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Use of a Cationic Hydridoaquopalladium(II) Complex As a Catalyst for Olefin Hydroesterification

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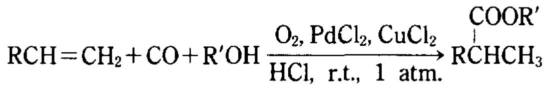
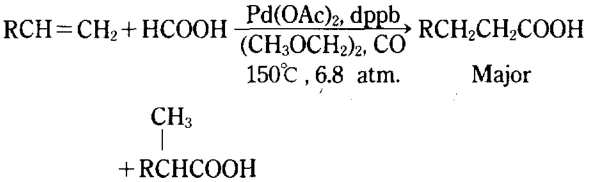
The cationic palladium complex, $(Cy_3P)_2Pd(H)(H_2O)^+BF_4^-$, **1**, catalyzes the hydroesterification of olefins to give straight-chain esters as the major products. The catalytic system consists of **1**, *p*-toluenesulfonic acid, 1,4-bis(diphenylphosphino) butane.

Introduction

A reaction which has been the subject of many publications and patents is the metal complex catalyzed hydroesterification and hydrocarboxylation of olefins.[1,2] Most of the research in this area has utilized palladium compounds as catalysts. For example, branched chain esters or acids are obtained in good yields when palladium chloride catalyzes the reaction of an olefin with carbon monoxide and an alcohol or water in the presence of copper(II) chloride, hydrochloric acid, and oxygen Eq. (1).[3] Another approach utilizes formic acid with palladium acetate and 1,4-bis(diphenylphosphino) butane [dppb] as the catalytic system for the regioselective synthesis of straight chain acids from olefins[4] Eq. (2) and for the conversion of alkynes to unsaturated acids.[5]



$$RCH=CH_2+CO+R'OH \xrightarrow[HCl,\ r.t.,\ 1\ atm.]{O_2,\ PdCl_2,\ CuCl_2} R\overset{\overset{COOR'}{|}}{C}HCH_3 \qquad (1)$$



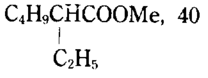
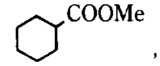
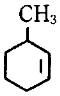
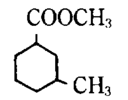
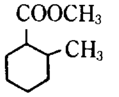
$$\begin{aligned} &RCH=CH_2+HCOOH \xrightarrow[(CH_3OCH_2)_2,\ CO]{Pd(OAc)_2,\ dppb} RCH_2CH_2COOH \qquad (2)\\ &\qquad\qquad\qquad\qquad 150℃,\ 6.8\ atm. \qquad\quad \text{Major}\\ &\quad +R\overset{\overset{CH_3}{|}}{C}HCOOH \end{aligned}$$

Recently, the cationic hydridoaquopalladium(II) complex, *trans*-$[(Cy_3P)_2Pd(H)(H_2O)]^+BF_4^-$ **1** was described in the literature.[6] The novel palladium complex has, in addition to bulky tricyclohexylphosphine ligands, hydrido and aquo ligands attached to the metal. It was of interest to assess the catalytic activity and regioselectivity of **1** for the hydroesterification reaction. The cationic palladium(II) diphosphine complexes, $[(dppp)Pd(solvent)_2][X]_2$, where X is a non or weakly coordinating anion, have been used for the carbonylation of olefins to ketones.[7] We now report the regioselective hydroesterification of olefins to straight chain esters, catalyzed by **1** under appropriate conditions.

Results and Discussion

No reaction occurred when styrene was treated with carbon monoxide and methanol in tetrahydrofuran (THF) at 20.4 atmospheres and 100℃ for 48 hours, using **1** as the catalyst [77/1.0 ratio of styrene: **1**]. Recently, Drent[8] showed that *p*-toluenesulfonic acid (*p*-TsOH) is an important component for the palladium catalyzed copolymerization of ethylene and carbon monoxide. When the reaction of styrene [**2**, *R* =Ph] was repeated in the presence of *p*-TsOH [2 : 1 ratio of *p*-TsOH/**1**], methyl 3-phenylpropionate [**3**, *R*=Ph] was formed in 26% yield and methyl 2-phenylpropionate [**4**, *R* =Ph] was isolated in 30% yield. Inferior results were obtain-

