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PAPER

Room temperature asymmetric Pd-catalyzed methoxycarbonylation of norbornene: highly selective catalysis and HP-NMR studies†

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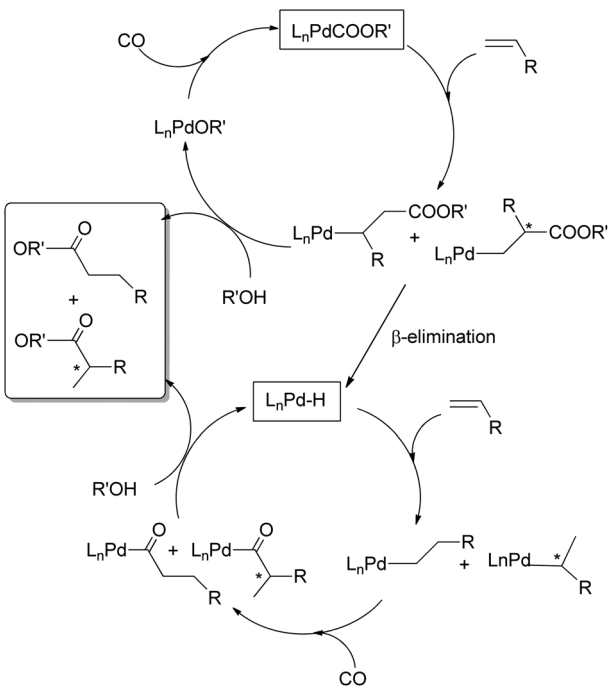
Palladium complexes bearing monodentate and bidentate phosphine ligands (**1–7**) were synthesised and used as catalyst precursors in the methoxycarbonylation of norbornene. The catalytic systems bearing ligands **1**, **3** and **4** afforded excellent conversions (>99%) and selectivity of the ester (>99%). NMR investigations showed that using complex **1a** as the precursor resulted in the protonated phosphine, **1**-H^+, being formed under catalytic conditions and thus the addition of acid is not required for the activation of this system since the reaction involving the precursor with methanol under CO pressure produces 2 equivalents of HCl and leads to the formation of the active species. The protonation of ligand **4** under methoxycarbonylation conditions was also observed and the diprotonated diphosphine was isolated and characterised. This compound was tested as a ligand and acid source in a catalysis and provided excellent conversion and high selectivity to the ester.

Introduction

Carbonylation reactions are among the most important industrial processes in homogeneous transition metal catalysis.[1] In these reactions, a low cost substrate is transformed in the presence of a metal catalyst into valuable compounds and/or intermediates for the fine chemical industry. The Pd-catalysed alkoxycarbonylation of alkenes is a process of interest for both academic and industrial researchers, which produces esters from simple alkenes.[2] In this reaction, excellent results can be achieved with substrates, such as ethene[3] and vinylarenes.[4] However, minor changes in the catalytic system and/or the reaction conditions were reported to greatly affect the selectivity of the catalytic process, usually leading to the formation of a variety of by-products, such as cooligomers, copolymers and ethers.[5] While the formation of the ether is explained by the addition of the alcohol across the alkene under acidic conditions, the copolymerization presents itself as a competing Pd-catalysed reaction that usually takes place under similar reaction conditions to those used in alkoxycarbonylations.

In the Pd-catalysed methoxycarbonylation of alkenes, two mechanisms have been proposed: the Pd–hydride and the Pd–carbomethoxy mechanisms (Scheme 1).[1d,6]



Scheme 1 The proposed mechanisms for the Pd-catalyzed alkoxycarbonylation of alkenes.

The first mechanism starts with the formation of a palladium hydride complex. Subsequent coordination of the substrate, followed by insertion into the Pd–H bond affords a Pd–alkyl complex which is transformed into an acyl complex by the migratory insertion of CO. Finally, methanolysis of the acyl intermediate yields the ester product(s) and regenerates the initial

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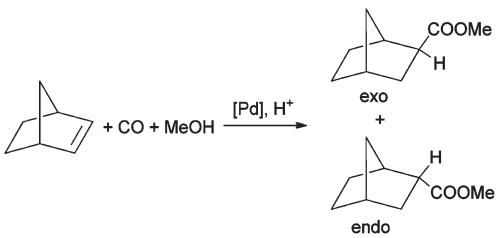
hydride species. The carbomethoxy mechanism starts with a Pd–OMe complex, which, after coordination and migratory insertion of CO, yields the corresponding carbomethoxy complex, Pd–COOMe. Coordination and insertion of the alkene followed by methanolysis yields the product and regenerates the initial catalyst. The production of the Pd–H species from the complexes formed in the carbomethoxy cycle has also been demonstrated to occur through the β-elimination of an unsaturated ester after alkene insertion. It is noteworthy that, in the case of cyclic substrates such as norbornene, this β-elimination process does not occur. Experimental evidence for the hydride mechanism have been reported for systems modified with monodentate and bidentate ligands.[7–10] Zacchini *et al.* observed that [PdH(L–L)(MeOH)X)] complexes (where L–L = 1,2-bis-$(CH_2PBu^t_2)_2C_6H_4$ and X = BF_4^- or $CF_3SO_3^-$) were formed by the reaction of [Pd(L–L)(dba)] with methanol and HBF_4 or CF_3SO_3H in the presence of oxygen or benzoquinone. The hydride complex $[PdH(L–L)(MeOH)]^+$ was shown to be a key intermediate in the catalytic methoxycarbonylation of ethene.[9] However, no mechanistic studies on the methoxycarbonylation of norbornene has been reported to date.

The asymmetric Pd-catalysed methoxycarbonylation of substrates, such as 2-vinyl-6-methoxynaphthalene,[11] 4-methoxystyrene,[12] α-methylstyrene[13] and acenaphthylene,[14] have been extensively studied. However, the alkoxycarbonylation of norbornene has been less well studied[15] (Scheme 2), although its functionalisation is particularly relevant since the product presents unique structural and chemical features and can produce valuable compounds with potential applications in the fragrance industry, such as in Dupical® and in sandalwood.[16] The functionalisation of this olefin generates three chiral carbon centres upon one C–C bond formation. In this process, chemo-, stereo-(*exo*/*endo*) and enantio-selectivity are important issues.[15a,c,d] In 1996, Zhou *et al.* first reported the asymmetric alkoxycarbonylation of norbornene using $Pd(OAc)_2$/DDPPI/*p*-TsOH as a catalytic system and achieved 72% chemoselectivity toward esters and 92% ee under 50 atm of CO at 120 °C (DDPPI = 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol).[15c,d] In 1997, Inoue *et al.* carried out the alkoxycarbonylation of various olefins using the cationic palladium complexes $[Pd(MeCN)_2(PPh_3)_2](BF_4)_2$ as catalysts. When norbornene was used as a substrate, up to 74% chemoselectivity toward esters was achieved.[15b]

In the alkoxycarbonylation reaction, the presence of acid is often required to promote catalytic activity *via* the formation of Pd–hydride species.[17] Under such conditions, neutral palladium complexes of the type $[PdHCl(PPh_3)_2]$ can be formed by oxidative addition of strong acids, such as HCl to Pd(0) complexes, including $[Pd(CO)(PPh_3)_3]$ or $[Pd(PPh_3)_4]$.[18] Related hydride complexes have also been reported with other monodentate phosphines, such as PCy_3 [8] and PBu_3.[19] From an industrial point of view, the use of acid is often an issue due to the corrosion of the reaction vessels. In this context, an interesting catalytic system, namely $PdCl_2$/NMDPP, was reported to afford high activity and excellent selectivities in the methoxycarbonylation of styrene in the absence of acid (NMDPP = neo-menthyl diphenyl phosphine).[11,20] To the best of our knowledge, the reason for which this catalytic system operates in the absence of acid has not been reported.

Recently, we briefly described the catalytic performance of a series of palladium systems bearing monodentate and bidentate phosphine ligands in the methoxycarbonylation of norbornene (Fig. 1).[15a] The effect of the acid was studied in detail and high activity and selectivity were achieved. Herein, we report further investigations into these catalytic systems, including some insights into the reaction mechanism using conventional and high pressure NMR methods.



Scheme 2 Methoxycarbonylation of norbornene catalyzed by palladium.

