROUP TO A METAL ATOM

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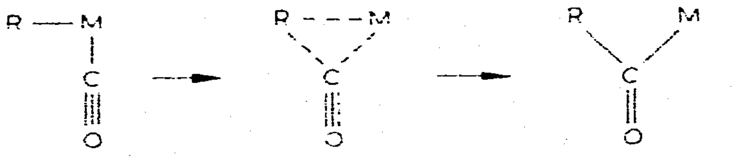
Summary

The stereochemistry of the oxidative addition of acetyl chloride to $RhCl(PAryl_3)_3$ and the subsequent isomerizations of the acetylrhodium products to other acetylrhodium complexes and then to methylrhodium complexes are studied by IR and both ^{31}P and ^{31}H NMR spectroscopy. There is no apparent correlation between the acetyl—methyl equilibrium constants and the nature of the *para* substituents on the tertiary phosphines, while ΔH and ΔS in the cases studied are about -2 kcal mol^{-1} and -8 eu, respectively.

The interconversion of acyl- and alkyl-metal carbonyl complexes (eq. 1) is a well-known reaction in organotransition metal chemistry [1].

$$RM(CO)L_n + L' \rightleftharpoons RCOML_nL' \qquad (1)$$

The mechanism of eq. 1 is believed to involve a 1,2 shift of the alkyl group R, from the metal to the coordinated carbon monoxide in a concerted process which probably involves a cyclic intermediate (eq. 2).



(2)

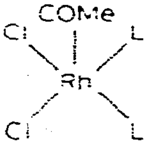
Such a process, which is consistent with the generally observed retention of configuration at the α-carbon of R [2—4], requires that R and CO occupy mutually *cis* coordination sites. In spite of numerous studies [1], however, it has been possible in only one system to reach conclusions about stereochemical changes at the metal centre. Using labelled carbon monoxide, Noack and Calderazzo were able to show that the reversible carbonylation of $CH_3Mn(CO)_5$ to give $CH_3COMn(CO)_5$ most probably involves methyl migration to one of the adjacent carbon monoxide groups [5, 6]. In addition, although many kinetic studies have been carried out [1], there is a notable paucity of thermodynamic data on alkyl—acyl conversions. Again only one investigation has appeared, that of Blake et al. on the conversion of complexes of the type $IrCl_2(COR)(PPh_3)_2$ to the corresponding alkyl derivatives in the solid state [7].

One of us has previously reported that the addition of acid chlorides to $RhCl(PPh_3)_3$ gives five-coordinated acyl complexes which, in some cases, isomerize to the corresponding octahedral alkyl carbonyl derivatives (eq. 3) [8].

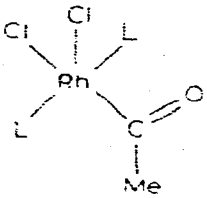
$$RhCl(PPh_3)_3 + RCOCl \rightarrow RhCl_2(COR)(PPh_3)_2 \rightleftharpoons RhRCl_2(CO)(PPh_3)_2 \qquad (3)$$

When $R = CH_3$, the position of the acyl--alkyl equilibrium is such that both species exist in easily detectable amounts in solution, an apparently unique situation in the organometallic literature and one which we have found permits the acquisition of reliable thermochemical data for the reaction. In addition, we find that the ^{31}P NMR and IR spectra of the complexes permit determination of the stereochemistry at the metal of each species in solution and, hence, of the stereochemical requirement for the alkyl—acyl conversion.

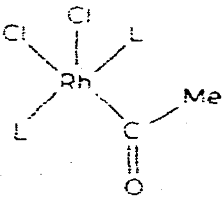
Addition of purified acetyl chloride to solutions of $RhClL_3$ ($L = (p\text{-}XC_6H_4)_3P$, X = F,H,Me) in methylene chloride yields yellow monomeric acetyl species of the type $RhCl_2(COMe)L_2$ (I). The complexes I isomerize in chloroform solution to orange monomeric acetyl complexes (II), and then to the methyl complexes (III) (eq. 4).



