Journal of Organometallic Chemistry, 179 (1979) C61—C64

Preliminary communication

THE KINETICS OF REDUCTIVE ELIMINATION OF METHYL CHLORIDE FROM $RhMeCl_2CO(PPh_3)_2$; NUCLEOPHILIC ATTACK BY A TERTIARY PHOSPHINE ON A COORDINATED METHYL GROUP

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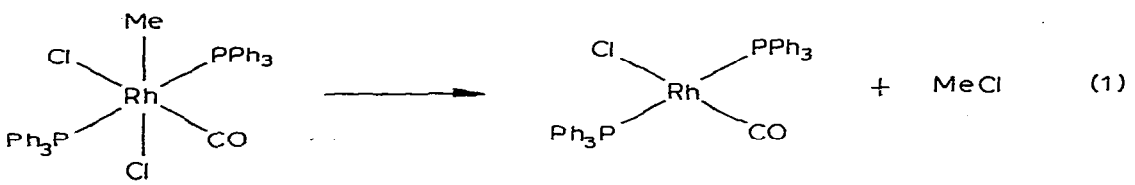
(Received July 17th, 1979)

Summary

The compound $RhMeCl_2CO(PPh_3)_2$ reductively eliminates methyl chloride in a first order, intramolecular process with an activation energy of 95.0 kJ mol^{-1}. In the presence of free triphenylphosphine, S_N2 attack on the methyl group by the phosphine occurs, yielding $PMePh_3^+Cl^-$ and *trans*-$RhClCO(PPh_3)_2$.

Although oxidative addition reactions of alkyl, aryl and vinyl halides to d^8 and d^{10} transition metal systems have been much studied in recent years [1], relatively little is known mechanistically about the reverse reactions, reductive eliminations. Thus while Stille et al. have reported some kinetic [2] and stereochemical [3,4] data which pertain to the reductive elimination of arylic and benzylic halides from rhodium(III), most work in this area seems to be concerned with reductive elimination of alkanes from, for instance, osmium(II) [5], platinum(II, IV) [6—8] and gold(III) [9—11].

During previous studies of the decarbonylation of acetyl chloride by $RhCl(PPh_3)_3$ [12,13], we have noted the facile reductive elimination of methyl chloride from $RhMeCl_2CO(PPh_3)_2$ (A) (eq. 1).



(A) (B)

As this reaction occurs over a convenient range of temperatures, the opportunity was presented of studying it kinetically with a view to possibly obtaining mechanistic information. The effort would be worthwhile, both in view of the

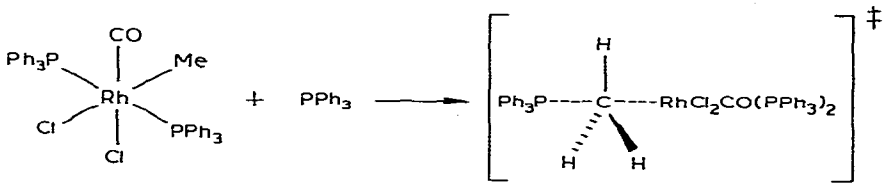
general importance of reductive elimination processes in organometallic chemistry, and because the results would complement data on oxidative addition reactions [1]. In the course of the work, as an added bonus, it was found that triphenylphosphine expedites the elimination reaction in a very novel manner.

Compound A exists in solution in equilibrium with a five-coordinated acyl isomer, $RhCl_2(COMe)(PPh_3)_2$ (C) the latter predominating [13]. Elimination from A is much slower than is equilibration between A and C. It was possible, therefore, to follow the rate of disappearance of A by monitoring both the proton-decoupled ^{31}P resonance of C (δ 23.6 ppm), or ν(CO) of A (2065 cm^{-1}) (the latter was chosen because ν(CO) of C is broadened by the presence of rotational isomers in solution).

Kinetic measurements were carried out on solutions of A (~0.1 *M*) in 2/1 $CHCl_3/1,2\text{-}C_2H_4Cl_2$ over the temperature range 314—333 K. Good first order and Arrhenius plots were obtained with $k_1 = (1.75 \pm 0.3) \times 10^{-4}$ sec^{-1} at 333 K, and an activation energy, E_a, of ~95.0 kJ mol^{-1}. These data are comparable in magnitude with similar data for the *p*-chlorophenyl and *p*-chlorobenzyl systems [2], and point to a mechanistic scheme involving an intramolecular reductive elimination process.