Results and discussion

Synthesis of the palladium complexes

The palladium complexes, $[PdCl_2(\mathbf{1})_2]$ (**1a**),[21] $[PdCl_2(\mathbf{3})]$ (**3a**),[6c] and $[PdCl_2(\mathbf{5})]$ (**5a**),[22] were synthesised according to previously reported methods. The complex $[PdCl_2(\mathbf{4})]$ (**4a**) was prepared by reaction of $[PdCl_2(COD)]$ in the presence of 1.1 equiv. of bidentate ligand **4** in dichloromethane at room temperature. The complex was isolated after precipitation with diethyl ether as an orange powder that recrystallizes in a mixture of THF–ether as red crystals. Single crystals suitable for X-ray diffraction were obtained from this mixture of solvents. The molecular structure of **4a** is shown in Fig. 2. Selected bond lengths and angles are listed in Table 1. The crystal structure, containing a lattice molecule of THF, shows the Pd atom adopting a distorted square planar coordination geometry. The Pd–Cl(1) and Pd–Cl(2) bond lengths were measured to be 2.3481(17) and 2.3529(17) Å, respectively, while the Pd–P bonds were also found to be comparable in length (2.3331(17) and 2.3206(16) Å for Pd–P(1) and Pd–P(2), respectively). These values are very similar to those previously reported for related Pd(II) dichloride complexes containing other phosphine ligands.[12]

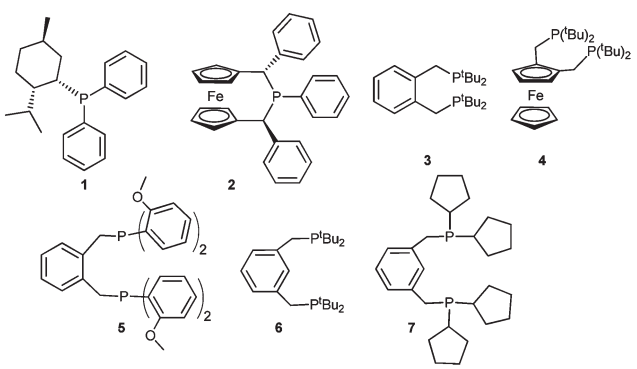


Fig. 1 The ligands used in this study.

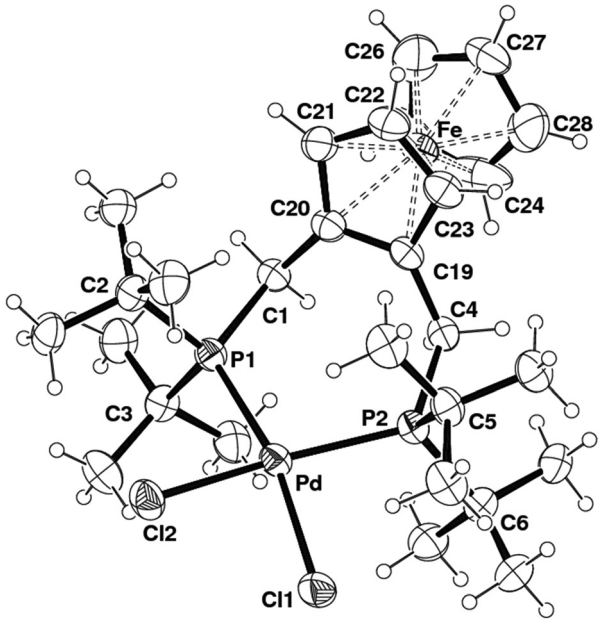


Fig. 2 An ORTEP diagram of complex **4a** (30% probability ellipsoids; solvent molecule omitted for clarity).

Table 1 Selected bond lengths (Å, top) and angles (°, bottom) for **4a**

Pd–P(1)	2.3331(17)	Pd–Cl(1)	2.3481(17)
Pd–P(2)	2.3206(16)	Pd–Cl(2)	2.3529(17)
P(1)–Pd–P(2)	103.95(6)	P(2)–Pd–Cl(1)	87.08(6)
P(1)–Pd–Cl(1)	163.23(6)	P(2)–Pd–Cl(2)	162.48(6)
P(1)–Pd–Cl(2)	88.24(6)	Cl(1)–Pd–Cl(2)	84.12(6)

The bite angle, P(1)–Pd–P(2), of diphosphine **4** when coordinated at the palladium center was 103.95(6)°, while the Cl(1)–Pd–Cl(2) bond angle was found to be narrower at 84.12(6)°, which is likely due to steric constraints.

Catalytic results

Palladium catalyzed methoxycarbonylation of norbornene using the monodentate ligands 1 and 2. Our group recently reported that using the phosphine ligands **1** and **2** (Fig. 1) in the Pd-catalyzed methoxycarbonylation of norbornene resulted in excellent conversions and selectivities at 70 °C. Furthermore, when using ligand **1**, the presence of acid was not required.[15a] Promising enantiomeric excess values and high conversions and selectivities were obtained using ligand **2** in the presence of trifluoroacetic acid. After optimisation of the reaction conditions, these catalytic systems were found to be highly active even at room temperature (Table 2).

When $PdCl_2$/(S)-NMDPP (**1**) was used as a catalytic system at room temperature (RT) without additional acid, total conversion (>99%) was achieved together with an excellent chemo- (>99%) and *exo*- selectivity (>99%) (Table 2, entry 1). However, the enantiomeric excess was low. When the reaction temperature was increased from room temperature to 70 °C, the catalytic results

Table 2 Methoxycarbonylation of norbornene using monodentate phosphine ligands **1** and **2**[a]

Entry	Catalyst	Acid	T (°C)	$C^{b,c}$ (%)	Chemo[b] (%)	% *exo* (ee)
1	$PdCl_2$/**1**	NO	RT	>99	>99	>99(3)
2	$PdCl_2$/**1**	NO	70	>99	>99	>99(9)
3	$[PdCl_2(\mathbf{1})_2]$ (**1a**)	NO	RT	>99	>99	>99(10)
4	$[PdCl_2(\mathbf{1})_2]$ (**1a**)	YES	RT	89	90	>99(10)
5	$[PdCl_2(\mathbf{1})_2]$ (**1a**)	NO	70	>99	>99	>99(11)
6	$PdCl_2$/**2**	YES	RT	25	>99	>99(33)
7	$PdCl_2$/**2**	YES	70	99	90	>99(40)
8	$[PdCl_2(PhCN)_2]$/**2**	YES	RT	14	>99	>99(46)
9	$PdCl_2$/**2**	NO	70	53	25	—

[a] Reaction conditions: Pd (0.021 mmol), TFA (0.210 mmol), norbornene (1.05 mmol), MeOH–THF (1 : 1), 30 bars of CO, 24 h. [b] All conversions and chemoselectivities toward the ester were determined by GC and GC-MS (chemo = chemoselectivity to the ester). [c] C = conversion.

remained unaltered (Table 2, entry 2). When the isolated $[PdCl_2(\mathbf{1})_2]$ (**1a**) system was probed as a catalytic precursor, both room temperature and 70 °C reactions yielded excellent conversions (>99%) (Table 2, entries 3 and 5) together with excellent chemo- (>99%) and *exo*-selectivities (>99%). However, the ee remained low. When this catalytic system was used under acidic conditions at room temperature, both the conversion and chemoselectivity decreased (89% and 90%, respectively); however, the *exo*-selectivity remained excellent (Table 2, entry 4). The addition of acid was thus detrimental and the methanol addition product, 2-methoxybicyclo[2.2.1]heptane, was identified as the by-product under these conditions.

When catalytic systems containing the (*S*,*S*)-ferrocenylphosphine (**2**)[23] ligand were used at room temperature in the presence of trifluoroacetic acid, excellent chemo- and *exo*-selectivities were achieved (Table 2, entries 6 and 8). It is noteworthy that when $[PdCl_2(PhCN)_2]$ was used as a precursor at room temperature, the enantioselectivity increased to 46% (Table 2, entry 8). However, the conversions were low under these conditions (25 and 14%). A significant increase in conversion (up to 99%) was observed when the temperature was increased to 70 °C. At this temperature, the *exo*-selectivity remained unchanged although the chemoselectivity and ee decreased to 90% and 40%, respectively (Table 2, entry 7). In the absence of any acid, both the conversion and the chemoselectivity of the reaction were drastically affected (Table 2, entry 9).

In view of the results obtained with $[PdCl_2(\mathbf{1})_2]$ (**1a**), in terms of the conversion and selectivity, larger substrate concentrations (from 50 to 1000 equiv./Pd) were used. The results are summarized in Table 3. Excellent conversion (>99%), chemo- (>99%) and *exo*-selectivities (>99%) were observed in the presence of 50 and 100 equiv. of norbornene (Table 3, entries 1 and 2). However, when the ratio of NBN : Pd was increased to 200, a decrease in chemoselectivity (71%) was observed, although both the conversion (>99%) and *exo*-selectivity remained excellent (>99%) (Table 3, entry 3). When the ratio of NBN : Pd was increased from 200 to 500 and 1000, a significant decrease in both conversion and chemoselectivity was observed (Table 3, entries 4 and 5). In all cases, co-oligomers were detected as the

Table 3 The effect of the norbornene concentration using complex **1a** in the palladium-catalyzed methoxycarbonylation of norbornene[a]

Entry	Catalyst	NBN (equiv.)	$C^{b,c}$ (%)	Chemo[b,c] (%)	% *exo* (ee)
1	[$PdCl_2$(**1**)$_2$](**1a**)	50	>99	>99	>99 (10)
2	[$PdCl_2$(**1**)$_2$](**1a**)	100	>99	>99	>99(6)
3	[$PdCl_2$(**1**)$_2$](**1a**)	200	>99	71	>99(7)
4	[$PdCl_2$(**1**)$_2$](**1a**)	500	42	40	>99(8)
5	[$PdCl_2$(**1**)$_2$](**1a**)	1000	23	26	>99(11)

[a] Reaction conditions: Pd (0.021 mmol), MeOH–THF (1 : 1), 30 bars of CO, RT, 24 h. [b] All conversions and chemoselectivities toward the ester were determined by GC and GC-MS. [c] *C* = conversion; Chemo = selectivity to the ester.

by-products of the reaction. Although the decrease in the conversion as a function of the norbornene concentration was predictable, the lower chemoselectivity observed in these experiments was unexpected. These results could be explained by an increase in the rate of substrate insertion into the Pd–C bond of the expected Pd–acyl intermediate when compared to the rate of the methanolysis step of the same species, thus forming oligomerisation products in preference to the esters.

