Journal of Organometallic Chemistry, 240 (1982) 447–451
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ENTHALPY CHANGES IN OXIDATIVE ADDITION REACTIONS OF IODINE WITH MONOMERIC AND DIMERIC RHODIUM(I) COMPLEXES

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(Received July 4th, 1982)

Summary

The heat of reaction for addition of iodine to the planar complexes RhCl(CO)dppe, $Rh(dppen)_2{}^+$, $Rh(dppe)_2{}^+$ and to the dimer $Rh_2Cl_2(CO)_2(dppm)_2$ has been obtained by a calorimetric method. Iodine forms stronger Rh–I bonds with RhCl(CO)dppe than with the bichelate complexes. The presence of metal–metal interaction in the iodine addition compound of $Rh_2Cl_2(CO)_2(dppm)_2$ makes a significant contribution to the enthalpy change for the oxidative addition. The stereochemistry of the complexes are discussed on the basis of IR and ^{31}P NMR spectra.

Introduction

The chemistry of planar rhodium(I) complexes is characterized by addition of small molecules resulting the formation of octahedral rhodium(III) compounds [1]. Activation of small molecules by metal complexes through oxidative addition has gained strong interest in recent years due to its implication in homogeneous catalysis [2–6]. Work on oxidative addition to square planar cationic complexes [7–15] and the binuclear complexes [17,18] of rhodium(I) are reported in the literature.

In the present study a calorimetric method has been used to obtain the heat of reaction for addition of iodine to rhodium(I) centers coordinated to chelating diphosphines. An attempt has also been made to determine the effect of interaction between the two rhodium centers when iodine adds to a binuclear rhodium(I) complex.

Experimental

The complexes $[Rh(dppe)_2]BF_4$ and $[Rh(dppen)_2]BF_4$, (dppe = Ph_2PCH_2-CH_2PPh_2, dppen = *cis*-$Ph_2PCH=CHPPh_2$) were synthesized by the same proce-

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0022-328X/82/0000–0000/$02.75

dure [13]. The complexes RhCl(CO)(dppe)$_2$ [19], [RhCl(CO)dppm]$_2$ [20] and [RhICl(CO)dppm]$_2$ [17] (dppm = $Ph_2PCH_2PPh_2$) were obtained by literature methods. The air-sensitive complexes and their solutions were carefully handled under N_2. Resublimed iodine (Mallinckrodt) was used as received. 1,2-Dichloroethane was distilled from P_4O_{10} and benzene was distilled and dried over calcium hydride before use. Nitrogen purged solvents were used on all occasions. Melting points were taken on a Mel-Temp apparatus and are uncorrected. IR and ^{31}P NMR were recorded on Perkin–Elmer model 621 and Nicolet 200 spectrometers respectively. The purity of the complexes were checked by elemental analyses performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

RhI$_2$Cl(CO)dppe. 0.041 g (0.16 mmol) of I_2 and 0.086 g (0.15 mmol) of RhCl(CO) dppe both in 1,2-dichloroethane were mixed together. The volume of the solution was reduced by blowing nitrogen over the solution until the complex started to crystallize out. The solid was filtered from the cold solution, washed three times with diethyl ether and dried in vacuo. The method yielded 0.12 g (97.6%) of the complex (m.p. 264°C dec). IR (Nujol): ν(Ir–CO) 2079, ν(Ir–Cl) 314 cm^{-1}. Anal. Found: C, 39.40; H, 3.08; Cl, 4.54; I, 31.04. $C_{27}H_{24}ClI_2P_2ORh$ calcd.: C, 39.62; H, 2.96; Cl, 4.33; I, 31.01%.

[RhI$_2$(dppen)$_2$]BF$_4$. Following the procedure described for RhI$_2$Cl(CO)dppe yielded 86.1% of the complex (m.p. 281°C dec) Anal. Found: C, 48.71; H, 3.56; I, 20.02. $C_{53}H_{46}ClI_2P_4BF_4Rh$ calcd.: (as hemisolvate of $C_2H_4Cl_2$): C, 49.51; H, 3.61; I, 19.74%.

