Organometallics **1992,** *11,* 20–22

Selectivity of the Carbonylation of Styrene by Cationic Palladium Complexes

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Received September 23, 1991

Summary: **$[Pd(CH_3CN)_4][BF_4]_2$ modified with different nitrogen and mono- or bidentate phosphorus ligands catalyzes the formation of (*E*)-1,5-diphenylpent-1-en-3-one from styrene and carbon monoxide; the use of hybrid ligands, particularly phosphine thioethers, switches the regioselectivity to bring about a largely selective formation of (*E*)-1,4-diphenylpent-1-en-3-one.**

A consequent exploitation of the synthetic potential of previously less investigated carbonylation reactions using cationic palladium complexes as the catalyst precursors[1,2] has opened the way to the synthesis of new carbonylation products from olefinic substrates.[3] When styrene is the substrate, $Pd(p\text{-}CH_3C_6H_4SO_3)_2(dppp)$ (dppp is 1,3-bis(diphenylphosphino)propane) brings about selective carbonylation to (*E*)-1,5-diphenylpent-1-en-3-one in aprotic solvents[4] (Scheme I). The formation of the saturated ketone 1,5-diphenylpentan-3-one can take place to a certain extent under high partial pressure of hydrogen, but in no case were more than trace amounts of branched products (e.g., (*E*)-1,4-diphenylpent-1-en-3-one, Scheme I) found.[4] In contrast, $Pd(p\text{-}CH_3C_6H_4SO_3)_2(1,10\text{-phen})$ (1,10-phen is 1,10-phenanthroline) (or the system formed "in situ" from $Pd(CH_3COO)_2/p\text{-}CH_3C_6H_4SO_3H$ and 1,10-phenanthroline or 2,2′-bipyridine) catalyzes the chemo-, regio-, and stereoselective formation of syndiotactic poly(1-oxo-2-phenyltrimethylene) in methanol solution in the presence of an oxidant (e.g., 1,4-benzoquinone).[5–7] These two catalytic systems display a remarkable difference in regioselectivity. Both for polymer chain growth and for ketone formation, the most straightforward mechanism which may be invoked involves alternate styrene and CO insertions. The growing of the polymer chain can be explained on the basis of consecutive secondary insertions of styrene units starting with a palladium–carbomethoxy species (Scheme II, path **1**–**2′b**–**3′b**).[7] In contrast, the formation of (*E*)-1,5-diphenylpent-1-en-3-one can be accounted for by assuming a first primary insertion of styrene into a palladium hydride species followed by a secondary insertion into a metal–acyl bond (Scheme II, path **1**–**2a**–**3a**).[4] The termination of the chain at this stage suggests that the carbon monoxide insertion into a metal–secondary hydrocarbyl bond such as in intermediate **3a** is unfavorable with respect to the insertion into a metal–primary hydrocarbyl, leading to exclusive β-hydrogen elimination. It seems worthwhile to mention that β-hydrogen elimination also represents a termination reaction of the polymer chain.[7]

Due to the fact that these catalytic systems appear to be the only ones able to carbonylate olefinic substrates selectively to α,β-enones,[8] we have investigated the influence of different ligands on the regiochemistry of the insertion reaction. This is also of interest in connection with the polymerization reaction, as it might be expected that the factors promoting carbon monoxide insertion into a metal–secondary hydrocarbyl bond should also favor the growing of the polymer chain. Since the cationic complex $[Pd(CH_3CN)_2(dppp)][BF_4]_2$ also promotes formation of (*E*)-1,5-diphenylpent-1-en-3-one even under high partial pressure of hydrogen, we chose $[Pd(CH_3CN)_4][BF_4]_2$ as the catalyst precursor, which allows an in situ screening of different ligands.[4]

