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Cationic palladium complexes with ketophosphine and phosphino enolate ligands and their reactivity towards C–C coupling reactions. Crystal structures of $[\overline{\text{PdMe}\{\text{Ph}_2\text{PCH}_2\text{C(O}})\text{Ph}\}\text{-}(\text{PCy}_3)](\text{PF}_6)$ and $[\overline{\text{Pd}\{\text{Ph}_2\text{PCH}\underline{\cdots}\text{C}(\underline{\cdots}\text{O}})\text{Ph}\}(\text{SMe}_2)_2](\text{PF}_6)$☆

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Dedicated to Professor S. Pasynkiewicz on the occasion of his 70th birthday, with our sincere congratulations

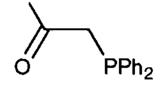
Abstract

Two types of monocationic Pd(II) complexes are reported, which contain either the functional P,O phosphine ligands $\text{Ph}_2\text{PCH}_2\text{C(O)Ph}$ or $\text{Ph}_2\text{PCH}_2\text{C(O)NPh}_2$ or an anionic chelating phosphino enolate. The first set of complexes includes $[\overline{\text{PdMe}\{\text{Ph}_2\text{PCH}_2\text{C(O}})\text{Ph}\}(\text{PPh}_3)](\text{PF}_6)$ (**1**), $[\overline{\text{PdMe}\{\text{Ph}_2\text{PCH}_2\text{C(O}})\text{Ph}\}(\text{PCy}_3)](\text{PF}_6)$ (**2**), $[\overline{\text{PdMe}\{\text{Ph}_2\text{PCH}_2\text{C(O}})\text{NPh}_2\}(\text{PPh}_3)](\text{PF}_6)$ (**3**), and the second $[\overline{\text{Pd}\{\text{Ph}_2\text{PCH}\underline{\cdots}\text{C}(\underline{\cdots}\text{O}})\text{Ph}\}(\text{SMe}_2)_2](\text{PF}_6)$ (**5**), which was obtained by an interesting ligand redistribution reaction between *cis*-$[\overline{\text{Pd}\{\text{Ph}_2\text{PCH}\underline{\cdots}\text{C}(\underline{\cdots}\text{O}})\text{Ph}\}_2]$ and $[\text{Pd}(\text{SMe}_2)_4](\text{PF}_6)_2$. Compounds **1** and **5** display catalytic activity for ethylene dimerization. A preliminary study on ethylene/CO copolymerization with complexes **1**–**3** identified compound **1** as a catalyst precursor. This led to the in situ preparation of an active species for ethylene/CO copolymerization, starting from a Pd(0) precursor and appropriate ligands. The structures of complexes **2** and **5** have been determined by X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cationic palladium complexes; Ketophosphine ligands; Phosphine enolate ligands; Ethylene dimerization; Ethylene/CO copolymerization

1. Introduction

Heteroditopic phosphine ligands containing oxygen functions, such as esters, ketones or amides, as in $\text{Ph}_2\text{PCH}_2\text{C(O)OEt}$ [1], $\text{Ph}_2\text{PCH}_2\text{C(O)Ph}$ (**I**) [2] or $\text{Ph}_2\text{PCH}_2\text{C(O)NPh}_2$ (**II**) [3] respectively, belong to a general family of ligands that possess a strong and a weak donor group.



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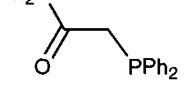

II

They have been found to confer interesting properties to their metal complexes, such as the selective binding to metal ions of different types (hard vs. soft), dynamic behaviour via reversible dissociation of the weaker metal–ligand bond, reversible binding of e.g. carbon monoxide or stereoelectronic control of the coordination sphere of the metal centre [4,5]. Furthermore, owing to the chelate effect, which makes these ligands behave formally as neutral four-electron donors, they generally impart greater stability to their complexes than monodentate phosphines, thus allowing isolation of reactive intermediates. The corresponding four-electron donor anionic phosphino enolate ligands $[\text{Ph}_2\text{PCH}\underline{\cdots}\text{C}(\underline{\cdots}\text{O})\text{R}]^-$ (R = OEt, Ph, NPh_2) are stronger chelates and, together with related *P,O* chelates, they confer special reactivity to their complexes, as found in the nickel-catalysed ethene oligomerization [6–9]. The

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☆ Non-SI unit employed: 1 atm = 101.325 kPa, 1 bar = 10^2 kPa.

