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RELATIVE STABILITIES OF ACYL- AND FORMYL-RHODIUM COMPLEXES

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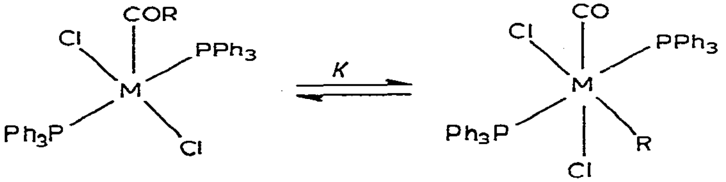
Summary

The various complexes $RhCl_2(COR)(PPh_3)_2$ and/or $RhRCl_2CO(PPh_3)_2$ (R = H, Me, Et, n-Pr, CH_2Cl, CH_2Ph, CH_2CH_2Ph, Cl) are generated in solution, and factors affecting the positions of equilibrium between the five-coordinate and six-coordinate isomers are discussed. The complex $RhCl_2(COMe)[(Ph_2P)_2(CH_2)_3]$ is far more stable with respect to isomerization to a six-coordinate methyl isomer than are any of the triphenylphosphine complexes studied.

Reversible 1,2 migration of an alkyl group between a coordinated carbonyl group and a *cis*-coordination site on a metal atom is a key feature of the chemistry of a wide variety of transition metal alkyl complexes, and has elicited much study [1]. We have previously utilized the oxidative addition reactions of a variety of acyl halides to $RhCl(PPh_3)_3$ and $IrCl(N_2)(PPh_3)_2$ to generate five-coordinate acyl species of the type $MCl_2(COR)(PPh_3)_2$ (M = Rh, Ir; R = alkyl) [2—4]. The latter isomerize in solution to six-coordinate complexes of the type $MRCl_2(CO)(PPh_3)_2$, reactions which occur with retention of configuration at both the α-carbon atom of R and, apparently, at the metal (eq. 1).



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Studies of the equilibrium constants and thermochemistry of eq. 1 showed that the alkyl migrations are generally exothermic [4—6] and involve small, negative entropy changes [4]. As the equilibrium constants decrease in the orders Ir > Rh and CF_3, Ph > Me, it was suggested that a major factor in determining the magnitudes of K is the M—R bond strength [4].

An interesting feature in the rhodium system was the observation that when

R = $PhCH_2CH_2$, K is sufficiently large that the six-coordinate species could be detected in solution using ^{31}P NMR spectroscopy. The rate of attainment of equilibrium from the acyl complex was slow, perhaps explaining why many previous studies of other, similar primary alkyl compounds had failed to observe such a species, and suggesting that other such species perhaps should be observable [4]. We report herein a study of the effects of varying the nature of R on the magnitude of K, including the case where R is hydrogen.

Experimental

^1H and $^{31}P\{^1H\}$ spectra were run on a Bruker HX60 NMR spectrometer on $CDCl_3$ solutions, infrared spectra on a Perkin—Elmer 180 instrument on Nujol mulls (<400 cm^{-1}) or $CHCl_3$ solutions. Analyses were carried out by Microanalysis Laboratories Ltd., Toronto. The compounds $RhCl_2(COEt)(PPh_3)_2$ [7], $RhCl_2(COCH_2Ph)(PPh_3)_2$ [8] and $RhCl_3CO(PPh_3)_2$ [9] have been prepared previously.

Dichloro-n-butyrylbis(triphenylphosphine)rhodium(III). The compound $RhCl_2(COCH_2CH_2CH_3)(PPh_3)_2$ was prepared by adding n-PrCOCl to a refluxing solution of $RhCl(PPh_3)_3$ in methylene chloride. After a few minutes, the solution was concentrated and the product was precipitated as orange crystals. Found: C, 62.71; H, 4.92. $C_{39}H_{31}Cl_2OP_2Rh$ calcd.: C, 62.44; H, 4.85%. The infrared spectrum of the compound exhibits ν(CO) at 1706 cm^{-1}, while the ^1H NMR spectrum exhibits methylene resonances at τ 7.21 ppm (C-2, triplet, J 7 Hz) and $\sim\tau$ 8.7 ppm (C-3, multiplet), a methyl resonance at τ 9.60 ppm (triplet, J 7 Hz).

