Does the Rhodium-catalysed addition of Perhaloalkanes to Alkenes (*i.e.* the Kharasch Reaction) proceed *via* an Oxidative-addition Mechanism?: the Crystal Structure of $RhBr(CCl_3)Cl(CO)(PMe_3)_2$

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Evidence is presented to show that rhodium(I)-catalysed Kharasch reactions may proceed *via* oxidative-addition of the perhalocarbon to the Rh followed by stepwise transfer to a coordinated alkene.

The Kharasch reaction is the general name given to the addition of perhaloalkanes to alkenes; the reaction is promoted by light, peroxides and a range of metal complexes. It has been extensively investigated and applied for over forty years.[1] The generally accepted mechanism for the metal-catalysed additions is the redox chain reaction shown below.[2]

$$[M^n] + RX \rightarrow [M^{n+1}]X + R^{\cdot} \qquad (1)$$

$$R^{\cdot} + R'CH{=}CH_2 \rightarrow R'C^{\cdot}HCH_2R \qquad (2)$$

$$[M^{n+1}]X + R'C^{\cdot}HCH_2R \rightarrow R'CHXCH_2R + [M^n] \qquad (3)$$

Our interest in these reactions was stimulated by a report that they could proceed enantioselectively in the presence of a chiral phosphine–rhodium(I) catalyst.[3] We examined a wide range of other transition metal catalysts and although many were more active than the reported rhodium system none produced any significant enantioselectivity. This prompted us to question what was special about the rhodium(I) phosphine catalyst and, given the propensity of such systems to undergo oxidative-addition, to consider whether in this case an alternative mechanism may operate. The following observations support this proposal.

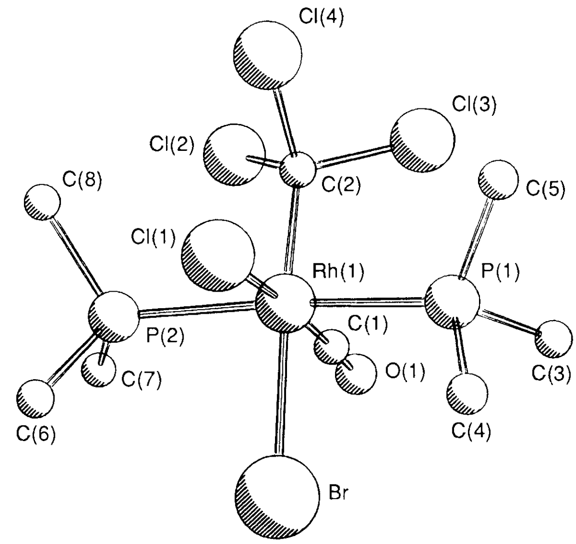

Fig. 1 Structure of $RhBr(CCl_3)Cl(CO)(PMe_3)_2$ **1**. Selected bond lengths (Å) and angles (°) for molecule 1 (see text): Rh(1)–Br(1) 2.581(4), Rh(1)–Cl(1) 2.352(5), Rh(1)–P(1) 2.387(5), Rh(1)–P(2) 2.383(6), Rh(1)–C(1) 1.874(17), Rh(1)–C(2) 2.004(18), Br(1)–Rh(1)–Cl(1) 94.1(1), Br(1)–Rh(1)–P(1) 87.7(1), Cl(1)–Rh(1)–P(1) 83.9(2), Br(1)–Rh(1)–P(2) 85.7(2), Cl(1)–Rh(1)–P(2) 82.8(2), Br(1)–Rh(1)–C(1) 81.3(6), P(1)–Rh(1)–C(1) 95.7(6), P(2)–Rh(1)–C(1) 97.0(6), Cl(1)–Rh(1)–C(2) 97.6(5), P(1)–Rh(1)–C(2) 95.1(5), P(2)–Rh(1)–C(2) 94.1(5), C(1)–Rh(1)–C(2) 87.0(8), P(1)–Rh(1)–P(2) 164.7(2), Cl(1)–Rh(1)–C(1) 175.4(6), Br(1)–Rh(1)–C(2) 168.2(4), mean Rh(1)–C(2)–Cl 116.3(9).

