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Insertion of CO and Strained Olefins into Organometallic (Ferrocenylmethyl)phosphane Palladium Complexes

Maria Michela Dell'Anna,[a] Daniela Giardina-Papa,[a] Susana Ibáñez,[b] Antonio Martín,[b] Piero Mastrorilli,*[a] Cosimo Francesco Nobile,[a] and Maurizio Peruzzini[c]

Dedicated to Prof. Fausto Calderazzo on the occasion of his 80th birthday

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The reaction of [Pd(cod)(CH_3)Cl] (cod = 1,5-cyclooctadiene) with the primary phosphane (ferrocenylmethyl)phosphane (PH_2CH_2Fc, **1**, 2 equiv.) affords *trans*-[Pd(PH_2CH_2Fc)$_2$(CH_3)Cl] (**2**) in 95 % yield. The intermediate chlorido-bridged dinuclear complex [Pd(PH_2CH_2Fc)(CH_3)(μ-Cl)]$_2$ (**3**) is traversed along the formation of **2**. Complex **3** may be isolated as a mixture of *anti*-**3a** and *syn*-**3b** isomers by treating [Pd(cod)(CH_3)Cl] with **1** (1 equiv.). For comparison, the analogous reactions of **1** with [Pt(cod)(CH_3)Cl] gives [Pt(PH_2CH_2Fc)$_2$(CH_3)Cl] as a mixture of *cis*-**4a** and *trans*-**4b** geometric isomers, regardless of the P/Pt molar ratio used. The insertion (at 1 atm and 253 K) of CO into the methyl–Pd bonds of either **2** or **3** gives the acetyl Pd complexes *trans*-[Pd(PH_2CH_2Fc)$_2$($COCH_3$)Cl] (**5**) and *anti*-[Pd(PH_2CH_2Fc)($COCH_3$)(μ-Cl)]$_2$ (**6**), respectively. The process leading from **3** to **6** occurs without fragmentation of the dinuclear core of the complexes, lending support to an associative mechanism with CO binding to the metal. Complex **6** undergoes facile insertion of strained olefins, such as norbornadiene or norbornene, into the acetyl–palladium bond, giving the complexes [Pd(κ^2*C,O*-$C_7H_8C(O)CH_3$)(Cl)(PH_2CH_2Fc)] (**7**) and [Pd(κ^2*C,O*-$C_7H_{10}C(O)CH_3$)(Cl)(PH_2CH_2Fc)] (**8**), respectively. Complexes **3** were tested as precatalysts for the vinylic polymerization of norbornene at 253 K, as well as for the alternate copolymerization of carbon monoxide with norbornene.

Introduction

The insertion of unsaturated molecules into M–C bonds of organometallic compounds is considered the key step of metal-catalyzed polymerization or copolymerization reactions. In this chemistry, an outstanding role is played by palladium complexes that are particularly suited to catalyze different processes including olefin oligomerization[1,2] and polymerization,[2] and olefin/CO copolymerization.[3] In particular, strained olefins are attractive substrates for copolymerization with CO, as the resulting copolymers and co-oligomers feature unique structural and chemical properties.[4] Moreover, strained olefins, such as norbornene and norbornadiene, proved useful to study the mechanism of insertion of the olefin into the metal–acyl bond during the chain-growth process,[3a] as the resulting products are quite stable due to the lack of β-hydrogen atoms accessible to the metal center.

A myriad of monodentate or bidentate ligands[5] have been used as ancillary ligands in studying the polymerization or copolymerization reactions catalyzed by organopalladium complexes, showing a strong influence of the nature of the ligand in determining the stereoregularity of the polymer.[6]

Although extensive work has been carried out on tertiary phosphane Pd complexes,[7] nothing has yet been reported on the insertion of olefins into the Pd–C bond of organometallic primary phosphane Pd complexes.

Following our recent studies dealing with the synthesis and reactivity of palladium complexes containing the air-stable primary phosphane (ferrocenylmethyl)phosphane (PH_2CH_2Fc, **1**),[8] we decided to synthesize (methyl)Pd complexes supported by such primary phosphanes and, thereafter, to investigate the insertion of CO and strained olefins, aimed at exploring these palladium complexes as catalyst precursors for either norbornene polymerization and CO/norbornene copolymerization.