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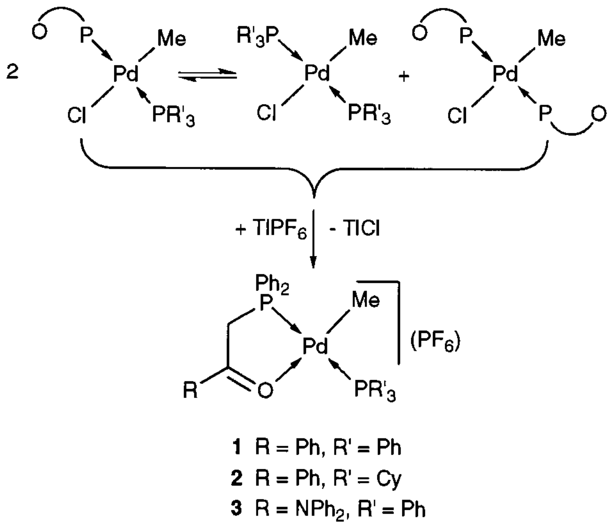
first palladium analogues of neutral SHOP-type nickel catalysts have been reported recently [10,11] and we were thus interested in preparing cationic palladium complexes with such ligands and examining their reactivity toward olefins in the presence and absence of carbon monoxide. The interest in the latter combination is mostly due to the recent developments and commercial applications of perfectly alternating polyketones [12,13].



Scheme 1.

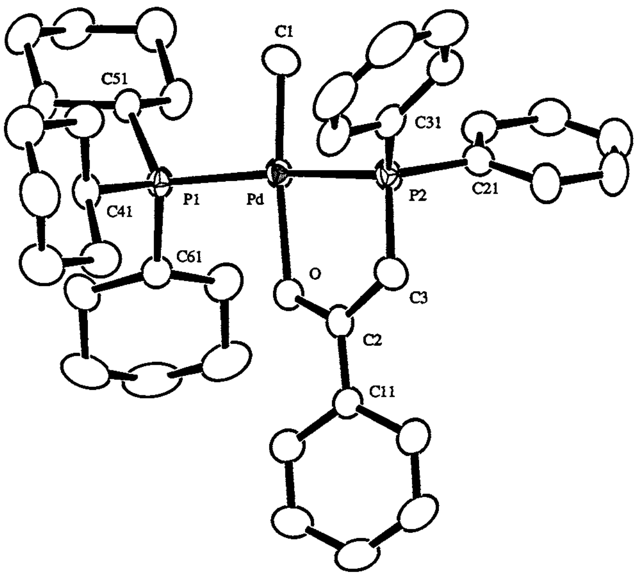


Fig. 1. View of the crystal structure of the cationic complex in $[PdMe\{Ph_2PCH_2C(O)Ph\}(PCy_3)](PF_6)$ (**2**).

Table 1

Selected bond distances (Å) and angles (°) for $[PdMe\{Ph_2PCH_2C(O)Ph\}(PCy_3)](PF_6)$ (**2**)

Bond distances			
Pd(1)–P(1)	2.3404(8)	C(2)–C(3)	1.497(5)
Pd(1)–P(2)	2.2859(9)	P(2)–C(3)	1.848(4)
Pd(1)–O(1)	2.191(2)	C(2)–O(1)	1.238(4)
Pd(1)–C(1)	2.029(4)		
Bond angles			
P(2)–Pd(1)–O(1)	81.30(6)	P(2)–C(3)–C(2)	112.0(2)
P(1)–Pd–C(1)	92.3(1)	C(3)–C(2)–O(1)	120.3(3)

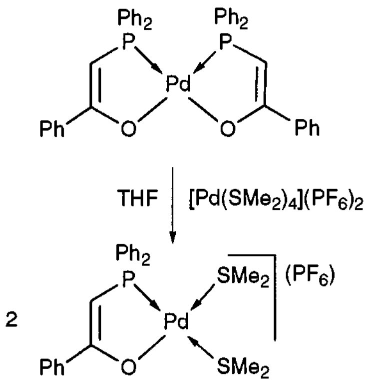
2. Results

The reaction of [PdMe(Cl)(COD)] with one equivalent each of the P,O ligand **I** or **II** and PPh_3 or PCy_3 in CH_2Cl_2 yielded in each case a mixture of three complexes in thermodynamic equilibrium, which prevented isolation of the mixed-phosphine complexes $[PdMe(Cl)(PR'_3)(P,O)]$ in pure form (Scheme 1) [10,11].

However, the addition of $TlPF_6$ to this mixture led to formation of the cationic complexes **1**–**3** in very high yield (Scheme 1). Their $\nu_{C=O}$ absorption appears in the IR spectrum around 1558 cm^{-1}, consistent with a chelation of the P,O ligands in a cationic complex [2]. The ligand arrangement in complex **2** was confirmed by an X-ray diffraction study (Fig. 1, Table 1).