Table 1. Hydroesterification of Olefins Catalyzed by **1**/*p*-TsOH/dppb[a]

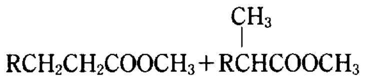
Olefin	Yield[b] (%)	Product distribution[c]	
2, R=Ph	97	**3**, 82	**4**, 18
2, R=*p*-$CH_3C_6H_4$	90	**3**, 79	**4**, 21
2, R=*p*-$(CH_3)_2CHCH_2$	77	**3**, 79	**4**, 21
2, R=*p*-BrC_6H_4	70	**3**, 81	**4**, 19
2, R=*p*-ClC_6H_4	90	**3**, 80	**4**, 20
2, R=*n*-C_5H_{11}	82	**3**, 77	**4**, 23
2, R=C_6H_{11}	75	**3**, 88	**4**. 12
$C_2H_5CH=CHC_3H_7$	75	$(C_3H_7)_2CHCOOMe$, 60	 $C_4H_9CH(C_2H_5)COOMe$, 40
	97	, 100	
	63	, 85	, 15
$CH_2=CHCOOCH_2$	58	**3**, 57	**4**, 43
$CH_2=CHOAc$	90	**3**, 45	**4**, 55

[a] Reaction conditions: olefin (0.1 mmol), dppb (5.2 mg, 0.012 mmol), *p*-TsOH (4.6 mg, 0.024 mmol), **1** (10.0 mg, 0.012 mmol), MeOH (0.2 mL), THF (5.0 mL), CO, 100°, 20.4 atm., 48 h. Products were identified by comparison of spectral results with those for authentic samples in most cases, and with literature data for *cis*-and *trans*-2- and -3-methylcyclohexane carboxylates. [b] Isolated yield. [c] Determined by NMR and by GC.

ed using toluene, methylene chloride, or methanol as the solvent. Although the mixture of **1** and *p*-TsOH does catalyze the hydroesterification process, the regioselectivity is poor.

The beneficial effect of dppb as an added ligand has been previously demonstrated.[4,9] When dppb was added, in an equimolar quantity relative to **1**, then the hydroesterification of styrene proceeded nicely, affording an 82 : 18 mixture of methyl 3-phenylpropionate **3** and methyl 2-phenylpropionate **4** in a total yield of 97% Eq. (3). Doubling the molar amount of

$$\underset{\mathbf{2}}{RCH=CH_2}+CO+CH_3OH\xrightarrow[p\text{-TsOH, dppb, THF}\;100℃,\ 2\text{ days, }20.4\text{ atm.}]{(Cy_3P)_2Pd(H)(H_2O)^+BF_4^-\ \mathbf{1}} \tag{3}$$



$$RCH_2CH_2COOCH_3+RCH(CH_3)COOCH_3$$

3 **4**

dppb has no effect on the product yields or ratios, while use of one-half an equlivalent of dppb relative to **1** resulted in lower yields. Monodentate phosphines were also tested as added ligands instead of dppb and gave inferior results [*e.g.*, PCy_3 effected conversion of styrene to **3** and **4** in 40% and 34% yields, respectively; $P(o\text{-}CH_3C_6H_4)_3$ gave **3** and **4** in a 1 : 1 ratio in 76% total yield]. Other alcohols can be used for the hydroesterification of styrene with **1** and dppb including ethanol [$PhCH_2CH_2COOC_2H_5$, 76% yield; $PhCH(CH_3)COOC_2H_5$, 15%] and isopropanol [$PhCH_2COOCH(CH_3)_2$, 56%; $PhCH(CH_3)COOCH(CH_3)_2$, 14%]. One can form the carboxylic acids by using water instead of alcohol, but the regioselectivity for the straight-chain acid product [$PhCH_2CH_2COOH$, 60%; $PhCH(CH_3)COOH$, 26%] is less than that found for the carbomethoxy ester by use of methanol. This result, however, is quite good in comparison with formic acid-$Pd(OAc)_2$-dppb.[4]

A series of olefins were reacted with CO and methanol in the presence of **1**, dppb, and *p*-TsOH, and the results are given in Table 1. Ring-substituted styrenes and terminal olefins (*e.g.*, 1-heptene, vinylcyclohexane) afford the straight-chain ester in good yield and regioselectivity. The internal acyclic olefin 3-heptene reacted, but in low regioselectivity. Cyclohexene and 3-methylcyclohexene gave esters in good yields. While the unsaturated esters, methyl acrylate and vinyl acetate, underwent hydroesterification, the regioselectivity was low in both cases.