[a] Dipartimento di Ingegneria delle Acque e di Chimica del Politecnico di Bari,
Via Orabona 4, 70125 Bari, Italy
Fax: +39-0805963611
E-mail: p.mastrorilli@poliba.it
[b] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain
[c] Istituto di Chimica dei Composti Organometallici (ICCOM-CNR),
Via Madonna del Piano 10, 50019 Sesto F.no (Florence), Italy

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Results and Discussion

Synthesis of (Methyl)Palladium (Ferrocenylmethyl)-phosphane Complexes

The reaction of [Pd(cod)(CH_3)Cl] with **1** (2 equiv.) in CH_2Cl_2 at 253 K afforded *trans*-[Pd(PH_2CH_2Fc)$_2$(CH_3)Cl] (**2**) in 95% yield. As complex **2** decomposed in solution at room temperature (see below), its NMR spectroscopic characterization was carried out at low temperature. At 200 K, the $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at –43.3 ppm, whereas the proton-coupled ^{31}P NMR spectrum gives rise to the characteristic multiplet associated to an $AA'X_2X'_2$ spin system (A = P; X = P-bonded H) with a strong A–A′ coupling.[9] The ^{31}P NMR spectrum was calculated (Figure 1) and the spectroscopic features reported in the Experimental Section were obtained. The large value of $J_{A,A'}$ = 464 Hz is a strong clue for the *trans* geometry of the complex.

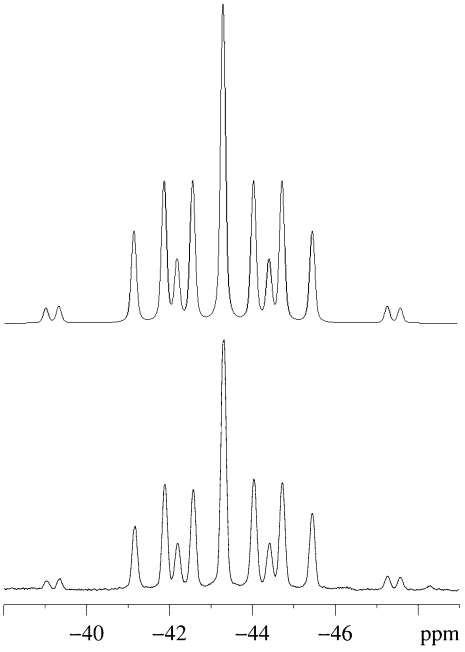
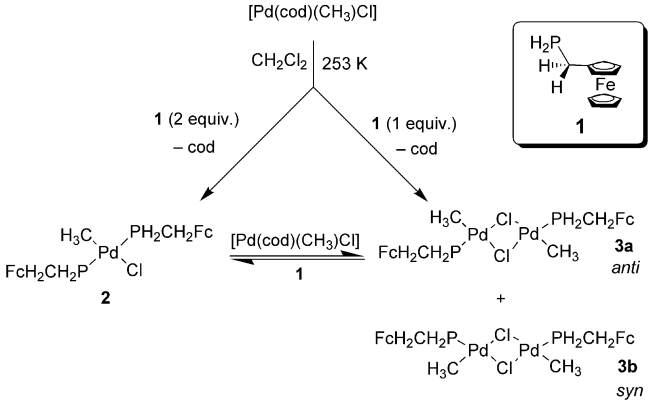


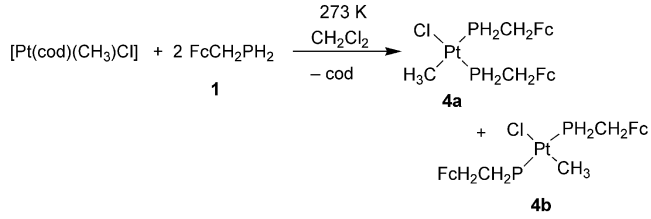
Figure 1. Experimental (bottom, CD_2Cl_2, T = 200 K) and calculated (top) ^{31}P NMR spectrum of **2**.

