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A NOVEL OXIDATIVE ADDITION INVOLVING C-H BOND CLEAVAGE ADJACENT TO A C=C DOUBLE BOND

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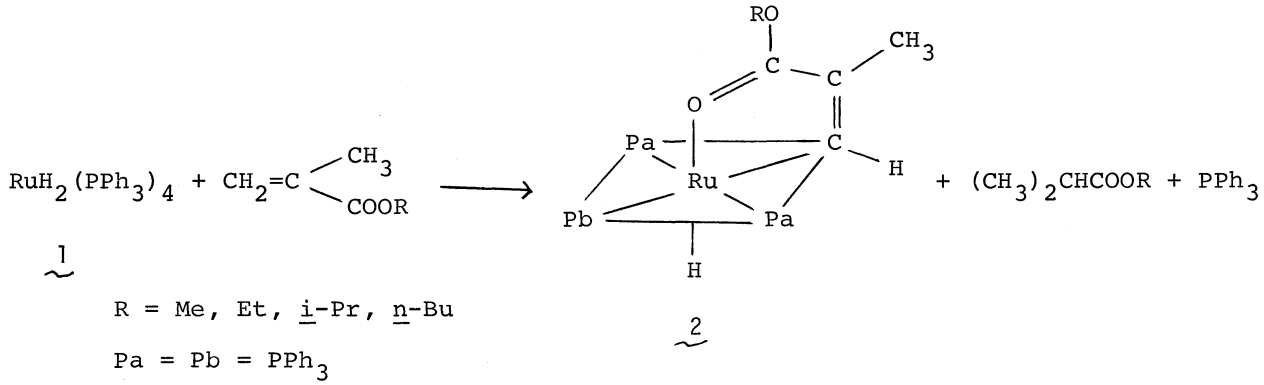
Dihydridotetrakis(triphenylphosphine)ruthenium(II) reacted with alkyl methacrylate to give hydrido(2-alkoxycarbonylpropenyl)tris(triphenylphosphine)ruthenium(II), $RuH(CH=C(CH_3)(COOR))(PPh_3)_3$ and an equimolar amount of alkyl isobutyrate per mole of the dihydride complex. Structure of the resultant complex was proposed from the results of IR and NMR spectroscopy and chemical reactions.

Selective activation of a C-H bond in an organic compound by a transition metal complex possesses a great potentiality of application in organic synthesis. Oxidative addition involving C-H bond cleavage has been postulated in ethylene dimerization[1], oxidative substitution of an olefin promoted by palladium compounds[2] and in H-D exchange in aliphatic and aromatic hydrocarbons catalyzed by platinum, palladium, titanium and niobium compounds[3], but unequivocal examples of oxidative addition involving C-H bond cleavage are limited to orthometallation and its analogous reactions in which C-H bond cleavage of a coordinated ligand is involved.[4,5]

We now report the first example of oxidative addition of the vinylic entity in alkyl methacrylate to a ruthenium complex affording a hydrido-alkenyl complex. Dihydridotetrakis(triphenylphosphine)ruthenium(II)[6,9] 1 reacts with olefins such as ethylene and styrene to afford olefin-coordinated complexes of the type $Ru(olefin)(PPh_3)_3$ and one mole equiv. of the hydrogenated products of the olefins.[7] Alkyl methacrylate (alkyl = Me, Et, i-Pr, n-Bu) reacts similarly with 1 at room temperature to give a complex with a composition of $Ru(alkyl\ methacrylate)(PPh_3)_3$ 2 releasing one mole equiv. of alkyl isobutyrate. Complex 2, however, was identified as hydrido(2-alkoxycarbonylpropenyl)tris(triphenylphosphine)ruthenium(II) on the basis of IR and NMR spectra, elemental analysis and chemical reactions.