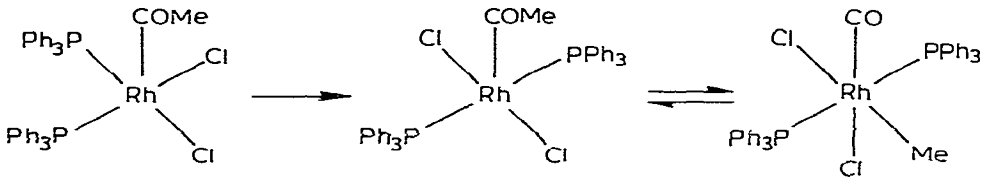
Carbonyldichloro(chloromethyl)bis(triphenylphosphine)rhodium(III). The compound $Rh(CH_2Cl)Cl_2CO(PPh_3)_2$ was prepared in a similar manner as tan crystals. Found: C, 60.28; H, 5.23. $C_{37}H_{32}Cl_3OP_2Rh$ calcd.: C, 58.82; H, 4.12%. The infrared spectrum exhibits ν(CO) at 2082 cm^{-1}, while the ^1H NMR spectrum exhibits the methylene resonance at τ 6.28 ppm (triplet of doublets, J(PH) 6.3 Hz, J(RhH) 2.7 Hz). A pale coloured, unstable acyl complex can be obtained if the solution is not heated (ν(CO) at 1713 cm^{-1}, methylene resonance at τ 4.66 ppm).

Carbonyldichlorohydridobis(triphenylphosphine)rhodium(III). The complex $RhHCl_2CO(PPh_3)_2$ is unstable with respect to loss of HCl, and the compound was formed in low concentrations by saturating a chloroform solution of $RhClCO(PPh_3)_2$ with anhydrous HCl. Formation of the hydride was confirmed by the appearance of a hydride resonance at τ 21.9 ppm (double triplet, J(PH) 10.3 Hz, J(RhH) 14.0 Hz), and a new carbonyl stretching band at 2071 cm^{-1}.

Acetyldichloro-1,3-bisdiphenylphosphinopropanerhodium(III). The complex $RhCl_2(COMe)[Ph_2P(CH_2)_3PPh_2]$ was prepared by adding a solution of the phosphine in methylene chloride to an equivalent amount of $[RhCl(C_2H_4)_2]_2$ suspended in methylene chloride under nitrogen. When ethylene evolution had ceased, acetyl chloride was added and the mixture was stirred at room temperature for 30 minutes. The solution was then filtered under nitrogen and the filtrate was concentrated under reduced pressure to give, on the addition of ethyl ether, a yellow precipitate of the product. Found: C, 54.88; H, 4.91. $C_{29}H_{29}Cl_2OP_2Rh$ calcd.: C, 55.35; H, 4.64%. The infrared spectrum exhibits ν(CO) at 1705 cm^{-1}, while the ^1H NMR spectrum exhibits the methyl resonance at τ 7.12 ppm.

Discussion

Addition of acetyl chloride to $RhCl(PPh_3)_3$ gives initially a rather unstable acetyl complex, previously referred to as acyl-I [4], which contains *cis*-triphenylphosphines and *cis*-chloride ligands. This compound isomerizes at room temperature, first to a second acetyl isomer, acyl-II, with mutually *trans*-triphenylphosphines, then to a six-coordinate methyl isomer (eq. 2).



(Acyl-I) (Acyl-II) (2)

Similar behaviour is to be expected for other alkyl complexes and, as before [3,4], we find that ^{31}P NMR spectroscopy permits facile structural assignments. Data are presented in Table 1, with data from previous studies for purposes of comparison, and with far infrared data.