When only 1 equivalent of **1** was treated with [Pd(cod)(CH_3)Cl] at 253 K, the chlorido-bridged (methyl)-palladium dimers *anti*-**3a** and *syn*-**3b** [Pd(PH_2CH_2Fc)-(CH_3)(μ-Cl)]$_2$ formed in quantitative yield. Their $^{31}P\{^1H\}$ NMR signals are undistinguishable at 260 K, where only a broad singlet is observed at –41.8 ppm, and differentiate at 200 K into two sharp singlets at –35.8 and –36.4 ppm in a 1.7:1 integral ratio, assigned to *anti*-**3a** and *syn*-**3b**, respectively. Complexes **3a**,**b** are stable at low temperatures (up to 273 K) but slowly decompose at room temperature, presumably due to demethanation and/or dehydrochlorination reactions. At low temperatures, addition of **1** to a solution of **3a** and **3b** resulted in a bridge-splitting reaction, leading to the quantitative formation of **2**, whereas introduction of fresh [Pd(cod)(CH_3)Cl] into a solution of **2** caused complete transformation into **3a**,**b** (Scheme 1). Such a behavior parallels that shown by other chlorido-bridged palladium dimers of tertiary phosphanes.[7a]



Scheme 1.

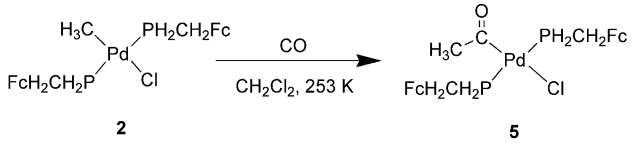
The analogous reaction of **1** with [Pt(cod)(CH_3)Cl] at 273 K in dichloromethane gave the mononuclear complex [Pt(PH_2CH_2Fc)$_2$(CH_3)Cl] as a mixture of *cis*-**4a** (ca. 70%) and *trans*-**4b** (ca. 30%) geometric isomers,[10] using either 2 or 1[11] equivalent of **1** (Scheme 2). The formation of **4a**,**b** even when 1 equivalent of **1** was used indicates that the undetected chlorido-bridged Pt dimeric intermediates related to **3a**,**b** should be significantly less stable than their Pd analogs.



Scheme 2.

Insertion Reactions of CO and Strained Olefins into Pd–C Bonds

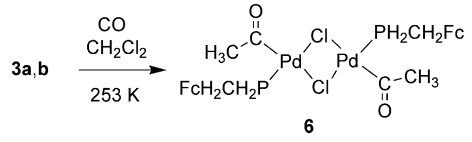
CO bubbling at atmospheric pressure through a CH_2Cl_2 solution of **2** at 253 K resulted in the instantaneous formation of the corresponding acetyl complex *trans*-[Pd(PH_2CH_2Fc)$_2$($COCH_3$)Cl] (**5**, Scheme 3) by CO insertion across the Pd–C bond. Complex **5** is indefinitely stable at room temperature in the solid state, but must be kept at a temperature lower than 273 K when dissolved in CH_2Cl_2. It is characterized by a strong IR stretching band at 1683 cm^{-1},[12,14a] and exhibits a ^{31}P NMR spectrum (δ_P = –64.2 ppm, $^2J_{P,P'}$ = 317 Hz) similar to that of **2** (see Supporting Information). Highly diagnostic for the formation of the acetyl group were the $^{13}C\{^1H\}$ $COCH_3$ resonances at 228.8 (δ_{CO}) and 43.1 (δ_{CH_3}) ppm as well as the ^1H NMR singlet at 2.15 ppm (δ_{CH_3}).



2 5

Scheme 3.

Similarly, bubbling carbon monoxide at atmospheric pressure through a CH_2Cl_2 suspension of **3a**,**b** at 253 K resulted in double regioselective carbonylation, quantitatively affording the *anti*-[Pd(PH_2CH_2Fc)($COCH_3$)(μ-Cl)]$_2$ bisacetylated species (**6**, Scheme 4). The variable-temperature (VT) $^{31}P\{^1H\}$ NMR spectrum of the homogeneous solution after reaction gave exclusively a very sharp singlet that moved from –55.4 ppm at 273 K to –52.2 ppm at 200 K. Single crystals of **6** obtained by slow diffusion of *n*-hexane into the dichloromethane reaction solution were submitted to XRD analysis, but were not of sufficient quality to warrant complete X-ray structure determination. Nonetheless, the collected data confirmed unambiguously for **6** the *anti* geometry shown in Figure 2.