Pd-catalyzed methoxycarbonylation of norbornene using the bidentate ligands 3–7. The $PdCl_2$/**3–7** *in situ* catalytic systems were tested in the palladium-catalyzed methoxycarbonylation of norbornene. The catalytic reactions were optimised and the results compared to those of the corresponding isolated complexes. The reactions were carried out at room temperature and 70 °C in the presence of acid and under 30 bar of CO during a period of 24 hours. The results are summarised in Table 4.

When the *in situ* $PdCl_2$/**3** system (Table 4, entry 1) was tested at room temperature, 19% conversion was obtained together with excellent chemo- (>99%) and stereoselectivities (>99%). However, when the reaction temperature was increased to 70 °C, a higher conversion was obtained (91%) (Table 4, entry 2). The chemo- and stereoselectivities were not affected by the reaction temperature. Similar behaviour was observed when the isolated complex, [$PdCl_2$(**3**)] (**3a**), was used as a precursor (Table 4, entries 3 and 4). When the *in situ* $PdCl_2$/**4** system was used at 70 °C, high conversion (75%) with excellent chemo- (>99%) and *exo*-selectivities (>99%) were obtained (Table 4, entry 5). However, when the reaction was performed at room temperature no conversion was observed (Table 4, entry 6). In contrast, when the isolated complex, [$PdCl_2$(**4**)] (**4a**), was used as a precursor, total conversion (99%) was achieved at both temperatures (Table 4, entries 7 and 8). This indicated that, under *in situ* conditions at room temperature, no active species were formed, while such species were efficiently formed from [$PdCl_2$(**4**)] (Table 4, entries 6 *vs.* 7).

When the *in situ* system containing ligand **5** was tested at 70 °C, the conversion was very poor (14%) and the chemoselectivity was only moderate (Table 4, entry 9). When the corresponding isolated palladium complex was tested, a higher conversion was obtained although the chemoselectivity to the ester slightly decreased (Table 4, entry 10). No catalytic activity was observed at room temperature with systems bearing this ligand. We previously reported that very low catalytic activity

Table 4 Palladium complexes bearing bidentate ligands (**3–7**) as catalyst precursors in the methoxycarbonylation of norbornene[a]

Entry	Precursor	*T* (°C)	$C^{b,c}$ (%)	Chemo[b] (%)	% *exo*
1	$PdCl_2$/**3**	RT	19	>99	>99
2	$PdCl_2$/**3**	70	91	>99	>99
3	[$PdCl_2$(**3**)] (**3a**)	RT	42	>99	>99
4	[$PdCl_2$(**3**)] (**3a**)	70	99	>99	>99
5	$PdCl_2$/**4**	70	75	>99	>99
6	$PdCl_2$/**4**	RT	0	—	—
7	[$PdCl_2$(**4**)] (**4a**)	RT	99	>99	>99
8	[$PdCl_2$(**4**)] (**4a**)	70	99	>99	>99
9	$PdCl_2$/**5**	70	14	89	>99
10	[$PdCl_2$(**5**)]	70	56	69	>99
11	$PdCl_2$/**6**	70	<5	<5	—
12	$PdCl_2$/**7**	70	<5	<5	—

[a] Reaction conditions: Pd (0.021 mmol), TFA (0.210 mmol), norbornene (1.05 mmol), MeOH–THF(1 : 1), 30 bars of CO, 24 h. [b] All conversions and chemoselectivities towards the ester were determined by GC and GC-MS. [c] *C* = conversion, Chemo = selectivity to the ester.

(<5%) was observed in this reaction using the *in situ* systems $PdCl_2$/**6–7** at 70 °C (Table 4, entries 11–12). To check whether the formation of the catalysts could explain these results, attempts to isolate the palladium dichloride complex, [$PdCl_2$(**7**)], by reaction of [$PdCl_2$(COD)] or [$PdCl_2$($PhCN)_2$] in the presence of the ligand were completed but the expected complex was not obtained. Instead, the formation of the palladium(II) pincer complex, **7a**, was observed and this species was characterized by multinuclear NMR spectroscopy, elemental analysis and X-ray diffraction.

Surprisingly, the molecular structure of complex **7a** showed the coordination of a bromide ligand to the palladium centre. To understand the origin of the presence of this ligand, several experiments were completed and electrospray mass spectroscopic analysis revealed that ligand **7**, which was purchased from a commercial source, was contaminated with one equivalent of HBr per ligand. It was thus concluded that the contamination of this reagent with HBr was responsible for the coordination of a bromide ligand in the palladium complex, **7a**. The molecular structure of **7a** is shown in Fig. 3 and a selection of bond lengths and angles are shown in Table 5.

The coordination sphere around the palladium atom was found to correspond to a distorted square-planar geometry, with P(1)–Pd–P(2) and C(12)–Pd–Br bond angles of 166.84(4) and 178.00(12)°, respectively, and *cis*-angles in the range of 83.33(12) to 97.06(3)°. The Pd–Br and Pd–C were found to be 2.5152(7) and 2.034(4) Å, respectively, whereas Pd–P bond lengths were closely comparable (mean 2.282 Å) and similar to those observed in the analogous [$PdBr(C_6H_3$-2,6-$CH_2PCy_2)_2$][24] and [$PdBr(C_6H_3$-2,6-$CH_2PPh_2)_2$] complexes.[25] All these values agree with those reported for similar palladium(II) pincer complexes.[24,25]

When complex **7a** was tested in the methoxycarbonylation reaction, no catalytic activity was observed. It was therefore concluded that the formation of this inactive species was occurring when the *in situ* system was used, thus explaining the lack of catalytic activity when systems containing ligands **6** and **7** were utilized. To ensure that the HBr impurity did not have an influence on the catalytic results, ligand **7** was purified by treatment with

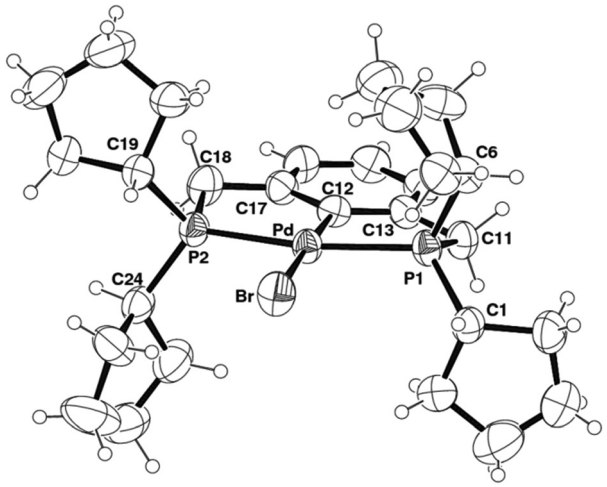


Fig. 3 An ORTEP diagram (30% probability of ellipsoids) of complex **7a**.

Table 5 Selected bond lengths (Å, top) and angles (°, bottom) for complex **7a**

Pd–P(1)	2.2828(12)	Pd–C(12)	2.034(4)
Pd–P(2)	2.2823(12)	Pd–Br	2.5152(7)
P(1)–Pd–P(2)	166.84(4)	C(12)–Pd–Br	178.00(12)
P(1)–Pd–C(12)	83.33(12)	P(1)–Pd–Br	95.74(3)
P(2)–Pd–C(12)	83.97(13)	P(2)–Pd–Br	97.06(3)

NEt_3 and used in the methoxycarbonylation of norbornene under the conditions previously described (Table 4). However, no conversion was again observed, showing that the presence of HBr did not influence the catalytic behaviour of this system under these conditions. When the synthesis of $PdCl_2$(**7**) was attempted using the purified ligand **7**, the $^{31}P\{^1H\}$ spectrum of the resulting species showed a singlet signal at δ 52.7 ppm, which was very similar to the signal observed for the pincer complex, **7a**, (δ 52.1). Very similar NMR features were previously reported for analogous Pd bromide and chloride pincer complexes.[26] It was therefore concluded that the analogue pincer complex containing a chloride ligand was formed.

Next, the variation of the substrate concentration was studied in the palladium-catalyzed methoxycarbonylation of norbornene with complex [$PdCl_2$(**4**)] (**4a**) as a catalyst precursor. The results are listed in Table 6.

When the catalytic reaction was carried out in the presence of 50 equiv. norbornene, an excellent conversion (99%) and chemo- (>99%) and stereoselectivities (>99% *exo*) were obtained (Table 6, entry 1). Identical results were achieved when the ratio of NBN : Pd was increased from 50 to 100 (Table 6, entry 2). However, when the ratio of NBN : Pd was increased from 100 to 200, the conversion drastically decreased (23%), although both the chemo- and stereoselectivity remained excellent (Table 6, entry 3). When the ratio of NBN : Pd was 500, practically no catalytic activity was observed (<5%) (Table 6, entry 4). Such a striking drop in the conversion was unexpected and could be due to the formation of inactive Pd species in the presence of a large excess of NBN, thus deactivating the catalyst.

