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Hemilabile ligands in palladium catalysed C–C linkages: the effect of the donor atom in the codimerisation of styrene with ethylene

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Abstract

Cationic η^3-2-methylallylpalladium(II) complexes with potentially hemilabile ligands XCH_2COOEt (X = NPh_2, PPh_2, OPh, SPh) or methylpicolinate have been prepared and their catalytic properties in the codimerisation of styrene with ethylene have been investigated. The catalytic activity decreases in the order of decreasing *trans* influence of X: $P \gg N \approx O > S >$ pyr. The relationship between catalytic activity and spectroscopic properties of the complexes is discussed.

Keywords: Codimerisation; Palladium; Styrene; Ethylene; Allyl; Hemilabile

1. Introduction

The catalytic codimerisation of olefins provides an interesting and powerful tool for selective C–C coupling reactions [1,2]. The codimerisation of styrene with ethylene to give 3-phenyl-1-butene is of particular interest, serving as a model reaction for the synthesis of compounds with pharmacological activity, e.g. Ibuprofen and Naproxen [3]. The first catalysts used for this reaction were simple transition metal salts like $RhCl_3$, $RuCl_3$ [4,5] or $PdCl_2$ [6]. As the development of organometallic chemistry proceeded, σ-alkyl, σ-aryl or π-allyl complexes of nickel and palladium were employed, in combination with a Lewis acid [7–11]. The latest generation of catalysts for this reaction consists of single component cationic metal complexes of nickel [12] or palladium [13]. These complexes bear in general one weakly bound ligand to provide a free coordination site. Parallel to the development of single component catalysts various in situ catalytic systems have been developed [14–16]. Asymmetric codimerisation reactions to give enantiomerically enriched products have been reported since 1988 [17–19]. However high enantioselectivities have been limited to the use of very active nickel catalysts at −70°C.

Since the concept of hemilabile bidentate ligands was introduced by Rauchfuss et al. [20] various combinations of different donors have

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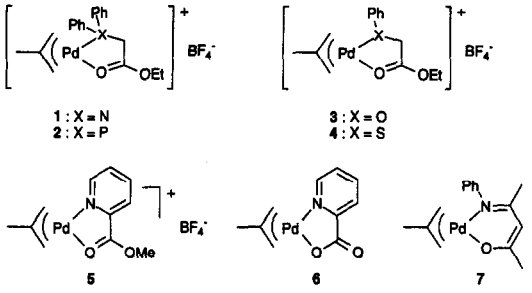


Fig. 1. Complexes **1–7**.

been studied, e.g. P^O [21–24], P^N [25–28], N^O [29] etc. The study of these ligands has proved to be extremely fruitful and interesting in both catalysis and coordination chemistry, due to their ability to provide a free coordination site under the appropriate conditions and concurrently stabilise active intermediates. Moreover, chelating anionic P^O ligands have been successfully applied in the nickel-catalysed oligomerisation of ethylene in the Shell Higher Olefin Process [30].

We have previously reported that changing the oxygen donor of a P^O ligand from a anionic oxygen to a neutral oxygen donor has a dramatic effect on the activity in the palladium catalysed oligomerisation of ethylene, the copolymerisation of ethylene with CO and the codimerisation of styrene with ethylene [13]. We now present a study on the effect of the other donor moiety on catalytic activity for the codimerisation of styrene with ethylene. Accordingly, we report here on the preparation of novel cationic palladium allyl complexes **1–5** with potentially hemilabile ligands such as substituted ethyl acetate XCH_2COOEt ($X = NPh_2$, PPh_2, OPh, SPh) or methylpicolinate (Fig. 1).

The catalytic properties of these complexes for the coreaction of ethylene with styrene have been investigated. An attempt has been made to correlate catalytic behaviour with NMR and IR spectroscopic data. For comparison the neutral complexes **6** and **7**, in which the palladium centre is a much weaker electrophile, have also been synthesised.