In conclusion, the cationic palladium(II) aquo hydride complex **1**, together with dppb and *p*-TsOH, is an effective system for the regioselective synthesis of straight-chain esters from simple acyclic and cyclic olefins, as well as styrene derivatives.

Experimental

General considerations. The following instrumentation was used to obtain spectral data: Bomem MB 100-C15 (FTIR), Varian XL-300 and/or Gemini 200 NMR spectrometers, and a VG 7070E mass spectrometer. Gas chromatography was effected using a Hewlett-Packard 5890 Series II instrument, equipped with 1.5% OV-17, 1.95% OV-210 on 100-120 mesh Chromosorb W.

The alkenes were purchased from commercial sources. Complex **1** was kindly prepared by Ms. M. Sommovigo.[6] All organic solvents were dried and distilled prior to use.

General procedure for olefin hydroesterification. A mixture of olefin [1.0 mmol], methanol [0.2 mL, 5.0 mmol], *p*-toluenesulfonic acid monohydrate [4.6 mg., 0.024 mmol], dppb [5.2 mg., 0.012 mmol] and the palladium catalyst **1** [10.0 mg., 0.012 mmol] in THF [5.0 mL] was stirred in an autoclave for 48 hours at 100℃ and 20.4 atmospheres. After cooling to room temperature, the autoclave was opened and the yellow homogeneous solution was passed through Celite, and the filtrate was concentrated by rotary evaporation. The carboxylic esters were purified by silica gel thin-layer chromatography using 2 : 1 hexane/ethyl acetate as the developer. The ratio of esters was determined by ^{1}H-NMR and by GC analyses, and by comparison with authentic materials in most cases.

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Hydroacylation of Alkynes with Alkylpentacarbonylchromate Anions

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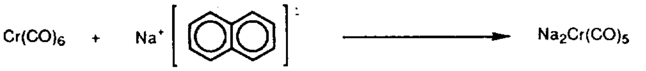
Various alkynes were hydroacylated with alkylpentacarbonylchromates in the presence of triphenylphosphine to give α,β-unsaturated ketones in good yields. The alkylpentacarbonylchromates were generated *in situ* from alkyl halides and disodium pentacarbonylchromate, $Na_2Cr(CO)_5$.

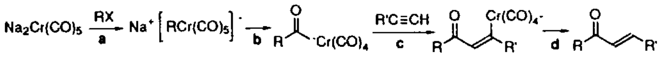
Introduction

In the last two decades, well defined direct carbonylations of organic compounds were developed to synthesize various carbonyl compounds. Some of these attempts involved fixation of carbon monoxide to non-carbonyl containing precursor using transition metal complexes. In this carbonylation chemistry external carbon monoxide which had to be introduced in high pressure[1] and special active catalysts[2] were needed. Others were focused on the reaction of transition metal complexes with acyl moiety were designed to introduce the carbonyl group[3]. These types of reactions needed to handle toxic carbon monoxide gas and involve special catalysts. Therefore they were not used widely for preparative methods of carbonyl compounds.

The preparation of a highly reactive species, disodium pentacarbonylchromate **3**, was reported by Ellis.[4] And a modified procedure was developed by Hegedus by the reaction of chromium hexacarbonyl **1** with sodium naphthalenide **2**.[5]



1 **2** **3**



3 **4** **5** **6** **7**

Scheme 1.

Treatment of this highly reactive species **3** with alkyl halides gives alkylpentacarbonylchromate monoanion complex **4** *via* nucleophilic oxidative addition.[6] However, due to its coordinatve saturation, these complexes **4** are fairly unreactive. Thus, it occurred to us that, if possible, intramolecular migratory insertion of an alkyl group to the carbonyl group on chromium metal in **4** would produce acyltetracarbonylchromate anion **5**, which is available for further reaction as shown in Scheme 1.

Consequently, the reaction of various alkylpentacarbonylchromate anions with alkynes was examined to synthesize directly α,β-unsaturated ketones. Easy preparation of these complexes may render us an advantage for this reaction. Various acyl groups are generated from migratory insertion, to carbon monoxide, of alkyl ligands on chromium metal, which are to be originated from alkyl halides.