Table 6 The effect of the norbornene concentration using complex **4a** in the Pd-catalyzed methoxycarbonylation reaction[a]

Entry	NBN (equiv.)	$C^{b,c}$ (%)	Chemo[b,c] (%)	% *exo*(ee)
1	50	99	>99	>99/—
2	100	99	>99	>99/—
3	200	23	>99	>99/—
4	500	<5	nd	nd

[a] Reaction conditions: [$PdCl_2$(**4**)] (0.021 mmol), TFA (0.210 mmol), MeOH–THF 5 ml (1 : 1), 30 bars of CO, RT. nd = not determined. [b] All conversions and chemoselectivities towards the ester were determined by GC and GC-MS. [c] *C* = conversion; Chemo = selectivity to the ester.

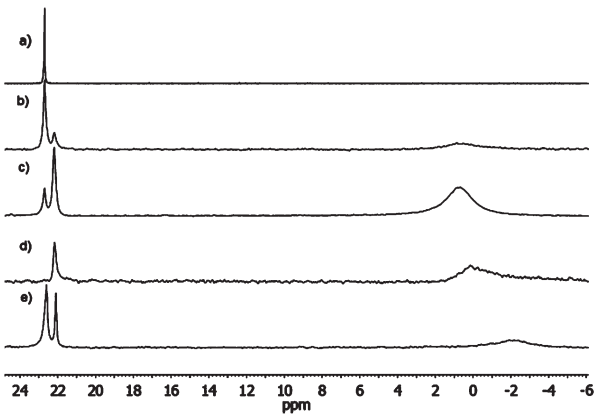


Fig. 4 The reaction sequence by $^{31}P\{^1H\}$ NMR spectroscopy at RT. (a) **1a** in CD_3OD–THF, (b) **1a** + 10 equiv. NBN + 30 atm CO in CD_3OD–THF after 5 h shaking and (c) after 4 days (d) after one week and (e) after releasing the CO pressure.

High pressure NMR (HP-NMR) studies

Reactivity of complex 1a under methoxycarbonylation conditions. To gain an insight into the activity of the palladium catalytic system containing monophosphine **1** in the absence of additional acid, the reactivity of this system in the presence of MeOH, CO and norbornene was studied by HP-NMR spectroscopy.

First, complex **1a** was reacted in the presence of all the reagents: norbornene (10 equiv.) and carbon monoxide (30 atm) in a solvent mixture of CD_3OD–THF. A 10 mm HP-NMR sapphire tube was therefore charged with a solution of complex [$PdCl_2$(**1**)$_2$] (**1a**) in a mixture of CD_3OD–THF (ratio 1 : 1 by volume). An initial $^{31}P\{^1H\}$ NMR spectrum was acquired at room temperature before pressurizing with CO. In the spectrum, a signal with singlet multiplicity at δ 22.7 corresponding to the starting material, [$PdCl_2$(**1**)$_2$] **1a**, was readily detected (Fig. 4a). When norbornene (10 equiv.) was added and the tube was charged with 30 atm of CO, the $^{31}P\{^1H\}$ NMR spectrum acquired at room temperature showed the presence of two new signals: a singlet resonance at δ 22.1 and a broad singlet at δ 0.79 (Fig. 4b). The starting material, **1a**, was also detected. At longer reaction times, the disappearance of the signal corresponding to the starting material, **1a**, and an increase in the intensity of the new signals at δ 22.1 and 0.79 was observed

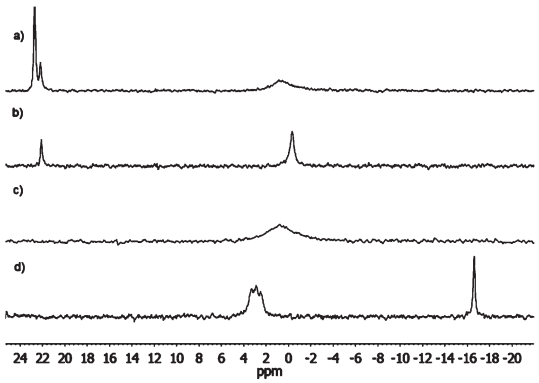


Fig. 5 The reaction sequence by $^{31}P\{^{1}H\}$ NMR spectroscopy of **1a** in CD_3OD–THF + 30 atm CO at variable temperatures: (a) at RT, (b) after 45 min at 343 K, (c) after 2 h at 373 K and (d) at 183 K.

(Fig. 4c and d). When the CO pressure was released and a new $^{31}P\{^{1}H\}$ NMR spectrum was acquired at room temperature, the signal corresponding to **1a** was again detected (Fig. 4e), indicating a reversible process involving CO.

When the experiment was repeated using ^{13}CO, two signals were detected at δ 177 and 185 in the corresponding $^{13}C\{^{1}H\}$ NMR spectra at room temperature. These signals were readily assigned to the ester product and free CO, respectively. No other signals could be detected in the carbonyl region of the spectrum at that stage.

When complex **1a** was placed under 30 atm of carbon monoxide in CD_3OD–THF at room temperature, the same three signals were detected by ^{31}P NMR spectroscopy (Fig. 5a), demonstrating that the formation of the corresponding species did not involve norbornene. After heating the sample to 343 K over 45 min, the signal corresponding to **1a** was not detected, indicating total conversion of the starting complex (Fig. 5b). When the sample was heated at 373 K, only the broad singlet at δ 0.79 was detected at this temperature (Fig. 5c). However, when this reaction mixture was cooled to room temperature, the signal at δ 0.79 resolved into two distinct resonances at δ 2.9 and −16.5 (Fig. 5d). The latter signal was readily assigned to the free ligand, **1**. The former signal resolved as a pseudo triplet (1 : 1 : 1) with J = 72 Hz, suggesting a direct P–D coupling.

To check whether this signal arose from the deuterated phosphine **1**-D^+, the stability of the free ligand, **1**, in MeOD was investigated. However, no reaction was observed even when the mixture was heated to 343 K over 24 h.

Previous reports have described the protonation of phosphine ligands under methoxycarbonylation conditions.[6,10] However, the protonation of the phosphine ligands usually occurs by reaction of the ligand with an excess of acid used to produce the active species from the Pd precursors. In this system, no additional acid was used. The detection of such a species therefore implied the *in situ* generation of acid from the catalytic mixture. To investigate whether the acid produced involved the metallic precursor, various palladium complexes were investigated as precursors (Table 7).

As previously mentioned, when $PdCl_2$/**1** was used as a catalytic system, excellent conversions and chemo- and *exo*-selectivities were obtained in the absence of any acid (Table 7, entry 1).

Table 7 The effect of the palladium precursor using ligand **1** in the palladium-catalyzed methoxycarbonylation of norbornene[a]

Entry	Catalyst	HCl (1 equiv.)	$C^{b,c}$ (%)	Chemo[b] (%)	% *exo*(ee)
1	$[PdCl_2)]$/**1**	NO	98	>99	>99(10)
2	$[Pd_2(dba)_3]$/**1**	NO	0	0	0
3	$[Pd_2(dba)_3]$/**1**	YES	65	>99	>99(7)
4	$Pd(OAc)_2$/**1**	NO	0	0	0
5	$Pd(OAc)_2$/**1**	YES	>99	>99	>99(9)

[a] Reaction conditions: Pd (0.021 mmol), L/Pd: 2, MeOH–THF (1 : 1), 30 bars of CO, 70 °C, 24 h. [b] All conversions and chemoselectivities towards the ester were determined by GC and GC-MS. [c] C = conversion, Chemo = selectivity to the ester.

However, when $[Pd_2(dba)_3]$ (entry 2) and $[Pd(OAc)_2]$ (entry 4) were tested in the presence of ligand **1** without any acid, no conversion was observed. These results suggests that palladium dichloride plays a crucial role in the activity and selectivity of the reaction. To corroborate this observation, we carried out the catalytic reaction using a $[Pd_2(dba)_3]$/**1** system in the presence of HCl (1 equiv.). A moderate conversion (65%) together with excellent chemo- and *exo*-selectivities (>99%) were achieved (Table 7, entry 3). Similarly, an excellent conversion (>99%) together with excellent chemo- (>99%) and *exo*-selectivities (>99%) were also obtained when $Pd(OAc)_2$/**1**/HCl (1 equiv.) (Table 7, entry 5) was used as a catalytic system.

The striking similarity of the results obtained using a Pd precursor containing chloride ligands without additional acid and those achieved using a chloride-free precursor in the presence of 1 equiv. of HCl clearly indicated that this acid could be generated *in situ* during catalysis.

In order to corroborate this hypothesis, the reactivity of ligand **1** in the presence of HCl was investigated by NMR spectroscopy.

A sample of ligand **1** was thus dissolved in a mixture MeOH–THF and the solution charged into a 5 mm NMR tube fitted with a Young's tap. In the corresponding $^{31}P\{^{1}H\}$ NMR spectrum, the expected singlet signal at δ −16.5 was readily detected (Fig. 6a). At this point, 1 equiv. of HCl was then added and a new $^{31}P\{^{1}H\}$ NMR spectrum was acquired. The signal corresponding to the free ligand was no longer present in the spectrum and only the previously detected signal at δ 0.79 was observed (Fig. 6b). At 183 K, however, the signal for the free ligand was again detected and the two signals at δ 2.9 and −16.5 (Fig. 6c) were observed as broad resonances.

