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# Ethene and styrene insertion into the Pd–acyl bond of [Pd(COMe)(P^N)(solv)]$O_3SCF_3$ and its role in the copolymerisation of olefins with carbon monoxide

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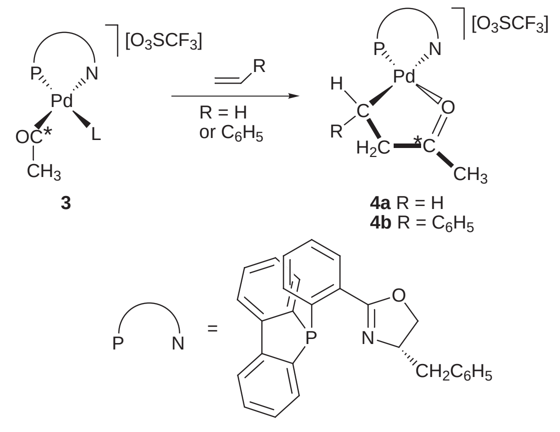
**Styrene has higher productivity than ethene during copolymerisation with carbon monoxide using [Pd(CO-$CH_3$)(P^N)(solv)]$O_3SCF_3$ (where P^N is a phosphanyl-dihydrooxazole ligand), while ethene, not styrene, is preferentially enchained during the terpolymerisation probably reflecting the different reactivity of the two possible alkyl intermediates toward carbon monoxide insertion.**

A good deal of attention has been paid to the alternating copolymerisation of olefins with carbon monoxide.[1–12] Although the newly developed commercial material, Carilon®, is, indeed, a terpolymer[13,14] less emphasis has been placed on terpolymerisation reactions[15–20] and on the factors determining the microstructure of the terpolymers during the catalytic process.

To understand the factors that determine the very high enantioface selection in the isotactic copolymerisation of styrene using {(*S*)-2-[2-(diphenylphosphino-κ*P*)phenyl]-4-benzyl-4,5-dihydrooxazole-κ*N*}diaquapalladium(II) trifluoromethanesulfonate **1** as the catalyst precursor[21,22] we studied the terpolymerisation of styrene, ethene and carbon monoxide.[23] Despite the copolymerisation activity shown by **1** being higher by a factor of about 3.5 for styrene than for ethene, in the terpolymerisation experiments using similar concentrations of the two olefins, more ethene is enchained than styrene in the terpolymers. Analogous experiments using (acetonitrile-κ*N*)-{(*S*)-2-[2-(5*H*-benzo[*b*]phosphindol-5-yl-κ*P*)phenyl]-4-benzyl-4,5-dihydrooxazole-κ*N*}methylpalladium(II) trifluoromethanesulfonate **2**[24] as the catalyst precursor give similar results (Table 1).† The terpolymerisation of ethene, styrene and carbon monoxide, using **2** with similar concentrations of ethene and styrene shows a productivity of 38.8 mmol (g Pd h)$^{-1}$ compared to a productivity of 130.0 mmol (g Pd h)$^{-1}$ in the copolymerisation of styrene and carbon monoxide and of 14.8 mmol (g Pd h)$^{-1}$ for the copolymerisation of ethene with the same catalyst precursor. Thus, the rate at which the terpolymer forms is close to that for the ethene copolymer. Furthermore, based on the chiroptical properties, enantioface selection for styrene is similar both in the ter- and co-polymerisation processes.

Styrene insertion into the palladium acetyl bond of **3** (the product of CO insertion of **2**) was found to take place with essentially complete selectivity and enantioselectivity to **4b** (Scheme 1).[24] In the reaction of **3** with ethene under atmospheric pressure, **4a** forms with the same selectivity, as determined by multinuclear NMR spectroscopy.‡ Using the same technique to determine the rate of the olefin insertion into the Pd–acyl bond of **3**, we found that at 0 °C **4a** forms about 4–5 times more rapidly than **4b** under comparable molar amounts of olefin.§ No further reaction with carbon monoxide is observed for **4a** and **4b** at normal pressure.[25,26] Consistent with the higher insertion rate of ethene into the Pd–acyl bond, an ethene concentration of about 81% was found in the terpolymer chains formed with **2** with similar concentrations of ethene and styrene.