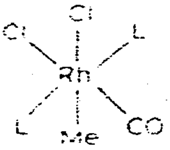
(I)



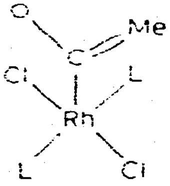
(IIa)



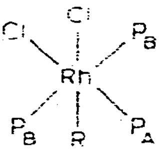
(IIb)



(III)



(V)



(VI)

$$\underset{\text{(I, Yellow)}}{RhCl_2(COMe)L_2} \rightarrow \underset{\text{(II, Orange)}}{RhCl_2(COMe)L_2} \rightleftharpoons \underset{\text{(III)}}{RhMeCl_2(CO)L_2} \qquad (4)$$

As noted perviously for $L = PPh_3$ [8], the isomerization of I to II to III can be followed using the ^1H NMR ($CDCl_3$) and solution IR ($CHCl_3$) spectra; in all cases, the spectral changes were as expected. (A broad resonance reported previously [8] at τ 8.37 ppm was found to occur only sporadically, exchanged with D_2O and did not contribute to the ^{31}P NMR spectrum. Thus it must be attributed to an impurity rather than to a second methylrhodium species.) Subsequent decomposition of III at room temperature to methyl chloride and the rhodium(I) species, *trans*-RhClCO(PPh$_3$)$_2$ (IV), is a relatively slow process.

Conversion of I to II to III to IV can be followed most easily using ^{1}H-decoupled ^{31}P NMR spectroscopy, which shows clearly that the two phosphorus nuclei are in equivalent positions in each complex. In addition, the great similarity in the ^{31}P NMR parameters for the complexes of all three tertiary phosphines strongly suggests that the structures of the species corresponding to I, II and III are the same in all cases; chemical shift and coupling constant data are listed in Table 1. Although it is not known whether the acyl complexes are square pyramidal or trigonal bipyramidal, the former seems much more likely on the basis of the reported crystal structure of RhMeI$_2$(PPh$_3$)$_2$ [9], which is a slightly distorted square pyramid with *trans*-iodides, *trans*-triphenylphosphines and an axial methyl group. On this basis, all of our spectroscopic data may be interpreted in terms of the structures illustrated.

The suggested structures of II and III are consistent with the methyl multiplet patterns in the ^{1}H spectra, which suggest that the two tertiary phosphines are in equivalent positions with respect to the methyl groups [8] while the suggestions for I and II are two of only three possible square pyramidal structures in which the phosphorus nuclei can be in equivalent positions. Comparison of the ^{31}P NMR parameters with data in the literature [10, 11] confirms the assignments. As the coordination numbers of I and II are identical, it is to be expected that J(Rh–P) of I, in which the phosphines are *trans* to Cl, should be larger than that of II, in which the phosphines are mutually *trans*. It is likewise to be expected that a phosphorus *trans* to chloride should resonate at lower field than a phosphorus *trans* to phosphorus [11, 12] (see also below). On going from II to III, the coordination number changes from five to six and, all other factors being equal,

TABLE 1

^{31}P NMR DATA IN CDCl$_3$ (δ(ppm) from external H$_3$PO$_4$; negative values are downfield)

Compound	L	δ(^{31}P) (ppm)	J(RhP) (Hz)
I	PPh$_3$	−29.8	145
I	P(C$_6$H$_4$F)$_3$	−28.1	146
I	P(C$_6$H$_4$Me)$_3$	−28.6	146
II	PPh$_3$	−23.6	108
II	P(C$_6$H$_4$F)$_3$	−21.7	108
II	P(C$_6$H$_4$Me)$_3$	−22.4	107
III	PPh$_3$	−18.7	90
III	P(C$_6$H$_4$F)$_3$	−16.9	91
III	P(C$_6$H$_4$Me)$_3$	−17.5	89
IV	PPh$_3$	−29.1	127
IV	P(C$_6$H$_4$F)$_3$	−27.0	126
IV	P(C$_6$H$_4$Me)$_3$	−27.0	126