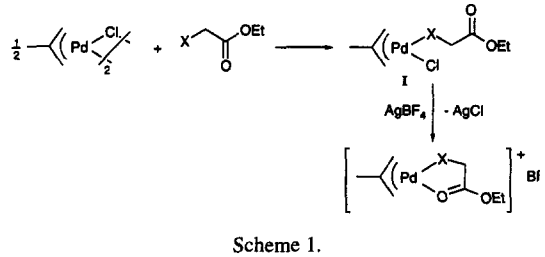
2. Results and discussion

2.1. Preparation and characterisation of complexes 1–7

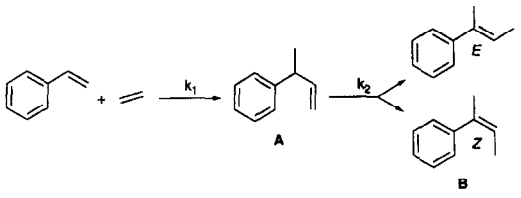
Complexes **1–7** were prepared according to Scheme 1 using a similar method to that described by Braunstein et al. [31]. The reaction of the appropriate ligand with di-μ-chloro-di-(η^3-2-methylallyl)dipalladium $[C_4H_7PdCl]_2$ in dichloromethane was monitored by ^1H NMR. Formation of an intermediate of the type $[C_4H_7PdCl(ligand)]$ (**I**) was only observed when Ph_2PCH_2COOEt was the ligand. Abstraction of the chloro ligand to allow coordination of the carbonyl moiety was achieved by addition of $AgBF_4$. For the preparation of the neutral complexes **6** and **7** the appropriate salts, thallium picolinate, $2\text{-}C_5H_4NCOOTl$ and potassium 4-phenylamino-3-penten-2-onate, K(PhNacac), were used. The newly formed palladium complexes **1–5** were isolated in almost quantitative yield as air sensitive solids (except for **4** which was obtained as an oil) and characterized by ^1H and ^{13}C NMR, IR, mass spectroscopy and by microanalysis. Selected NMR data are given in Table 3. The spectroscopic properties will be discussed in detail later.

2.2. Codimerisation of styrene with ethylene

The codimerisation of styrene with ethylene was carried out in CH_2Cl_2 at room temperature under 30 bar of ethylene in the presence of each complex, **1–7**. The reaction mixture was analyzed at regular time intervals by gas chromatography. 3-Phenyl-1-butene, **A**, the initial



Scheme 1.



Scheme 2.

product of the codimerisation reaction, is subsequently isomerized to *Z*- and *E*-2-phenyl-2-butene, **B** (Scheme 2). Small amounts of 1- and 2-butenes, due to ethylene dimerisation, and traces of other dimerisation products including styrene dimer are also observed. These products were not analyzed further.

Complexes **1–4** were found to be active codimerisation catalysts. Conversions of styrene and the selectivities for 3-phenyl-1-butene and the isomers are summarized in Table 1. The activity of the catalyst is expressed in terms of the turnover frequency (TOF – moles styrene/moles catalyst/h). With complex **5** as the catalyst only traces of butenes were found. The complexes **6** and **7**, which were tested for reasons that will be discussed later, were found to be totally inactive for codimerisation under

Table 1
Codimerisation of styrene with ethylene by complexes **1–4**

Complex	Time/ h	Conversion/ % [a]	Selectivity/%			TOF [b]
			A	B(*Z*)	B(*E*)	
1 (N)	3	28	58	12	30	37
	6	47	37	20	43	28
	16	91	4	30	66	22
2 (P)	1	41	92	2	6	180
	2	55	78	5	17	119
	3	100	9	21	70	
3 (O)	3	33	60	12	28	41
	6	64	20	24	56	41
	14	83	8	29	63	26
4 (S)	3	10	100	0	0	13
	9	26	57	13	30	11
	16	67	17	25	58	16

Conditions: [styrene]/[Pd] = 400; 30 bar ethylene; in CH_2Cl_2; at 25°C.

[a] Conversion of styrene, determined by GC.

[b] TOF = $mol_{styrene} \cdot mol_{cat}^{-1} \cdot h^{-1}$.

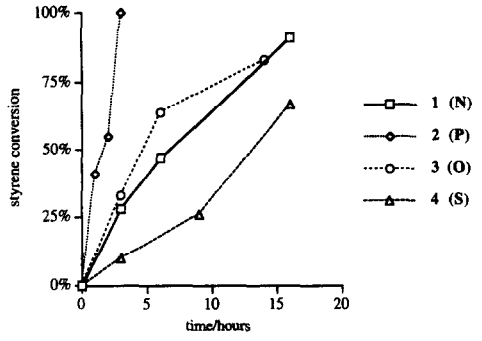


Fig. 2. Conversion of styrene versus time for complex **1–4**.

the reaction conditions employed. The activity of complexes **1–4** can be compared by their TOF or by the conversion of styrene versus time as the same amount of catalyst was used for each experiment. The data from Table 1 are plotted in Fig. 2 and from these plots it is readily seen that based on the ligand donor moiety, the activity decreases in the order P ≫ O ≈ N > S. Complex **2** bearing the Ph_2PCH_2COOEt ligand is by far the most active catalyst for the codimerisation reaction under the conditions employed.

