Mild selective metathesis of alkane C–H bonds and C–X bonds of polyhalogenomethane $CH_{4-n}X_n$ (X = Cl, n = 4; Br, I, n = 3) catalysed with chlorotris(triphenylphosphine)rhodium(I)

Andrei N. Vedernikov,* Rafael R. Sharifullin and Boris N. Solomonov

Department of Organic Chemistry, Kazan State University, 420008 Kazan, Russian Federation. E-mail: Andrei.Vedernikov@ksu.ru

Alkanes RH (n-C_6H_{14}, cyclo-C_6H_{12}) and toluene react with polyhalogenomethanes CCl_4, $CHBr_3$ and CHI_3 at 80–110 °C under catalysis with Wilkinson's complex, $RhCl(PPh_3)_3$, to produce halogenohydrocarbons RX and $CHCl_3$, CH_2Br_2 or CH_2I_2 respectively with unusually high selectivity which decreases in the order: $C\text{–}H_{\text{secondary}} >> C\text{–}H_{\text{benzylic}} > C\text{–}H_{\text{primary}}$.

Rhodium(I) complexes are well known as both reagents[1] and catalysts[1–4] for alkane and arene C–H bond activation in photochemical processes. Only one type of thermal alkane functionalization catalysed with a rhodium(I) complex is known, namely dehydrogenation.[3,5] The first described reaction was cyclooctane dehydrogenation in the presence of chlorotris(triarylphosphine)rhodium(I) complexes.[3]

We report here a new thermal hydrocarbon functionalization catalysed with Wilkinson's complex, $RhCl(PPh_3)_3$, **1**:

$$RH + CH_{4-n}X_n \rightarrow R\text{–}X + CH_{5-n}X_{n-1} \qquad (1)$$

$$RH = \text{cyclo-}C_6H_{12},\ \text{n-}C_6H_{14},\ PhMe$$
$$X = Cl,\ n = 4;\ Br,\ I,\ n = 3$$

The reaction proceeds selectively under mild conditions (80–110 °C) and gives metathesis products of hydrocarbon C–H bonds and C–X bonds (X = Cl, Br, I) of the polyhalogenomethanes CCl_4, $CHBr_3$, CHI_3, usually in catalytic yields on rhodium. Though non-catalytic reactions of alkanes with CCl_4[6] and CBr_4[7] are known to proceed at high temperature and/or in the presence of radical reaction initiators such as benzoyl peroxide; no reactions of alkanes with either bromoform or iodoform have been reported.

Some results for metathesis (1) are listed in the Table 1.[†] A typical RX yield *versus* reaction time plot for cyclohexane and toluene metathesis with CCl_4 is shown in Figure 1. The slight curvative of the lines indicate that catalyst deactivation takes place during the reaction. Indeed, after several hours of reaction a small amount of yellow rhodium-containing precipitate was formed. No metathesis product was obtained in the absence of complex **1** or in the sole presence of triphenylphosphine which could be formed during partial decomposition of the starting complex.

Table 1 Results for hydrocarbons RH and polyhalogenomethanes $CH_{4-n}X_n$ metathesis (1) in the presence of Wilkinson's complex **1**.

RH	**1**/ mmol dm^{-3}	$CH_{4-n}X_n$ / mmol dm^{-3}	T / °C	Time / min	Yield of R–X[a] % on **1** (% on polyhalogenomethane)[b]
$PhCH_2$–H[c]	3.62	CCl_4	110	24	14(0.03)
		1767		77	48(0.10)
				154	100(0.20)
Cy–H	0.82	CCl_4	110	3	153(0.49)
		255		33	2630(8.46)
				53	4360(14.0)
Cy–H	0.82	CCl_4	80	11	199(0.64)
		255		23	303(0.97)
				59	523(1.68)
n-C_6H_{14}	0.82	CCl_4	80	30	300(0.96)[d]
		255		80	600(1.92)[d]
Cy–H	0.47	$CHBr_3$	80	47	23(0.77)
		14		90	65(2.18)
				131	73(2.45)
$PhCH_2$–H[c]	0.65	CHI_3	110	112	19(2.05)
		6		350	53(5.74)
Cy–H	0.41	CHI_3	80	52	70(5.74)
		5		124	163(13.4)

[a] According to GLC. [b] Hydrocarbon is in excess with respect to polyhalogenomethane in all cases. [c] No tolyl halogenides were detected. [d] Sum of 2- and 3-hexyl derivatives (1.2:1 ratio), yield of 1-halogeno derivative less than 1.5% on rhodium.