When a ^{1}H coupled ^{31}P NMR spectrum was acquired at this temperature, the ^{31}P signal resonating at δ 0.79 exhibited a doublet multiplicity (Fig. 6d) characteristic of a direct P–H coupling ($^{1}J_{P-H}$ = 506 Hz).[27,28]

Attempts to isolate the protonated phosphine by evaporation of the solvent under reduced pressure failed to produce the protonated phosphine, as ligand **1** was the only product obtained each time. This indicated that an equilibrium between ligand **1** and its protonated form, **1**-H^+, was taking place.

The species detected under CO pressure was therefore identified as the protonated phosphine, **1**-H^+, in equilibrium with monophosphine **1** (Scheme 3). The detection of species **1**-H^+ under methoxycarbonylation conditions can be explained by the

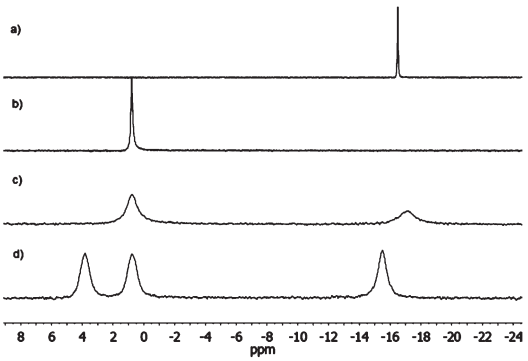
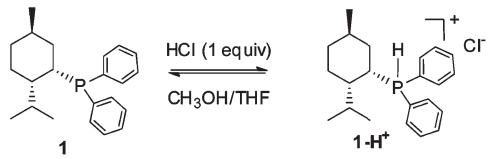


Fig. 6 The reaction sequence by $^{31}P\{^{1}H\}$ NMR spectroscopy of **1** in MeOH–THF: (a) at RT, (b) + 1 equiv. HCl at RT, (c) + 1 equiv. HCl at 183 K and (d) ^{1}H-coupled ^{31}P NMR spectrum of **1** + 1 equiv. HCl at 183 K.

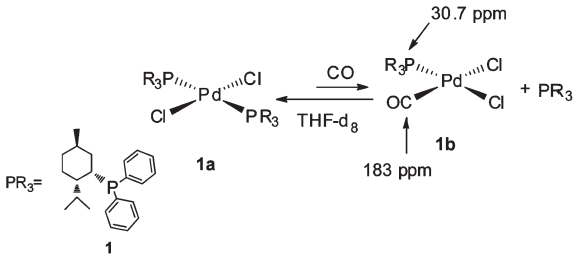


Scheme 3 The reaction of ligand **1** in the presence of HCl (1 equiv.) in MeOH–THF.

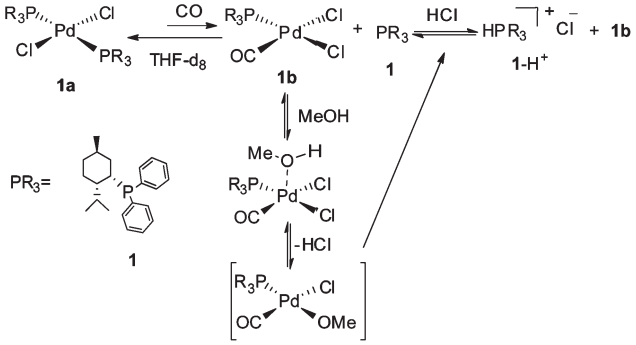
in situ production of HCl from the $PdCl_2$ precursor, which reacts with the free phosphine present in solution.

As previously mentioned, when the reaction of complex **1a** in the presence of norbornene and carbon monoxide (30 atm) was performed in CD_3OD–THF, no carbonyl containing species could be detected. The rapid reaction of such species in the presence of methanol could explain this result. To confirm this hypothesis, the reaction was repeated in neat THF-d_8.

A solution of precursor **1a** in a mixture of THF-d_8 was prepared and placed in a 10 mm high pressure (HP)-NMR tube. After pressurizing the tube with 30 atm of CO enriched with ^{13}CO, a $^{31}P\{^{1}H\}$ NMR spectrum was acquired at room temperature and the signal at δ 22.7 corresponding to the starting material, **1a**, was readily detected. Under these conditions, no other signals were observed. However, at longer reaction times, a new singlet signal was detected at δ 30.7. The detection of this signal indicates that **1a** was reacting under these conditions. When the temperature was decreased to 193 K, the same signals were observed, together with a broad resonance at δ −16.5, which was readily assigned to the free ligand, **1**. The detection of free ligand **1** in solution suggested that a substitution reaction had taken place. In the corresponding $^{13}C\{^{1}H\}$ NMR spectrum acquired at room temperature, two signals were detected in the carbonyl region of the spectrum at δ 185 and 183. The former singlet signal was readily assigned to free CO. The latter signal was detected as a broad singlet and was attributed to a carbonyl ligand coordinated to palladium. The presence of the new ^{31}P signals at δ 30.7 suggested that the Pd–CO species contained a phosphorus ligand. Furthermore, the broad singlet multiplicity of the ^{13}C signal suggested the *cis* arrangement of the CO and phosphine ligand.



Scheme 4 Proposed structure for the complex $[PdCl_2(\mathbf{1})(CO)]$ **1b**.



Scheme 5 The proposed mechanism for the formation of **1**-H^+.

When the CO pressure was released from the NMR tube and a new spectrum was acquired. The signal at δ 30.7 was not detected, suggesting that the reaction of **1a** in the presence of CO to form the new product was reversible. This species was identified as the complex $[PdCl_2(\mathbf{1})(CO)]$ **1b** (Scheme 4).

Interestingly, the protonation of the phosphine was not observed when the reaction was carried out in the absence of methanol. The *in situ* generation of HCl was previously reported by the reaction of a Pd complex containing chloride ligands in methanol.[29] We concluded that similar reactivity was taking place in the presence of MeOH from the previously identified species $[PdCl_2(\mathbf{1})(CO)]$ **1b**, which is generated from complex **1a** under CO. A mechanism matching our observations in this study is proposed in Scheme 5.

Such a formation of HCl from a Pd chloride species and an alcohol has previously been described during the Wacker process.[30]

Reactivity of complex 4a under methoxycarbonylation conditions. A 10 mm HP-NMR sapphire tube was charged with a solution of complex **4a** in CD_3OD–THF and a $^{31}P\{^{1}H\}$ spectrum was acquired (Fig. 7a). The signal corresponding to the starting material, **4a**, at δ 44.0 was readily detected. Two broad signals with low intensity at δ 19.1 and 37.7 were also detected at this stage. The corresponding species could not be identified unambiguously. At this point, 10 equiv. of TFA, 50 equiv. of norbornene and 30 atm of CO were added and the reaction was monitored by ^{31}P NMR spectroscopy. In the first $^{31}P\{^{1}H\}$ NMR spectrum at room temperature (Fig. 7b), two signals at δ 36.9 and 38.1 with complex multiplicity suggesting the formation of species containing a direct P–D coupling were detected (Fig. 7b). A broad resonance at 46.1 and a singlet resonance at δ 53.1 (major species) were also observed.

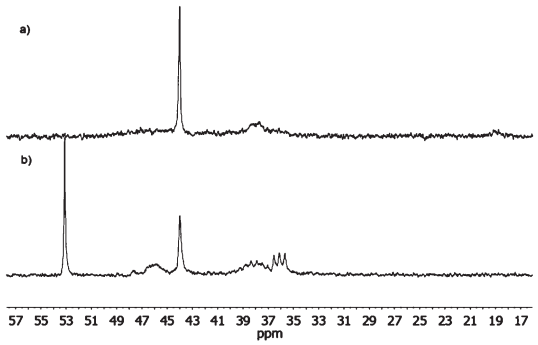


Fig. 7 The reaction sequence by $^{31}P\{^{1}H\}$ NMR spectroscopy. (a) **4a** in CD_3OD–THF at RT, (b) **4a** + 10 equiv. TFA + 50 equiv. NBN + 30 atm of CO in CD_3OD–THF at RT.

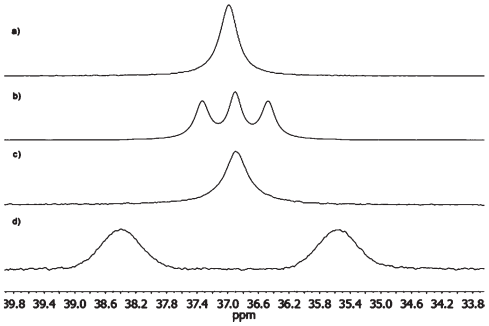


Fig. 8 The reaction sequence by $^{31}P\{^{1}H\}$ NMR spectroscopy. (a) Ligand **4** + 10 equiv. TFA in CD_3OD–THF at RT, (b) **4** + 10 equiv. TFA in CD_3OD–THF at 213 K, (c) **4** + 10 equiv. TFA in CD_2Cl_2 at RT and (d) an ^{1}H-coupled ^{31}P NMR spectrum of **4** + 10 equiv. TFA in CD_2Cl_2 at 193 K.

