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A Bimetallic Ruthenium Ethylene Complex as a Catalyst Precursor for the Kharasch Reaction

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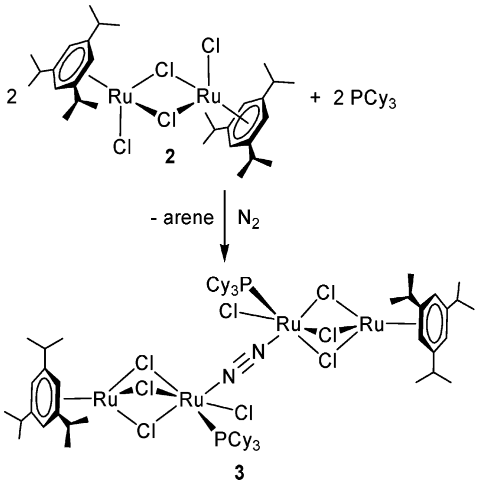
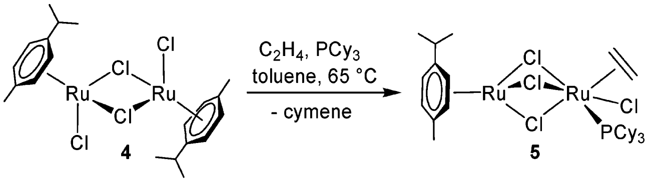
Summary: A bimetallic complex, in which a $RuCl_2(\eta^2\text{-}C_2H_4)(PCy_3)$ fragment is connected via three chloro bridges to a (η^6-p-cymene)$RuCl_2$ fragment, has been synthesized and characterized by single-crystal X-ray crystallography. This complex was used to catalyze the atom transfer radical addition of CCl_4 and $CHCl_3$ to olefins at temperatures between 0 and 40 °C. Turnover frequencies of up to 1550 h^{-1} were observed, making the new complex one of the most active catalysts for this type of reaction described so far.

In 1973, Matsumoto and co-workers reported that the complex [$RuCl_2(PPh_3)_3$] (**1**) can be used as a catalyst for the addition of polychloromethanes to 1-olefins.[1] This type of reaction proceeds via a radical mechanism and is commonly referred to as the “Kharasch reaction”.[2] For a long time, complex **1** was one of the most active catalysts for the Kharasch reaction and several applications in organic synthesis were reported.[3] Over the last 6 years, a number of ruthenium-based catalysts with superior performance have been described.[4,5] Our group has recently shown that a mixture of the dimeric complex [$(1,3,5\text{-}C_6H_3{}^iPr_3)RuCl_2]_2$ (**2**) and PCy_3 can be used to catalyze the addition of $CHCl_3$ to aromatic olefins under exceptionally mild conditions.[6] As a product of the reaction between **2** and PCy_3, the tetranuclear complex **3** has been identified, which itself proved to be a very efficient catalyst (Scheme 1). The general utility of complex **3** in atom transfer radical reactions, however, is limited by its very low solubility. Therefore, we have investigated whether it is possible to replace the bridging nitrogen ligand with other labile two-electron-donor ligands. Furthermore, we wanted to substitute the $(1,3,5\text{-}C_6H_3{}^iPr_3)$Ru fragment by a (cymene)Ru fragment, which would allow us to use the commercially available complex [$(cymene)RuCl_2]_2$ (**4**) as the starting material.