The dimensions within the five-membered *P*,*O* chelate are similar to those in $[Pd\{Ph_2PCH_2C(O)Ph\}_2](BF_4)(B_2F_7)$ [14]. It is interesting to compare the present data with those previously reported for $[PdMe\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}(PPh_3)]$ [10]. Note that on going from a neutral to an anionic *P*,*O* chelate the P–Pd–O bite angle increases by 2° and the Pd–O distance increases by 0.07 Å due to the different nature of the oxygen donor atoms (ketonic vs. enolate). All other angles and distances remain surprisingly similar. The cationic nature of the Pd centre in **2** was expected to have a more significant effect on the metal coordination sphere.

Another cationic complex was prepared with a chelating *phosphino enolate* ligand. It was obtained by an interesting ligand exchange reaction involving migration of the anionic chelating ligand from *cis*-$[Pd\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_2]$ to the electrophilic palladium complex $[Pd(SMe_2)_4](PF_6)_2$ (Eq. (1)).



5 (1)

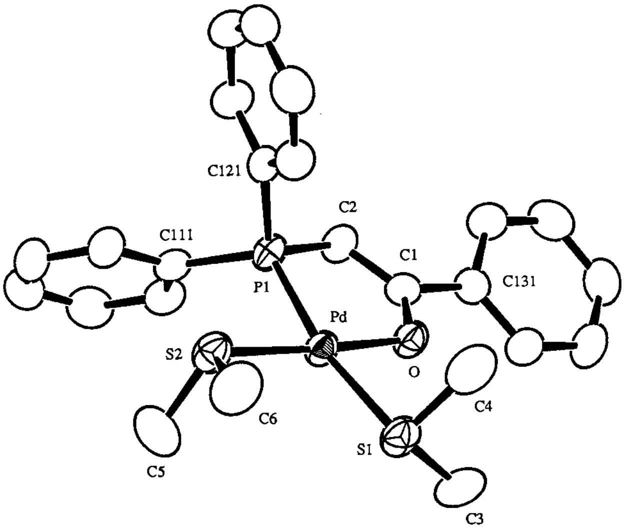


Fig. 2. View of the crystal structure of the cationic complex in $[\overline{\mathrm{Pd}\{\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}\}(\mathrm{SMe_2})_2](\mathrm{PF_6})$ (**5**).

Table 2
Selected bond distances (Å) and angles (°) for $[\overline{\mathrm{Pd}\{\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}\}(\mathrm{SMe_2})_2](\mathrm{PF_6})$ (**5**)

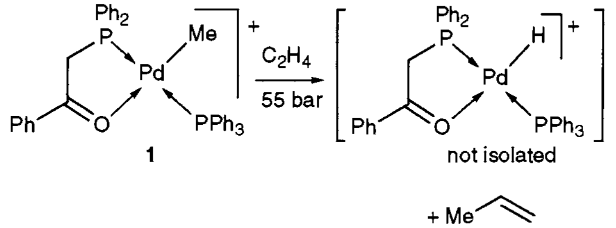
Bond distances			
Pd(1)–S(1)	2.412(2)	C(1)–C(2)	1.357(8)
Pd(1)–S(2)	2.299(2)	P(1)–C(2)	1.760(6)
Pd(1)–P(1)	2.241(2)	O(1)–C(1)	1.324(7)
Pd–O(1)	2.016(4)		
Bond angles			
P(1)–Pd(1)–O(1)	83.9(1)	P(1)–C(2)–C(1)	114.2(4)
S(1)–Pd(1)–S(2)	97.21(6)	C(2)–C(1)–O(1)	123.3(5)

The latter reagent was prepared by reaction of $Pd(OAc)_2$ with excess SMe_2 in CH_2Cl_2, followed by addition of HPF_6 (see Section 5). It is noteworthy that $[Pd(NCMe)_4]^{2+}$ could not be used as an electrophile in Eq. (1) owing to reaction between the activated acetonitrile ligand and the nucleophilic enolate carbon centre. Related observations were made in the reactions of $[PtCl_2(NCPh)_2]$ with $\mathrm{Li[Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O})\mathrm{Y}]$ (Y = CN, CO_2Et, NPh_2), which yielded the complexes *trans*-$\overline{\mathrm{Pt[Ph_2PC\{{=}C(N}}\mathrm{H)Ph\}\{C(O)Y\}]_2}$ [15–17]. In the IR spectra of compound **5** the band at 1510 cm^{-1} is typical for a $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ vibration of the enolate moiety [2].

