

RADICAL REACTIONS IN THE COORDINATION SPHERE I.
ADDITION OF CARBON TETRACHLORIDE AND CHLOROFORM TO 1-OLEFINS
CATALYZED BY RUTHENIUM(II) COMPLEXES.

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Recently considerable attention has been directed to the radical reactions brought about by the interaction of a transition metal salt or complex with an organic halide.¹⁾ For example, the addition of polyhaloalkanes to a variety of olefins is known to be initiated by metal halides²⁾ and by metal carbonyls.³⁾ The transition metal-phosphine complexes which are often utilized for homogeneous hydrogenation catalysts⁴⁾ might also be expected to activate organic halides and, in fact, zero-valent transition metal-phosphine complexes such as tetrakis(triphenylphosphine)platinum(0) and bis(triphenylphosphine)nickel dicarbonyl with carbon tetrachloride have been used as an initiator for free radical polymerization.⁵⁾ This communication deals with our finding that the ruthenium(II)-triphenylphosphine complexes catalyzed effectively the addition of carbon tetrachloride and chloroform to 1-olefins.

In the presence of either dichlorotris(triphenylphosphine)ruthenium(II) (A) or dichlorotetrakis(triphenylphosphine)ruthenium(II) (B), the addition of polychloromethanes such as carbon tetrachloride and chloroform to 1-olefins proceeded smoothly under mild conditions to afford the corresponding 1:1 adducts. The results of addition reactions are listed in the Table. The good yields of the adducts indicate that the ruthenium catalyzed reaction was accompanied by but little telomerization. It was also found that the complex (A) is a better catalyst compared to the complex (B).

In a typical procedure, 1.16 g (10.3 mmol) of 1-octene and 3.35 g (21.8

mmol) of carbon tetrachloride were allowed to react in a sealed tube at 80°C with 0.05 g (0.05 mmol) of the complex (A). After 4 hours, the resulting mixture was subjected to glpc analysis which indicated that 75 % of 1-octene was consumed and 1,1,1,3-tetrachlorononane was produced in a 97 % yield based on the olefin consumption.

The reaction was slower for chloroform and more vigorous conditions were required to achieve the high conversion. Thus, heating of a 3:1 mixture of chloroform and 1-octene at 140°C with 1 mol% of the complex (A) or (B) afforded

Table Addition of carbon tetrachloride and chloroform to 1-olefins in the presence of dichlorotris(triphenylphosphine)ruthenium(II) (A) or dichlorotetrakis(triphenylphosphine)ruthenium(II) (B).^{a)}

Olefin	Halide	Catalyst	Condition	Adduct(yield,%) ^{e)}	Conversion(%) ^{f)}
1-octene ^{b)}	CCl ₄	A ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₆ H ₁₃ (97)	76
1-octene	CCl ₄	B ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₆ H ₁₃ (100)	60
1-octene	CHCl ₃	A ^{d)}	140°C, 15 hr	CHCl ₂ CH ₂ CHClC ₆ H ₁₃ (67)	75
1-octene	CHCl ₃	B ^{d)}	140°C, 15 hr	CHCl ₂ CH ₂ CHClC ₆ H ₁₃ (66)	71
1-nonene	CCl ₄	A ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₇ H ₁₅ (95)	80
1-nonene	CCl ₄	B ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₇ H ₁₅ (92)	48
1-heptene	CCl ₄	A ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₅ H ₁₁ (99)	68
1-heptene	CCl ₄	B ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₅ H ₁₁ (81)	45
1-hexene	CCl ₄	A ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₄ H ₉ (88)	90
1-hexene	CCl ₄	B ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₄ H ₉ (88)	42
styrene ^{g)}	CCl ₄	A ^{c)}	80°C, 4 hr	CCl ₃ CH ₂ CHClC ₆ H ₅ (92)	98

a) A 3:1 mixture of a halide and an olefin was used unless otherwise indicated.

b) A 2:1 mixture was used. c) The catalyst concentration was 0.5 mol% based on the olefin charged. d) The catalyst concentration was 1 mol% based on the olefin charged. e) Yields were determined by glpc (based on the olefin consumption).

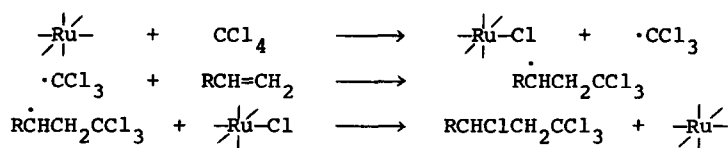
f) Conversion was (final concentration of the olefin)/(initial concentration of the olefin). g) In preliminary experiments it was found that other easily polymerizable olefins such as methyl acrylate and acrylonitrile add carbon tetrachloride at 100°C to yield the corresponding 1:1 adducts in ca. 20-40% yields.

1,1,3-trichlorononane in a yield of 67 % or 66 % respectively. In addition to this adduct, there were also produced 1,1-dichlorononane, 1,1,3-trichlorononane and 1,1,1,3-tetrachlorononane though in much lesser amounts. The formation of these products has previously been reported in the metal chloride systems.²⁾ Isomerization of 1-octene to 2-octene was observed to occur to a small extent in the reaction of chloroform. This is not unexpected, since it has been shown by Hudson et al.,⁶⁾ and Lyons⁷⁾ that the complex (A) and (B) slowly isomerized olefins.

Other transition metal-phosphine complexes such as chlorotris(triphenylphosphine)rhodium(I), dichlorobis(triphenylphosphine)palladium(II), dibromobis(triphenylphosphine)nickel(II) and dichlorobis(triphenylphosphine)nickel(II) also effected the reaction of carbon tetrachloride with 1-octene, but the conversion was invariably low at temperatures around 80°C.

The results in the Table indicate that the present system has some significant advantages when compared to previous methods: (a) The use of polar solvents such as alcohols or nitriles is no longer necessary whereas cuprous or ferrous chloride catalysis technique must employ solvents to ensure the reasonable yields of products. (b) The reaction can be carried out under mild conditions. Thus, for the reaction of carbon tetrachloride to 1-octene the ruthenium complexes catalyzed reaction gives 60-76 % yield of the adduct at 80°C while dicobalt octacarbonyl gives 19 % yield at 160°C.^{3e)}

Finally, by the analogy of the previously proposed mechanism^{2b,c,d)} for the cuprous or ferrous chloride catalyzed reaction, our results are likely to be accounted for in terms of the following propagation steps,



Supporting evidence was obtained for the homolytic mechanism since the reaction was completely inhibited by adding a small amount of galvinoxyl to the reaction mixture.

Application of these catalyst systems to other combinations of an olefin and a halide is at present underway.

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