Some of the results obtained are shown in Table I, where the difference between the conversion of the substrate and the extent of carbonylation is related to the formation of polystyrene. Under 160 bar of an equimolar mixture of hydrogen and carbon monoxide in tetrahydrofuran solution, the phenanthroline ligand brings about a selective formation of the straight-chain ketones with prevalence of the unsaturated one (run 13). Some hydroformylation also takes place, but to a small extent. The catalytic activity is very much reduced under 1 bar of hydrogen; however, when methanol is the solvent (run 14) the unsaturated ketone is formed with good selectivity. No higher cooligomerization products between styrene and carbon monoxide were found in these experiments. The selectivity of the systems seems therefore rather comparable to that observed using a series of diphosphine ligands with different chelate-ring sizes. For these ligands a similar catalytic activity was observed in the case of dppp and diop (runs 1 and 3), whereas the systems containing dppe have much lower activity (run 2). In contrast, a change in the regioselectivity is observed when the phosphine–thioether hybrid ligands $Ph_2PCH_2CH_2SR$ are used (runs 8–11). In fact, these ligands bring about some depression of the catalytic activity but formation of the branched ketone (*E*)-1,4-diphenylpent-1-en-3-one becomes substantial. When $Ph_2PCH_2CH_2SC_2H_5$ (run 9) is the ligand, the regioselectivity ratio is about 10:1 in favor of the branched isomer. Almost no regioselectivity is observed in the case of the ligand $Ph_2PCH_2CH_2SC_6H_5$, (*E*)-1,5-diphenylpent-1-en-3-one and (*E*)-1,4-diphenylpent-1-en-3-one being formed in equimolar amounts. The selectivity toward the branched ketone increases on going from the methyl to the ethyl substituent but decreases for the cyclohexyl group. Also, in the case of the thio–phosphino ligands no cooligomeric products having higher molecular weight were observed. The system modified by the ligand $Ph_2PCH_2SC_6H_5$ similarly to that containing $Ph_2PCH_2CH_2N(CH_3)_2$, gives results comparable (runs 6 and 12) to those obtained with diphenylethylphosphine (run 5), probably reflecting the monodentate nature of these ligands. The catalytic system containing

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[1] Mrowca, J. J. U.S. Patent 3,876,672, 1972; *Chem. Abstr.* **1976,** *84,* 30432. Cf. also: Belg. Patent 825,835, 1975.

[2] Waller, F. J. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1982,** *27,* 611.