1

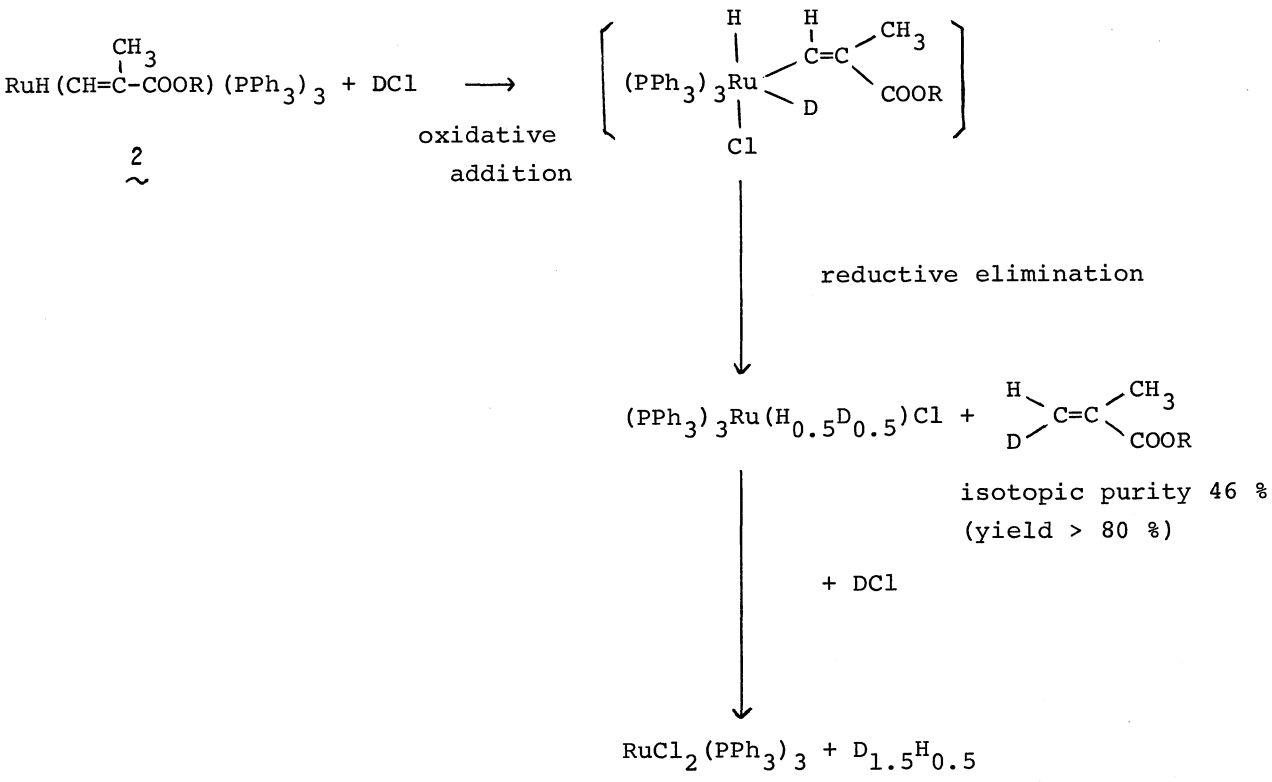
R = Me, Et, i-Pr, n-Bu

Pa = Pb = PPh_3

2

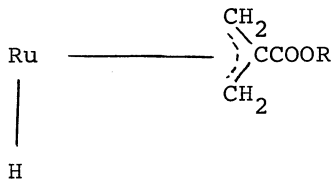
IR spectra of 2 (R = Me, Et, i-Pr, n-Bu) show a ν(Ru-H) band at 1960 - 1980 cm^{-1} and a ν(C=O) band at 1580 cm^{-1}. The large shift of the ν(C=O) band of the methacrylic ester to lower frequency from that of the free ester suggests a ring forming coordination of the C=O moiety to ruthenium. ^{1}H NMR spectra of 2 in $C_6D_5CD_3$ at 100 MHz show the resonance of a hydridic hydrogen at δ ∿ -18 ppm (up-field from internal TMS) as doublets of a triplet ($^{2}J_{P_b-H}$, 12Hz; $^{2}J_{P_a-H}$, 28Hz). The signal of the vinylic proton appears at a very low field δ ∿ 8.2 ppm as a quartet ($^{3}J_{P_a-H} = {}^{3}J_{P_a-H}$, 4Hz). $^{31}P\{^{1}H\}$ NMR spectrum of 2 shows the presence of two kinds of the triphenylphosphine ligands, a doublet ($^{2}J_{P_a-P_b}$, 22Hz) at -52 ppm (down-field from external triphenylphosphine) due to two triphenylphosphine ligands (P_a) and a triplet at -48 ppm due to the unique triphenylphosphine (P_b) trans to the vinylic entity.