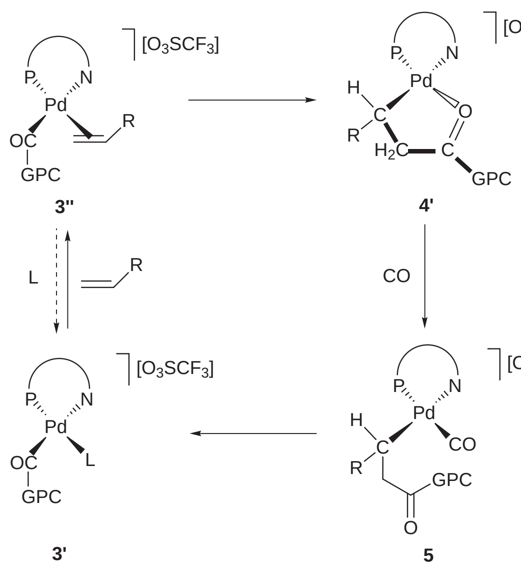
**Scheme 1**

The reported results contribute to an understanding of the kinetic role of the various reaction steps in the copolymerisation process (Scheme 2). With the catalyst systems used, coordination of the olefin is favoured for ethene with respect to styrene and does not appear to be completely reversible. Since insertion is more rapid for ethene than for styrene, the turnover frequency of the process must be limited by the successive step from **4′** to **3′**. Both coordination of carbon monoxide and the opening of the chelation ring to form intermediate **5** (the relative order of the two events is not fixed) are expected to be easier for species **4′a** than for species **4′b** due to steric and entropic factors respectively. Therefore, the smaller reactivity of ethene compared to styrene most probably reflects a more difficult insertion of carbon monoxide into a palladium–primary carbon atom bond (**5a**) than insertion into the palladium–secondary benzylic carbon bond (**5b**).

**Table 1** Polymerisation reactions using [(P^N)Pd($CH_3$)($CH_3CN$)][$O_3SCF_3$] **2** as the catalyst precursor

| Styrene/ mmol | Ethene/ mmol | CO/bar | Productivity/ mmol (g Pd h)$^{-1}$ | Polymer composition $C_2H_4CO:C_8H_8CO$ | Δε[a]/l mol$^{-1}$ cm$^{-1}$ | M$_n$[b]/ g mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 435 | 0 | 320 | 130.0 | 0:100 | −11.75 | 7500 |
| 435 | 385 | 300 | 38.8 | 81:19 | −13.02[c] | 8000 |
| — | 456 | 300 | 14.8 | 100:0 | — | 4500 |

[a] From the circular dichroism spectra measured at 282 nm in $(CF_3)_2CHOH–CHCl_3$ 1:10. [b] Estimated from end groups in the $^1H$ NMR spectra. [c] Extrapolated to 100% styrene units.



**a** R = H
**b** R = C$_6$H$_5$

(GPC = growing polymer chain)

**Scheme 2**

## Notes and references

† A general procedure for copolymerisation and terpolymerisation reactions is described in ref. 23.

‡ Selected spectroscopic data for **4a**: $^1$H NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 0.98–1.04 (m, 1H, $CH_3{}^{13}COCH_2C\mathit{H}_2$), 1.15–1.21 (m, 1H, $CH_3{}^{13}COCH_2C\mathit{H}_2$), 2.38 [d, $^2J$(C,H) = 5.8, 3H, $C\mathit{H}_3{}^{13}COCH_2CH_2$], 2.72–2.80 (m, 1H, $CH_3{}^{13}COC\mathit{H}_2CH_2$), 2.82–2.89 (m, 1H, $CH_3{}^{13}COC\mathit{H}_2CH_2$). $^{31}$P NMR (121.5 MHz, $CD_2Cl_2$, 0 °C): $\delta$ 25.34 [d, $^3J$(C,P) = 1.6]. $^{13}$C NMR (75.5 MHz, $CD_2Cl_2$, 0 °C): $\delta$ 23.2 (s, $CH_3{}^{13}COCH_2\mathit{C}H_2$), 28.0 [dd, $^1J$(C,C) = 40.0, $^4J$(P,C) = 2.1, 1C, $\mathit{C}H_3{}^{13}COCH_2CH_2$], 50.7 [d, $^1J$(C,C) = 40.3, $CH_3{}^{13}CO\mathit{C}H_2CH_2$], 235.4 [d, $^3J$(P,C) = 1.6, $CH_3{}^{13}\mathit{C}OCH_2CH_2$]. Assignments were made on the basis of HMQC, COSY, NOESY and $^{31}$P-{$^1$H} NMR spectroscopic techniques.

§ The amount of ethene dissolved in the $CD_2Cl_2$ solution at 0 °C was determined in preliminary experiments using octamethylcyclotetrasiloxane as an internal standard. Because of the relatively high relaxation time of the protons in ethene, the cycle time was set at 40 s for these quantitative measurements.

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