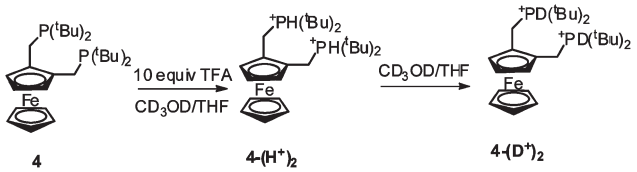
When the experiment was repeated using ^{13}CO, in the corresponding $^{13}C\{^{1}H\}$ NMR spectrum at room temperature, two singlet resonances were detected at δ 185 and 177. The former signal was readily assigned to free CO. This signal appeared as a broad singlet suggesting some fluxional behaviour. The latter signal corresponds to the ester product indicating that the methoxycarbonylation reaction was taking place under these conditions. No other carbonyl species were detected at this stage.

In order to identify the corresponding signals observed during this experiment, the reactivity of complex **4a** was investigated in a step-wise manner with regards to TFA, CO and norbornene.

A solution of complex **4a** in CD_3OD–THF was prepared and transferred to a 5 mm NMR tube and TFA (10 equiv.) was added. A $^{31}P\{^{1}H\}$ NMR spectrum was acquired and the signal at δ 44.0, corresponding to the starting material **4a**, was readily detected. Under these conditions, the previously detected singlet resonance at δ 36.9 was observed with a high intensity, indicating that this signal arose from the reaction of complex **4a** or ligand **4** in the presence of TFA.

To corroborate this hypothesis, a sample of ligand **4** was dissolved in a CD_3OD–THF mixture (ratio 1 : 1 by volume) and charged into a 5 mm NMR tube fitted with a Young's tap. When a $^{31}P\{^{1}H\}$ NMR spectrum was acquired, one singlet resonance at δ 22.8, which can be readily assigned to free ligand **4**, was detected. When TFA (10 equiv.) was added, the singlet signal at δ 36.9 was observed as the only signal at room temperature (Fig. 8a). When a $^{31}P\{^{1}H\}$ NMR spectrum was acquired at 193 K, this signal appeared as a pseudo triplet with a 1 : 1 : 1 intensity pattern (Fig. 8b). The multiplicity of this signal indicates the formation of a species containing deuterium with a P–D bond (J_{P-D} = 69 Hz), suggesting that H/D exchange had taken place.

The experiment was then repeated in a CH_3OH–THF mixture and, after evaporation of the solvent, the residue was re-dissolved in CD_2Cl_2. In the $^{31}P\{^{1}H\}$ NMR spectrum at 193 K, the signal at δ 36.9 was detected as a single resonance (Fig. 8c). When the ^{1}H-coupled ^{31}P NMR spectrum was acquired at 193 K, this peak exhibited a doublet multiplicity J_{P-H} = 460 Hz (Fig. 8d), which is characteristic of a compound containing a P–H moiety. The species corresponding to this signal was therefore identified as the diprotonated diphosphine $[Fe(\eta^5\text{-}C_5H_5)\text{-}(\eta^5\text{-}C_5H_3)\text{-}(^{+}H(^{t}Bu_2)_2P)_2]$ **4**-$(H^{+})_2$ (Scheme 6).

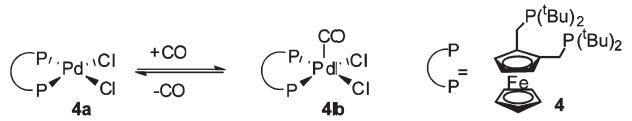


Scheme 6 The reactivity of ligand **4** in the presence of TFA in CD_3OD–THF.

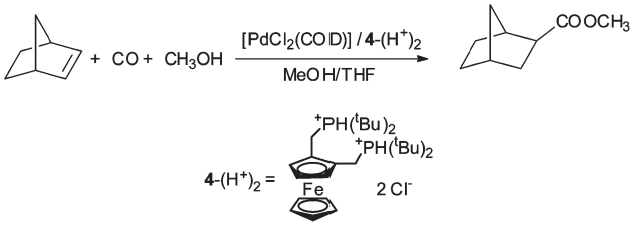
These experiments showed that the previously observed resonance at δ 36.9 was arising from the reaction product of ligand **4** and TFA, namely the diprotonated species, **4**-$(H^{+})_2$.

When complex **4a** was placed under 30 atm of CO in the presence of TFA (10 equiv.) in CD_3OD–THF at room temperature, the previously observed signals at δ 46.1 (a broad multiplet), 44.0 (complex **4a**), 38.1 (a broad multiplet) and 36.9 (diprotonated phosphine, **4**-$(H^{+})_2$) were detected in the corresponding $^{31}P\{^{1}H\}$NMR spectrum. The resonance at δ 53.1 (s) was also observed at this point, suggesting that the corresponding species was formed in the presence of CO. When the CO pressure was removed, the signal at δ 53.1 (s) was not observed anymore. This indicated that the formation of this species involved a reversible reaction with CO. When the experiment was repeated using ^{13}C-enriched CO, in the corresponding $^{13}C\{^{1}H\}$NMR spectrum recorded at 213 K, only the singlet resonance for free CO was detected at δ 185. The broadness of the signal suggested a fluxional behaviour that could be explained by the reversible formation of species **4b** containing a CO ligand rapidly exchanging with free CO (Scheme 7).

As previously mentioned, when the reactivity of complex **4a** under methoxycarbonylation conditions was studied in CD_3OD–THF, the formation of the diprotonated phosphine, **4**-$(H^{+})_2$, was evidenced. Interestingly, it was observed that the intensity of the signal corresponding to this species decreasing during the experiment, which suggested that this species may react during the catalytic reaction. To confirm this hypothesis, species **4**-$(H^{+})_2$ was tested as an acid and ligand source in the Pd-methoxycarbonylation of norbornene using $[PdCl_2(COD)]$ and $[Pd(OAc)_2]$ as palladium precursors with 30 bars of CO pressure at room temperature over 24 hours (Scheme 8). The catalytic results suggested



Scheme 7 The proposed structure for species **4b**.



Scheme 8 Pd-catalysed methoxycarbonylation of norbornene using the $[PdCl_2(COD)]$/**4**-$(H^+)_2$ system as a catalytic precursor.

total conversion (>99%) and high chemoselectivity (85%) when $[PdCl_2(COD)]$ was used as a precursor. Interestingly, when $[Pd(OAc)_2]$ was used as a Pd precursor, no conversion was obtained, indicating that the presence of chloride in the solution is crucial to obtain catalytic activity with this system.

When the catalytic reaction was performed using complex **4a** in the presence of only 2 equiv. of TFA, identical results for the conversion (>99%) and similar results in terms of the chemoselectivity (>99%) to those achieved with the $[PdCl_2(COD)]$/diprotonated diphosphine catalytic system were obtained. In view of these results, the reactivity of the Pd precursor in the presence of **4**-$(H^+)_2$ was investigated by NMR spectroscopy.

First, the stability of the diprotonated diphosphine, **4**-$(H^+)_2$, in CH_3OH–THF-d_8 was examined. A solution of the diprotonated diphosphine, **4**-$(H^+)_2$, in CH_3OH–THF-d_8 was charged into a 5 mm NMR tube fitted with a Young's tap. The broad singlet at δ 36.9 corresponding to the starting material, **4**-$(H^+)_2$, was readily detected in the corresponding ^1H and $^{31}P\{^1H\}$NMR spectra acquired at room temperature. After several hours at this temperature, no new signals were observed, indicating that compound **4**-$(H^+)_2$ was stable under these conditions.

Then, in a 5 mm NMR tube fitted with a Young's tap, a solution of the diprotonated diphosphine, **4**-$(H^+)_2$, and $[PdCl_2(COD)]$ (1 equiv.) in CH_3OH–THF-d_8 was prepared at 213 K and the reaction was monitored by ^1H and ^{31}P NMR spectroscopy in a pre-cooled spectrometer at 213 K. In the first $^{31}P\{^1H\}$ NMR spectrum, the resonance at δ 36.9, which corresponds to the diprotonated diphosphine **4**-$(H^+)_2$ (Fig. 9a), was the only signal detected at this stage. When the temperature of the sample was increased to room temperature, the solution rapidly darkened and several resonances attributed to decomposition products were observed by NMR spectroscopy.

The experiment was therefore repeated at a low temperature. At 233 K, two new signals were observed at δ 34.0 and 41.2 as two mutually coupled doublets (dd, $^2J_{P-P}$ = 18 Hz) (Fig. 9b). In the corresponding ^1H NMR spectrum, a hydride signal was detected as a doublet of doublets at δ −11.0 (dd, $^2J_P{}^a{}_{-H}$ = 19 Hz and $^2J_P{}^b{}_{-H}$ = 193 Hz) (Fig. 10).

The coupling pattern of this signal clearly indicates that the corresponding hydride complex contained two inequivalent

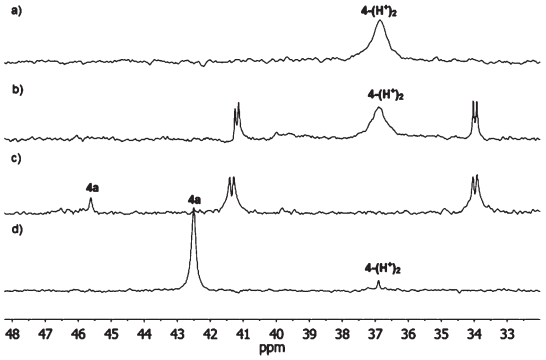


Fig. 9 The reaction sequence by $^{31}P\{^1H\}$NMR spectroscopy. The reactivity of diprotonated diphosphine **4**-$(H^+)_2$ and $[PdCl_2(COD)]$ in CH_3OH–THF-d_8. (a) The initial spectrum at 213 K, (b) at 233 K after a few minutes, (c) at 253 K after a few minutes, and (d) the spectrum after increasing the temperature to RT.