[RhI$_2$(dppe)$_2$]BF$_4$. The method described above was used to give 85.7% of the complex (m.p. 158°C dec). Anal. Found: C, 49.83; H, 4.16; I, 18.97. $C_{53}H_{50}$-$ClI_2P_4BF_4Rh$ (as hemisolvate of $C_2H_4Cl_2$) calcd.: C, 49.35; H, 3.91; I, 19.68%.

Calorimetry

The Tronac 450-4 titration calorimeter has been previously described [21]. In general, 0.03–0.05 g of the metal complex was placed in a 2 ml volumetric flask which was then purged with a slow stream of N_2 for 25–30 min. N_2 swept 1,2-dichloroethane was added to the mark and the solution transferred to the titration buret. A 0.007–0.010 g of I_2 was placed in the dewar which was then gently flushed with argon for 25–30 min. 1,2-Dichloroethane (40 ml) was added to the dewar through a Teflon delivery tube. A series of 10–15 aliquots of the metal complex solution was added to the iodine solution and the heat changes for each addition were evaluated using standard techniques [22]. As the reactions were quantitative, ΔH values were calculated directly from experimental heat data. No heat was observed when the solution of the metal complex was titrated into the solvent 1,2-dichloroethane. The standard resistance heater was calibrated periodically by HCl/tris(hydroxymethyl)aminomethane titration. The observed $\Delta H = -47.49 \pm 1.0$ kJ mol^{-1} is consistent with the literature value of -47.49 kJ mol^{-1} [22].

Results and discussion

When a solution of rhodium(I) complex was titrated into a solution of iodine, heat was evolved reaching the end point with equimolar amounts of the reactants. Further addition of the titrant produced no heat change unequivocally showing 1/1

TABLE I

ENTHALPY OF REACTION FOR ADDITION OF IODINE TO RHODIUM(I) COMPLEXES IN 1,2-DICHLOROETHANE AT 25°C

Complex [b]	$-\Delta H$ [a] (kJ mol^{-1})
RhCl(CO)dppe	143±2
[Rh(dppen)$_2$]BF$_4$	118±6
[Rh(dppe)$_2$]BF$_4$	110±2
[RhCl(CO)dppm]$_2$	147±2

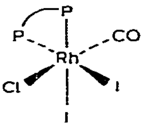
[a] Error limits are 1 standard deviation. [b] Also determined $\Delta H = -123$ kJ mol^{-1} for formation of $RhI_2Cl(CO)(PMePh_2)_2$.

stoichiometry. The reaction in each case was virtually quantitative with $K > 10^4$ l mol^{-1}. The stoichiometry was further confirmed by isolation of adducts. Enthalpy data for reactions between iodine and the rhodium(I) complexes are shown in Table 1. Each value is the average of between five to eight titrations on at least two independently prepared samples of the metal complex. Data in Table 1 are comparable to those obtained [21] with other rhodium(I) complexes of the type $RhX(CO)L_2$ (X = halogen, L = tertiary phosphine). It is observed that iodine forms stronger bonds with rhodium in RhCl(CO)dppe compared to the cationic complexes of $[Rh(dppen)_2]^+$ and $[Rh(dppe)_2]^+$ presumably due to less steric hindrance from one chelating phosphine ligand compared to two present in the cationic complexes. Of the last two, the Rh–I bond order in the former is slightly greater than in the latter. The analogous cobalt complexes with O_2 and the iridium complexes with tetrachloro-1,2-benzoquinone ($O_2C_6Cl_4$) show the same bond order trend as observed in the iodine adducts of the cationic compounds. $[Co(dppen)_2]^+$ forms a well characterized complex with O_2 while $[Co(dppe)_2]^+$ decomposes to more than one reaction product on exposure to air [7]. The iridium analog of the former produced a stable addition compound with $O_2C_6Cl_4$ ($-\Delta H = 179 \times 8$ kJ mol^{-1}) [13] and that of the latter gave neither well defined titration data nor satisfactory elemental analyses required for formation of an addition compound [23].