The reaction regioselectivity is typical of that for classical organic chemistry. Namely, benzylic C–H bonds are activated in toluene and secondary C–H bonds are more reactive than primary ones in n-hexane. According to the data in Table 1, the secondary C–H bond of n-hexane is at least two orders of magnitude more reactive at 80 °C as compared with the primary bond. Indeed, after 80 min of the reaction a 600% yield on rhodium of secondary hexyl chlorides was obtained whereas the primary product was not detected (detection limit near 1.5% on rhodium). After statistical correction for the number of C–H bonds involved in the reaction it corresponds to a ratio of more than 300:1. Surprisingly, cyclohexane is roughly 100 times more reactive than toluene (see Figure 1). This conclusion has been checked by concurrent toluene/n-hexane metathesis. Thus, very high selectivity of secondary alkane C–H bond halogenation in comparision to primary alkane or benzylic C–H bonds is observed under catalysis with complex **1**.

In order to learn more about the mechanism of reaction (1) we conducted a kinetic study which revealed that the reaction is first order in each reagent and is inhibited by triphenylphosphine additives (by a factor of 6 at a 20:1 ligand to metal ratio). Analysis of cyclohexane reactivity at 80 °C allows us to conclude that the activity of polyhalogenomethanes increases

---

[†] A typical reaction procedure was as follows: In a Schlenk-type flask 3-5 µmol of complex **1**, 0.8 ml of hydrocarbon (toluene or mixture of 0.5 ml of alkane and 0.3 ml of benzene added in order to increase solubility of complex) and 1 µl of n-decan as internal standard for GLC were placed. The mixture was deaerated by 2–3 cycles of consecutive freezing with liquid nitrogen–pumping–melting under argon. The necessary reagent (*e.g.*, 20 µl of liquid polyhalogenomethane or 20 µl of a benzene solution of iodoform) was injected into a flask and the mixture heated at 80–110 °C. A sample of the reaction mixture was periodically extracted and analysed by GLC. The products were identified by GC-MS. The stability of the products under the reaction conditions was checked in additional experiments.

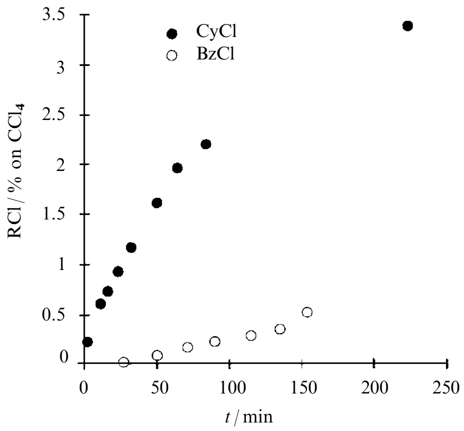

Figure 1 Comparison of the reactivity of cyclohexane (80 °C, [CyH] = 5.4 mol dm^{-3}, [CCl$_4$] = 0.26 mol dm^{-3}, [Rh] = 0.8 mmol dm^{-3}) and toluene (110 °C, [PhMe] = 9.8 mol dm^{-3}, [CCl$_4$] = 0.41 mol dm^{-3}, [Rh] = 3.9 mmol dm^{-3}) in metathesis with CCl$_4$.

in the order $CCl_4 < CHBr_3 < CHI_3$. Although radical traps such as benzoquinone inhibit reaction (1) slightly, the low reactivity of toluene in comparison with cyclohexane contradicts a radical chain reaction mechanism. Indeed, no dimers such as R_2 or C_2Cl_6 were detected in CCl_4 containing reaction mixtures. At the same time, addition of an excess of iodine into a hot toluene solution of complex **1** results immediately in benzyl iodide formation in 3% yield on rhodium. Benzyl iodide is formed in 100% yield on iodine after 0.5 h heating when iodine is added to the corresponding CCl_4 containing reaction mixture. These facts indicate that the formation of organorhodium compounds which smoothly undergo halogenolysis[8] takes place in the reaction mixtures. Thus we can conclude that Wilkinson's complex selectively activates hydrocarbon C–H bonds. We suppose that reaction (1) can proceed *via* the unstable and labile products of hydrocarbon oxidative addition to the rhodium(I) complex **2**:

$$\mathrm{RH + RhCl(L)_3 \rightleftharpoons \underset{\mathbf{2}}{R{-}RhCl(H)(L)_3}} \tag{2}$$