J(Rh—P) should decrease by 5/6, exactly the observed ratio. (Two other possible structures for III would involve the methyl and carbonyl groups, both ligands of high *trans* influence, being mutually *trans*, an unlikely situation). The IR spectra are also consistent with the suggested structures, exhibiting the two ν(Rh—Cl) expected for the *cis*-chlorides of each, and apparently ruling out the third possible acetyl isomer with *trans*, equivalent phosphines and *trans*-chlorides (V). The latter possibility is also ruled out for II on the basis of the observed ν(C=O), which is a doublet (1716, ~ 1735 (sh) cm^{-1}). The doublet structure may be attributed to the presence of rotational isomerism about the Rh—acetyl bond, as in IIa and IIb, an unlikely situation for V [13]*. As II, with a vacant site *cis* to the acetyl group, can isomerize readily to the alkyl derivative, while I apparently does not, the case for a mechanism involving a 1,2 shift of the alkyl group from the metal to the coordinated carbonyl group would appear to be greatly strengthened.

Equilibrium constants for the II $\rightleftharpoons$ III interconversion have been obtained for the complexes of all three phosphines from both the ^{1}H and ^{31}P spectra. Values of 0.29 ± 0.02, 0.35 ± 0.01 and 0.38 ± 0.02 are found for the PPh_3, $P(C_6H_4F)_3$ and $P(C_6H_4Me)_3$ complexes, respectively, and thus there is no correlation with the nature of the *para* substituent. Variable temperature equilibrium constant studies of the triphenylphosphine system show that $\Delta H = -1.7 \pm 0.1$ kcal mol^{-1} and $\Delta S = -8.2 \pm 0.4$ eu; similar results are found for the other complexes. ΔH is much less negative than the values for the reaction of similar iridium complexes in the solid state [7], and clearly cannot be attributed to a specific bond making/breaking step. It may be noted, however, that the direction of change of ΔH on going from the iridium to the rhodium systems parallels the expected decrease in the strength of the metal—alkyl bonds.

Comparing the equilibrium discussed here with similar equilibria of aryl and primary alkyl complexes [3, 8], it has been shown that RCOM $\rightleftharpoons$ RM(CO) equilibrium constants decrease in the order aryl > methyl > primary alkyl, also possibly reflecting a decrease in the metal—carbon σ bond strength [14]. The small entropy change is consistent with a unimolecular process, the negative sign probably reflecting increased crowding and thus increased steric inhibition to internal rotations in the octahedral species.

In a related study, pertinent to the above, we have prepared the complexes $RhMeCl_2(PMe_2Ph)_3$ and $RhPhCl_2(PMe_2Ph)_3$ by refluxing solutions of *mer*-$RhCl_3$-$(PMe_2Ph)_3$ with dimethyl- and diphenyl-mercury, respectively. The mode of preparation of these compounds is in itself very interesting, as attempts to prepare similar complexes using Grignard reagents failed [15]. The ^{1}H NMR spectra [16] indicate that the compounds have structure VI while the ^{31}P NMR spectral parameters are $\delta(P_A)$ −1.87, $\delta(P_B)$ 5.45 ppm, $J(Rh—P_A) \approx 136$ Hz, $J(Rh—P_B)$ 97 Hz, J_{AB} 28 Hz. Consistent with the assignments discussed above for triarylphosphinerhodium complexes, the chemical shift of P_A (*trans* to Cl) is to lower field than that of P_B (*trans* to phosphorus), while $J(Rh—P_A)$ is larger than $J(Rh—P_B)$.

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* Space-filling molecular models suggest that a conformation in which the acetyl group is eclipsed with two PPh_3 would be of relatively high energy.

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