Journal of Organometallic Chemistry, 306 (1986) 133–138
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE OXIDATIVE ADDITION OF 1-HALOALKANES TO MONOMERIC *trans*-$[RhX(CO)(PR_3)_2]$ (X = Cl, Br; R = aryl) AND DIMERIC *trans*-$[Rh(\mu\text{-}X)(CO)(PPh_3)]_2$ (X = Cl, I)

F.R. HARTLEY*, S.G. MURRAY*, D.M. POTTER

The Royal Military College of Science, Shrivenham, Wiltshire, SN6 8LA (Great Britain)

and J.R. CHIPPERFIELD

Department of Chemistry, The University of Hull, Hull, HU6 7RX (Great Britain)

(Received November 12th, 1985)

Summary

The oxidative addition of 1-bromopropane to *trans*-$[RhBr(CO)\{P(p\text{-}EtC_6H_4)_3\}_2]$ has been found to follow pseudo first-order kinetics and give only an acylrhodium(III) product. The reaction is not catalysed by added bromide ion in chloroform solution, indicating that an anionic intermediate such as $[RhBr_2(CO)\{P(p\text{-}EtC_6H_4)_3\}]^-$ does not play an important part in this reaction. The oxidative addition of iodomethane to *trans*-$[Rh(\mu\text{-}X)(CO)(PPh_3)]_2$ (X = Cl and I) is pseudo first-order, the reactivity increasing on replacing chloride by iodide.

Introduction

The oxidative addition of iodomethane to *trans*-$[RhCl(CO)(PR_3)_2]$ (I) has recently been shown [1] to be more complicated than once thought [2]. A mechanism involving the anionic intermediate $[RhClI(CO)(PR_3)]^-$ has been proposed [1], although the possibility of halide exchange between iodomethane and I to give *trans*-$[RhI(CO)(PR_3)_2]$ complicates this system. Thus it was decided to study systems in which the same halogen was present in both the 1-haloalkane and the rhodium(I) complex *trans*-$[RhX(CO)(PR_3)_2]$ (II). The systems chosen were the addition of 1-bromopropane to *trans*-$[RhBr(CO)\{P(p\text{-}EtC_6H_4)_3\}_2]$ as well as the addition of iodomethane to *trans*-$[RhI(CO)(PPh_3)_2]$. Unfortunately, during the preparation of II (X = I; R = *para*-substituted phenyl) the phosphine was found to dissociate readily to give dimeric *trans*-$[Rh(\mu\text{-}I)(CO)(PR_3)]_2$ (III) [3]. Although the oxidative addition of iodomethane to *trans*-$[RhI(CO)(PR_3)_2]$, has been reported previously [2–4], it was not realised that the dimer III (R = Ph) was present. The reactivity of *trans*-$[Rh(\mu\text{-}Cl)(CO)(PPh_3)]_2$ to both oxidative addition [5] and reduc-

0022-328X/86/$03.50

tive elimination [6] has been compared to that of monomeric rhodium(I) species and has been found to be greater. It would be expected, therefore, that the dimer would play an important part in the mechanism of oxidative addition of iodomethane to *trans*-[RhI(CO)(PPh_3)$_2$]. To further understand the role played by *trans*-[Rh(μ-I)(CO)(PPh_3)]$_2$ in the latter system, the oxidative addition of iodomethane to *trans*-[Rh(μ-X)(CO)(PPh_3)]$_2$ (III, X = Cl and I) was also investigated.

Experimental

The infrared spectra were monitored by use of a Perkin–Elmer model 577 spectrometer. Solution infrared cells fitted with potassium bromide windows were mounted in a methanol-jacketted cell housing which was maintained at constant temperature by a Techne C100 circulating bath coupled to a Techne 1000 refrigeration unit.

Synthesis of reaction substrates

Trans-[RhX(CO)(PR_3)$_2$] (II, X = Br and I; R = Ph and *p*-EtC_6H_4) were prepared by the literature method [3]. The complexes *trans*-[Rh(μ-X)(CO)(PPh_3)]$_2$ (III, X = Cl and I) were prepared by a modified literature method [7] under an atmosphere of nitrogen and in the dark.