6

Scheme 4.

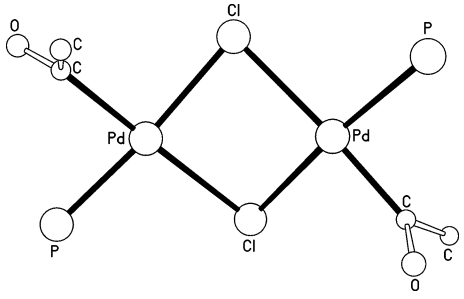


Figure 2. Core of complex **6**.

Two mechanisms were proposed to account for the carbonylation reaction of square-planar (alkyl)Pd complexes, both involving migration of the alkyl group from the metal to the carbonyl group.[13] The first mechanism requires the associative formation of a five-coordinate CO adduct, followed by migration of the alkyl group onto the neighboring carbonyl ligand.[13,14] In contrast, the alternative pathway proceeds by initial ligand dissociation, followed by CO coordination, to afford the four-coordinated species [PdClR(CO)L]. Subsequent alkyl migration and ligand reassociation steps eventually afforded the square-planar acyl derivative.[13,15]

In order to determine which mechanism is responsible for the carbonylation of **3a**,**b**, the reaction was repeated by using ^{13}CO and was monitored by multinuclear NMR at low temperature. Thus, in the NMR tube test experiment, 1.0 mL of ^{13}CO was added at 200 K to 0.5 mL of a CD_2Cl_2 solution containing 0.019 mmol of **3a**,**b**. Apart from the signals of unreacted **3a**,**b** (–36.7, –37.3 ppm), five new singlets (–36.5, –37.0, –51.6, –51.7, and –52.2 ppm, respectively, the last one ascribable to **6**), were observed in the $^{31}P\{^1H\}$ NMR spectrum (Figure 3b), all transforming into triplets ($^1J_{P,H} \approx 370$ Hz) in the proton-coupled spectrum. Inspection of the related $^{13}C\{^1H\}$ NMR spectrum showed four signals in the acetyl region at 220.6, 220.3, 219.3, and 217.7 ppm (Figure S14), the last one ascribable to **6**. Further addition of a second portion of ^{13}CO (1.0 mL) to the reaction mixture caused a progressive decrease in intensity of the $^{31}P\{^1H\}$ NMR signals at –36.5, –37.0, –51.6, and –51.7 ppm (Figure 3e) accompanied by a corresponding increase in the signal at –52.2 ppm, indicating that **6** was becoming the only NMR-detectable Pd species after ca. 1 h (Figure 3f).[16] The corresponding $^{13}C\{^1H\}$ and ^1H NMR spectra recorded 1 h after the addition of the second portion of ^{13}CO showed in the acetyl region only the singlet at 217.7 ppm [^{13}C NMR, $\delta_{^{13}CO(CH_3)}$] associated through 2D ^1H–^{13}C HMBC NMR with a doublet at 2.33 ppm [$\delta_{^{13}CO(CH_3)}$] in the ^1H NMR spectrum ($^2J_{H,C} = 5.2$ Hz). The absence of $^{13}C\{^1H\}$ NMR signals in the region where palladium carbonyl groups are usually found (190–160 ppm)[17] suggests that in our case the only observable intermediates are dipalladium compounds bearing one or two acetyl groups formed without bridge splitting of the parent compounds **3a**,**b**. On this basis, the three $^{13}C\{^1H\}$ NMR signals at 220.6, 220.3, and 219.3 ppm may be assigned to the acetyl groups of the three putative intermediates shown in Scheme 5, with the $^{31}P\{^1H\}$ NMR signals at –36.5 and –37.0 ppm belonging to the PH_2CH_2Fc unit *cis* to the CH_3 group in intermediates **A** and **B** and the $^{31}P\{^1H\}$ NMR resonances at –51.6 and –51.7 ppm ascribed to the PH_2CH_2Fc ligand *cis* to the acetyl groups in intermediates **A**, **B**, and **C**.[18] An irreversible isomerization from **C** to **6**

