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The first example of palladium catalysed non-perfectly alternating copolymerisation of ethene and carbon monoxide†

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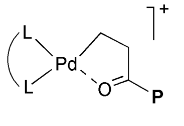
Non-alternating ethene–CO copolymerisation is catalysed by a new series of [P-O]Pd catalysts based on *o*-alkoxy derivatives of diphenylphosphinobenzene sulfonic acid

The palladium catalysed alternating copolymerisation of ethene and carbon monoxide has attracted considerable interest[1] since efficient catalysts were discovered nearly two decades ago.[2] Whilst double CO insertion in this copolymerisation does not occur for thermodynamic reasons,[3] the lack of double ethene insertions produced by these cationic palladium(II) complexes is remarkable considering the same species efficiently dimerizes ethene to butenes; even high ethene–CO ratios (~10) produce exclusively error-free polyketone until all CO is consumed.[4] The perfect alternation is attributed to the cationic Pd–alkyl oxo-chelate **A**,[5] in which CO insertion is kinetically favoured over that of C_2H_4, despite a thermodynamic preference for pure olefin polymerisation.[6] The metal catalysed non-alternating copolymerisation of CO and ethene would open up a series of new materials, but has yet to be demonstrated.[7]



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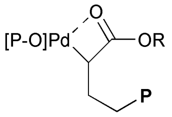

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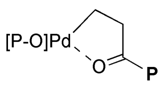
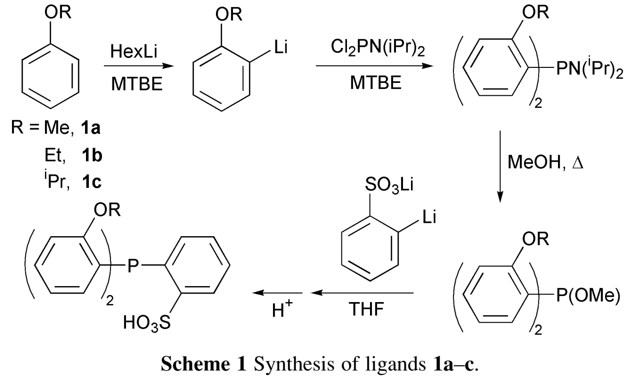


C

We recently reported[8] a neutral [P-O]Pd catalyst for the copolymerisation of ethene with alkylacrylates; the acrylate is incorporated into linear polyethylene, consistent with a mechanism involving direct C_2H_4 insertion into Pd–alkyl oxo-chelate **B**.

We report here that the same family of P-O ligand (**1**)-modified palladium catalysts co-activate ethene and CO to generate a high molecular weight non-alternating copolymer.[9]

The ligands **1a–c** were synthesised as outlined in Scheme 1,[10] and their *in situ* combination with $Pd(OAc)_2$ afforded active catalysts for the copolymerisation experiments shown in Table 1.

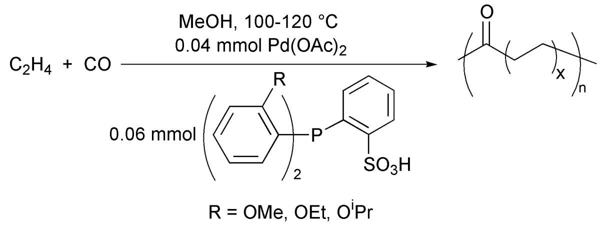


Scheme 1 Synthesis of ligands **1a**–**c**.

A high molecular weight (>30 000) polyketone was made in all experiments as no ester or ketone end groups were detected by $^{13}C\{^1H\}$ NMR spectroscopy. Resonances in the CH_2 region of these spectra were assigned to double, triple and quadruple ethene insertions (Fig. 1).

