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Catalysis by Phosphine Complexes of Silylruthenium Hydrides of the Addition of Carbon Tetrachloride to 1-Octene[1]

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Synopsis. Phosphine complexes of silylruthenium hydrides of types $[RuH_3(SiR_3)(PPh_3)_3]$ (where R_3Si= Et_3Si, Me_2PhSi, and $(MeO)_3Si$) and $[RuH(SiR_3)(PPh_3)_2]$ (where R_3Si= Cl_2MeSi and $(MeO)_3Si$) were found to be much more effective catalysts for the addition of carbon tetrachloride to 1-octene than $RuCl_2(PPh_3)_3$ or $RuH_2(PPh_3)_4$.

The addition reactions of carbon tetrachloride with olefins have been carried out with the aid of various catalysts (*e.g.*, peroxides, metal carbonyls and metal salts, *etc.*).[2] We have recently found that the addition reactions were effectively catalyzed by a homogeneous ruthenium catalyst, dichlorotris(triphenylphosphine)-ruthenium(II).[3,4] This catalyst was shown to have definite advantages (*e.g.*, high yields of 1: 1 adducts, unique selectivities and simplicity of the system, *etc.*)[3,4] compared to usual free-radical addition reactions. Even more effective catalysts have now been found as described below.

We have prepared phosphine complexes of silylruthenium hydrides of types $[RuH_3(SiR_3)(PPh_3)_3]$ (where R_3Si=Et_3Si, Me_2PhSi, and $(MeO)_3Si$) and $[RuH(SiR_3)(PPh_3)_2]$ (where R_3Si=Cl_2MeSi and $(MeO)_3Si$) by the reactions of $RuH_2(PPh_3)_4$ or $RuCl_2(PPh_3)_3$ with hydrosilanes.[5] and tested the catalytic efficiencies of these complexes for the reaction between carbon tetrachloride and 1-octene. All experiments were carried out in an argon atmosphere under reflux conditions using a 1: 3 mixture of the olefin and the chloride. The results are presented in Table 1 together with those for the reactions catalyzed by $RuCl_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$. The Table also shows the turnover number of these complexes.

$$n\text{-}C_6H_{13}CH{=}CH_2 + CCl_4 \xrightarrow{[Ru]} n\text{-}C_6H_{13}CHClCH_2CCl_3$$

$$[Ru] = RuH_3(SiR_3)(PPh_3)_3,\ RuH(SiR_3)(PPh_3)_2$$

An inspection of the Table clearly indicates that seven-coordinate ruthenium complexes, $RuH_3(SiR_3)(PPh_3)_3$, are particularly excellent catalysts for the addition reaction. With these catalysts, the 1: 1 adduct was obtained in 57—85% yields with turn-over number 2650—4250 while the values for $RuCl_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$ amounted to be 130 and 370, respectively. Therefore, it is apparent that these silylruthenium complexes are 20—32 times more active than the dichlororuthenium complex and 7—11 times more active than the dihydroruthenium complex.

Although the turn-over number of the complexes, $RuH(SiR_3)(PPh_3)_2$, were smaller than those of the trihydrido analogs, these four-coordinate complexes were also found to be 2—7 times effective than $RuCl_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$.

It has been known that phosphine complexes of ruthenium hydrides often catalyze double-bond migration in some unsaturated system.[6] Such migration, however, was not found in the present system and only the terminal adduct, 1,1,1,3-tetrachlorononane, was obtained under the conditions employed.

TABLE 1. REACTIONS OF CARBON TETRACHLORIDE WITH 1-OCTENE CATALYZED BY PHOSPHINE COMPLEXES OF SILYLRUTHENIUM HYDRIDES[a]

Catalyst	Catalyst concentration, mol%[c]	Yield of the 1: 1 adduct, %[d]	Catalytic efficiency[e]
$RuH_3(SiMe_2Ph)L_3$	0.02	57	2850
$RuH_3(SiMe_2Ph)L_3$	0.02	85	4250
$RuH_3(SiEt_3)L_3$	0.02	58	2900
$RuH_3[Si(OMe)_3]L_3$	0.02	53	2650
$RuH(SiCl_2Me)L_2$	0.05	44	880
$RuH[Si(OMe)_3]L_2$	0.05	46	920
RuH_2L_4	0.10	37	370
$RuCl_2L_3$	0.15	20	130
($L=PPh_3$)			

a) Reactions were carried out in an argon atmosphere under reflux conditions for 5 h using 50 mmol of the olefin and 150 mmol of the chloride. b) The system was carefully degassed by freeze-pump-thaw cycles and then flushed well with argon prior to the reaction. c) Based on the olefin charged. d) Yields (*via* GLC) of the adduct, 1,1,1,3-tetrachlorononane, are based on the olefin charged. e) The catalytic efficiency is meant by (moles of the adduct)/(moles of the catalyst).

Experimental

1-Octene and carbon tetrachloride were commercially available and purified by distillation prior to use. The complexes $RuCl_2(PPh_3)_3$,[7] $RuH_2(PPh_3)_4$,[8] $RuH_3(SiR_3)(PPh_3)_3$,[5] and $RuH(SiR_3)(PPh_3)_2$[5] were prepared according to literature directions.

Procedure for Testing the Catalytic Efficiencies of Phosphine Complexes of Silylruthenium Hydrides. All runs were conducted in essentially the same manner; therefore, only the reacttion catalyzed by the $RuH_3(SiMe_2Ph)(PPh_3)_3$ complex is described in detail.

In a 50-ml round bottomed flask, equipped with a reflux condenser and a magnetic stirring bar were placed 5.61 g (50 mmol) of 1-octene, 23.05 g (150 mmol) of carbon tetrachloride and 0.11 g (0.010 mmol) of the complex. The system was flushed with argon and the solution was refluxed for 5 h with stirring. GLC analysis of the resulting mixture disclosed that the 1: 1 adduct, 1,1,1,3-tetrachlorononane, had been produced in 57% yield based on the olefin charged. Structural assignment for this adduct was performed by comparing their physical properties (IR and NMR spectra and

GLC retention times, *etc.*) with those of an authetic sample after isolation by GLC.

Another reaction was carried out with a slight modification in order to optimize the yield of the 1: 1 adduct. Thus, the same mixture of the olefin, the chloride and the catalyst was cooled in liquid nitrogen, evacuated at 0.3 mm, flushed well with argon and then heated under reflux for 5 h. GLC analysis of the resulting mixture showed production of the 1: 1 adduct in 85% yield.

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