Codimerisation followed by isomerisation of the initial product 3-phenyl-1-butene to *Z*- and *E*-2-phenyl-2-butene is a consecutive reaction [5,11]. The selectivity for 3-phenyl-1-butene will therefore depend on the rate constants k_1 and k_2 (see Scheme 2). In Fig. 3 the selectivity for 3-phenyl-1-butene is plotted against the conversion of styrene. In general, the selectivity for

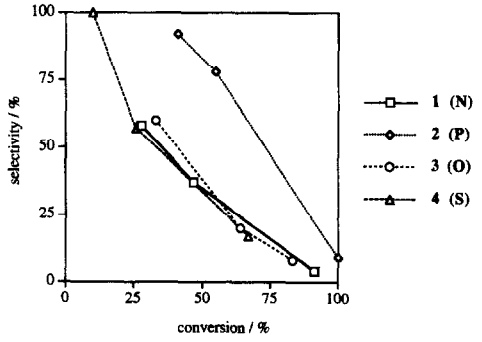


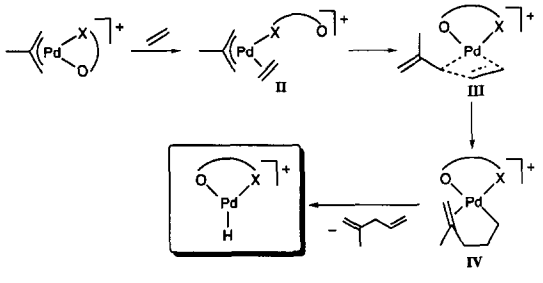
Fig. 3. Selectivity for 3-phenyl-1-butene versus conversion of styrene.

3-phenyl-1-butene is the highest at low conversion. However, for example at 50% conversion the selectivity is 80% using complex **2** compared to approximately 40% for the other complexes. Complex **2** obviously has a larger overall codimerisation rate (k_1) compared to the isomerisation rate (k_2).

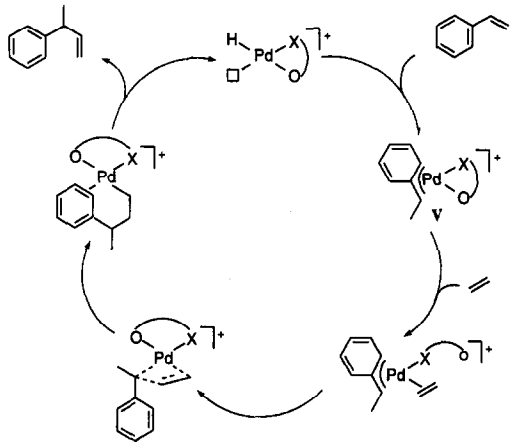
2.3. Mechanism for the codimerisation of styrene with ethylene

Several mechanistic studies on the nickel or palladium catalysed codimerisation of 1,3-dienes with ethylene have been reported [7,32]. In general, the mechanisms feature a metal hydride complex as the catalytic species. Palladium hydride complexes are usually not stable enough to be isolated but can be generated in situ e.g. using allyl complexes as the catalyst precursor [33]. Insertion of ethylene into the palladium allyl bond followed by β-elimination of 2-methyl-1,4-pentadiene provides the catalyst as depicted in Scheme 3.

In complexes containing chelating ligands the hydride formation reaction may be facilitated by the use of hemilabile X^O ligands. NMR studies on the complex $[C_4H_7Pd(PhSCH_2COOMe\text{-}\kappa^2\text{-}S,O)]BF_4$ (**4'**) showed that upon addition of ethylene the ^{1}H-NMR signal of the methoxy group and the ^{13}C-NMR signal of the carbonyl C-atom change to similar chemical shifts as those observed for the free ligand. This indicates that the weakly coordinated oxygen donor is possibly displaced by ethylene, leading to an



Scheme 3.



Scheme 4.

intermediate of type **II** (Scheme 3). Similar allyl–olefin palladium complexes have been reported previously [34,35]. Subsequent insertion of ethylene into the palladium allyl bond would lead to intermediate **IV**. Pentenyl complexes, like intermediate **IV**, have been isolated from the insertion of strained olefins, e.g. norbornene, into the palladium allyl bond [36–38]. Finally, β-elimination of 2-methyl-1,4-pentadiene from intermediate **IV** and recoordination of the ester moiety would provide the hydride complex. Evidence for such a mechanism has been provided previously [39].

Besides metal hydride formation through β-elimination, the reverse reaction is also well documented. The reaction of palladium hydride complexes with 1,3-dienes often yields allyl complexes [40]. The use of styrene as a 1,3-diene results in the formation of η^3-α-methylbenzyl palladium complex **V**, as depicted in Scheme 4. Complexes of this kind, stabilized by the use of bulky bidentate phosphine ligands and large non-coordinating anions, have been isolated and structurally and spectroscopically characterized [41–43]. Subsequent insertion of ethylene into the palladium benzyl bond followed by β-elimination of 3-phenyl-1-butene regenerates the palladium hydride complex as the active catalytic species.

