semidione, on the other hand, is symmetric with respect to this symmetry element.

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Catalytic Dimerization of Ethylene and Propylene by Nitrogentris(triphenylphosphine)cobalt Hydride

Sir:

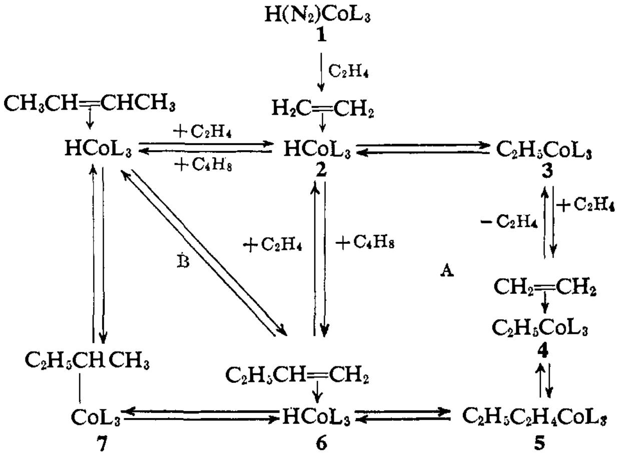
Nitrogentris(triphenylphosphine)cobalt hydride ($H(N_2)Co(PPh_3)_3$,[1] **1**) exhibits remarkably versatile chemical properties. It combines reversibly with H_2,[2,3] C_2H_4,[2] and NH_3,[2] forms a carbonyl complex by reaction with carbon monoxide[2,3] or by abstraction of CO from aldehydes,[3] and reacts with CO_2 to give a formate complex, $HCO_2Co(PPh_3)_3$.[4] The cobalt complex also catalyzes the hydrogenation of ethylene,[5] oxidation of triphenylphosphine to triphenylphosphine oxide,[5,6] and reduction of N_2O.[6] We wish to report now another example of catalytic activities of the complex, dimerizations of ethylene and propylene.

Many papers have been published reporting the ethylene dimerization by soluble catalysts based on Ti,[7,8] Ni,[8] Rh,[9] Ru,[9] and Pd[10] compounds and on mixed systems of cobalt and organoaluminum compounds.[11] However no report has been made, to our knowledge, on the catalytic dimerization using an isolated cobalt complex. Concerning the dimerization of propylene, only a few catalyst systems based on $RhCl_3$[9] and nickel compounds[8] have been reported.

The catalytic dimerizations of ethylene and propylene by **1** take place at ambient temperature and pressure and proceed with substantial rates even at 0°. In a typical example of the ethylene dimerization, 192 mmol of ethylene with an initial pressure of 710 mm was brought in contact with 10 ml of a *m*-xylene solution containing 0.55 g (0.63 mmol) of **1** at room temperature (25–30°). The solution absorbed ethylene with an initial rate of *ca.* 100 cc (NTP)/hr, but the rate of ethylene absorption decayed with time under this condition, accompanied by the color change of the original solution to dark brown, presumably by the partial decomposition of the catalyst. The deterioration of the catalyst was less marked at 0°. The products were separated by distillation and preparative vapor phase chromatography and identified by vpc, ir, and mass spectroscopy. After the reaction time of 32 hr, 41 mmol of butenes was produced, consisting of 72% *trans*-2-butene, 26% *cis*-2-butene, and 2% of 1-butene. In addition to butenes, small amounts of ethylene trimers and ethane (0.57 mmol) were found. This system also catalyzes the isomerization of 1-butene to 2-butenes. The isomerization takes place very rapidly at room temperature and gives a butene mixture with the same composition as obtained in the ethylene dimerization by **1**.

The propylene dimerization was carried out in a similar manner as ethylene. Complex **1** (0.23 g, 0.32 mmol) in 7 ml of *m*-xylene was stirred at 25° in contact with 190 mmol of propylene with an initial pressure of 753 mm for 47 hr. About 17 mmol of propylene dimers was produced, containing 2-methyl-1-pentene as the main product with two other unidentified dimers of minor quantities. The addition of 3 mol of tri-*n*-butylphosphine/mol of **1** reduced the dimerization rate considerably, but triphenylphosphine had little effect on the rate.

The mechanisms of ethylene dimerization and butene isomerization by $RhCl_3 \cdot 3H_2O$ were discussed in detail by Cramer. The dimerization mechanism by the present cobalt complex appears to be simpler compared with the one by $RhCl_3 \cdot 3H_2O$, where the activation of $RhCl_3 \cdot 3H_2O$, the presence of a cocatalyst such as HCl, and the formal change of the oxidation state of Rh are required. Since the presence of a cobalt–hydride bond in the original complex (**1**) has been established,[4,12,13] the following mechanism involving the insertion of ethylene between Co–H bond seems to be reasonable for the ethylene dimerization. Evidently complex **1** is only a precursor of the active species, and the coordinated N_2 is displaced by ethylene from **1** as confirmed by the examination of the ir spectrum of the catalyst solution.[2] An unstable crystalline complex which releases on pyrolysis 0.9 mol of C_2H_4/g-atom of cobalt with a small amount of C_2H_6 and has a composi-



L = triphenylphosphine

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tion corresponding to **2** could be isolated from a reaction mixture of cobalt acetylacetonate and diethylaluminum monoethoxide in ether under argon atmosphere. The isolation of this complex suggests the presence of complex **2** in the catalyst solution as an active species of dimerization.