According to the results of the iodinolysis of toluene solutions of complex **1**, which gives only a 3% yield of benzyl iodide on rhodium, the reaction of compound **1** with hydrocarbons can proceed by the thermodynamically unfavourable oxidative addition of the hydrocarbon to the rhodium(I) complex; thus the weakest C–H bond undergoes reaction, as takes place in the case of its isolobal analogue dihalogenobis(triphenylphosphine)palladium(II).[9] Reaction (2) can be compared with the final stage of the well known catalytic cycle of Wilkinson's-complex-catalysed alkene hydrogenation, *i.e.* the reductive elimination of the hydrocarbon from hydridoorganorhodium(III).[10a] We propose a catalytic cycle of reaction (1) which includes along with the stage (2) at least two more stages:

$$\mathrm{R{-}RhCl(H)(L)_3 + CCl_4 \rightarrow \underset{\mathbf{3}}{R{-}RhCl_2(L)_3} + CHCl_3} \tag{3}$$

$$\mathrm{R{-}RhCl_2(L)_3 \rightleftharpoons RhCl(L)_3 + RCl} \tag{4}$$

Reaction (3) is the well known exchange of hydrido for halogenido ligands in transition metal complexes.[10b] On the basis of the analogy between $RhCl(PPh_3)_3$ and $PdCl_2(PPh_3)_2$ one can explain the unusually high cyclohexane/toluene selectivity in reaction (1): cleavage of the benzylic C–H bond, which is expected to be more reactive with respect to rhodium(I) as compared with the secondary alkane C–H bond, gives the more stable organorhodium intermediates **2**,**3**. At the same time the pentamethylcyclopentadienyl(trimethylphosphine)rhodium(I) complex preferentially activates aromatic C–H bonds in toluene and primary C–H bonds in n-alkanes.[1a] Thus, depending on the ligand environment, complexes of a particular metal can possess entirely different selectivity in the activation of C–H bonds.

A possible alternative scheme for the catalytic cycle of reaction (1) includes polyhalogenomethane C–X bond activation with complex **1** leading to a polyhalogenomethyl free radical. However, this does not explain either the cyclohexane/toluene or hexane secondary/primary C–H bond selectivity in the metathesis (1).

This work was made possible in part by grant no. RHH300 from the International Science Foundation, grant no. 94-03-08412a from the Russian Foundation for Basic Research and grant no. 94-9.4-04 from the Competition Centre of Fundamental Natural Sciences.

References

1 (*a*) W. D. Jones, in *Activation and Functionalization of Alkanes*, ed. C. L. Hill, John Wiley, New York, 1989, ch. 4; (*b*) R. G. Bergman, *Science*, 1984, **223**, 902; (*c*) R. Crabtree, *Chem. Rev.*, 1985, **85**, 245; (*d*) J. Halpern, *Inorg. Chim. Acta*, 1985, **100**, 41; (*e*) A. A. Bengali, B. A. Arndtsen, P. M. Burger, R. H. Burger, B. H. Weiller, K. R. Kyle, C. B. Moore and R. G. Bergman, *Pure Appl. Chem.*, 1995, **67**, 281.

2 K. Nomura and Y. Saito, *J. Chem. Soc., Chem. Commun.*, 1988, 161.

3 F. Takahiro and Y. Saito, *J. Chem. Soc., Chem. Commun.*, 1990, 757.

4 T. Sakakura and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1987, 758.

5 J. A. Miller and L. K. Knox, *J. Chem. Soc., Chem. Commun.*, 1994, 1449.

6 J. P. West and L. Schmerling, *J. Am. Chem. Soc.*, 1950, **72**, 3225.

7 *Beilsteins Handbuch der Organischen Chemie*, Vierte Aufl., Springer-Verlag, Berlin, 1972, Band 1, Teil 1, S. 85.

8 *Comprehensive Organometallic Chemistry. The Synthesis, Reactions and Structures of Organometallic Compounds*, ed. G. Wilkinson, Pergamon Press, Oxford, 1982, vol. 5, ch. 35.

9 A. N. Vedernikov, A. I. Kuramshin and B. N. Solomonov, *Zh. Org. Khim.*, 1993, **29**, 2129 (*Russ. J. Org. Chem.*, 1993, **29**, 1767); *J. Chem. Soc., Chem. Commun.*, 1994, 121.

10 (*a*) J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, California, 1987, ch. 10; (*b*) ch. 3.

Received: Cambridge, 26th October 1995; Com. 5/07067H
Moscow, 15th December 1995