Scheme 1



Scheme 2



As a potential substitute for the μ-N_2 ligand of the catalyst precursor **3**, olefins appeared to be of special interest, since olefin π-complexes have been discussed as intermediates in the catalytic cycle of ruthenium-catalyzed Kharasch reactions.[4a] We therefore investigated the reaction of complex **4** with 1 equiv of PCy_3 in the presence of various olefins. When the reaction was performed under an atmosphere of ethylene, complex **5** could be obtained in the form of red crystals in 80% yield (Scheme 2).[7]

Complex **5** is quite soluble in methylene chloride and moderately soluble in aromatic solvents such as benzene

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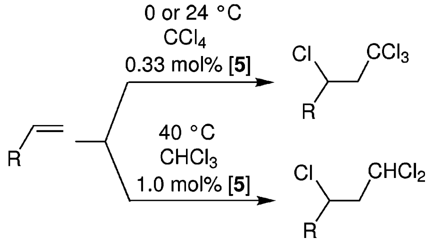
(7) A solution of complex **4** (100 mg, 163 μmol) and PCy_3 (45.6 mg, 163 μmol) in toluene (10 mL) under an atmosphere of ethylene was heated to 60 °C for 9 h. Upon cooling to room temperature, crystals of complex **5** formed, which were isolated after 24 h and washed with pentane (yield 80%). ^{1}H NMR (400 MHz, toluene-d_8 + C_2H_4): δ (ppm) 1.28 (d, ^3J = 7 Hz, 6 H, p-$CH_3C_6H_4CH(C\mathit{H}_3)_2$), 1.27−1.31 (m, 6 H, PCy_3), 1.74−1.95 (m, 18 H, PCy_3), 2.11 (s, 3 H, p-$C\mathit{H}_3C_6H_4CH(CH_3)_2$), 2.16−2.22 (m, 6 H, PCy_3), 2.51 (m, 3 H, PCy_3), 2.88 (sept, ^3J = 7 Hz, 3 H, p-$CH_3C_6H_4C\mathit{H}(CH_3)_2$), 4.17 (m, 2 H, C_2H_4), 4.66 (m, 2 H, C_2H_4), 5.04 (d, ^3J = 6 Hz, 1 H, p-$CH_3C_6\mathit{H}_4CH(CH_3)_2$), 5.25 (d, ^3J = 6 Hz, 1 H, p-$CH_3C_6\mathit{H}_4CH(CH_3)_2$), 5.33 (d, ^3J = 6 Hz, 1 H, p-$CH_3C_6\mathit{H}_4CH(CH_3)_2$), 5.51 (d, ^3J = 6 Hz, 1 H, p-$CH_3C_6\mathit{H}_4CH(CH_3)_2$). ^{13}C NMR (101 MHz, toluene-d_8 + C_2H_4): δ (ppm) 18.74, 22.13, 22.49 (s, CH_3, cymene), 27.00 (s, PCy_3), 28.24−28.37 (m, PCy_3), 29.76 (m, PCy_3), 31.36 (s, $\mathit{C}H(CH_3)_2$), 61.03 (d, $^2J_{PC}$ = 2 Hz, C_2H_4), 78.19, 78.65, 79.33, 80.05 (s, CH, cymene), 96.40, 99.79 (s, C, cymene). ^{31}P NMR (162 MHz, toluene-d_8 + C_2H_4): δ (ppm) 44.37 (s). Anal. Calcd for **5**·(toluene): C, 50.57; H, 6.77. Found: C, 50.25; H, 6.72.

10.1021/om050027x CCC: $30.25

Table 1. Kharasch Addition of $CXCl_3$ (X = H, Cl) to Olefins Catalyzed by Complex 5[a]



entry	olefin	$CXCl_3$	$CXCl_3$: olefin	time (h)	temp (°C)	conversn (%)	yield (%)
1[c]	styrene	CCl_4	4	2	24	98	98
2[c]	styrene	CCl_4	4	10	0	≥99	≥99
3[b,c]	*p*-methoxystyrene	CCl_4	4	1	24	96	96
4	methyl methacrylate	CCl_4	4	5	24	78	62
5	methyl methacrylate	CCl_4	4	12	0	≥99	86
6	*n*-butyl acrylate	CCl_4	4	5	24	80	60
7	*n*-butyl acrylate	CCl_4	4	48	0	79	55
8[b,c]	1-decene	CCl_4	1.5	24	24	92	81
9[c]	styrene	$CHCl_3$	4	48	40	94	94
10[c]	*p*-chlorostyrene	$CHCl_3$	4	48	40	93	89
11	methyl methacrylate	$CHCl_3$	4	48	40	92	25

