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Chlorine and Hydrogen Transfer in a Reversible Metathesis of Organorhodium(III) and Organic Compounds

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Hydridoalkylrhodium(III) complexes are important intermediates in hydrogenation of alkenes and in sp^3 carbon–hydrogen bond activation of some aliphatic compounds [1]. Simple hydridoalkylrhodium compounds which bear acyclic alkyl groups with no atoms, such as phosphorous, that strongly bind to rhodium are unstable above about −10 °C. They collapse to an aliphatic rhodium-free compound that sometimes can equilibrate with the rhodium containing adduct. In the presence of carbon tetrabromide or another polyhalogenated methane, hydridoalkylrhodium complexes instead give monohalogenated derivatives of the organic precursor. Reversible interconversion of the monohalogenated organic compound, the hydridoalkylrhodium species, and a rhodium-coordinated alkene is described in this paper. This previously unpublished intermolecular equilibration proceeds with interchange of hydrogen and chlorine between rhodium ions and an organic moiety. This report extends the range of known chemical reactions of hydridoalkylrhodium compounds.

Experimental

Rhodium-mediated Hydrogen and Chlorine Transfer to Organic Moieties

The system for study consists of tris(triphenylphosphine)chlororhodium(I) and 2-ethoxyethanol (the monoethyl ether of ethylene glycol) (0.14 and 0.055 M, respectively, in 99.8% deuterochloroform that contains 1% *v*/*v* tetramethylsilane)**. These reactants proceed through either of two reaction intermediates, rhodium-bound ethoxyethene (ethyl vinyl ether) or ethoxyacetaldehyde, to ultimately yield rhodium-free organic products. Eighty-five percent of the final products derive from the aldehyde and 15% from the alkene. (The alkene arises from rhodium-promoted dehydration of 2-ethoxyethanol, and the aldehydic intermediate [2] is a dehydrogenated product of this same alcohol.) This alkene, ethoxyethene, has been isolated from a related reaction of rhodium(I) with 1,2-diethoxyethane [2], and appropriate NMR lines for the free alkene are observed in the ongoing reaction system with 2-ethoxyethanol [$^{13}C\{^1H\}$ NMR (30 °C): 152.3 ± 0.7 ppm]. In the system with 2-ethoxyethanol (rather than diethoxyethane), ethoxyethene actually is isolated as a derivative, as either diethyl ether or 2-chloroethyl ethyl ether. The hydrogen that is essential for formation of diethyl ether can be contributed by $H_2[RhCl(PPh_3)_2]_2$ (**2**), a spectroscopically identified component of the reaction under study (Table 1), a known hydrogenation agent for alkenes [3]†, and a product of $RhCl(PPh_3)_3$(I) and hydrogen-donating organic compounds [4] (such as, in this case, the starting material 2-ethoxyethanol). The dihydrido rhodium complex **2** also participates in magnetization transfer both with the proton of monodeuterodichloromethane (**5**) and with a species that possesses ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR lines which are appropriate for the hydridoalkylrhodium complex (**3**) in Scheme 1 (*cf.* Table 1). These observed proton–proton interconnectivities are characterized by diminution of the intensities for ^1H resonances that are listed in Table 1 for compounds **2**, **3**, and **5**††.

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**See right-hand column.

**Unwanted competing reactions with water and dioxygen were rigorously avoided by extended drying of the liquid starting materials (for >12 h over activated 3A molecular sieves), by purging them for >15 min in iced, serum stoppered containers (with a dry, deoxygenated dinitrogen stream that was flowed through an Oxi-Clear No. DGP-250 cartridge), and by maintenance of all reaction mixtures under the purified nitrogen. After a reaction interval of 4–4.5 days at ⩽30 °C volatile components were isolated from the reaction mixture by bulb-to-bulb transfer at <60 °C and <0.2 Torr. Characterization of each volatile component was based on comparison with known values for its GC–MS retention time and fragmentation pattern, as well as ^1H and $^{13}C\{^1H\}$ NMR spectra. Products in the ethoxyacetaldehyde pathway (2,4-di-*O*-ethylthreose and 2,4,6-tri-*O*-ethyl-β-glucose or galactose) are known, were independently synthesized (for purposes of comparison), and have been reported elsewhere [2]. Organic products constituted 82% of the volatile mixture, which was composed of the threose (<10%) and hexose (53%), the starting alcohol (18%), ethoxyacetaldehyde (<10%), diethyl ether (<10%), and 2-chloroethyl ethyl ether (10%). Quantitation was based on relative NMR line intensities and limits of GC–MS detection.