Complex **5** is a rare example of a cationic complex containing a disymmetric anionic chelating ligand. In its crystal structure, established by X-ray diffraction (Fig. 2, Table 2), the Pd–S bond distances are in the expected range and that *trans* to the phosphorus atom is longer than that *trans* to oxygen, consistent with the different *trans* influences of the phosphorus and oxygen donor atoms [18,19]. The C(1)–C(2) bond distance of 1.357(8) Å indicates a C=C double-bond character and is comparable with that in other coordinated phosphino enolate type systems [10,16,20,21]. This bond is shorter by about 0.10 Å than the corresponding C(2)–C(3) bond in the neutral ligand of **2**. Similarly, on going from the neutral to the anionic form of the *P*,*O* chelate, the C–O bond distance increases from 1.238(4) to 1.324(4) Å. This is in accordance with the existence of a more single-bond character for the C–O bond in complex **5**. The P(1)–Pd(1)–O(1) bite angle of 83.9° is consistent with previous findings [10,16,20,21].

2.1. Catalytic studies

We first studied the reactivity of some complexes toward ethylene alone. Complex **1** was found to dimerize ethylene and the influence of the solvent was examined by running the reaction in CH_2Cl_2, in the molten salt $(BMI)PF_6$ (BMI = butylmethylimidazolium) [22,23] or in MeOH. In the latter case, addition of a phosphonium triflate allowed solubilization of the complex. GC analysis showed the presence of propylene, indicative of the formation of a palladium hydride species according to Eq (2).



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(2)

Quantitative formation of propylene was observed in CH_2Cl_2, whereas it was only partial in $(BMI)PF_6$, probably due to the low solubility of the complex, and in MeOH where significant decomposition to palladium metal was observed. Heterolytic cleavage of the Pd–Me bond in MeOH to give methane and Pd–OMe could also reduce the amount of propylene formed. Complex **1** catalyses ethylene dimerization and from the results shown in Table 3, a clear relationship appears between the quantities of propylene and butenes formed. This is consistent with the involvement of a palladium hydride in the catalytic cycle. Very small amounts of hexenes were detected, in accord with the β-elimination reaction leading to 1-butene being much favoured over chain growth. The selectivity of **1** for butenes ($>99.5\%$) is also favoured by the slow rate of reaction. The presence of *cis*- and *trans*-2-butenes results from the well-known ability of palladium hydrides to isomerize 1-butene [24]. For comparison it was interesting to test the activity of the cationic complex **5** for ethylene dimerization (Table 3). The selectivity for butenes was again very high (99%) and the presence of *cis*- and *trans*-2-butenes was also observed.

Table 3
Catalytic results for ethylene oligomerization with complexes **1** and **5** [a]

Run	Catalyst	Mol C_3H_6 mol Pd^{-1}	Mass % of oligomers				C_2H_4 conversion (%)	TON [b]
			1-butene	*trans*-2-Butene	*cis*-2-Butene	Hexenes		
1 [c]	**1**	1.0	58	23	19	<0.5	5	164
2 [d]	**1**	0.3	50	33	16	1	1	22
3 [e]	**1**	0.4	49	30	21	0	1	6
4 [f]	**5**		66	22	11	1	4	98

[a] Catalytic test run at 85°C, under 55 bar of C_2H_4 for 3 h.

[b] Turnover numbers are given as moles of substrate converted per mole of palladium during the entire experiment.

[c] 0.23 mmol of catalyst, 20 ml of CH_2Cl_2.

[d] 0.26 mmol of catalyst, 4 ml of [BMI](PF_6), 2 ml of heptane.

[e] 0.23 mmol of catalyst, 0.46 mmol of $[P^{n}Bu_4](CF_3SO_3)$, 5 ml of CH_2Cl_2, 30 ml of MeOH.

[f] 0.33 mmol of catalyst, 20 ml of CH_2Cl_2.

Other C–C coupling reactions of current academic and industrial interest include the copolymerization of olefins with carbon monoxide to yield polyketones [12,25–32]. Complexes **1**–**3** were therefore also tested for catalytic ethylene/CO copolymerization. Preliminary results show that these complexes are active, with **1** giving better results than **2** or **3** (see Table 4). Activities are expressed both as TON h^{-1} (moles of substrate converted per moles of Pd per hour) and in grams of polyketone per gram of palladium per hour and are based on the mass of the insoluble polymer collected after reaction (details in Section 5). The characterization of the perfectly alternating polyketones (elemental analysis, melting point, IR, ^{13}C-NMR spectra) is in agreement with the literature data [33,34]. The $^{13}C\{^1H\}$-NMR spectra of the polyketones formed show the characteristic singlets at $\delta = 35.0$ ($-CH_2-$) and 212.0 (C=O) and no resonance for end groups could be detected. This is indicative of long polymer chains with more than 400 monomeric units [33,35].