[a] Reaction conditions: **5**:olefin = 1:300 (CCl_4) or 1:100 ($CHCl_3$); [**5**] = 4.6 mM (CCl_4) or 13.8 mM ($CHCl_3$); solvent, toluene-d_8; all reactions were performed under an atmosphere of dry dinitrogen. The conversion is based on the consumption of styrene, and the yield is based on the formation of product, as determined by GC or ^1H NMR spectroscopy after the time given. [b] Solvent, CD_2Cl_2. [c] Solvent saturated with D_2O.

and toluene. NMR spectroscopy indicated the presence of a cymene, a PCy_3, and a C_2H_4 ligands in a ratio of 1:1:1. In solution, the last ligand was found to be rather labile. All spectra were thus recorded under an atmosphere of ethylene. For the aromatic protons of the arene ligand, four signals were observed in the ^1H NMR spectra. This indicated that complex **5** is chiral, in agreement with the structure depicted in Scheme 2.

Analysis of complex **5** by X-ray crystallography confirmed that the (cymene)$RuCl_2$ fragment is indeed connected via three chloro bridges to the $RuCl_2(C_2H_4)PCy_3$ fragment (Figure 1).[8,9] The Ru−Cl bond lengths of the bridging chloro ligands (2.42−2.54 Å) are larger than the Ru−Cl bond distance found for the terminal chloro ligand (Ru1−Cl4 = 2.3948(6) Å). The bond distances between the ethylene carbon atoms and the ruthenium atom (Ru1−C1 = 2.172(2), Ru1−C2 = 2.159(2) Å) as well as the carbon−carbon distance of the coordinated olefin (C1−C2 = 1.386(4) Å) are within the expected range.[10]

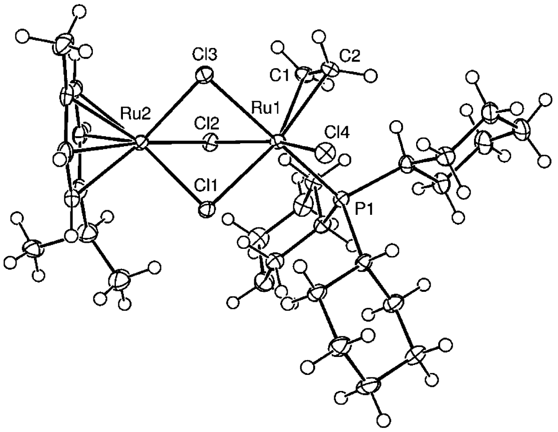


Figure 1. Graphic representation of the molecular structure of **5** in the crystal. The solvent molecule (toluene) is not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 = 2.4878(6), Ru1−Cl2 = 2.4513(7), Ru1−Cl3 = 2.5356(6), Ru1−P1 = 2.3133(7), Ru1−Cl4 = 2.3948(6), Ru1−C1 = 2.172(2), Ru1−C2 = 2.159(2), C1−C2 = 1.386(4), Ru2−Cl1 = 2.4281(6), Ru2−Cl2 = 2.4152(6), Ru2−Cl3 = 2.4396(7); P1−Ru1−Cl3 = 178.46(2), P1−Ru1−Cl4 = 88.72(2), P1−Ru1−Cl1 = 101.67(2).