Table 2
IR data [ν(CO)] for complexes **1–5** [a]

Complex	ν(CO)/cm^{-1} ligand	ν(CO)/cm^{-1} complex	Δν(CO)/cm^{-1}
1 (N)	1747	1665	82
2 (P)	1732	1629	103
3 (O)	1757	1682	75
4 (S)	1733	1660	73
5 (N-pyr)	1726	1661	65

[a] In CH_2Cl_2 solution.

2.4. Spectroscopic properties and their relation to catalytic activity

2.4.1. IR spectroscopy

Complexation of the ester function via the carbonyl oxygen is demonstrated by the change in the C=O stretching frequency in the IR spectrum. In comparison with the free ligand a difference [Δν(CO)] of 70–100 cm^{-1} is observed upon coordination (Table 2). However, it is difficult to draw any definitive conclusions from the differences in shifts for the C=O stretching frequencies [Δν(CO)], as two effects could be responsible for the observed changes. The most obvious effect is that coordination of the carbonyl oxygen atom, resulting in a Pd–O bond, will cause a shift to lower wavenumbers. The nature of the hetero atom in the β-position also seems to have an effect on the C=O stretching frequency as can be seen from the IR data of the free ligands and this effect will change upon coordination of the hetero atom.

However, the most notable aspect is that the largest value for Δν(CO) is observed for complex **2**, which is 20–30 cm^{-1} greater than the values for the other complexes. There appears to be a correlation between the observed catalytic activities for the codimerisation of styrene and ethylene and Δν(CO). Complex **2** shows a much higher activity for this reaction than the other complexes (vide supra). In addition, complex **5**, for which the Δν(CO) value is considerably lower, shows very little catalytic activity under the same reaction conditions. This suggests that, if the shift of Δν(CO) is proportional to the Pd–O bond strength, a strong Pd–O interaction favours a higher catalytic activity. However, while hemilability is important [13], care should be taken in interpreting this trend. It is more likely, that the opening of the chelate is not the rate determining step and catalytic activity is more dependant on the *trans* influence of X.

2.4.2. NMR spectroscopy

In general, in a square-planar η^3-allyl complex substituted with two additional ligands with differing electronic properties some asymmetry in the bonding of the allyl group can be observed. The degree of asymmetry is reflected in a change in the chemical shifts of the terminal allylic carbon atoms and sometimes the allylic protons. It has been suggested that the changes in the ^{13}C chemical shifts of the allylic carbons are related to the donor capacity of the *trans* ligand [44]. Additionally, in η^3-allyl palladium

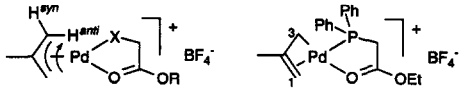
Table 3
^1H and ^{13}C NMR data for compounds **1–7** [a]

Compound	Allylic H^{syn}		Allylic H^{anti}		Allylic C		δ(C=O)	δ(C=O)	Δδ(C=O)
	H^1	H^4	H^2	H^3	C^1	C^3	ligand	complex	
1 (N)	3.96	3.96	3.20 (br)	3.20 (br)	63.7	63.7	170.9	178.6	8
2 (P) [b,c]	4.96	3.26	4.09	2.76	76.1	36.3	170.4	179.7	9
3 (O)	3.85	3.85	2.98	2.98	66.1	66.1	169.0	173.6	5
4 (S)	4.36	4.36	3.51	3.51	66.7	66.7	169.6	175.0	5
5	4.29	4.29	3.32	3.32	61.4	61.4	165.7	172.6	7
6 [c]	4.00	3.67	2.99	2.99	58.3	55.5			
7 [c]	3.56 (d)	2.38	2.77	1.96	59.5	57.7			

[a] In $CDCl_3$ solution.
[b] ^1H-NMR data were recorded at 253 K.
[c] Assignment: H^1(*syn*)H^2(*anti*)C^1, H^4(*syn*)H^3(*anti*)C^3.

complexes various dynamic intramolecular processes can operate. These can give rise to *syn–anti* isomerism as well as *syn–syn* and *anti–anti* proton exchange processes (apparent rotation of the allyl group). The mechanisms underlying these dynamic processes have been extensively studied during the last 30 years [45–50].