As can be seen, the acyl compounds are divided into two groups, a group of three, in which the triphenylphosphine complexes have phosphorus chemical shifts of about 30 ppm, $J(RhP)$ of about 140 Hz, and $\nu(RhCl)$ in the ranges 308—316 and 273—288 cm^{-1}, and a group of five with triphenylphosphine-phosphorus chemical shifts of about 23.5 ppm, $J(RhP)$ of about 108 Hz and $\nu(RhCl)$ in the ranges 344—357 and 308—326 cm^{-1}. All ^{31}P resonances are doublets, indicating equivalent phosphorus atoms in each compound.

We have previously presented arguments [4] for concluding that acyl-I has the structure indicated in eq. 1, and it is gratifying to note that the diphosphine complex, which must have essentially the same structure, has a very similar far

TABLE 1

^{31}P NMR AND FAR INFRARED SPECTROSCOPIC DATA FOR THE COMPLEXES $RhCl_2(COR)(PPh_3)_2$ AND $RhRCl_2CO(PPh_3)_2$

Complex	δ (ppm)[a]	J(Rh—P) (Hz)	ν(Rh—Cl) (cm^{-1})
$RhCl_2(COMe)(PPh_3)_2$ (acyl-I)	29.8	145	314, 273
$RhCl_2(COCH_2Cl)(PPh_3)_2$	29.9	140	308, 288
$RhCl_2(COMe)[Ph_2P)_2(CH_2)_3]$	23.4	136	316, 288(sh)
$RhCl_2(COMe)(PPh_3)_2$ (acyl-II)	23.6	108	357, 328
$RhCl_2(COEt)(PPh_3)_2$	23.5	108	344, 310
$RhCl_2(COPr\text{-}n)(PPh_3)_2$	23.3	109	347, 308
$RhCl_2(COCH_2Ph)(PPh_3)_2$	23.4	108	356, 326
$RhCl_2(COCH_2CH_2Ph)(PPh_3)_2$	23.2	108	348, 308
$RhHCl_2CO(PPh_3)_2$	25.0	87	—
$RhMeCl_2CO(PPh_3)_2$	18.7	90	304, 248
$Rh(CH_2Cl)Cl_2CO(PPh_3)_2$	17.9	90	308, 254
$Rh(CH_2CH_2Ph)Cl_2CO(PPh_3)_2$	15.9	89	—
$RhCl_3CO(PPh_3)_2$	12.9	77	—

[a] Downfield from external H_3PO_4.

infrared spectrum. The ^{31}P chemical shift of this compound is not directly comparable with the chemical shifts of the triphenylphosphine complexes, and it is possible that the similarity of the rhodium—phosphorus coupling constant with that of acyl-I is fortuitous.

It is apparent from the data that $RhCl_2(COCH_2Cl)(PPh_3)_2$ must also have a structure similar to that of acyl-I. No other acyl species was observed in the ^{31}P NMR spectrum during the smooth conversion of this compound to $Rh(CH_2Cl)Cl_2CO(PPh_3)_2$, although it is not at all clear why a chloroacetyl species with *trans*-phosphines and *trans*-chlorides should not be stable. Possibly the isomer with *trans*-chlorides isomerizes to the six-coordinated species too rapidly to be detected.

The data in Table 1 indicate that the remaining five acetyl complexes all have the same structure, as shown in eq. 1, established by a crystal structure determination of $RhCl_2(COCH_2CH_2Ph)(PPh_3)_2$ [4]. The six-coordinated complexes probably all have the stereochemistry about the rhodium exhibited by the methyl complex, as illustrated in eq. 1, although the data for this series are less conclusive. The ^1H NMR spectra of $RhHCl_2CO(PPh_3)_2$, $RhMeCl_2CO(PPh_3)_2$ [4], and $Rh(CH_2Cl)Cl_2CO(PPh_3)_2$ are all consistent with this type of structure, as is the ^1H spectrum of the iridium analogue of $Rh(CH_2CH_2Ph)Cl_2CO(PPh_3)_2$ [2]. In addition, the ^{31}P NMR and far infrared data exhibit reasonable consistency throughout the series, although the ^{31}P chemical shifts are obviously very sensitive to electronic effects.