Having established the structure of complex **5**, we next investigated its ability to catalyze the Kharasch addition of CCl_4 and $CHCl_3$ to olefins. With CCl_4 and styrene as the substrates and 0.33 mol % of complex **5**, a very fast and clean addition reaction was observed at room temperature. After only 30 min, a yield of 88% was obtained, and after 2 h, the reaction was complete (Table 1, entry 1). The initial turnover frequency was determined to be 1100 h^{-1} at 24 °C and 1550 h^{-1} at 40 °C.[11] These values are comparable to those found for the most active ruthenium catalyst described so far, a half-sandwich carborane complex of the formula $[RuH(9\text{-}SEtPh\text{-}7\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)_2]$.[5c,d] The activity of the new catalyst **5** was so high that the addition of CCl_4 to styrene could be performed at 0 °C. After 10

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(8) Crystal data for complex **5**·(toluene): $C_{37}H_{59}Cl_4PRu_2$, M_r = 878.75, triclinic, a = 9.6834(5) Å, b = 10.1191(6) Å, c = 21.2946(13) Å, α = 94.104(5)°, β = 92.837(5)°, γ = 113.374(5)°, V = 1903.54(18) Å^3, T = 140(2) K, space group $P\bar{1}$, Z = 2, μ(Mo Kα) = 1.141 mm^{-1}, 11 226 reflections collected, 5878 independent reflections, R_{int} = 0.0265, $R_1(I > 2\sigma(I))$ = 0.0236, wR_2(all data) = 0.0613.

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(11) To measure the initial rates, the reactions were performed with 0.1−0.2 mol % of complex **5**. The initial TOF was calculated from the yield determined after 5 min.

h, quantitative conversion was observed (entry 2). When the substrate to catalyst concentration ratio was increased to 2000:1 (0.05 mol % of **5**), it was still possible to obtain a yield of 90% (TON = 1800).[12] However, due to partial catalyst deactivation, significantly longer reaction times were required (21 d).

Other olefins such as 4-methoxystyrene (entry 3) and acrylates (entry 4−7) were also converted to the corresponding CCl_4 adducts in good yields at 0 or 24 °C using 0.33 mol % of complex **5**. As expected, a reaction temperature of 0 °C resulted in slower rates (entry 5 and 7). For methyl methacrylate (MMA) as the substrate, however, the low reaction temperature was found to be beneficial, because the reaction proceeded with slightly fewer side products[13] and gave a higher TON.

With 1-decene, a difficult substrate for Kharasch additions, a conversion of 92% and a yield of 81% was determined after 24 h (entry 8). Here, it was advantageous to use a relatively low CCl_4 to olefin ratio of 1.5:1. For higher ratios, faster rates and fewer side products were observed but the lifetime of the catalyst was reduced and the final yield was therefore lower.

For addition reactions with the significantly less active substrate $CHCl_3$, the reaction temperature was increased to 40 °C and a catalyst concentration of 1.0 mol % was employed. Under these conditions, the chloroform adducts of the aromatic substrates styrene and *p*-chlorostyrene were obtained in very good yields (entries 9 and 10). It should be noted that, so far, there have been only very few catalysts for which synthetically useful yields of over 80% for this type of reaction have been reported.[5b,h,6] For MMA, a conversion of 92% was determined after 48 h (entry 11). The yield of the desired addition product, however, was very modest, due to competing polymerization reactions.

Interestingly, for the aromatic olefins styrene, *p*-methoxystyrene, and *p*-chlorostyrene, catalyst **5** gave slightly better results when the solvents (CH_2Cl_2 and toluene) contained small amounts of water. For 1-decene and *n*-butyl acrylate, traces of water did not effect the reaction, whereas for MMA, water was detrimental to the addition reaction. Currently, we have no explanation for this “water-effect”, but it is interesting to note that an increased activity in the presence of small amounts of water was also observed for some other polynuclear catalysts, which were recently described by our group.[5a] For the data summarized in Table 1, the “optimal” solvents ($\pm H_2O$) were employed.