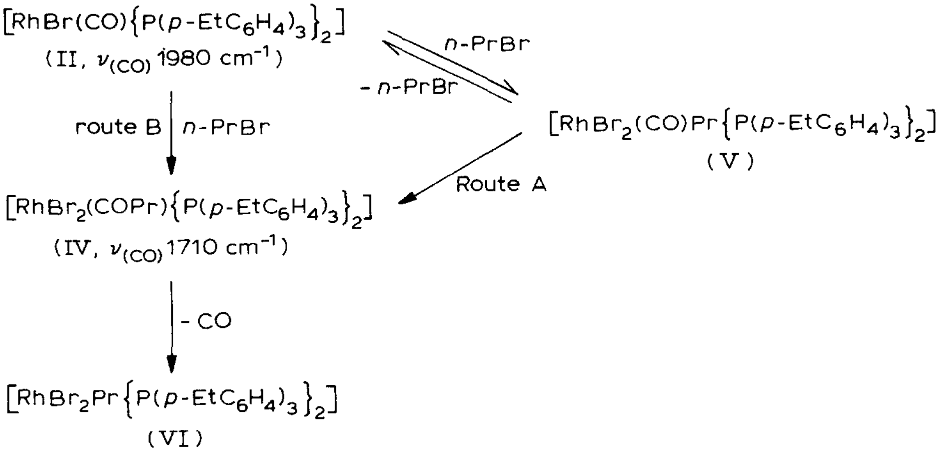
Kinetic measurements

Solutions of *trans*-[RhX(CO)(PPh_3)$_2$] (II, X = Cl and I) and *trans*-[RhX(CO)-(PPh_3)]$_2$ (III, X = Cl and I) in iodomethane and *trans*-[RhBr(CO)(PR_3)$_2$] (R = Ph and *p*-EtC_6H_4) in 1-bromopropane were prepared and their infrared spectra between 2200 and 1600 cm^{-1} monitored as a function of time. The haloalkanes were redistilled under an atmosphere of nitrogen, freeze-degassed twice and stored under nitrogen prior to use. *Trans*-[RhI(CO)(PPh_3)$_2$] was subjected to a high vacuum (0.08 mmHg) to remove any oxygen absorbed onto the surface of the complex and then stored under nitrogen, at 25°C, until addition of the iodomethane. The reaction mixture was then transferred to the infrared cell which had been flushed out by nitrogen using a syringe. The rate of reaction between 1-bromopropane and *trans*-[RhBr(CO){P(*p*-EtC_6H_4)$_3$}$_2$] was also measured in chloroform solution in the presence and absence of added tetra-n-propylammonium bromide. The kinetic data were analysed by a pseudo first-order method which proved satisfactory for all systems except the oxidative addition of iodomethane to *trans*-[RhI(CO)(PPh_3)$_2$] where the system was complex and did not exhibit pseudo first-order behaviour.

Results

Reaction of trans-[RhBr(CO)(PR_3)$_2$] (R = Ph and p-EtC_6H_4) with 1-bromopropane

A pseudo first-order plot was obtained for the reaction of *trans*-[RhBr(CO){P(*p*-EtC_6H_4)$_3$}$_2$] (II) with 1-bromopropane by following the decrease in the infrared absorption at 1980 cm^{-1} due to ν(CO) in II. The infrared spectrum showed the only product to be a acylrhodium complex, whose structure was assigned as [RhBr(COPr){P(*p*-EtC_6H_4)$_3$}$_2$] (IV) by comparison with earlier work [1,2]. Infrared spectroscopy showed no ν(CO) corresponding to [$RhBr_2$(CO)Pr{P(*p*-EtC_6H_4)$_3$}$_2$] (V). Thus the reaction is not complicated by either halide exchange or



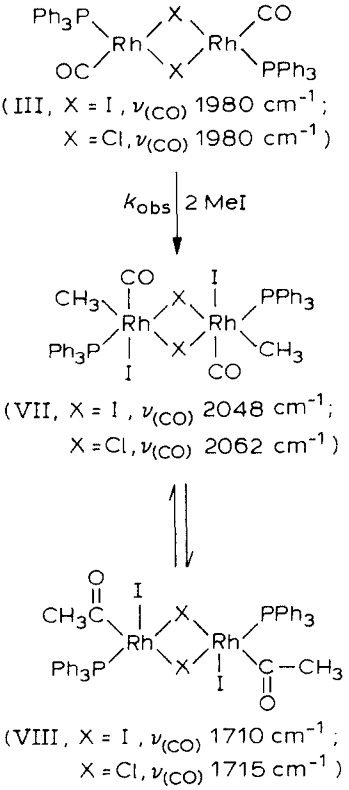
SCHEME 1

dimerisation in spite of the fact that due to the lower reactivity of the 1-bromoalkane the reaction was followed at 40°C.

Two reaction routes are possible (Scheme 1), there could be either a fast propyl transfer to give an acyl complex, IV, from V, which is in equilibrium with II as shown in route A, or simultaneous addition and transfer as shown in route B. The rhodium(III) complex IV was observed to slowly decarbonylate, the expected product being VI. Similar decarbonylations have been reported previously [8]. The reaction was studied in the presence and absence of added tetra-n-propylammonium bromide in chloroform, but two otherwise identical reactions showed no significant difference in rate (Table 2). This indicates that the anionic intermediate $[RhBr_2(CO)\{P(p\text{-}EtC_6H_4)_3\}]^-$ does not play an important role in the oxidative addition of 1-bromopropane to II. The oxidative addition of 1-bromopropane to *trans*-$[RhBr(CO)(PPh_3)_2]$ occurred at a rate too slow to measure even at 40°C. Wilkinson found no reaction occurred between bromoethane and *trans*-$[RhCl(CO)(PPh_3)_2]$ at 25°C [2].