Only small changes in the chemical shift of the central allylic carbon (C^2) or the methyl group is apparent for complexes **1–5** on substitution at palladium. For the complexes **1**, **3**, **4** and **5** the terminal carbon atoms appear as one slightly broadened signal at around 65 ppm (Table 3), indicating that there is no asymmetry evident within the allyl ligand at room temperature. This apparent lack of asymmetry is somewhat surprising considering the different substituents attached to the palladium centre in these complexes. Dissimilar electronic properties would be expected for the carbonyl oxygen donor compared to the other donor species. However, VT ^{13}C NMR studies on complex $[C_4H_7Pd(PhSCH_2COOMe\text{-}\kappa^2\text{-}S,O)]BF_4$ (**4′**) provided clarification for these observations. Further broadening of the signal at 67.3 ppm occurred upon lowering the temperature, and at −40°C the signal disappears completely. (The methyl ester, complex **4′**, was used instead of the ethyl ester, complex **4**, to eliminate interference from the CH_2 signal at 64.9 ppm). Lowering the temperature to −80°C reveals two signals at 73.4 and 71.4 ppm, indicating that the expected asymmetry induced by the different trans ligands is obscured by fluxional behaviour (rotation) of the allyl ligand, which is occurring at room temperature (see Fig. 4a). For complex **2** the chemical shifts for the terminal carbon atoms C^1 and C^3 are well separated at room temperature (36.3 and 76.1 ppm respectively), indicating an asymmetric structure as depicted in Fig. 4b. The strong *trans* influence of the phosphorus and the weak *trans* influence of the carbonyl oxygen induce an asymmetrical η^3-allyl coordination mode [51].



a: R = Et; X = NPh_2 (1), OPh (3), SPh (4)
R = Me; X = SPh (4′), 2-pyr (5)

b: 2

Fig. 4. Different allyl coordination modes for complexes **1–5**.

In ^1H NMR the *anti* protons are generally at higher field than the *syn* protons. At room temperature the complexes **3** and **4** (X = O, S) show two sharp singlets, representing signals for the equivalent *syn* and the *anti* protons. At lower temperatures, broadening of these signals occurs, however, providing no clear information. Similar results are obtained for complex **1** (X = N) except that the *anti* protons already appear at room temperature as a broad singlet, indicating some lowering in the rate of rotation for the allyl group in this complex. In contrast, all four *syn* and *anti* protons for complex **2** (X = P) appear as separate signals, which are considerably broadened at room temperature. This broadening, which is reduced upon cooling, must be ascribed to a different exchange process from that described above. All *syn* and *anti* protons in complex **2** have a unique chemical shift indicating a structure that is consistent with a static η^3-allyl group as depicted in Fig. 4b.

In order to investigate whether asymmetry in the allyl ligand is in general an essential feature for catalytic activity we synthesised complex **6** and **7** and investigated their catalytic properties for the codimerization of styrene and ethylene. From their NMR spectra and X-ray diffraction studies these complexes are known to have some asymmetry in the allyl ligand at room temperature [52–54]. Under the same reaction conditions these complexes showed no catalytic activity at all. However, these are neutral rather than cationic complexes.

As noted for the change in the C=O stretching frequency in the IR spectrum, a downfield shift of the chemical shifts [δ(C=O)] in the ^{13}C NMR is observed upon coordination of the carbonyl moiety. A similar order for the differences Δδ(C=O) is obtained, again with com-

plex **2** giving the highest value (see Table 3). The coordination of the oxygen atom will be the main influence on the chemical shift, however the effect of the β-hetero atom on the chemical shift of the carbonyl C atom cannot be excluded. However, as the δ(C=O) of the free ligands are all the same (within 2 ppm) this does not seem to be significant. Therefore the differences Δδ(C=O) must be generated either from the different *trans* influence of the donor opposite the carbonyl ligand (the σ-bonded carbon of the allyl ligand) or the different *cis* influence (the π-bonded part of the allyl ligand) (see Fig. 4b).

In conclusion, the hemilability of the X^O ligand in the complexes used in this study is essential for catalytic activity in the codimerisation of ethylene and styrene. The relative bond strength of the dative Pd–O bond does not seem to be important, as complex **2** where X = P shows the highest catalytic activity but seems to have the strongest Pd–O interaction. The observed higher activity may be ascribed to the strong *trans* influence of the phosphorus atom, causing an unsymmetrical coordination mode of the allyl ligand in this complex and facilitating the olefin insertion reaction to produce the hydride complex (see Scheme 3). As the intermediate **V** in Scheme 4 is also an allyl-type complex this argument for the enhancing effect in ethylene insertion of P^O versus other X^O ligands will also apply here.

3. Experimental section

3.1. General remarks

All reactions and manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk techniques. All solvents were dried and purified by standard methods and freshly distilled before use. Styrene (Aldrich) was distilled and stored at 5°C. The starting materials $[C_4H_7PdCl]_2$ [55], Ph_2NCH_2COOEt, $PhOCH_2COOEt$, $PhSCH_2COOEt$ [56,57], Ph_2PCH_2COOEt [21], $2\text{-}C_5H_4NCOOTl$ [29] and K(Ph–HNacac) [58] were synthesized according to known methods. They were fully characterized by multinuclear NMR and by IR. To compare the differences upon coordination we have listed the spectroscopic data of these ligands. For several of them the NMR data have not been reported before.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-300 or a Varian Gemini-200 NMR spectrometer. Chemical shifts (δ) are reported in ppm relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P). Infrared (IR) spectra were recorded on a Bruker IFS-66 FTIR spectrometer. CH_2Cl_2 solutions were used in the mid-IR range (4000–400 cm^{-1}). Liquid secondary ion mass spectroscopy (LSIMS) measurements were recorded on a Kratos Concept ISQ spectrometer using 10 kV cesium ions as the primary beam, 5.3 kV accelerating voltage and scanning m/z of 1400 to 100 at 2 sec/decade (resolution = 1000). Samples were dissolved in *m*-nitrobenzyl alcohol. Microanalysis were performed by the Central Science Laboratory, University of Tasmania on a Carlo Erba CHNS–O EA elemental analyzer. Codimerisation products were analysed by gas chromatography using a Hewlett Packard 5890 gas chromatograph fitted with a SGE 50QC3/BP1-0.5 capillary column.