With regard to the mechanism of the reaction, it seems likely that the ethylene ligand of complex **5** is initially cleaved off to provide a free coordination site at which subsequent catalytic transformations can occur. This hypothesis was substantiated by the isolation and structural characterization[14] of the mixed-valence $Ru^{II}-Ru^{III}$ complex $[(\text{cymene})Ru(\mu\text{-}Cl)_3RuCl_2(PCy_3)]$ (**6**) (Figure 2), which was obtained by reaction of complex **5** with CCl_4.[15] The formation of this complex is in accord with the general assumption that a reversible oxidation of the metal complex is a key step in ATRA reactions.[4,5]

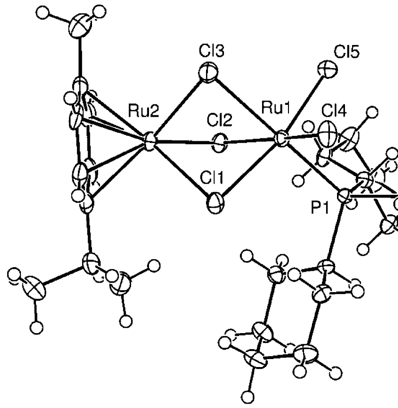

Figure 2. Graphic representation of the molecular structure of **6** in the crystal. The solvent molecule (CCl_4) is not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 = 2.4398(12), Ru1−Cl2 = 2.4300(11), Ru1−Cl3 = 2.5588(13), Ru1−P1 = 2.3304(13), Ru1−Cl4 = 2.3192(12), Ru1−Cl5 = 2.3014(13), Ru2−Cl1 = 2.4454(11), Ru2−Cl2 = 2.4548(13), Ru2−Cl3 = 2.4264(12); P1−Ru1−Cl3 = 177.80(4), P1−Ru1−Cl4 = 92.12(4), P1−Ru1−Cl1 = 101.53(4).

In summary, we have described the synthesis and the structure of a new bimetallic Ru−ethylene complex (**5**). This complex turned out to be a potent catalyst for the Kharasch reaction of CCl_4 or $CHCl_3$ and olefins. With turnover frequencies of over 1000 h^{-1} at ambient temperatures, it is one of the most active catalysts described so far. From a practical perspective it is an advantage that complex **5** can be obtained in a one-step procedure from commercially available starting materials. Currently we are investigating whether complex **5** can be used as a catalyst for other reactions, such as the closely related atom transfer radical polymerization of olefins.[16]

Supporting Information Available: Crystallographic data, as CIF files, of complexes **5** and **6**. This material is available free of charge on the Internet at http://pubs.acs.org.

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[12] Reaction conditions: **5**:styrene:CCl_4 = 1:2000:4000; temperature, 24 °C; solvent, toluene-d_8 saturated with D_2O.

[13] Lower values for the yield compared to the conversion are frequently found for Kharasch reactions. This is mainly due to polymerization reactions which compete with the addition reaction.

[14] Crystal data for complex **6**·CCl_4: $C_{29}H_{47}Cl_9PRu_2$, $M_r = 947.83$, monoclinic, $a = 20.3160(16)$ Å, $b = 10.0742(7)$ Å, $c = 21.2411(16)$ Å, $\beta = 118.213(8)°$, $V = 3830.9(5)$ Å^3, $T = 140(2)$ K, space group $P2_1/c$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 1.478$ mm^{-1}, 21 514 reflections collected, 6447 independent reflections, $R_{int} = 0.0515$, $R_1(I > 2\sigma(I)) = 0.0362$, wR_2(all data) = 0.0758.

[15] Red crystals of **6** were obtained upon heating a solution of complex **5** (20.1 mg, 25.6 μmol) in a mixture of toluene (0.5 mL) and CCl_4 (1.0 mL) to 40 °C for 2 h under an inert atmosphere. After cooling to room temperature, the product was isolated, washed with hexane (2 × 1 mL) and pentane (1 mL), and dried under vacuum (yield 83%). Anal. Calcd for $C_{28}H_{47}Cl_5PRu_2\cdot{}^3/_4CCl_4$: C, 37.97; H, 5.21. Found: C, 37.64; H, 5.11. A GC-MS analysis of the reaction mixture revealed the presence of hexachloroethane and of the Kharasch adduct of ethylene, 1,1,1,3-tetrachloropropane.

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