†For a discussion of magnetization transfer ('spin saturation transfer', 'SST', 'Forsén-Hoffmann double-resonance'), see ref. 3.

††Homonuclear magnetization transfer was achieved upon implementation of the HMG double irradiation mode of a JEOL FX-90Q NMR spectrometer. For the pair **2** and **5**, the constant frequency pulsed irradiation was at the ^1H resonance of **5**; for **2** and **3** it was at the high field proton resonance of **2**.

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TABLE 1. Resonances that Participate in Magnetization Transfer among Compounds 1–3, 5, 6[a, b]

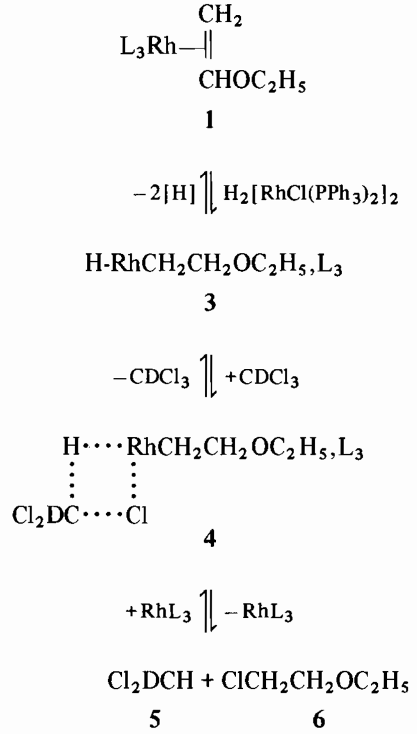
Reaction component	Chemical shift (ppm)		
	^{1}H	^{13}C{^{1}H}	^{31}P{^{1}H} or ^{31}P
$Rh(CH_2{:}CHOC_2H_5)Cl(\underline{P}Ph_3)_2$ (1)			36.40 (± 0.08)[c]
$\underline{H}_2[RhCl(PPh_3)_2]_2$ (2)	−16.29 [d, J (H–Rh) 23 Hz][d]		
$\underline{H}Rh\underline{C}H_2CH_2OC_2H_5,Cl,(\underline{P}Ph_3)_2$ (3)	−15.84 [J (H–X) 11 Hz]	19.90 (± 0.02, C-1)[e]	43.09 (± 0.11) [dd, [f] J (P–X′) 15 ± 4 Hz, J (Rh–P) 139 ± 1 Hz]
$\underline{H}CDCl_2$ (5)	5.29–5.26		
$Cl\underline{C}H_2\underline{C}H_2OC_2H_5$ (6)		70.73 (± 0.03, C–O), 43.67 (± 0.03, C–Cl)	

[a] Ref. 3. [b] At −50 °C in $CDCl_3$. Tabulated values are for underlined atoms in each molecule. [c] *cf.* ^{31}P NMR lines for $Rh(C_2H_4)Cl(PPh_3)_2$; ref. 4. [d] Ref. 5. [e] This ^{13}C resonance became a triplet upon off-resonance irradiation in the ^{1}H frequency region. No other ^{13}C resonance upfield of 42.0 ppm was impacted upon double irradiation of ^{1}H and ^{13}C frequencies. Carbon resonances for the Rh–CH_2 unit are within *ca.* ±6–8 ppm of those for the corresponding H–CH_2 molecules (refs. 6, 7). The methyl carbon of $H{-}CH_2CH_2OC_2H_5$ has a resonance at 14.52 ppm. [f] The ^{31}P{^{1}H} resonance is a singlet at 30 °C and a doublet at −50 °C. Double irradiation with continuous irradiation in the proton region provided this d–d. [Double irradiation can lengthen the lifetime of exchanging species ten-fold (ref. 8).] This J (Rh–P) is appropriate for a penta-coordinated trigonal bipyramidal complex (ref. 9).

