Inorganica Chimica Acta, **44** (1980) L135–L136

Activation of Water. 3. Oxidative Addition of Water to Rhodium(I) Hydrido Compounds and Application as Catalyst for Deuteration of Aromatic Hydrocarbons and Hydrogen with D_2O

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Received October 5, 1979

The metal-assisted H–D exchange reaction of aromatic hydrocarbons has received considerable interest because it implies activation of C–H bond by metal [1]. Generally D_2 is employed as deuterium source. Metal complexes, *e.g.* $RhCl_3$ [2] and $PtCl_4^{2-}$ [3], were reported to be active in acidic media for the exchange with D_2O. Recently we reported oxidative addition of water to PtL_3 (L = $P(i\text{-}Pr)_3$, PEt_3) to generate the hydrido hydroxo species HPtOH which serves as a potent catalyst for H–D exchange between D_2O and aliphatic hydrogens attached to the α-carbon atoms of carbonyl compounds or α-olefinic, allylic, and aldehydic hydrogens of α, β-unsaturated carbonyl compounds [4]. However, the PtL_3/D_2O system was incapable of exchanging aromatic hydrogens. Rh(I) hydrides, $RhH[P(i\text{-}Pr)_3]_3$ (*I*) and $Rh_2H_2(\mu\text{-}N_2)[P(c\text{-}C_6H_{11})_3]_4$ (*II*) [5] were found much more versatile than the PtL_3/H_2O system as reported here.

Oxidative addition of H_2O to *I* took place at room temperature in pyridine to give $\{RhH_2(pyridine)_2[P(i\text{-}Pr)_3]_2\}OH$(*III*) [Rh–H, δ –20.3(q), J(H–Rh) = J(H–P) = 16.8 Hz; CH_3, δ 1.08(q), $^3J(H\text{–}P) + {}^5J(H\text{–}P)$ = 12.8 Hz, J(H–H) = 6.4 Hz]. Although *III* is stable in aqueous pyridine, a facile reductive elimination of H_2O occurs in dry solvent to regenerate *I*, indicating reversibility of H_2O addition. The formation of *III* was confirmed by isolation of the BPh_4^- salt (ν(Rh–H) 2076 and 2112 cm^{-1}) as colorless crystals. A similar addition of H_2O to *II* in pyridine followed by metathesis reaction with $NaBPh_4$ gave $\{RhH_2(pyridine)_2[P(c\text{-}C_6H_{11})_3]_2\}BPh_4$ (ν(Rh–H) 2005 and 2020 cm^{-1}).

When D_2O was employed in the above reaction, a facile deuteration of pyridine was observed. Thus, a gentle heating (80 °C, 20 h) of a mixture of *I*(0.1 mmol), pyridine(5.4 mmol), and D_2O(27 mmol) gave deuterated pyridine without positional preference, deuteration at 2,6-, 3,5-, and 4-positions being 62, 59, and 58%, respectively. Compound *II* also showed a comparable activity.

A wide range of aromatic compounds, *e.g.* $PhCH_3$, $PhOCH_3$, PhF, and $C_{10}H_8$ were deuterated with D_2O by the catalysis with *I*. *I* is more active than the system $RhCl_3$–CH_3CO_2D–D_2O [2]. Remarkably, deuterium incorporation into the CH_3 group was observed for $PhCH_3$ and $PhOCH_3$ (Table I). This is in sharp contrast to $(\eta\text{-}C_5H_5)_2NbH_3$ and $IrH_5(PPhMe_2)_2$ which are inactive for deuteration of the corresponding CH_3 hydrogens with D_2 [6].

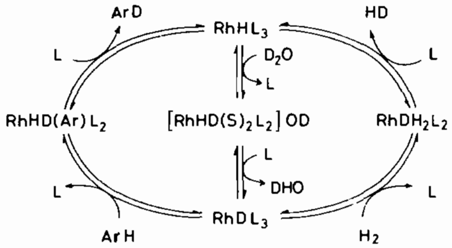
TABLE I. H–D Exchange of PhX with D_2O[a] Deuteration (%).

X	*m*-H	*o, p*-H	CH_3
$N(CH_3)_2$	65	32	0
OCH_3	54	54	48
CH_3	50		12
$COCH_3$	33[b]	5[c]	61
F	53	54	

[a] PhX(5 mmol)–D_2O(25 mmol)–*I*(0.1 mmol) in THF (3 ml) at 80 °C for 20 h. [b] *m, p*-H. [c] *o*-H.