Catalytic experiments were first run in CH_2Cl_2 but the copolymer obtained was grey, owing to the presence of palladium metal, while the product obtained from runs in acetonitrile was white. However, a similar productivity was observed in both solvents. We therefore performed all of our subsequent copolymerization tests in acetonitrile. A beneficial effect of added *p*-hydroquinone was observed, consistent with previous observations on palladium-catalysed carbon–carbon coupling reactions [36,37].

Note that another reasonable route to generate a palladium hydride species is to oxidize Pd(0) by a strong organic acid such as CF_3COOH, in the presence of **I** and PPh_3 in order to stabilize an intermediate analogous to that in Eq. (2). Thus, mixing one equivalent of $[Pd(dba)_2]$ (dba = dibenzylideneacetone) with an equimolar amount of **I** and PPh_3 and 10 equivalents of CF_3COOH generated an active system for the production of polyketones (TON $h^{-1} = 51$). In the absence of acid, no catalysis was observed. These experiments suggest that the addition of a Brönsted acid such as *p*-hydroquinone or CF_3COOH has a beneficial effect on the catalytic copolymerization reaction and that this catalysis can also be performed from Pd(0) precursors.

3. Discussion

With the hemilabile P,O ligands used in this work, neither chelation could be obtained by displacement of the COD ligand from [PdMe(Cl)(COD)], nor a neutral complex bearing both the functional phosphine and an auxiliary ligand (PR_3) be isolated in a pure form. Nevertheless, addition of a chloride abstractor to the equilibrium mixture of Scheme 1 led to selective formation of the mixed-phosphine cationic complexes **1**–**3**. This lucky situation results from redistribution of phosphine ligands leading to the thermodynamically preferred product. Similar ligand redistributions have previously been observed when R = NPh_2 upon deprotonation of such an equilibrium mixture with NaOMe to give selectively the phosphino enolate complex $[PdMe\{Ph_2PCH \overset{...}{=} C(\overset{...}{=} O)NPh_2\}(PR_3)]$ [10,11].

Table 4
Catalytic results for ethylene/CO copolymerization with complexes **1**–**3** [a]

Run	Catalyst	TON (h^{-1}) [b]	g(PK) $g(Pd)^{-1}$ h^{-1}
1	**1**	43	23
2 [c]	**1**	41	22
3 [d]	**1**	235	124
4	**2**	32	17
5	**3**	14	7

[a] Catalytic conditions: 40 ml CH_3CN, initial $p(CO) = 30$ bar, initial $p(\text{ethylene}) = 30$ bar, $n(\text{catalyst}) = 0.11$ mmol, 3 h reaction time.

[b] Moles of substrate converted per mole of palladium per hour.

[c] In the presence of 1.1 mmol of *p*-benzoquinone.

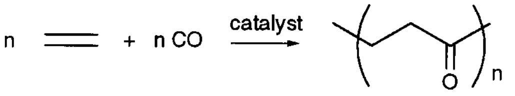
[d] In the presence of 1.1 mmol of *p*-hydroquinone.

3.1. Catalytic ethylene dimerization

In the catalytic studies on ethylene oligomerization, the high selectivity of **1** for butenes is in accord with that of other cationic palladium complexes containing monodentate or chelating phosphines [38,39]. However, the catalytic activity of **1** is much lower than that of $[Pd(O_3SCF_3)_2(dppp)]$ [39] or of $[Pd(\eta^3\text{-allyl})\{Ph_2P(CH_2)_nC(O)OMe\}](SbF_6)$ [40]. Complex **5** catalyses ethylene dimerization with a selectivity of 99% although ethylene conversion was low. There are precedents in the literature for cationic palladium complexes being catalytic precursors for this reaction although they do not contain a Pd–C bond. Thus, for example, $[Pd(NCMe)_4](BF_4)_2$ dimerizes ethylene catalytically [34,41], whereas $[Pd(acac)(NCMe)_2](BF_4)$ dimerizes methyl acrylate only stoichiometrically [42]. The reaction mechanism could proceed via ethylene insertion into a palladium hydride bond, followed by further ethylene insertion into the resulting Pd–carbon bond and by β-elimination of 1-butene or via a carbocationic-type mechanism, which has been suggested for electrophilic cationic catalysts [25,41].

3.2. Ethylene/CO copolymerization

In recent years several groups have reported on the Pd(II)-catalysed alternating copolymerization of olefins with carbon monoxide to yield polyketones (Eq. (3)) with very attractive physical properties [13].