Reaction of trans-$[Rh(\mu\text{-}X)(CO)(PPh_3)]_2$ *with iodomethane*

The oxidative addition of iodomethane to *trans*-$[Rh(\mu\text{-}I)(CO)(PPh_3)]_2$ was found to follow a pseudo first-order rate law with iodomethane always present in a large excess. The observed rate constant (k_{obs}) was obtained by measurement of the decrease of the carbonyl absorption in the infrared due to *trans*-$[Rh(\mu\text{-}I)(CO)(PPh_3)]_2$ (ν(CO) 1980 cm^{-1}). The reaction products are the rhodium(III) alkyl complex (VII) and the rhodium(III) acetyl complex (VIII), which are in equilibrium. $[Rh(\mu\text{-}Cl)X(CO)(Me)(PMe_3)]_2$ (X = Cl, Br and I) equilibrate in an identical manner to give the acyl complex $[Rh(\mu\text{-}Cl)X(COMe)(PMe_3)]_2$ [9]. In Scheme 2 the assumption has been made that VII is the initial product although this may not necessarily be the case. The molecular structures of VII (X = Cl and I) have been assigned by comparison with $[Rh(\mu\text{-}Cl)Br(CO)Me(PMe_2Ph)]_2$, the crystal structure of which has been reported [9]. The oxidative addition of iodomethane to *trans*-$[Rh(\mu\text{-}Cl)(CO)(PPh_3)]_2$ (Scheme 2) also gave pseudo first-order kinetics. As shown in Table 1 the rate of oxidative addition (k_{obs}) of iodomethane to the



SCHEME 2

TABLE 1

OBSERVED RATE CONSTANTS FOR THE REACTION OF 1-HALOALKANES WITH $[RhX(CO)(PR_3)_2]$ AND $[Rh(\mu\text{-}X)(CO)(PR_3)]_2$

Complex	Haloalkane	T (°C)	k_{obs} (s^{-1})
$[Rh(\mu\text{-}I)(CO)(PPh_3)]_2$	MeI	20	2.3×10^{-3}
$[Rh(\mu\text{-}Cl)(CO)(PPh_3)]_2$	MeI	20	5.3×10^{-4}
$[RhCl(CO)(PPh_3)_2]$	MeI	20	1.17×10^{-4}
$[RhBr(CO)(PEt_2Ph)_2]$	MeBr	25	6.0×10^{-7} [a]
$[RhBr(CO)\{P(p\text{-}EtC_6H_4)_3\}_2]$	n-PrBr	40	4.25×10^{-5}

[a] Data from ref. 10.

TABLE 2

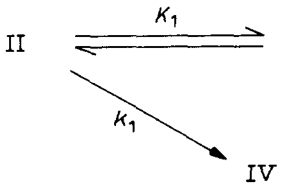
OBSERVED RATE CONSTANTS FOR THE REACTION OF 1-BROMOPROPANE WITH *trans*-$[RhBr(CO)\{P(p\text{-}EtC_6H_4)_3\}_2]$ IN THE PRESENCE AND ABSENCE OF ADDED BROMIDE ION IN CHLOROFORM

Complex	T (°C)	$[Pr_4N^+Br^-]$ (M)	[n-PrBr] (M)	k_{obs} (s^{-1})
trans-$[RhBr(CO)\{P(p\text{-}EtC_6H_4)_3\}_2]$	40	0.0185	2.53	3.44×10^{-5}
trans-$[RhBr(CO)\{P(p\text{-}EtC_6H_4)_3\}_2]$	40	0.0	2.53	3.41×10^{-5}

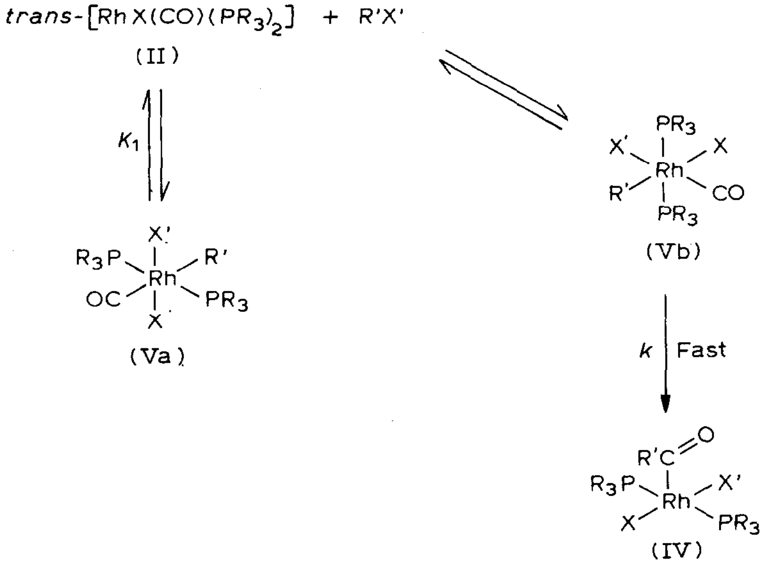
monomeric *trans*-[RhCl(CO)(PPh$_3$)$_2$] is only slightly slower than that observed for the dimeric *trans*-[Rh(μ-Cl)(CO)(PPh$_3$)]$_2$ although a direct comparison cannot be made due to the possibility of halide exchange in the monomeric system [1].