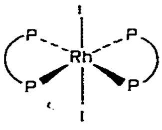
Titration of I_2 solution with a solution of [RhCl(CO)dppm]$_2$ indicates that only one iodine atom is coordinated to each metal center. This is in accord with the spectrophotometric titration data [17] which led to the conclusion that the iodine addition product of the binuclear rhodium(I) complex is a rhodium(II) compound. The enthalpy change for addition of I_2 to [RhCl(CO)dppm]$_2$, ($-\Delta H = 147$ kJ mol^{-1}) is significant when compared to 123 kJ mol^{-1} for formation of the monomeric $RhI_2(CO)(PMePh_2)_2$. Since two Rh–I bonds are formed in both the complexes, the difference in enthalpy changed (24 kJ mol^{-1}) may be attributed to the enthalpy contribution for formation of Rh–Rh bond in the dimeric complex [RhICl(CO)dppm]$_2$. The total enthalpy change cannot be clearly factored between Rh–I and Rh–Rh bond enthalpy contributions because the metal–metal bond may exert a strong *trans*-influence [24] on the metal–iodine bond in the linear I–Rh–Rh–I system.

The infrared spectra of the cationic complexes of iodine show absorptions characteristic of the presence of BF_4^-. The CO stretching frequency shifts to higher wave number when iodine adds to RCl(CO)(dppe) and $[RhCl(CO)dppm]_2$, which indicates decreased back-donation from Rh to CO owing to oxidation. When RhCl(CO)(dppe) adds to I_2, ν(CO) increases from 2010 to 2070 cm^{-1} and the ν(Rh–Cl) shifts from 290 to 314 cm^{-1}. The observed shift in the Rh–Cl frequency suggests that the Cl is *trans* to CO [25]. The increase in ν(CO) for the dimer $[RhCl(CO)dppm]_2$ on addition to I_2 by 51 cm^{-1} compared to ~ 105 cm^{-1} when I_2 added to the monomer RhCl(CO)(dppm) indicates the formation of the rhodium(II) dimer $[RhICl(CO)dppm]_2$.

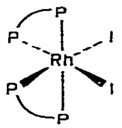
The ^{31}P NMR spectra of $RhI_2Cl(CO)dppe$ consists of a doublet, *J*(Rh–P) 98 Hz, showing the presence of two equivalent phosphorus atoms. This together with IR data showing Cl *trans* to CO leads to the stereochemistry as shown in I. The spectrum for $RhI_2(dppe)_2$ has a simple doublet *J*(Rh–P) 83 Hz indicating that all four phosphorus atoms are equivalent as in II. The ^{31}P resonances obtained for



(I)



(II)



(III)

$[RhI_2(dppen)_2]BF_4$ were complex showing three signals: one doublet *J*(Rh–P) 87 Hz and two doublets of triplets *J*(Rh–P) 87 and 106 Hz. The interpretation of the complex spectra was aided by reported observations [26,27]. The simple doublet suggests that all the four phosphorus atoms are equivalent as in II. The two pairs of triplets observed presumably reflect the stereochemistry as in III with equivalent *trans* phosphorus *J*(Rh–P) 87 Hz and equivalent *cis* phosphorus *trans* to iodine showing larger *J*(Rh–P) 106 Hz. The preceding observations suggest that the complex $[RhI_2(dppen)_2]^+$ is a mixture of isomers II and III. The low solubility of $[RhICl(CO)dppm]_2$ in CD_2Cl_2 precluded recording of a satisfactory spectrum. As the metal–metal interaction depends on the geometry of the bridging chelate ligand and the complex $[RhI(CNR)_2dppm]_2^{2+}$ (R = methyl, n-butyl and cyclohexyl) is observed to be diamagnetic [18], the complex $[RhICl(CO)dppm]_2$ having the same bridging ligand to span the two metal atoms presumably has the identical basic structure with Rh–Rh bond as proposed earlier [17]. The rather small difference between the ΔH for addition of I_2 to the dimer as compared to the monomeric complexes is surprising. Whether this indicates a weak Rh–Rh bond in the adduct or a compensating effect of strong Rh–Rh bonding and weakened Rh–I bonds cannot be decided by the experiments reported here.

Acknowledgement

The support of The Robert A. Welch Foundation and The National Science Foundation (Grant No. SPI-7926970) is gratefully acknowledged. We thank Ray Bulls for assistance with the ^{31}P NMR spectra.

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