(3)

In 1996, Shell started up a plant with an annual capacity of 20 000 t, and marketed its polymer under the trade name Carilon®. Other chemical companies (Akzo Nobel, BASF, BP, Enichem) filed patents and several research groups are very active in this field in order to develop new classes of catalysts and to understand the different steps involved in the overall catalytic process [12,25–32]. Catalysts are usually of the type $[Pd(solvent)_2(L_2)]^{2+}$ or $[PdMe(solvent)(L_2)]^{+}$ where L_2 is a diphosphine or diimine ligand. The activity of complex **1** is more than three times higher than that of its analogue **3**, where ligand **I** has been replaced by ligand **II**. This shows the inhibiting effect of an electron donating group on the ligand backbone. Similarly, we found compound **2** to be less productive than **1**. The inhibitory effect of the highly basic PCy_3 in carbonylation reactions of neutral palladium alkyl or aryl complexes [43] or in ethylene/CO copolymerization with cationic alkyl palladium complexes has been previously noted [27]. The activity of complex **1** in ethylene/CO copolymerization remains fairly low compared with cationic palladium catalysts with bidentate P,P or N,N-ligands [32,33], but is in the range observed with heteroditopic bidentate ligands [27,44,45]. The copolymerization catalysts of the type $[Pd(solvent)_2L_2]^{2+}$ (L = P or N donors) generally show a higher activity in methanol in the presence of added oxidants like benzoquinone. The latter allow oxidation to Pd^{2+} of some mono- or dinuclear Pd(0) species generated in the course of the catalysis which can then re-enter the catalytic cycle [12,29]. Under our catalytic conditions, *p*-benzoquinone had no significant effect on the productivity while the reactivity of **1** was enhanced by a factor of five (runs 2 and 3) upon addition of *p*-hydroquinone. The fact that *p*-hydroquinone had a positive effect on the productivity, while *p*-benzoquinone had none appears intriguing and in order to evaluate the possible role of the –OH function in *p*-hydroquinone, we performed a catalytic experiment in the presence of MeOH. Addition of 1 ml of MeOH to the acetonitrile solution of the catalyst led to a major decrease in the productivity of polyketones, under otherwise similar catalytic conditions. Thus it appears unlikely that the OH group of the *p*-hydroquinone has by itself any beneficial effect.

4. Conclusions

Our previous studies on the reactivity toward ethylene oligomerization of neutral palladium alkyl and aryl complexes containing phosphino enolate ligands have shown that in the case of the alkyl compounds, mono-insertion of ethylene into the Pd–Me bond resulted in the formation of propylene and an unstable palladium hydride species [11]. The behaviour of these complexes contrasts with that of their nickel analogues that yielded oligomeric products with high efficiency [6–8]. With the aim of increasing the reactivity of such complexes, we investigated the synthesis of cationic palladium analogues. We thus prepared two families of monocationic complexes, **1**–**3** and **5**, respectively, with either the neutral or the anionic form of the ligand. Compounds **1** and **5** displayed catalytic activity for ethylene dimerization. A preliminary study on ethylene/CO copolymerization with complexes **1**–**3** allowed us to identify compound **1** as a catalyst precursor. This led to the in situ preparation of an active species for ethylene/CO copolymerization starting from a Pd(0) precursor and appropriate ligands.

5. Experimental

All reactions were performed under purified nitrogen or carbon monoxide. Solvents were purified and dried under nitrogen by conventional methods. The ^1H- and

$^{31}P\{^1H\}$-NMR spectra were recorded at 300.13 and 121.5 MHz on a FT Bruker AC300 instrument and IR spectra in the 4000–400 cm^{-1} range on a Bruker IFS66 FT spectrometer. The ligands $Ph_2PCH_2C(O)Ph$ [2] and $Ph_2PCH_2C(O)NPh_2$ [3] and the complex [PdMe(Cl)(COD)] [46] were prepared according to literature procedures.

*5.1. [PdMe{$Ph_2PCH_2C(O)Ph$}(PPh_3)](PF_6) (**1**)*

A mixture of [PdMe(Cl)(COD)] (0.400 g, 1.50 mmol), **I** (0.458 g, 1.50 mmol) and PPh_3 (0.396 g, 1.50 mmol) was stirred in CH_2Cl_2 (30 ml) for 1 h. Solid $TlPF_6$ (0.492 g, 1.50 mmol) was added and the mixture was stirred again overnight. The suspension was then filtered over Celite and the pale yellow solution was concentrated in vacuo. Addition of Et_2O afforded colorless crystals, which were filtered, washed with Et_2O, and dried in vacuo, yield: 1.12 g (90%). Anal. Calc. for $C_{39}H_{35}F_6OP_3Pd{\cdot}0.5CH_2Cl_2$: C, 54.16; H, 4.13. Found: C, 54.25; H, 4.21%. IR (CH_2Cl_2): 1608 (s), 1593 (s), 1583 (w), 1575 (s), $\nu_{C=O} = 1558$ (s) cm^{-1}. ^1H-NMR (CD_2Cl_2): δ 0.91 (t, 3H, $^3J_{PH} = 5.8$ Hz, CH_3), 4.61 (dd, 2H, $^2J_{PH} = 6.1$, $^4J_{PH} = 2.6$ Hz, PCH_2), 7.82–6.50 (m, 30H, phenyl). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): AB spin system: δ_A 25.4, δ_B 28.7 ($^2J_{PP} = 385$ Hz), -143.7 (sept., 1P, PF_6^-, $^1J_{PF} = 713$ Hz).