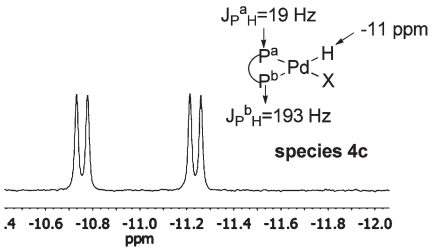


Fig. 10 The hydride region of the ^1H NMR spectrum of a solution of diprotonated diphosphine **4**-$(H^+)_2$ and $[PdCl_2(COD)]$ in CH_3OH–THF-d_8 at 233K.

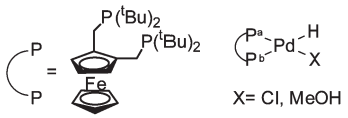


Fig. 11 The proposed structure of species **4c**.

phosphorus centres. The values of these coupling constants are characteristic of *trans* ($^2J_P{}^b{}_{-H}$ = 193 Hz) and *cis* ($^2J_P{}^a{}_{-H}$ = 19 Hz) couplings. The corresponding species was therefore identified as the diphosphine Pd hydride species **4c** (Fig. 11).

No information on the nature of the remaining X ligand could be obtained by NMR techniques at this point. Interestingly, in the ^1H spectrum, a singlet resonance at δ 4.5 was also observed and attributed to H_2.

The sample was then slowly heated to 253 K and a new $^{31}P\{^1H\}$ NMR spectrum was acquired. At this temperature, the signals at δ 34.0 and 41.2 (dd, $^2J_{P-P}$ = 18 Hz) were detected together with a singlet signal at δ 45.6. This signal was attributed to complex **4a**, although the formation of an intermediate species can not be discarded. All the signals remained unchanged at this temperature (Fig. 9c). However, the signal of the diprotonated phosphine, **4**-$(H^+)_2$, was not detected at this point. When the sample was slowly heated to room temperature, the signals for the species, **4c**, were not detected, which is in agreement with the previous results. At this temperature, signals for **4a** and **4**-$(H^+)_2$ were readily detected (Fig. 9d).

In order to gain more information about the other unknown X ligand in complex **4c**, the hydride species [PdH(MeOH)(**4**)][TfO] was synthesised according to a previously reported procedure[6b] and its NMR features were compared to those of **4c**. The $^{31}P\{^{1}H\}$ NMR spectrum of [PdH(MeOH)(**4**)][TfO] presented two mutually coupled ^{31}P signals at δ 30.1 (d, J_{P-P} = 21.7 Hz) and 76.1 (d, J_{P-P} = 21.7 Hz), which disagrees with the signals observed for species **4c**. It was therefore concluded that species **4c** does not contain a MeOH ligand and the nature of the unknown ligand is proposed to be a chloride, which remains from the Pd dichloride precursor (Fig. 11).

Conclusions

A series of palladium complexes bearing monodentate and bidentate phosphine ligands were synthesised and used as catalyst precursors for the methoxycarbonylation of norbornene. The new complexes, [$PdCl_2$(**4**)] **4a** and [PdBr(**7**)] **7a**, were characterised by multinuclear NMR spectroscopy and X-ray crystallography.

In the methoxycarbonylation of norbornene, ligands **1**, **3** and **4** afforded excellent conversions (>99%) and selectivities toward the ester formation (>99%).

Excellent conversions and chemo- and *exo*-selectivities were achieved without any additional acid at room temperature using [$PdCl_2$(**1**)$_2$] **1a** as a catalytic precursor. NMR investigations showed that the protonated phosphine, **1**-H^+, is formed under catalytic conditions by the reaction of free ligand **1** and *in situ* generated HCl. The addition of acid is thus not required with this system since the reaction of the precursor with methanol under CO pressure produces 2 equiv. of HCl and leads to the formation of the active species.

The catalytic system containing ligand **4** [$PdCl_2$(**4**)] afforded an excellent conversion and chemo- and *exo*-selectivities at room temperature under acidic conditions. The protonation of ligand **4** under methoxycarbonylation conditions was observed and the isolation and characterization of the diprotonated diphosphine was carried out. This diprotonated compound was tested under catalytic conditions as a ligand and acid source with [$PdCl_2$(COD)] as a precursor and an excellent conversion and high selectivity toward the ester were achieved. Once more, the presence of chloride ligands in the precursor was revealed to be crucial to achieve a high level of activity and selectivity. The reaction of the diprotonated ligand with [$PdCl_2$(COD)] evidenced the formation of the Pd hydride species, [PdCl(H)(**4**)].

Experimental

General methods

All palladium complexes were synthesized using standard Schlenk techniques under a nitrogen atmosphere. Diethyl ether and THF were distilled over sodium benzophenone and dichloromethane was distilled over P_2O_5. All solvents were deoxygenated before use. Ligand **3**[22] and the palladium complexes [$PdCl_2$(NCPh)$_2$],[31] [$PdCl_2$(COD)],[32] [$PdCl_2$(**1**)$_2$] (**1a**),[21] [$PdCl_2$(**3**)](**3a**)[6c] and [$PdCl_2$(**5**)] (**5a**),[22] were prepared according to the literature methods. Ligands **2** and **4** were generously supplied by Dr Angela Marinetti from the Institut de Chimie des Substances Naturelles C.N.R.S., and Dr Graham Eastham from Lucite International, respectively. $PdCl_2$ was purchased from Johnson Matthey Inc. and used without further purification. All other reagents were used as received from commercial suppliers. Deuterated solvents used for routine NMR measurements were dried over molecular sieves. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Varian Mercury 400 spectrometer (400.14, 100.63 and 161.98 MHz, respectively). Chemical shifts were referenced to either TMS as an internal standard (^{1}H, $^{13}C\{^{1}H\}$ NMR spectra) or 85% H_3PO_4 as an external standard ($^{31}P\{^{1}H\}$NMR spectra). Gas chromatography analyses were performed using a Hewlett–Packard 5890 series II chromatograph with a flame ionization detector and Ultra-2 (5% diphenylsilicone, 95% dimethylsilicone) (25 m × 0.2 mm Ø) capillary column. Enantiomeric excesses were determined by GC analysis (Chiraldex-GTA capillar column 30 m × 0.25 mm × 0.12 μm film thickness).

HP-NMR measurements

In a typical experiment, the NMR tube was charged under N_2 with a solution containing the palladium precursor (0.021 mmol), TFA (when needed, 0.210 mmol) and norbornene (1.05 mmol) in a mixture of CD_3OD–THF (ratio 1 : 1 by volume) (2 ml) as the solvent. The tube was then pressurized with CO to the desired pressure.

Crystal data for structures [$PdCl_2$(4)] (4a·THF) and [PdBr(7)] (7a). Data collection for the crystal structures of compounds **4a**·THF and **7a** was carried out at 293(2) K on an Enraf Nonius CAD4 single crystal diffractometer (Mo-Kα radiation, λ = 0.71073 Å). Cell refinement, indexing and scaling of all the data set were performed using the Denzo and Scalepack programs.[33] The structure was solved by direct methods and subsequent Fourier analyses[31] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[34] The THF molecule appears slightly disordered in **4a** leading to unreliable C–C distances. The large thermal motion (or disorder) in the THF lattice molecule of **4a** and in one cyclopentyl ring of **7a** led to short C(sp^3)–C(sp^3) distances (in the range of 1.34–1.41 Å). All the calculations were performed using the WinGX System, Version 1.80.05.[35]

4a·THF: $C_{28}H_{48}Cl_2FeP_2Pd{\cdot}C_4H_8O$, M = 751.86, monoclinic, space group $P2_1/n$, a = 11.558(3), b = 14.646(3), c = 20.721(4) Å, β = 94.29(3)°, V = 3497.8(13) Å^3, Z = 4, final R_1 = 0.0510, wR_2 = 0.1159 for the observed data $I > 2\sigma(I)$, R_1 = 0.1008, wR_2 = 0.1354 (all data), S = 0.894 for 352 parameters and 6015 reflections, residuals in ΔF map 0.668, −0.406 e Å^{-3}.

7a: $C_{28}H_{43}BrP_2Pd$, M = 627.87, orthorhombic, space group $Pbca$, a = 15.151(3), b = 17.180(4), c = 21.361(4) Å, V = 5560 (2) Å^3, Z = 8, final R_1 = 0.0395, wR_2 = 0.0959 for the observed data $I > 2\sigma(I)$, R_1 = 0.0852, wR_2 = 0.1079 (all data), S = 0.860 for 289 parameters and 5864 reflections, residuals in ΔF map 0.382, −0.697 e Å^{-3}.