If the species **2** or **3** should exist in the system, further coordination of ethylene to the complex and ensuing insertion between ethyl-cobalt bonds are the most reasonable steps expected. Displacement of butene by ethylene through a butene-hydride intermediate (**6**) will regenerate **2**, and the cyclic process A will yield butene catalytically. Why ethane is formed is not clear at the moment, but a possible cause is hydrogen abstraction by the ethyl group from the *ortho* positions of the phenyl groups in the triphenylphosphine ligands.[13] The result of the independent isomerization experiment of 1-butene by **1** giving the same composition of butene isomers as obtained in the catalytic dimerization implies that another cycle, B, is operating in the dimerization reaction.

The propylene dimerization may proceed with a similar mechanism to that of ethylene dimerization involving the insertion of propylene molecules between the Co–H bond and the replacement of propylene dimers by propylene.

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Solvolytic α-Deuterium Effects for Different Leaving Groups

Sir:

It has recently been found that *p*-methylbenzyl-α-d_2 chloride shows nearly the same isotope rate effect at 25° in 94% (by weight) trifluoroethanol–water (1.146 per D) and 70% trifluoroethanol–water (1.140) as has been reported for α-phenylethyl-α-*d* chloride at 25° in various ethanol–water mixtures (1.146–1.153).[1] This finding suggests that the α-deuterium effect for a limiting reaction is primarily a function of the leaving group and not of the structure of the particular alkyl group. Some typical solvolyses show effects about 3% smaller for ionization of the C–Br bond than of the C–Cl bond.[1]

Such isotope effects are related to changes in force constants at the position of isotopic substitution.[2] If the isotope effects and especially the relative bromide–chloride isotope effects do not depend on the particular alkyl group, it is appropriate to carry out model calculations on the methyl halides for which force fields obtained from vibrational data are available.[3] The conditions under which such calculations on the methyl halides should give significant information about the experimental systems have been discussed.[4]

With the use of the methyl halide force fields and geometries,[3] we have calculated, in the harmonic approximation, the equilibrium constant, K_{ex}, for $CH_3Cl + CH_2DBr \rightleftharpoons CH_2DCl + CH_3Br$ to be 1.037 at 25°. Detailed calculations indicate that this isotope effect reflects mainly the fact that force constants involving H–C–halide bending motion are larger in chloride than in bromide.

We designate by R the ratio of k_H/k_D in alkyl chloride solvolysis to the same quantity for an alkyl bromide. It is then straightforward to show, within the transition-state theory framework,[5] that $R = [(\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger})_{Cl}/(\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger})_{Br}][K_{ex}/K_{ex}{}^{\ddagger}]$ where $(\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger})_{Cl}$ is the isotope effect, H/D, on the frequency corresponding to the reaction coordinate in the chloride and $K_{ex}{}^{\ddagger}$ is the exchange equilibrium constant analogous to K_{ex} for the corresponding transition states but with the degree of freedom for the reaction coordinate missing.[6]

Calculations have been carried out with reasonable transition-state models which give essential agreement with the experimental k_H/k_D values for the chlorides and bromides, respectively.[7] The transition-state force fields for the chloride and for the bromide were chosen to be the same, so, as expected, $K_{ex}{}^{\ddagger}$ is found to be very close to unity.[2] The ratio of $\nu_L{}^{\ddagger}$ ratios in the expression for R is calculated to be 0.995 where the transition state has a planar CH_3 group, the C–halogen stretch force constant is set equal to -0.5 mdyn/Å, and all C–halogen stretch–interaction force constants are set equal to 0.0. This calculated value for the ratio of $\nu_L{}^{\ddagger}$ ratios is very close to that which one evaluates on the basis of methyl and halide fragment masses;[5] this ratio would be expected to be even closer to unity for larger molecules such as the α-phenylethyl halides.

Since, in our model, the $\nu_L{}^{\ddagger}$ ratios and $K_{ex}{}^{\ddagger}$ are very close to unity, the kinetic isotope effect, R, reduces essentially to K_{ex}, the equilibrium constant for isotopic exchange between the reactants. *We take the near agreement between the experimental value of R and the calculated value* K_{ex} *to indicate that the force constants in the transition states of these limiting solvolysis reactions depend much less strongly on the particular halide than do the force constants of the reactants.*

In line with the above, it follows that the force constants for motion involving H–C–halogen bending are much more independent of halogen in the transition state than in the reactant. In our model calculations, reduction of force constants for this bending motion is the main contributor to the isotope effect.

Some time ago, Seltzer characterized as "normal" for limiting solvolysis an α-isotope effect of about 12% at 105° (or 15% at 25°),[8] and it was then possible to argue that the aqueous hydrolyses of alkyl halides and arylsulfonates were limiting only when the α-isotope effect did not differ from this value by more than a few per cent.[9] We can now make more precise mechanistic arguments by estimating how the effect will vary with the leaving group.

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