*5.2. [PdMe{$Ph_2PCH_2C(O)Ph$}(PCy_3)](PF_6) (**2**)*

Following the procedure described for **1**, but starting from [PdMe(Cl)(COD)] (0.335 g, 1.26 mmol), **I** (0.384 g, 1.26 mmol), PCy_3 (0.354 g, 1.26 mmol) and $TlPF_6$ (0.412 g, 1.26 mmol), **2** was obtained after crystallization from a 1:3 mixture of CH_2Cl_2–Et_2O as white crystals, yield: 0.998 g (93%). Anal. Calc. for $C_{39}H_{53}F_6OP_3Pd$: C, 55.03; H, 6.26. Found: C, 54.81; H, 6.25%. IR (CH_2Cl_2): 1609 (s), 1593 (s), 1575 (s) 1558 (s) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 0.80 (t, 3H, $^3J_{PH} = 5.5$ Hz, CH_3), 1.30–2.00 (m, 33H, cyclohexyl), 4.65 (d, 2H, $^2J_{PH} = 10.8$ Hz, PCH_2), 7.30–8.15 (m, 15H, phenyl). $^{31}P\{^1H\}$-NMR ($CDCl_3$): AB spin system: δ_A 24.9, δ_B 33.8 ($^2J_{PP} = 365$ Hz), -143.6 (sept., 1P, PF_6^-, $^1J_{PF} = 711$ Hz).

*5.3. [PdMe{$Ph_2PCH_2C(O)NPh_2$}(PPh_3)](PF_6) (**3**)*

Following the procedure described for **1**, but starting from [PdMe(Cl)(COD)] (0.300 g, 1.13 mmol), **II** (0.447 g, 1.13 mmol), PPh_3 (0.297 g, 1.13 mmol) and $TlPF_6$ (0.395 g, 1.13 mmol), **3** was obtained after crystallization from a 1:3 mixture of CH_2Cl_2–Et_2O as white needles, yield: 0.880 g (78%). Anal. Calc. for $C_{51}H_{45}F_6NOP_3Pd{\cdot}1.25CH_2Cl_2$: C, 56.67; H, 4.32; N, 1.27. Found: C, 56.63; H, 4.63; N, 1.44%. ^1H-NMR (CD_2Cl_2): δ 0.65 (dd, 3H, $^3J_{PH} = 5.9$, 5.0 Hz, CH_3), 3.80 (dd, 2H, $^2J_{PH} = 6.2$, $^4J_{PH} = 2.1$ Hz, PCH_2), 7.60–7.00 (m, 35H, phenyl). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): AB spin system: δ_A 24.3, δ_B 27.6 ($^2J_{PP} = 391$ Hz), -143.6 (sept., 1P, PF_6^-, $^1J_{PF} = 714$ Hz).

*5.4. [Pd(SMe_2)$_4$](PF_6)$_2$ (**4**)*

Pure dimethylsulfide (5 ml) was added to a solution of $Pd(OAc)_2$ (0.500 g, 2.23 mmol) in CH_2Cl_2 (10 ml). Within a few seconds the solution went from brown to yellow and after 5 min of stirring excess HPF_6 (1 ml, 75% in H_2O, 9.95 mmol) was added. After 30 min the yellow precipitate formed was isolated, washed with Et_2O (3×15 ml) and THF (2×15 ml), and dried in vacuo, yield: 1.070 g (75%). Anal. Calc. for $C_8H_{24}F_{12}P_2PdS_4$: C, 14.90; H, 3.75. Found: C, 14.55; H, 3.63%. ^1H-NMR (acetone-d_6): δ 2.65 (s, $S(CH_3)_2$).