MS analysis

The MS spectrum was obtained by direct injection on an 6210 LC/TOF mass spectrometer (Agilent Technologies, Palo Alto,

USA), equipped with an electrospray ionisation source. MS source parameters were set with a gas temperature of 250 °C, a drying gas flow of 5 l min^{-1}, a nebulizer gas pressure of 12 psi and a capillary voltage of 3500 V. Data acquisition was realised both in the negative and positive centroid acquisition mode, with a skimmer voltage of 65 V, a fragmentor voltage of 150 V and an acquisition range from 50 to 1500 *m*/*z*, at a rate of 1.02 spectra per sec. The instrument was calibrated in the positive and negative ion modes using a tuning mixture and an internal reference standard was used to calibrate the exact mass during the analysis (both from Agilent Technologies, Palo Alto and USA). The average of the scans obtained were, in the positive mode, the protonated ion (*m*/*z* 443.3010) and, in the negative mode, the bromide ion with *m*/*z* values of 78.9200 and 80.9178.

Catalysis

High-pressure experiments were carried out in a Berghof autoclave and the reaction mixtures were magnetically stirred and electrically heated. In a typical experiment, a solution of the palladium precursor (0.021 mmol), TFA (0.210 mmol) and norbornene (1.05 mmol) in 5 ml of a mixture of THF–CH_3OH (1 : 1) were introduced into the evacuated autoclave. Carbon monoxide was introduced and the system was then heated. When a thermal equilibrium was reached, stirring was initiated. After reaction, the autoclave was cooled to room temperature and depressurized. The product was filtered in a short column of celite and the solvent was removed under vacuum. The conversions and chemo- and stereo-selectivities were determined by GC, GC-MS and NMR analyses.

Synthesis of [$PdCl_2$(1)$_2$] (1a). The synthesis of this compound was carried out according to a previous report[21] and the NMR characterization was completed. A solution of ligand **1** (173.48 mg, 0.53 mmol) in dichloromethane (5 ml) was added to a solution of [$PdCl_2$(PhCN)$_2$] (100.00 mg, 0.26 mmol) in dichloromethane (3 ml) at room temperature. The resulting yellow solution was stirred for 1 h and concentrated under vacuum. The addition of diethyl ether yielded the precipitation of a pale yellow solid, which was filtered and washed with diethyl ether before being dried under vacuum. Yield: 166.3 mg (75%).

^{1}H NMR (CD_2Cl_2, 400.14 MHz, ppm): δ 0.65 (d, J_{HH} = 6.8 Hz, CH_3), 1.02 (d, J_{HH} = 6.0 Hz, CH_3), 1.06 (d, J_{HH} = 7.2 Hz, CH_3), 1.15 (m, CH_2), 1.45 (m, CH_2), 1.55 (m, CH_2), 1.63 (m, CH_2), 1.69 (m, CH_2), 1.85 (s br. CH), 2.55 (m, CH), 2.61 (m, CH), 3.70 (m, P–CH), 7.31–7.44 (m, Ar), 7.62–7.69 (m, Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.63 MHz, ppm): δ 18.76 (s, CH_3), 21.32 (brs, CH_2), 21.43 (s, CH_3), 25.17 (s, CH_3), 28.6 (t, J_{PC} = 8.0 Hz, CH), 29.73 (brs, CH_2), 31.66 (t, J_{PC} = 6.8 Hz, CH), 32.8 (m, CH), 32.9 (s, CH_2), 33.08 (s, CH_2), 40.37 (s, CH), 127.6 (t, J_{PC} = 10.1 Hz, Ar), 128.6 (t, J_{PC} = 8.5 Hz, Ar), 13 009 (s, Ar), 13 066 (s, Ar), 133.41 (t, J_{PC} = 10.4 Hz, Ar), 137.03 (t, J_{PC} = 11.1 Hz, Ar). ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.98 MHz, ppm): δ 22.7 (s). Anal. Calc. for $C_{44}H_{58}P_2PdCl_2$ (826.20 g mol^{-1}): Calc.: C, 63.96; H, 7.08%. Found: C, 62.53; H, 6.92%.

Synthesis of [$PdCl_2$(4)] (4a). A solution of ligand **4** (269.70 mg, 0.54 mmol) in dichloromethane (10 ml) was added to a solution of [$PdCl_2$(COD)] (146.00 mg, 0.51 mmol) in dichloromethane (5 ml). The resulting red solution was stirred for 1 h and concentrated under reduced pressure. Addition of diethyl ether led to the precipitation of an orange solid, which was filtered off, washed with diethyl ether and dried under vacuum. The orange solid was recrystallized from CH_2Cl_2–ether to obtain complex **4a** as red crystals. Yield: 300.5 mg (82%).

^{1}H NMR (CD_2Cl_2, 400.14 MHz, ppm): δ 1.48 (d, 18H, J_{HP} = 13.6 Hz, *t*-Bu), 1.51 (d, 18H, J_{HP} = 13.6 Hz, *t*-Bu), 3.16 (dd, 2H, J_{HH} = 4.8 Hz, J_{HP} = 14.4 Hz, RCH_2P), 3.44 (m, 2H, RCH_2P), 4.10 (s, 5H, Cp-ring), 4.18 (m, 3H, C_5H_3-ring), 4.50 (d, 1H, J_{HH} = 4.0 Hz, C_5H_3-ring). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.63 MHz, ppm): δ 25.0 (m, CH_2), 30.0 (m, CH_3), 30.8 (m, CH_3), 31.8 (s, *tert*-C), 32.3 (s, *tert*-C), 66.3 (s, CH), 70.7 (s, Cp), 71.5 (s, Cp subst), 82.3 (s, C quat.). ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.98 MHz, ppm): δ 44.0 (s). Anal. Calc. for $C_{28}H_{48}FeP_2PdCl_2$ (679.79 g mol^{-1}): Calc.: C, 49.42; H, 7.06%. Found: C, 48.31 H, 7.00%.

Synthesis of diprotonated phosphine 4-(H^+)$_2$. Bidentate ligand **4** (65.1 mg, 0.129 mmol) was dissolved in a mixture MeOH–THF (ratio 1 : 1 by volume) (2 ml) and TFA (100 µl, 1.29 mmol) was added to the solution. The reaction was stirred for a few minutes at room temperature. Then, the yellow solution was concentrated under vacuum and diethyl ether was added to precipitate compound **4**-(H^+)$_2$ as a yellow powder. Yield: 62.5 mg (96%).

^{1}H NMR (THF-d_8, 400.14 MHz, ppm): δ 1.3 (d, 18H, J_{HP} = 13.2 Hz, CH_3), 1.4 (d, 18H, J_{HP} = 13.2 Hz, CH_3), 3.3 (d, 4H, J_{HH} = 7.2 Hz, CH_2), 4.0 (t, 1H, J_{HH} = 2.8 Hz, C_5H_3-ring), 4.1 (s, 5H, C_5H_3-ring), 4.5 (d, 2H, J_{HH} = 2.4 Hz, C_5H_3-ring). ^{13}C{^{1}H} NMR (THF-d_8, 100.63 MHz, ppm): δ 29.4 (d, J_{PC} = 9.1 Hz, CH_3), 20.0 (brs, CH_2), 33.4 (s, *tert*-C), 33.70 (s, *tert*-C), 66.6 (s, CH, Cp), 71.3 (s, CH, Cp), 71.8 (m, CH, Cp), 83.9 (m, C, Cp). ^{31}P{^{1}H} NMR (THF-d_8, 161.98 MHz, ppm): δ 36.9 (s). Calc. for $C_{28}H_{50}FeP_2$ (504.49 g mol^{-1}): Calc.: C, 66.66; H, 9.99%. Found: C, 67.53; H, 10.83%.

Synthesis of [PdBr(7)] (7a). A solid sample of [$PdCl_2$(PhCN)$_2$] (141.47 mg, 0.37 mmol) was added to a solution of ligand **7** (217.51 mg, 0.49 mmol) in 2-methoxyethanol (10 ml). The yellow solution was refluxed for 30 min, then allowed to cool and the solvent was removed to leave a yellow powder. Extraction with hot ethanol and cooling followed by reduction of the volume gave a white solid. The solid was recrystallized from a mixture of CH_2Cl_2–pentane to obtain complex **7a** as colourless crystals. Yield: 185.3 mg (60%).

^{1}H NMR (CD_2Cl_2, 400.14 MHz, ppm): δ 1.58 (m, 8H, –CH_2–), 1.72 (m, 8H, –CH_2–), 1,85 (m, 8H, P–CH_2), 2,06 (m, 8H, P–CH_2), 2.47 (m, 4H, P–CH), 3.23 (t, J = 11.6 Hz, 4H, P–CH_2Ar), 6.90–7.30 (m, 3H, Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.63 MHz, ppm): δ 26.20 (m, CH_2), 26.54 (m, CH_2), 28.90 (s, CH_2), 29.34, (s, CH_2), 35.50 (t, $J_{(C-P)}$ = 9.0 Hz, P–CH_2Ar), 35.58 (d, $J_{(C-P)}$ = 3.0 Hz, P–CH), 122.41, 122.51, 122.62, 124.91, 150,41, 16 102. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.98 MHz, ppm): δ 52.1 (s). Anal. Calc. for $C_{28}H_{43}P_2PdBr$ (627.91 g mol^{-1}): Calc.: C, 53.56; H, 6.90%. Found: C, 54.16; H, 6.72%.

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