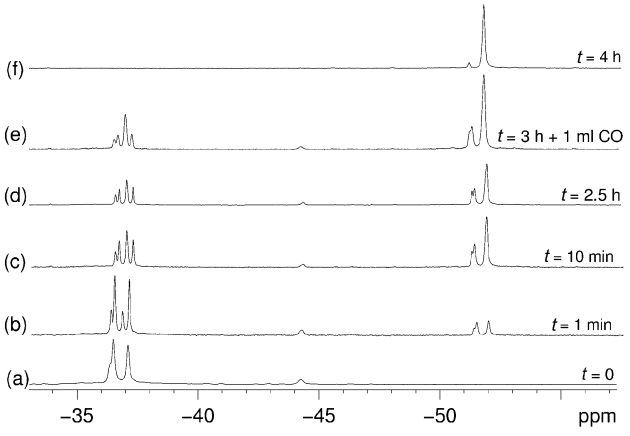
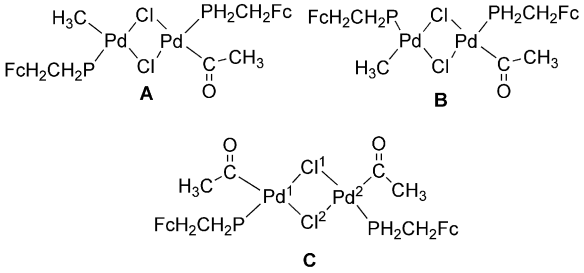


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture: **3a**,**b** + ^{13}CO (200 K, CD_2Cl_2). Spectrum recorded (a) in the absence of ^{13}CO; (b) t = 1 min after the first addition of 1 mL (at ambient conditions) of ^{13}CO to the NMR solution; (c) t = 10 min after the first addition of ^{13}CO; (d) t = 2.5 h after the first addition of ^{13}CO; (e) t = 3 h after the first addition of ^{13}CO and immediately after the second addition of 1 mL of ^{13}CO to the NMR solution; (f) t = 4 h after the first addition of ^{13}CO. The signal at ca. –44 ppm is due to residual **2** coming from the synthesis of **3a**,**b**.

(by Pd^2–Cl^2 bond breaking followed by rotation about the Pd^2–Cl^1 bond and restoring of the Pd^2–Cl^2 bond, Scheme 5) might account for the selective formation of *anti* diacetyl compound **6**. The results of the in situ study seem to favor an associative mechanism for the carbonylation of **3a**,**b**.



Scheme 5. Proposed intermediates in the carbonylation of **3a**,**b**.

The insertion of strained olefins such as norbornene (NBE) and norbornadiene (NBD) into the Pd–acetyl bond of **5** and **6** was also investigated. Whereas mononuclear complex **5** did not react with norbornadiene in thf at 273 K, dinuclear complex **6** smoothly inserted either NBD or NBE to give products **7** and **8**, respectively (Scheme 6). Complexes **7** and **8** are stable at room temperature in the solid state and up to 273 K in solution.