Since in many cases reductive elimination reactions involve prior dissociation of a neutral ligand and are retarded in the presence of excess free ligand [2,6,7,9,10], rates of disappearance of A were studied in the presence of free triphenylphosphine (1—20-fold excess). Interestingly, while an equimolar amount of the phosphine does not have a significant effect on K_1, larger amounts actually have an accelerating effect, K_1 in the presence of 10- to 20-fold excesses being constant at about triple the value of K_1 in the absence of free phosphine. While the kinetics in the presence of free phosphine are complicated and have not yet been fully elucidated, it appears that decomposition of A in the presence of free ligand involves two pathways, one of which involves attack by free phosphine.

The nature of the latter, which appears to be unprecedented, was determined by ^1H and ^{31}P NMR spectroscopy of the reactant solutions. It was noted that, as the ^{31}P resonances of A and C diminished and that of B increased in intensity, a singlet at δ 21.3 ppm in the ^{31}P spectrum and a doublet at δ 3.30 ppm (*J* 13 Hz) in the ^1H spectrum also appeared and increased in intensity. These resonances were attributed to the formation of the phosphonium salt, $MePh_3P^+Cl^-$, by comparison with the spectra of an authentic sample. As the salt formed at a rate faster than that with which free MeCl reacts with PPh_3, it would seem that its for-



(D)

$$D \longrightarrow [Ph_3PMe]^+ + [RhCl_2CO(PPh_3)]^- \longrightarrow PMePh_3^+Cl^- + RhClCO(PPh_3)_2 \quad (2)$$

mation must involve direct nucleophilic attack by the phosphine on the methyl carbon atom, a rhodium(I) species being the leaving group (eq. 2).

While coordinated olefin [14] and dienyl [14,15] ligands are known to undergo nucleophilic attack by tertiary phosphines, the reaction is unknown for coordinated alkyl groups. However, there are reports of somewhat similar substitution reactions, of presumably S_N2 character, in which halide ion attacks "activated" alkyl groups in cationic complexes. Thus halide ions attack the α-carbon atoms of the compounds [alkylCo(dioximato)$_2$ L]$^+$ [16] and [η^5-$C_5H_5Fe(CO)_2$benzyl]$^+$* to give the alkyl halides, with inversion of configuration, and a metal complex in a lower oxidation state. On the other hand, the methyl group of the neutral compound, A, is presumably activated only by the strongly electrophilic rhodium(III), suggesting that such reactions may be rather general**.

The results reported herein may have relevance to similar studies with aryl- and benzyl-rhodium systems [2]. As mentioned above, the values of k_1 and E_a for the methyl systems are comparable with those reported for the aryl and benzyl compounds. An apparently complicating factor with the latter two, however, was that added triphenylphosphine had a marked retarding effect on the reductive elimination of chlorobenzene from the aryl complex, but no effect on the rate of reductive elimination of benzyl chloride from the benzyl analogue. It now seems possible that prior dissociation of phosphine is a common feature of reductive elimination reactions in this rhodium system. If, as seems likely, a benzyl group coordinated to rhodium(III) can also undergo nucleophilic attack by triphenylphosphine, then it is possible that the rate of decomposition of the benzyl compound, like that of A, may be unaffected by free phosphine under certain conditions because of a balancing of the two decomposition paths.

Dissociation of neutral ligands is now recognized as a common feature in reductive elimination reactions yielding hydrocarbons [6,7,9,10]. Interestingly, a recent report has shown that dissociation of tertiary phosphine also occurs prior to oxidative addition of aryl halides to iridium(I) compounds [18]; the suggestion was made that earlier kinetic studies on similar oxidative addition reactions should be re-evaluated for the possible effects of added neutral ligands.

Acknowledgements

We thank Queen's University and the National Sciences and Engineering Research Council of Canada for financial support, Johnson Matthey, Ltd., for a loan of rhodium trichloride and Professor B.K. Hunter for assistance obtaining the ^{31}P NMR spectra.

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*As yet unpublished experiments with (*R*)-(−)-η^5-$C_5H_5Fe(CO)_2$CHDPh have demonstrated inversion of configuration in the chemistry described in ref. 17.

**We cannot at this time rule out the prior dissociation of chloride ion to give a cationic intermediate, although this seems relatively unlikely.

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