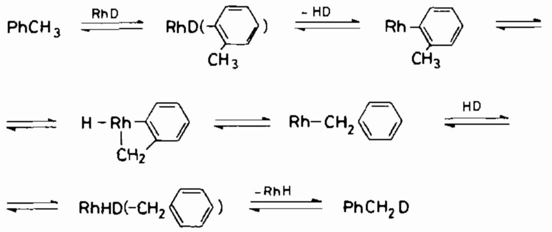
The faster deuteration of PhF compared to $PhOCH_3$ [relative rate; *o, p*-H(PhF) 9.8, *m*-H(PhF) 5.6, *o, p*-H($PhOCH_3$) 1.9, *m*-H($PhOCH_3$) 5.0, CH_3O 1.0] is consistent with a mechanism involving oxidative addition of ArH to *I* as rate-determining step [6]. Although formation of the σ-aryl species C_6H_4FRh was not detected in the mixture of *I* and PhF, an adduct $Rh_2(C_6F_5)_2(N_2)[P(c\text{-}C_6H_{11})_3]_4 \cdot 2C_6H_5CH_3$ (*IV*) [^{19}F nmr (benzene-d_6, upfield from $CFCl_3$) 103.4 (2F, m) and 165.0 (3F, m)] was obtained as yellow crystals by treating *II* with C_6F_5H in n-hexane at room temperature under N_2. The ir spectrum shows a band assignable to ν(N≡N) at 2130 cm^{-1}. This is probably due to a partial dissociation, $IV \rightleftharpoons Rh(N_2)(C_6F_5)L_2 + Rh(C_6F_5)L_2$ (L = $P(c\text{-}C_6H_{11})_3$). A similar dissociation was found for $Rh_2H_2(\mu\text{-}N_2)L_2$ (L = $P(i\text{-}Pr)_3$, $P(c\text{-}C_6H_{11})_3$) [7]. Oxidative addition of PhF to a low-valent transition metal compound has a precedent [8]. The coordinated dinitrogen in *IV* is readily replaced by L(CO or PhCN) to give quantitatively $Rh(C_6F_5)L[P(c\text{-}C_6H_{11})_3]_2$ (ν(CO) 1945, ν(CN) 2180 cm^{-1}) as yellow crystals.

The results suggest that the H–D exchange of aromatic hydrogens with D_2O catalyzed by *I* proceeds via initial formation of $RhD[P(i\text{-}Pr)_3]_3$ (*V*) through addition of D_2O to *I* followed by reductive elimination of DHO from the adduct $\{RhDH(pyridine)_2[P(i\text{-}Pr)_3]_2\}OD$. The oxidative addition of ArH to *V* and subsequent elimination of ArD from $RhHD(Ar)[P(i\text{-}Pr)_3]_2$ complete a catalytic cycle (*Scheme I*). The reversible oxidative addition of ArH to *I* also accounts for hydrogen scrambling between aromatic hydrocarbons catalyzed by *I*. Thus, a gentle heating (80 °C) of a mixture of *I* (0.1 mmol), $C_{10}H_8$ (5 mmol), and C_6D_6 (25 mmol) gave per-deuterated naphthalene, deuteration at α- and β-positions being 33 and 77%, respectively.



L = P(i-Pr)$_3$, S = solvent

Scheme I.



(auxiliary P(i-Pr)$_3$ ligands are omitted for clarity)

Scheme II.

The exchange of methyl hydrogens of $PhCH_3$ and $PhOCH_3$, may be explained by double oxidative addition leading to four- and five-membered ring intermediates, $HRhCH_2$-*o*-C_6H_4 and $HRhCH_2O$-*o*-C_6H_4, respectively (*Scheme II*). Consistent with this postulate is the faster rate of exchange of methyl hydrogens of $PhOCH_3$, which could occur through a five-membered ring intermediate, than that of $PhCH_3$ which requires a four-membered ring.

H–D exchange of H_2 with D_2O can also be catalyzed by *I* and *II*. Thus, a reaction (80 °C, 20 h) of D_2O (0.11 mol) and H_2 (0.45 mol, 100 atm) in presence of *II* (0.1 mmol) gave 75% H_2O, 22% DHO, and 3% D_2O. A similar result was obtained by catalysis of *I*. The H–D exchange of H_2 with D_2O must involve RhH_2D species (Scheme I). In fact, the trigonal bipyramidal trihydride RhH_3L_2 (L = P(i-Pr)$_3$, P(c-C_6H_{11})$_3$), [7] was isolated by treating *I* and *II* with H_2.

The catalytic cycles (Scheme I) are supported by the observation that *I* also can catalyze H–D exchange of benzene with D_2 under ambient conditions.

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