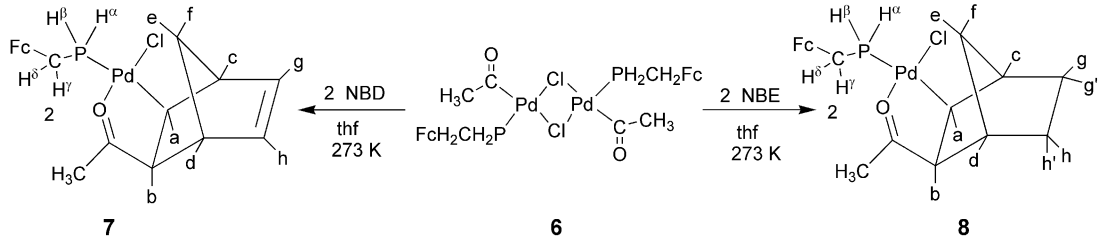
The $^{31}P\{^1H\}$ NMR spectrum of **7** features a singlet at –36.0 ppm splitting into a triplet ($^1J_{P,H}$ = 366 Hz) in the proton-coupled ^{31}P spectrum. A thorough ^1H NMR analysis carried out by running a variety of bidimensional NMR experiments (^1H COSY, ^1H–^{13}C HMQC, ^1H–^{31}P HMQC), allowed us to assign to **7** the solution structure shown in Scheme 6, and to extract all the relevant spectroscopic features reported in the Experimental Section. Notably, the $^3J_{H^a,H^b}$ = 6.2 Hz coupling constant indicates H^a and H^b as *endo* protons in the norbornene framework,[19] suggesting that the addition of Pd and of the acetyl group occurred on the *exo* side of NBD. Moreover, the stereochemistry of **7** (i.e., P *trans* to CH^a)[20] is consistent with a concerted process involving acyl migration on the *exo* face of the olefin, with both the acyl group and the olefin being coordinated to the metal.[19b] The unusually low carbonyl stretching frequency (1623 cm^{-1}) of the acyl group in the IR spectrum is consistent with the coordination of the carbonyl oxygen atom to the metal center.[19] No trace of dinuclear compounds, which could have been generated from double insertion of both NBD C=C bonds into Pd–Ac bonds,[21] was ever observed, even when an equimolar amount of NBD was added to **6**. Moreover, complex **7** was completely inert with respect to the insertion of a second CO molecule.[22]

Apart from the absence of vinyl protons, similar spectroscopic features were found for complex **8** obtained after NBE insertion into **6**. The reaction of **6** with unstrained olefins, such as ethylene or styrene, was also briefly investigated, leading to decomposition products (ethylene),[23] whereas insertion of styrene did not occur at all.

Polymerization of NBE

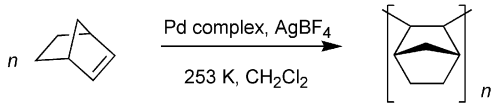
The homopolymerization of bicyclic olefins, such as NBE, can occur by three routes: cationic polymerization, ring-opening metathesis polymerization, and vinyl addition polymerization.[24] Addition polymers of NBE exhibit a combination of properties that make them amenable for many electronic and optical applications. Late-transition metals, particularly nickel and palladium, are active catalysts for addition polymerization.[24] Several palladium complexes[7c–7e,25–30] have been successfully employed as precatalysts for the vinyl addition polymerization of NBE.

Complexes **3a**,**b** were tested as precatalysts for the homopolymerization of NBE, after chloride abstraction by $AgBF_4$,[31] and the main results are collected in Table 1. The polymerization was carried out in dichloromethane at 253 K to minimize catalyst decomposition and to maximize the polymer stereoregularity.[32] Precatalysts **3a**,**b** were employed either as isolated species or generated in situ without taking care of cod removal. By using pure **3a**,**b**, the polymerization of NBE (NBE/Pd molar ratio = 400) proceeded with a TOF of 57 h^{-1} (at 50% conversion) and resulted in the quantitative formation of white, insoluble, vinyl addition poly(norbornene) (polyNBE1) as shown by both the IR spectrum and the ^1H NMR spectrum of its light fraction. In particular, no olefinic protons were detected in the ^1H NMR spectrum and no band in the 1680–1620 cm^{-1} region was present in the IR spectrum[33] of polyNBE1. TGA measurements showed a decomposition temperature of ca. 409 °C, which is higher than that (335 °C) observed, for example, for the polymer obtained by using $[Pd(NCMe)_4](BF_4)_2$ as the palladium precatalyst.[25a] The molecular weight and polydispersity values were not determined be-



Scheme 6.

Table 1. NBE polymerization reactions catalyzed by **3a**,**b** (T = 253 K, reaction time = 12 h, solvent = CH_2Cl_2).