3.2. Characterisation of ligands

3.2.1. Ph_2NCH_2COOEt

IR (CH_2Cl_2): ν(C=O) 1747 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.29–6.92 (m, 10H, C_6H_5), 4.41 (s, 2H, NCH_2), 4.17 (q, 2H, J = 7.1 Hz, CH_2CH_3), 1.22 (t, 3H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9 (*C*O), 147.5, 129.4, 121.9, 120.7 (aromatic carbons), 61.1 (CH_2CH_3), 54.2 (NCH_2), 14.2 (CH_2CH_3).

3.2.2. Ph_2PCH_2COOEt

IR (CH_2Cl_2): ν(C=O) 1732 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.50–7.30 (m, 10H, C_6H_5), 4.02 (q, 2H, J = 7.1 Hz, CH_2CH_3), 3.11 (s, 2H, PCH_2), 1.10 (t, 3H, J = 7.1 Hz,

CH_2CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4 (d, $J = 7.5$ Hz, *C*O), 137.2, 132.6, 129.1, 128.6 (aromatic carbons), 60.8 (CH_2CH_3), 35.2 (d, $J = 21.6$ Hz, PCH_2), 14.0 (CH_2CH_3).

3.2.3. $PhOCH_2COOEt$

IR (CH_2C_2): ν(C=O) 1757 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.33–6.89 (m, 5H, C_6H_5), 4.61 (s, 2H, OCH_2), 4.26 (q, 2H, $J =$ 7.1 Hz, CH_2CH_3), 1.28 (t, 3H, $J = 7.1$ Hz, CH_2CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.0 (*C*O), 157.8, 128.5, 121.7, 114.6 (aromatic carbons), 65.4 (OCH_2), 61.3 (CH_2CH_3), 14.1 (CH_2CH_3).

3.2.4. $PhSCH_2COOEt$

IR (CH_2Cl_2): ν(C=O) 1733 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.43–7.20 (m, 5H, C_6H_5), 4.14 (q, 2H, $J = 7.1$ Hz, CH_2CH_3), 3.62 (s, 2H, SCH_2), 1.20 (t, 3H, $J = 7.1$ Hz, CH_2CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.6 (*C*O), 135.0, 129.9, 129.0, 126.9 (aromatic carbons), 61.5 (CH_2CH_3), 36.7 (SCH_2), 14.1 (CH_2CH_3).

3.2.5. $PhSCH_2COOMe$

^1H NMR (200 MHz, $CDCl_3$): δ 7.43–7.24 (m, 5H, C_6H_5), 3.70 (s, 3H, OCH_3), 3.64 (s, 2H, SCH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1 (*C*O), 135.0, 129.8, 129.1, 127.0 (aromatic carbons), 52.5 (OCH_3), 36.4 (SCH_2).

3.2.6. $2\text{-}C_5H_4NCOOMe$

IR (CH_2Cl_2): ν(C=O) 1726 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.77 (dd, 1H, $J = 5.7$ Hz, $J = 0.9$ Hz, H^6), 8.18–7.47 (m, 3H, H^{3-5}), 4.02 (s, 3H, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.7 (*C*O), 149.8, 147.9, 137.1, 127.0, 125.1 (pyridyl carbons), 52.9 (OCH_3).

3.3. Preparation of complexes

The appropriate ligand (5 mmol) was added to a solution of $[C_4H_7PdCl]_2$ (2.5 mmol) in CH_2Cl_2 (5 ml). After stirring for 30 minutes at room temperature this solution was added to a suspension of $AgBF_4$ (5 mmol) in 5 ml CH_2Cl_2. After stirring for a further 5 minutes, during which time AgCl precipitated, the mixture was filtered through Celite and the CH_2Cl_2 was evaporated. The product was washed with hexane. Although dried in vacuo the complexes usually contained some CH_2Cl_2.