The activities for C_2H_4–CO copolymerisation with these neutral catalysts are low compared to classical dppp-based cationic palladium systems. With the bis-*o*-Me substituted ligand **1a** the proportion of ethene incorporated into the linear copolymer increases linearly with C_2H_4:CO ratio (entries 1–3) and with temperature (entries 2,4,5). Comparison of entries 2, 6 and 7 illustrates the effect of varying the *o*-alkoxy group on the

Table 1 Pd catalysed non-alternating C_2H_4–CO copolymerisation‡



Entry	[P-O]	*T*/°C	C_2= /bar	CO/bar	Activity[a]/ gmmol^{-1} h^{-1}	Non-alt C_2= insertions (%)[b]
1	**1a**	110	20	30	190	2.4
2	**1a**	110	30	20	123	7.3
3	**1a**	110	30	10	49	15.2
4	**1a**	100	30	20	86	4.7
5	**1a**	120	30	20	108	11.0
6	**1b**	110	30	20	103	11.9
7	**1c**	110	30	20	108	18.3

[a] Based on Pd over experiment run time (2.0–2.2 h). [b] Total mol % C_2H_4 of copolymer involved in non-alternation, calculated from $^{13}C\{^1H\}$ NMR spectra (measured in 1,1,1,3,3,3-hexafluoropropan-2-ol–C_6D_6).

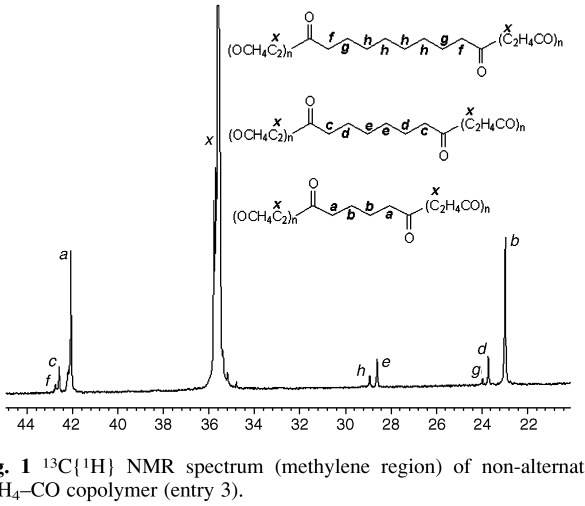


Fig. 1 $^{13}C\{^1H\}$ NMR spectrum (methylene region) of non-alternating C_2H_4–CO copolymer (entry 3).

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† Electronic supplementary information (ESI) available: ligand syntheses and NMR analyses of copolymers. See http://www.rsc.org/suppdata/cc/b1/b111629k/

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[P-O] ligand; the amount of ethene built into the copolymer increases with steric hindrance. This trend is displayed graphically in Fig. 2, including the proportion of double, triple and higher ethene insertions.

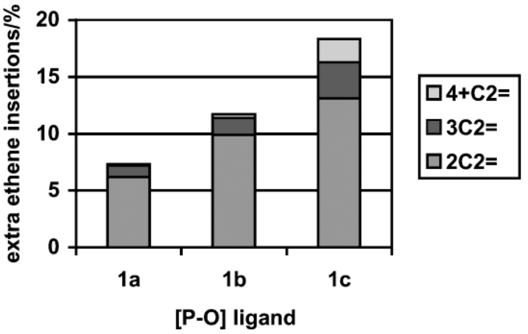

Fig. 2 Effect of [P-O] ligand on C_2H_4–CO non-alternation.

Many of the cationic palladium complexes that are highly active for C_2H_4–CO copolymerisation also dimerize C_2H_4 to butenes in the absence of CO.[4] Inspection of the resonances in the $^{13}C\{^1H\}$ NMR spectrum (Fig. 1) corresponding to the double ethene insertions (***a*** and ***b***) indicates that they do not originate from insertion of hypothetically formed but-1-ene. This was unequivocally demonstrated by an analogous C_2H_4 (30bar)–CO (20bar)–but-1-ene (20 ml) terpolymerisation experiment in which the differing signals for double and triple ethene and but-1-ene insertions can be seen in the $^{13}C\{^1H\}$ NMR spectrum of the terpolymer (Fig. 3).