(*i*) Addition of excess $CBrCl_3$ to a benzene solution of $RhCl(CO)(PMe_3)_2$ immediately gave the oxidative-addition product $RhBr(CCl_3)Cl(CO)(PMe_3)_2$ **1**.†

(*ii*) $RhCl(CO)(PMe_3)_2$ and $RhBr(CCl_3)Cl(CO)(PMe_3)_2$ are active catalysts for the addition of $CBrCl_3$ to styrene; the catalytic activities are comparable to that reported for the rhodium(I)–diop system.[3]‡

(*iii*) With the known[4] heterogeneous catalyst $Pd(OAc)_2$–$Ph_2P(CH_2)_4PPh_2$–K_2CO_3 (1 : 1 : 100) in benzene under a CO atmosphere, a mixture of CCl_4–CBr_4–oct-1-ene (1 : 1 : 2) at 40 °C gave the adducts $C_6H_{13}CHClCH_2CCl_3$ and $C_6H_{13}CHBrCH_2CBr_3$, together with the crossover products $C_6H_{13}CHBrCH_2CCl_3$ and $C_6H_{13}CHClCH_2CBr_3$ in the ratio 10 : 100 : 15 : 2. Similar observations using the catalysts $[Fe(C_5H_5)(CO)_2]_2$ have been interpreted as support for the redox chain mechanism outlined above.[5] In contrast, a similar experiment using $RhCl(CO)(PMe_3)_2$ as a catalyst gave only $C_6H_{13}CHClCH_2CCl_3$ and $C_6H_{13}CHBrCH_2CBr_3$ in the ratio 9 : 100, and none of the crossover products.

(*iv*) At 70 °C $[Rh(cod)(PPh_3)_2]PF_6$ (cod = cycloocta-1,5-diene) catalyses the addition of both CBr_4 and $CBrCl_3$ to cod to give the corresponding *cis*-5-bromo-6-trihalomethylcyclo-oct-1-ene;§ none of the corresponding *trans*-isomers was detected. Addition to a non-coordinated alkene should lead to an approximately equal mixture of *cis* and *trans* isomers.[6]

We therefore suggest that rhodium(I)-catalysed addition of perhaloalkanes to alkenes proceeds, at least in part, *via* a mechanism analogous to the addition of hydrogen to alkenes *i.e.* initial oxidative-addition of the perhaloalkane to the rhodium followed by rapid stepwise transfer to a coordinated alkene. This not only rationalises why the $[Rh(cyclooctene)_2Cl]_2$–diop is more stereoselective than any of the Cu^I, Fe^{II}, Ru^{II} catalysts we tried but should also allow more stereoselective catalysts to be designed.

The trichloromethane complex **1** is also of interest given its ease of formation and the recent interest in elaborating metal-halocarbon complexes.[7] Although the structures of trichloromethyl complexes of Hg^{II},[8,9] Au^{II} and Au^{III}[10] have been reported this is the first structural characterisation of a transition metal trichloromethyl complex. The crystal structure consists of two visually indistinguishable molecules; their crystallographic independence is confirmed by their different packing environments. The structure of one of the molecules is illustrated in Fig. 1.

Each molecule contains an octahedrally coordinated rhodium(III) although there are significant deviations of the *trans* ligands from colinearity with the metal. Principally, all angles subtended by the trichloromethyl ligand exceed 90°, except for that to the carbonyl ligand: the explanation seems to be purely steric in origin. The mean C–Cl distance of 1.843(18) Å is longer than that found in Au^{II} or Au^{III} trichloromethyl complexes [*i.e.* 1.795(17) and 1.785(10) Å].[10]

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† *Selected spectroscopic data* for $RhBr(CCl_3)Cl(CO)(PMe_3)_2$ **1** ν_{CO}/cm^{-1} 2084s (CH_2Cl_2); δ_H (250 MHz, $CDCl_3$) 1.87 (t, *J* 4 Hz, Me); δ_P [referenced to H_3PO_4 (101 MHz, C_6D_6)] −1.9 (d, *J* 87 Hz); δ_C (101 MHz, CD_2Cl_2) 15.2 (t, 18 Hz, PMe_3), 86.1 (d of t's, 4.5 and 46 Hz, $-CCl_3$), 180.3 (d of t's, 8 and 64 Hz, -CO).

Crystal data for **1**, $C_8H_{18}BrCl_4OP_2Rh$; *M* = 516.80. Crystallises from diethyl ether as yellow bricks (0.425 × 0.25 × 0.20 mm). Triclinic, a = 8.897(7), b = 14.243(17), c = 14.771(19) Å, α = 98.87(9), β = 95.41(8), γ = 93.01(8)°, U = 1837(3) Å^3; D_c = 1.869 g cm^{-3}, Z = 4. Space group $P\bar{1}$ (C_i^1, No. 2), Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 38.16 cm^{-1}. Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω scan method. The 4757 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption. The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods (SHELXTL 83). Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement with unit weights converged at a final *R* 0.0723, with allowance for the thermal anisotropy of all non-hydrogen atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

‡ diop = 3,4-bis[(diphenylphosphinyl)methyl]-2,2-dimethyl-1,3-dioxolane.

§ Confirmed by X-ray crystallography *cis*-5-bromo-6-tribromomethylcyclooct-1-ene.