3.3.1. $[C_4H_7Pd(Ph_2NCH_2COOEt\text{-}\kappa^2\text{-}N,O)]BF_4$ (1)

Green–brown solid; 93% yield. Anal. Calcd. for $C_{20}H_{24}NO_2PdBF_4 \cdot 0.2\ CH_2Cl_2$: C, 46.60; H, 4.72; N, 2.69. Found: C, 46.62; H, 5.08; N, 2.71. IR (CH_2Cl_2): ν(C=O) 1665 cm^{-1}. Mass spectrum: m/z 416 $[M]^+$, 361 $[M - C_4H_7]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.46–7.22 (m, 10H, C_6H_5), 4.65 (s, 2H, NCH_2), 4.43 (q, 2H, $J = 7.1$ Hz, CH_2CH_3), 3.96 (s, 2H, H^{syn}), 3.20 (br. s, 2H, H^{anti}), 2.18 (s, 3H, CH_3), 1.34 (t, 3H, $J = 7.1$ Hz, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.6 (*C*O), 147.5, 132.2, 130.2, 126.8, 122.1 (aromatic carbons and CCH_3), 65.6 (CH_2CH_3), 63.7 (allylic CH_2), 60.3 (NCH_2), 22.1 (CCH_3), 14.2 (CH_2CH_3).

3.3.2. $[C_4H_7Pd(Ph_2PCH_2COOEt\text{-}\kappa^2\text{-}P,O)]BF_4$ (2)

Brown–yellow solid; 92% yield. IR (CH_2Cl_2): ν(C=O) 1629 cm^{-1}. Mass spectrum: m/z 433 $[M]^+$, 378 $[M - C_4H_7]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.61–7.28 (m, 10H, C_6H_5), 5.03 (br.s, 1H, H^1), 4.28 (q, 2H, $J = 7.1$ Hz, CH_2CH_3), 3.83 (d, 2H, $J = 10.5$ Hz, PCH_2), 3.49 (br.s, 1H, H^2), 3.17, 3.10 (br.m, 2H, H^4 and H^3), 2.14 (s, 3H, CH_3), 1.22 (t, 3H, $J = 7.1$ Hz, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.7 (d, $J = 9.8$ Hz, *C*O), 136.5–128.9 (aromatic carbons and CCH_3), 76.1 (allylic C^1), 66.0 (CH_2CH_3), 37.3 (d, $J = 25.7$ Hz, PCH_2), 36.3 (allylic C^3), 23.7 (CCH_3), 14.2 (CH_2CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ 20.3 (s).

3.3.3. $[C_4H_7Pd(PhOCH_2COOEt\text{-}\kappa^2\text{-}O,O)]BF_4$ (3)

Grey solid; 88% yield. Anal. Calcd. for $C_{14}H_{19}O_3PdBF_4 \cdot 0.5\ CH_2Cl_2$: C, 36.98; H,

4.28. Found: C, 37.02; H, 4.48. IR (CH_2Cl_2): ν(C=O) 1682 cm^{-1}. Mass spectrum: *m/z* 340 $[M]^+$, 285 $[M-C_4H_7]^+$, 161 $[C_4H_7Pd]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.46–7.06 (m, 5H, C_6H_5), 4.78 (s, 2H, OCH_2), 4.38 (q, 2H, J = 7.1 Hz, CH_2CH_3), 3.85 (s, 2H, H^{syn}), 2.98 (s, 2H, H^{anti}), 2.15 (s, 3H, CH_3), 1.35 (t, 3H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6 (*C*O), 157.6, 129.6, 120.4, 113.4 (aromatic carbons), 131.7 (*C*CH_3), 66.1 (allylic CH_2), 64.0 (*C*H_2CH_3), 62.9 (O*C*H_2), 22.0 (C*C*H_3), 13.9 (CH_2CH_3).

3.3.4. [$C_4H_7Pd(PhSCH_2COOEt$-κ^2-*S,O*)]BF_4 (*4*)

Orange oil; 82% yield. IR (CH_2Cl_2): ν(C=O) 1660 cm^{-1}. Mass spectrum: *m/z* 356 $[M]^+$, 301 $[M-C_4H_7]^+$, 161 $[C_4H_7Pd]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.73–7.45 (m, 5H, C_6H_5), 4.36 (q, 2H, J = 7.1 Hz, CH_2CH_3), 4.36 (s, 2H, H^{syn}), 4.21 (s, 2H, SCH_2), 3.51 (s, 2H, H^{anti}), 2.21 (s, 3H, CH_3), 1.29 (t, 3H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0 (*C*O), 135.5, 132.1, 130.8, 130.2, 129.5 (aromatic carbons and *C*CH_3), 66.7 (allylic CH_2), 64.9 (*C*H_2CH_3), 42.5 (S*C*H_2), 22.5 (C*C*H_3), 13.7 (CH_2CH_3).