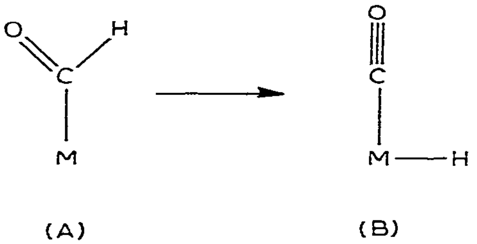
Acyl $\rightleftharpoons$ alkyl equilibrium constants were measured using ^{31}P NMR spectroscopy in $CDCl_3$ solution; Overhauser effects appeared to be negligible. In most cases, only one species could be detected, and thus only upper or lower estimates could be obtained. Since up to half an hour appears to be necessary for the phenethyl and chloromethyl systems to reach equilibrium, all the others were allowed at least an hour before spectra were run.

As reported previously [4], the equilibrium constant, K, for the methyl system is 0.29 ± 0.02. Surprisingly, while K for the phenethyl system is ~ 0.06, the octahedral isomers of the ethyl, n-propyl and benzyl systems could not be detected, and thus K for these systems must be less than ~ 0.02. In contrast, acyl species for the chloromethyl, hydrido and chloro systems could not be detected, and thus K for these systems must be greater than ~ 40. Contrary to our expectations, therefore, there is no apparent correlation between the steric requirements of R and the magnitude of K, and it is not at all clear why the phenethyl complex provides such a contrast to the other alkyl complexes. The diphosphine complex also provides contrast, as it is seemingly quite robust. This compound, which of course cannot convert to an isomer with mutually *trans*-phosphorus ligands, remains unchanged after refluxing in chloroform for one hour, conditions under which the triphenylphosphine analogue is completely converted to $RhClCO(PPh_3)_2$. The much greater stability of $RhCl_2(COMe)$diphos may be attributed to the fact that methyl migration would lead to an octahedral complex in which a methyl group would be *trans* to a phosphorus, an unlikely occurrence.

The driving forces for the formation of the six-coordinate chloromethyl and trichloro species are undoubtedly the bond strengths of the rhodium—carbon and rhodium—chloride bonds being formed. Both would be expected to be stronger than, say, rhodium—methyl or —ethyl bonds because of the highly electronegative chlorine.

The stability of the hydride complex, $RhHCl_2CO(PPh_3)_2$, with respect to isomerization to the formyl complex, $RhCl_2(COH)(PPh_3)_2$, which could not be detected, is noteworthy in view of current interest in the possible roles of formyl complexes in catalytic systems [10]. The reluctance of the hydride to isomerize to a formyl species does not appear to be a result solely of kinetic stability of the former, if the rates of similar isomerizations of other compounds in Table 1 be any guide. The hydridocarbonyl species must be the thermodynamically preferred species, consistent apparently with the chemical behaviour of those formyl complexes which have been reported [11—14].

Indeed, formyl complexes might be expected, on the basis of consideration of bonds being formed and broken in a general reaction such as eq. 3, to be unstable. Factors favouring the conversion of A to B would be the formation of a new metal—hydrogen bond and possibly of a stronger metal—carbon bond (greater back-bonding), and the conversion of the carbon—oxygen moiety from a double bond to a triple bond. On the other hand, only a carbon—hydrogen bond is being broken. It would seem then that, all other factors being equal, the difference in C—H and M—H bond strengths would have to be very large for the reverse of process of eq. 3 to be sufficiently exothermic that the formyl compound would be thermodynamically preferred.



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A similar argument would apply to the primary alkyl compounds considered above, and it is probable that congestion in the octahedral isomers [4] is an important factor leading to their apparent lack of stability. Although few reliable thermodynamic data for the strengths of metal—carbon and metal—hydrogen bonds are available in the literature, it seems very unlikely that they are significantly weaker than carbon—hydrogen bonds [15].

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