Pyrolysis of 2 at 200°C liberates over 80 % equiv. of the coordinated methacrylic ester with a small amount of its hydrogenation product and benzene arising from the decomposition of the triphenylphosphine ligand. Dry DCl (isotopic purity > 95 %) reacted with 2 (R = Me) at room temperature to afford one mole equiv. of methyl cis-β-d_1-methacrylate (isotopic purity 46 %) and one mole equiv. of hydrogen gas containing H_2, HD and D_2 in a ratio of 6 : 34 : 60. The result indicates that the vinylic entity in 2 is bonded with ruthenium at the cis position from the ester group as shown in the formula of 2 and DCl oxidatively adds to 2 to release a 1 : 1 mixture of methyl cis-β-d_1-methacrylate and undeuterated ester and produced $RuDCl(PPh_3)_3$ and $RuHCl(PPh_3)_3$, which react further with DCl to liberate the isotopic mixture of D_2, HD and H_2.



Complex 2 (R = Me, Et) reacted with an excess amount of methyl iodide at room temperature to liberate 1 mole equiv. of methane and a mixture of alkyl methacrylate, alkyl angelate and alkyl tiglate and a small amount of alkyl isobutyrate as confirmed by glc-mass spectroscopic analysis. Introduction of the methyl group on reaction of 2 with methyl iodide at the β-position of the alkyl methacrylate gives a promise of a potential applicability for substitution at a specific position of the olefin.

Reaction of ethyl cis-β-d_1-methacrylate[8] (isotopic purity 72 %) with 1 gives 2 in which the deuterium content at the hydridic hydrogen was small. Ethyl cis-β-d_1-methacrylate used was converted to ethyl methacrylate which contains ca. 14 % of deuterium at vinylic positions and the α-methyl group. The result indicates that a rapid scrambling of vinyl protons of the ethyl methacrylate took place prior to the hydrogenation of the ethyl methacrylate and the formation of 2 (R = Et). The triphenylphosphine ligand was not deuterated. $RuD_2(PPh_3\text{-}d_6)_4$[9], in which 87 % of the hydridic hydrogens and ortho-hydrogens of the triphenylphosphine ligands was deuterated, reacted with ethyl methacrylate to give a hydrido-vinylic complex RuH-$(CH{=}C(CH_3)CO_2Et)(PPh_3\text{-}d_6)$ 3. Formation of the Ru-H bond as revealed by IR spectrum of 3 indicates that the hydridic hydrogen in 2 comes neither from the original hydridic hydrogen in 1 nor from ortho-hydrogens in the triphenylphosphine ligands but from the hydrogen adjacent to the double bond in ethyl methacrylate. Thermolysis of 3 at 200°C liberated ethyl methacrylate in which ca. 70 % of the vinylic protons and of the α-methyl protons were deuterated, calculated value of deuteration being 68 % on assumption of random exchange of the CH_2= and α-methyl protons of ethyl methacrylate with ortho-deuteriums of the triphenylphosphine ligands. The scrambling suggests that a hydrido-π-allylic species as



is involved in the thermolysis with the participation of ortho-metallation of the triphenylphosphine ligands. The NMR spectrum of 2 (R = i-Pr) in pyridine showed some broadening of the α-methyl proton signal at 100°C. Above the temperature, decomposition was too extensive to observe the coalescence of the methyl resonance with the vinylic resonance.

The present result indicates that a seemingly simple π-olefin complex as judged from its composition alone was actually a product of a new type of oxidative addition and exhibits quite different behavior from that of an ordinary π-olefin complex.

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