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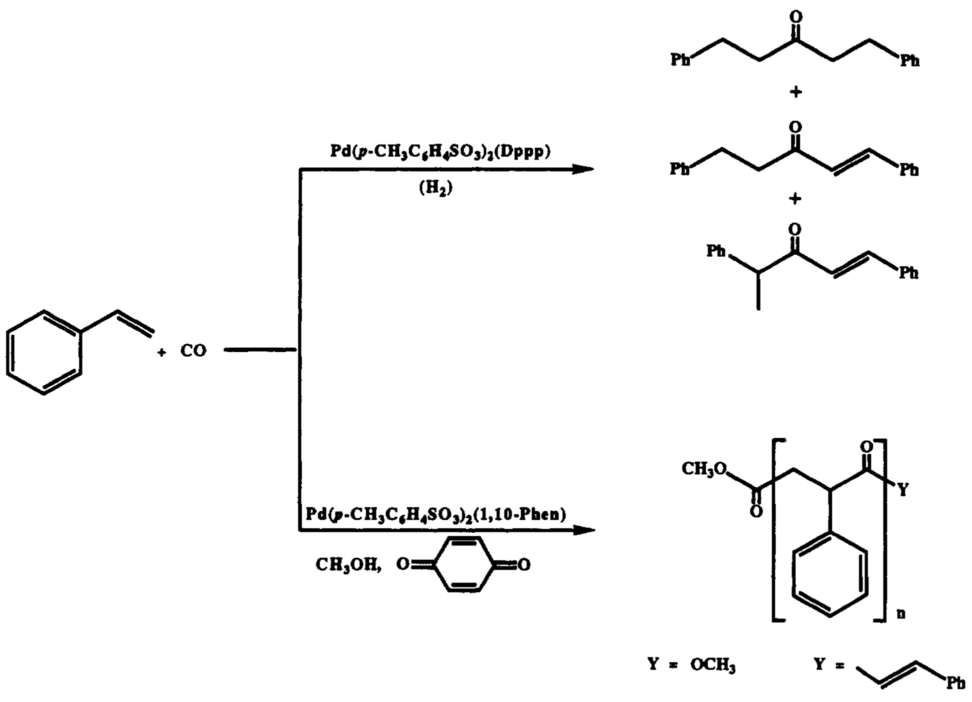
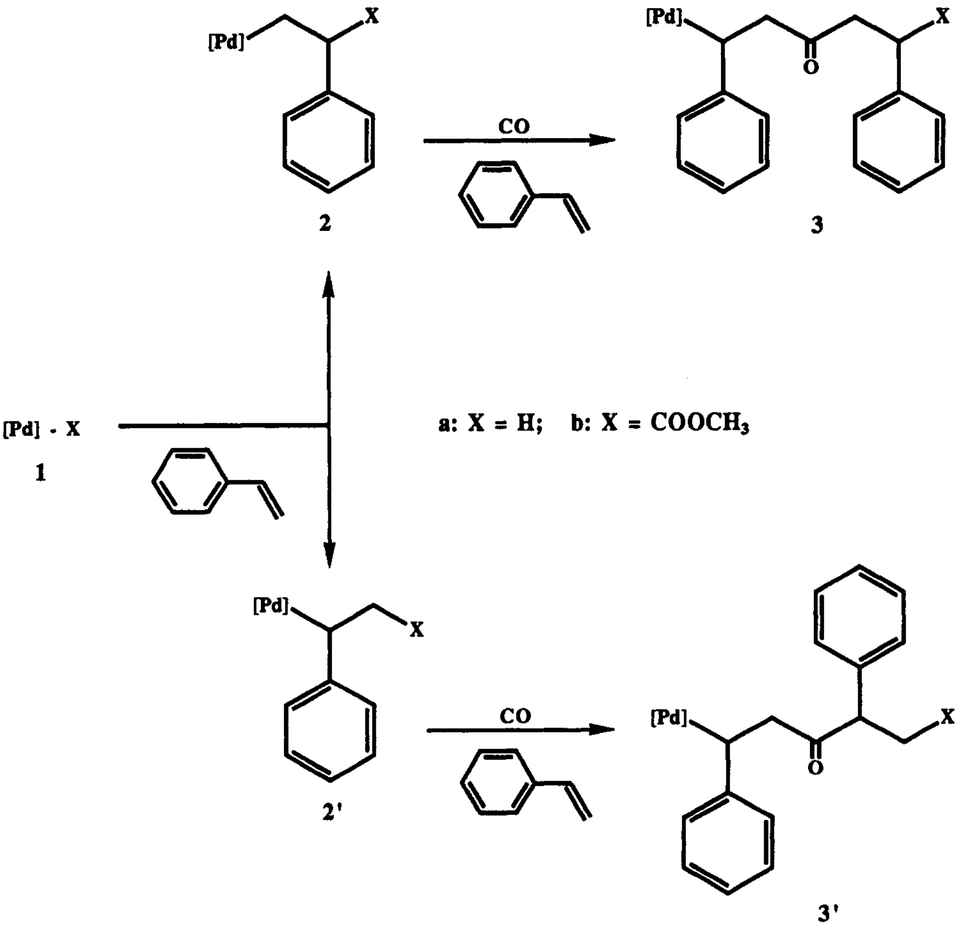
Scheme I



Scheme II



$Ph_2PCH_2CH_2(2\text{-}NC_5H_4)$, even though of low reactivity, causes a selective formation of ketones, the regioselectivity ratio being close to unity (run 7). The catalytic activity of the system containing $C_2H_5SCH_2CH_2SC_2H_5$ is very low (run 15); however, for this ligand the straight-chain ketones are strongly preferred. In contrast, the catalytic system $Pd(CH_3COO)_2/p\text{-}CH_3C_6H_4SO_3H$ modified by $C_2H_5SCH_2CH_2SC_2H_5$ was found to promote formation of atactic poly(1-oxo-2-phenyltrimethylene)[9] in methanol.

Some interesting aspects arise from the present results. In contrast to other carbonylation reactions of aromatic

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[9] Van Dorn, J. A.; Drent, E. Eur. Pat. Appl. 345,847, 1972; *Chem. Abstr.* **1990**, *112*, 199339.