*5.5. [Pd{$Ph_2PCH{\cdots}C({\cdots}O)Ph$}($SMe_2$)$_2$]($PF_6$) (**5**)*

In 20 ml of THF were mixed together *cis*-[Pd{$Ph_2PCH{\cdots}C({\cdots}O)Ph$}$_2$] (0.230 g, 0.32 mmol) and [Pd(SMe_2)$_4$](PF_6)$_2$ (0.207 g, 0.32 mmol). After stirring for 5 h the solution was filtered over Celite, and the solvent was removed in vacuo. The orange powder was washed with a 1:1 mixture of Et_2O–pentane (2×10 ml) and dried in vacuo. Anal. Calc. for $C_{24}H_{28}F_6OP_2PdS_2$: C, 42.46; H, 4.16. Found: C, 42.39; H, 4.20%. IR (CH_2Cl_2): $\nu(C{\cdots}O) + \nu(C{\cdots}C) = 1510$ cm^{-1}. ^1H-NMR (acetone-d_6): δ 2.45 (s, 6H, $S(CH_3)_2$), 2.60 (s, 6H, $S(CH_3)_2$), 5.05 (d, 1H, $^2J_{PH} = 4.9$ Hz, PCH), 7.40–8.00 (m, 15H, phenyl). $^{31}P\{^1H\}$-NMR (acetone-d_6): δ 43.0 (s).

5.6. Crystallographic analyses

The crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer. The unit cell was determined and refined from 15 randomly selected reflections, obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 5. All data processing was performed on a Digital Equipment Corp. Vaxstation 3520 by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures [47a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [47b]. Lorentz/polarization (Lp) and absorption corrections (based on three azimutal psi scans) were applied to the data. Full-matrix least-squares refinements minimized the function: $\Sigma_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Table 5
Selected crystallographic data for complexes **2** and **5**

Compound	**2**	**5**
Formula	$PdF_6P_3OC_{39}H_{53}$	$PdF_6P_2S_2OC_{24}H_{28}$
Formula weight (g mol^{-1})	851.16	678.94
Crystal color	Colorless	Colorless
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Temperature (K)	293	293
a (Å)	11.743(1)	10.720(1)
b (Å)	16.375(2)	13.800(2)
c (Å)	10.8348(9)	10.670(1)
α (°)	92.736(8)	97.69(1)
β (°)	108.162(6)	98.85(1)
γ (°)	85.770(9)	112.582(9)
V (Å^3)	1973.5(3)	1407.6(3)
Z	2	2
$\rho_{Calc.}$ (g cm^{-3})	1.43	1.60
Radiation, λ (Å)	Mo–K$_\alpha$, 0.71069	Mo–K$_\alpha$, 0.71069
μ (mm^{-1})	0.65	0.98
Correction (three psi scans)	(Transmission factors 0.92–1.00)	(Transmission factors 0.86–1.00)
Scan mode	ω	ω
θ Limits (°)	0.0/24.0	0.0/22.5
No. of reflections ($I > 3\sigma(I)$)	5478	3120
No. of variables	452	326
Residuals (R; R_w) [a]	0.033; 0.042	0.041; 0.049
Goodness of fit (GOF) [a]	2.49	3.03
Max. peak in final difference map (e Å^{-3})	0.55	1.01

[a] $R = \Sigma_{hkl}(\|F_{obs}| - |F_{calc}\|)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF^2_{obs}]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Both compounds crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure in both cases. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated, d(C–H) = 0.95 Å, and were included in the structure factor calculations, $B_{iso} = 6.0$ Å^2, without refinement.

5.7. Catalytic experiments

5.7.1. Ethylene oligomerization reactions

The reactions were performed in a stainless-steel reactor (80 ml), equipped with a double jacket for thermoregulation and a magnetic stirring bar. After drying and purging the reactor with ethylene, the complex in the proper solvent mixture was introduced. Temperature and pressure were slowly raised to reach 85°C and 55 bar. The total quantity of ethylene introduced was determined by weight difference of the cylinder. The reactor was isolated and ethylene consumption was monitored by pressure variation on the manometer. After reaction, the reactor was progressively cooled overnight, the gas phase depressurized and analysed by GC (HP 5890, series II) using a capillary PONA column (methylsilicone, 50 m, int. diameter 0.2 mm, film thickness 0.1 μm), an HP 3388 integrator and the following conditions: injection and flame ionization detector 250°C, programed for 0°C during 10 min, then 8°C increase/min until 250°C and this temperature was maintained for 10 min.

5.7.2. Ethylene/CO copolymerization reactions

The copolymerization reactions were carried out in an 80 ml Pyrex glass beaker placed into a stainless-steel autoclave of ca. 100 ml in order to prevent contamination by metallic species. The catalyst was introduced into solution and the autoclave was then pressurized with the mixture of monomers to the required pressure. The reactor was heated to 85°C and the polymerization was carried out isothermally, while maintaining a constant pressure level by a continuous feed of monomers. After 3 h, the autoclave was cooled to room temperature, the residual pressure discharged, and the polymer removed by filtration, washed with methanol, and vacuum dried.

6. Supplementary material

Complete tables of crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, hydrogen atom coordinates, and least-squares planes for complexes **2** and **5**, CCDC nos. 140273 and 140274, respectively, have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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