Melt processing of a perfectly alternating C_2H_4–CO copolymer is achieved by reducing its melting point from *ca.* 260 to 220 °C with 6% propene incorporation. The melting points of non-alternating copolymers made by catalysts from **1a** (entry 2, 234 °C), **1b** (entry 6, 231 °C) and **1c** (entry 7, 229 °C) are similarly reduced, reflecting relatively decreased interactions between polymer chains and demonstrating the control this family of catalysts engenders on the copolymer physical properties.

There is no doubt that the active catalyst is based on a P-O chelate of ligands **1a–c** with palladium; copolymer propagation can only proceed when such bidentate coordination forces the growing polymer chain and fourth coordination site into mutually *cis*- environments (*cf.* termination *via cis–trans* isomerisation).[1–6] With regard to multiple ethene insertions, we suggest that this novel catalysis is facilitated by stereoelectronic destabilization of neutral chelate **C** to an extent that C_2H_4 can effectively compete with CO for the next insertion. The reduced electrostatic attraction between palladium and carbonyl is also apparent from the low catalyst activity relative to cationic Pd systems; transition state stabilization during rate-determining olefin insertion into the Pd-acyl is reduced as a function of chelate **C** stability.[6]

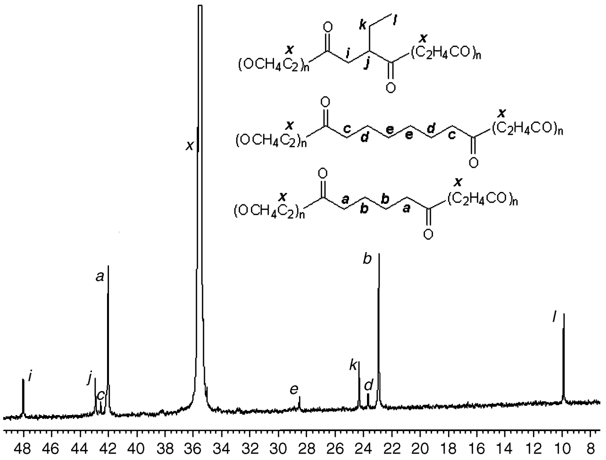

Fig. 3 $^{13}C\{^1H\}$ NMR spectrum (methylene region) of the non-alternating C_2H_4–CO–but-1-ene terpolymer.

In summary, neutral palladium catalysts derived from [P-O] ligands **1a–c** catalyse the first example of non-alternating ethene–CO insertion copolymerisation. The degree of non-alternation (observed by $^{13}C\{^1H\}$ NMR analysis and manifested in the copolymer melting point) can be tuned by reaction temperature, relative C_2H_4 and CO concentrations, and ancillary ligand.

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Notes and references

‡ Typical reaction conditions: 0.04 mmol (9 mg) $Pd(OAc)_2$, 0.06 mmol (23 mg) **1a** and 100 ml MeOH were transferred to a 250 ml Hastelloy C autoclave. The autoclave was quickly closed and flushed 3 times with 40 bar N_2 before charging with 30 bar C_2H_4 and 20 bar CO. After *ca.* 15 min the autoclave was heated to, and maintained at 110 °C for 2 hours by a Thermo-Electric temperature control unit (care was taken in all cases to stop the experiment before all CO was consumed). After this time, the cooled contents of the autoclave were filtered, the polymer washed with 2 × 100 ml methanol and dried *in vacuo*.

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9 For preliminary work with the unsubstituted diphenylphosphinobenzene sulfonic acid ligand, see E. Drent and D. H. L. Pello, *Eur. Pat. Appl.*, 1995, EP0632084 (to Shell).

10 The free ligands exist as zwitterions; for experimental and NMR data, see ESI†.