3.3.5. [$C_4H_7Pd(PhSCH_2COOMe$-κ^2-*S,O*)]BF_4 (*4'*)

Yellow solid; 95% yield. ^1H NMR (200 MHz, $CDCl_3$): δ 7.66–7.44 (m, 5H, C_6H_5), 4.34 (s, 2H, H^{syn}), 4.21 (s, 2H, SCH_2), 3.89 (s, 3H, OCH_3), 3.53 (s, 2H, H^{anti}), 2.20 (s, 3H, CCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.0 (*C*O), 135.4, 132.2, 130.9, 130.3, 129.6 (aromatic carbons and *C*CH_3), 67.3 (allylic CH_2), 55.5 (O*C*H_3), 42.9 (S*C*H_2), 22.7 (C*C*H_3).

3.3.6. [$C_4H_7Pd(2$-$C_5H_4NCOOMe$-κ^2-*N,O*)]BF_4 (*5*)

White solid; 83% yield. Anal. Calcd. for $C_{11}H_{14}NO_2PdBF_4$: C, 34.28; H, 3.66; N, 3.63. Found: C, 34.10; H, 3.62; N, 3.64. IR (CH_2Cl_2): ν(C=O) 1671 cm^{-1}. Mass spectrum: *m/z* 298 $[M]^+$, 243 $[M-C_4H_7]^+$, 161 $[C_4H_7Pd]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ 8.96 (dd, 1H, J = 5.2 Hz, J = 0.8 Hz, pyr-H^6), 8.33–7.91 (m, 3H, pyr-H^{3-5}), 4.29 (s, 2H, H^{syn}), 4.25 (s, 3H, OCH_3), 3.32 (s, 2H, H^{anti}), 2.28 (s, 3H, CCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.6 (*C*O), 154.2, 144.6, 141.1, 131.8, 127.8 (pyridyl carbons), 133.8 (*C*CH_3), 61.4 (allylic CH_2), 56.3 (O*C*H_3), 22.9 (C*C*H_3).

3.3.7. [$C_4H_7Pd(2$-C_5H_4NCOO-κ^2-*N,O*)] (*6*)

Off-white solid; 99% yield; ^1H NMR (200 MHz, $CDCl_3$): δ 8.47, 8.26, 8.02, 7.55 (m, pyr-H^{3-6}), 4.00 (br s, 1H, H^1), 3.67 (br s, 1H, H^4), 2.99 (s, 2H, H^{anti}), 2.20 (s, 3H, CCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.4 (*C*O), 152.5, 151.2, 139.5, 130.5, 127.3, 126.8 (pyridyl carbons and *C*CH_3), 58.3 (C^1), 55.5 (C^3), 23.5 (C*C*H_3).

3.3.8. [C_4H_7Pd(4-phenylamino-3-penten-2-onato-κ^2-*N,O*)]BF_4 (*7*)

Purple solid; 33% yield; ^1H NMR (300 MHz, $CDCl_3$): δ 7.31–7.01 (m, 5H, C_6H_5), 5.01 (s, 1H, CC*H*C), 2.08, 2.02 (2s, H, NCCH_3 and OCCH_3), 1.68 (s, 3H, allyl-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.4 (*C*O), 164.6 (*C*N), 157.5, 131.0, 129.2, 124.4 (aromatic carbons), 123.5 (*C*CH_3), 98.0 (C*C*HC), 59.5 (allylic C^1), 57.7 (allylic C^3), 27.6 (OC*C*H_3), 24.0 (C*C*H_3) 23.5 (NC*C*H_3).

3.3.9. Characterisation of intermediate [$C_4H_7Pd(Ph_2PCH_2COOEt)Cl$]

^1H NMR (200 MHz, $CDCl_3$): δ 7.69–7.39 (m, 10H, C_6H_5), 3.88 (q, 2H, J = 7.1 Hz, CH_2CH_3), 3.64 (d, 2H, J = 8.5 Hz, PCH_2), 3.15 (br.s, H^1–H^4), 1.94 (s, 3H, CH_3), 1.00 (t, 3H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.8 (d, J = 5.0 Hz, *C*O), 133.6–128.9 (aromatic carbons and *C*CH_3), 61.6 (*C*H_2CH_3), 34.6 (d, J = 17.5 Hz, P*C*H_2), 23.8 (C*C*H_3), 14.3 (CH_2CH_3).

3.4. Codimerisation of styrene and ethylene

To a solution of the complex (0.05 mmol) in CH_2Cl_2 (20 ml) was added ca. 2 g of styrene

(40 mmol). After stirring for 5 min. this solution was transferred into a 75 ml steel autoclave, which was equipped with a glass inlet and a magnetic stirring bar. The autoclave was pressurised with ethylene to 30 bar (6–7 g) and stirred at room temperature. After the appropriate time the excess ethylene was released and the catalyst was destroyed by adding a saturated KOH/MeOH solution (1 ml). A sample was filtered through Celite before GC analysis. Quantitative analysis were performed using n-nonane as a standard.

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