Table I. Influence of the Ligand on the Carbonylation of Styrene Using $[Pd(CH_3CN)_4][BF_4]_2/L$ (1/1) as the Catalyst Precursor[a]

run	ligand	substrate convern, %	carbonylation products, %	selectivity, %		
				SK[b]	(*E*)-LK[b]	(*E*)-BK[b]
1	$Ph_2PCH_2CH_2CH_2PPh_2$	68	61	25	74	1
2	$Ph_2PCH_2CH_2PPh_2$	44	4	23	75	2
3	diop[c]	60	56	16	79	1
4	diop-dbp[d]	60	55	24	74	2
5	$Ph_2PCH_2CH_3$	53	51	26	69	4
6	$Ph_2PCH_2CH_2N(CH_3)_2$	64	58[e]	9	72	~0
7	$Ph_2PCH_2CH_2(2\text{-}NC_5H_4)$	12	9	~0	52	48
8	$Ph_2PCH_2CH_2SCH_3$	21	14	2	55	41
9	$Ph_2PCH_2CH_2SC_2H_5$	40	25	2	7	71[f]
10	$Ph_2PCH_2CH_2S(c\text{-}C_6H_{11})$	39	29	1.5	27	69
11	$Ph_2PCH_2CH_2SC_6H_5$	53	41	1	48	49
12	$Ph_2PCH_2SC_6H_5$	88	52	20	78	2
13	1,10-phenanthroline	89	62[g]	26	66	1
14	1,10-phenanthroline[h]	27	27[g]	3	75	11
15	$C_2H_5SCH_2CH_2SC_2H_5$	20	1	28	68	4

[a] Reaction conditions (except run 14): 0.25 mmol of catalyst; 6.5 mL of styrene; 25 mL of tetrahydrofuran; $p(CO) = p(H_2) = 80$ bar; $T = 100$ °C; 20 h. [b] SK = 1,5-diphenylpentan-3-one; (*E*)-LK = (*E*)-1,5-diphenylpent-1-en-3-one; (*E*)-BK = (*E*)-1,4-diphenylpent-1-en-3-one. [c] Diop = [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphine). [d] Diop-dbp = [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)-bis(methylene)]bis(5*H*-benzo[*b*]phosphindole). [e] ~18% hydroformylation (n/b = 40/60). [f] ~20% isomeric unidentified ketones were formed. [g] ~7% hydroformylation (n/b = 67/33). [h] In methanol as the solvent and in the presence of ~1 atm of H_2.

substrates (e.g., the palladium-catalyzed carbonylation to esters[10]) no significant change in regioselectivity on going from bidentate to monodentate phosphines or to dibenzophosphole (runs 5 and 4) types of ligands was observed. Nevertheless, the selectivity for the carbonylation reaction of styrene can be shifted toward the formation of (*E*)-1,4-diphenylpent-1-en-3-one using the thio–phosphino ligands. In the case of the thioethyl ligand, the selectivity to the branched isomer is higher than 90%. This could appear rather surprising since phosphines containing thioether groups have normally been used in order to open the possibility of having vacant coordination sites due to the loose coordination of sulfur.[11] For palladium(II) compounds a stronger coordination of sulfur donors can be expected, however.[12] This change in regioselectivity in the formation of the branched ketones, which is interpreted on the basis of path **1**–**2′a**–**3′a** in Scheme II, seems to be determined both by steric and by electronic effects. However, we do not know at the moment whether this indicates that the first styrene unit preferentially undergoes a secondary insertion, or if this change is determined by the relative rates of carbon monoxide insertion into intermediates **2a** and **2′a**. Moreover, since the ligands $Ph_2PCH_2CH_2(2\text{-}NC_5H_4)$ and $Ph_2PCH_2CH_2SC_2H_5$ are able to promote CO insertion into a metal–secondary hydrocarbyl bond, as in the case of the polymer chain growth, it is not clear why a second insertion of carbon monoxide does not take place after the second styrene unit has been inserted, giving intermediate **3′a**. Such an observation casts some doubt on the proposed mechanism for the copolymerization reaction.[13] Chain growth could be determined by the presence of the oxidant (e.g., 1,4-dibenzoquinone), possibly due to coordination at the catalytic site. However, the presence of the oxidant does not seems necessary when $C_2H_5SCH_2CH_2SC_2H_5$ is the ligand. An alternative explanation would imply a different mechanism for the chain growth during the formation of the copolymer. In fact, the first-formed polymeric product could have a structure different from a simple polyketone structure, as observed in the case of propylene[14] or norbornene,[15] where a spiroketal enchainment was identified as the kinetic structure for the produced copolymers.

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