Discussion

Sigma Bond Cleavage upon Equilibration of Rhodium Complexes

Equilibria shown in Scheme 1 are in complete and full agreement with the observation of magnetization transfer upon proton transfer at −50 °C in deuterochloroform. (For a system such as this one with several exchanging sites, mathematical analysis of rates of reactions is non-trivial; however, meaningful semi-quantitative and qualitative relationships can be described [10].) Observation of this phenomenon requires that the overall rate for the reversible sequence in Scheme 1 be in the range of 10^{-5} to 1 s^{-1} [10] (where this latter value is that of the pulse interval of the observation frequency in the double irradiation experiments). The equilibration of **1** and **3** (*cf.* Scheme 1) has precedent in a literature report; magnetization transfer has been reported for reversible intramolecular interconversion of hydridobis(triisopropylphosphine)ethylrhodium (at a rate of 0.29 ± 0.04 s^{-1} at −40 °C [11]). In this intramolecular case, as in the intermolecular one in Scheme 1 with rhodium-complexed ethoxyethene, equilibration of the free and rhodium-bound alkenes is not observed. (It proceeds at a rate outside the range that is correct for magnetization transfer.)



where $L_3 = Cl,(PPh_3)_2$

Scheme 1.

The chlorinated organic products in the reaction mixture, $HCDCl_2$ (**5**) and $ClCH_2CH_2OC_2H_5$ (**6**), are known compounds that have been identified by GC–MS, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Besides the solvent $CDCl_3$, no other chlorinated or deuterated compounds have been detected in the final organic product mixture from tris(triphenylphosphine)-chlororhodium(I) and 2-ethoxyethanol. It is notable that (a) only one chlorine atom of $CDCl_3$ is hydrogenolyzed, and that (b) hydrogen (but neither deuterium nor chlorine) of $HCDCl_2$ (**5**) is exchanged. All of these observations are compatible with selective C–H cleavage of **5** at a rhodium center, as shown in Scheme 1. [Dichloromethane can be cleaved at a C–H bond rather than a C–Cl link [12], and a large k_H/k_D for $CHDCl_2$ is consistent with its participation at (or adjacent to) the rate-determining step in a reaction sequence [13].] Deuterochloroform donates the chlorine for formation of 2-chloroethyl ethyl ether (**6**). The solvent deuterochloroform has an essential role in this chemistry; no chloro ether **6** arises when dideuterodichloromethane is the alternative solvent.

A key organometallic complex, **4**, can form either from the hydridoalkylrhodium compound **3** and deuterochloroform or from bis(triphenylphosphine)-dichloro(β-ethoxyethyl)rhodium(III) and monodeuterodichloromethane (**5**). Although participating bonds are shown as equivalent in **4** in Scheme 1, the strengths of these bonds may actually differ considerably. The participation of the common species **4** in these sigma-bond metatheses is further indicated by heteronuclear magnetization transfers* between $HCDCl_2$ (**5**) and other reaction components (Table 1). Upon double irradiation, intensities decreased for the underlined resonances of $Rh\underline{C}H_2$ in **3** and $Cl\underline{C}H_2$-$\underline{C}H_2OC_2H_5$ (**6**).

Conclusions

These experimental observations establish the fate of CX_3 of a starting material CX_3,X' (where X = a halogen atom and X′ = a halogen or hydrogen atom) in a system with hydrido rhodium compounds. Evidence has been presented above for rhodium mediated equilibration and sigma-bond metatheses of these reactants and their products.

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*The SEL irradiation mode for a JEOL FX-90Q spectrometer was utilized at −50 °C with continuous wave irradiation at the proton frequency of $HCDCl_2$ (5.29–5.26 ppm).