Discussion

The results presented here and in earlier work [1,4] suggest a mechanism for the oxidative addition of 1-haloalkanes to *trans*-[RhX(CO)(PR$_3$)$_2$] (II, X = Cl and Br; R = phenyl and *para*-substituted aryl) in which acyl, V, and alkyl, IV, complexes are formed independently from II as shown in Scheme 3. This has been explained by a mechanism involving the anionic intermediate [RhX$_2$(CO)(PR$_3$)]$^-$ formed by dissociation of a phosphine ligand which immediately forms a quaternary phosphonium salt by reaction with the 1-haloalkane [1]. The addition of 1-bromopropane to II (X = Br and R = p-EtC$_6$H$_4$) yields only the rhodium(III) acyl product IV, as shown in Scheme 1. This supports the general mechanism shown in Scheme 3 although in this case the formation of V does not occur as the value of K_1 does not favour its formation. A mechanism involving formation of the acyl complex IV



SCHEME 3



SCHEME 4

without a rhodium(III) alkyl complex as intermediate is unlikely. It is improbable that this intermediate is the anionic complex $[RhBr_3(CO)Pr\{P(p\text{-}EtC_6H_4)_3\}]^-$ formed by the oxidative addition of 1-bromopropane to $[RhBr_2(CO)\{P(p\text{-}EtC_6H_4)_3\}]_2^-$ as this reaction was found not to be catalysed by the addition of extra bromide ion. An alternative simpler explanation is that the intermediate is an isomer of V, in which carbonyl insertion into the rhodium(III)–methyl bond is sterically favoured (i.e. isomer Vb in Scheme 4) which reacts rapidly to form the acyl complex IV.

The oxidative addition of iodomethane to *trans*-$[Rh(\mu\text{-}X)(CO)(PPh_3)]_2$ was found to be dependent on the halide ion in the order I > Cl. The addition of 1-bromoalkanes to *trans*-$[RhBr(CO)(PR_3)_2]$ (II, $PR_3 = P(p\text{-}EtC_6H_4)_3$ and PEt_2Ph) [10] is slow (Table 1) due to the lower electrophilicity of the substrate. The rate of oxidative addition has been found to be dependent on the coordinated phosphine in *trans*-$[RhBr(CO)(PR_3)_2]$, decreasing in the order $R = p\text{-}EtC_6H_4 \gg Ph$.

Acknowledgements

We thank the European Office of the US Army for financial support under the auspices of grant DAJA-81-C-0594 and Johnson-Matthey plc for the loan of rhodium salts.

References

1 S. Franks, F.R. Hartley and J.R. Chipperfield, Inorg. Chem., 20 (1981) 3238.
2 I.C. Douek and G. Wilkinson, J. Chem. Soc. A, (1969) 2604.
3 F.R. Hartley, S.G. Murray and D.M. Potter, J. Organomet. Chem., 254 (1983) 119.
4 D. Forster, J. Am. Chem. Soc., 97 (1975) 951.
5 P. Uguagliati, A. Palazzi, G. Deganello and U. Belluco, Inorg. Chem., 9 (1970) 724; these authors erroneously assigned the structure of $[Rh(\mu\text{-}Cl)(CO)(PPh_3)]_2$ as $[RhCl(CO)_2(PPh_3)]$, see ref. 7.
6 P.D. Bartlet and J.S. McKennis, J. Am. Chem. Soc., 99 (1977) 5334.
7 D.F. Steele and T.A. Stephenson, J. Chem. Soc., Dalton Trans., (1972) 2161.
8 J. Kampmeier, R.M. Rodehorst and J.B. Philip, J. Am. Chem. Soc., 101 (1981) 1847.
9 M.J. Doyle, A. Mayanza, J.J. Bonnet, P. Kalke and R. Poilblanc, J. Organomet. Chem., 146 (1978) 293.
10 A.G. Constable, C.R. Langrick, B. Shabazadek and B.L. Shaw, Inorg. Chim. Acta, 65 (1982) L151.