Polymer	Catalyst	NBE/Pd	Yield [%][c]	T_d[a] [°C]	M_n[b] [Da]	M_w/M_n[b]	(g Polymer)/(g Pd)
polyNBE1	**3a**,**b**	400	73	409	[d]	[d]	257
polyNBE2	**3a**,**b** in situ[e]	400	70	410	[d]	[d]	247
polyNBE3	**3a**,**b** in situ[e]	50	72	409	4303	1.41	32
polyNBE4	**2** in situ[f]	400	59	389	[d]	[d]	208

[a] Temperature of 5% mass loss determined by thermal gravimetric analysis. [b] Determined by GPC analyses. [c] Isolated yield. [d] Not determined due to insolubility. [e] Obtained by mixing [(cod)Pd(CH_3)Cl] with **1**. [f] Obtained by mixing [(cod)Pd(CH_3)Cl] with **1** (2 equiv.).

cause of the scarce solubility of polyNBE1 in organic solvents. Similar results were found for PolyNBE2 obtained by employing **3a**,**b** generated in situ (Table 1).

In order to obtain a polymer soluble enough for $^{13}C\{^1H\}$ NMR spectroscopic analysis, the polymerization reaction was carried out by using an NBE/Pd molar ratio of 50. The resulting polymer, polyNBE3, obtained in the presence of cod, showed high solubility in $CHCl_3$ at room temperature, allowing complete NMR characterization in solution. The ^1H NMR spectrum of polyNBE3 is similar to those of other NBE vinyl addition polymers obtained with Pd[7e] or Ni[34–36] catalysts, the only difference being the presence in the spectrum of polyNBE3 of three weak broad signals at 5.53, 5.63, and 5.79 ppm,[37] ascribable to the vinyl protons of cod embodied in the polymer.[38]

The $^{13}C\{^1H\}$ APT spectrum of polyNBE3 shows that the resonances of the methine carbon atoms fall in the 35–56 ppm range, whereas those of the methylene carbon atoms fall between 27 and 38 ppm.

The polymer is *exo* enchained, as its $^{13}C\{^1H\}$ NMR spectrum does not exhibit resonances in the 20–24 ppm region.[34] It is noteworthy that although the chemical shift assignments are essentially the same for polyNBE3 and other vinyl addition poly(norbornenes),[32,34,35] the number of observed resonances within each chemical shift region is different, likely reflecting differences in the polymer architecture. Although the broad, unresolved nature of the $^{13}C\{^1H\}$ NMR spectrum of polyNBE3 made it difficult to assign the exact stereochemistry to the enchainment of norbornene in the polymer, some hypotheses can be put forward (see Supporting Information).

TGA measurements showed a decomposition temperature of ca. 409 °C and GPC analyses gave number-average molecular weight of 4303 Da and a polydispersity of 1.41 (Table 1).

Also, complex **2** was active as a precatalyst in the NBE polymerization after chloride abstraction with $AgBF_4$. The polymerization was carried out under the same experimental condition employed for the synthesis of polyNBE2 and the yield of vinyl polymer polyNBE4 was 59% (Table 1).

NMR Spectroscopic Monitoring of Polymerization Experiments

In a recent paper, Espinet et al. found that palladium complexes bearing poorly coordinating and bulky ligands are very active precatalysts for NBE polymerization. This effect was interpreted to result from easy replacement of the weakly coordinated ligands by NBE along with the formation of the catalytically active species.[39] Hence, it seemed reasonable to check whether in our polymerization reaction the primary phosphane ligand remained coordinated to palladium. To this purpose, we analyzed, by multinuclear NMR spectroscopic experiments, two different polymerization reactions carried out at low temperature in an NMR tube.

In the first experiment, a CD_2Cl_2 solution of **3a**,**b** was treated with $AgBF_4$ (1 equiv. with respect to Pd) at 253 K and then NBE (3 equiv., also with respect to Pd) was added to the resulting mixture. The ^{31}P NMR spectrum of the green suspension (180 K) consisted of three broad triplets ($^1J_{P,H}$ = 330–374 Hz) centered at –44, –51, and –65 ppm. Further addition of NBE to this suspension did not result in any polymerization reaction. These results may be explained with the formation of catalytically inactive monochlorido-bridged cationic dinuclear species derived from the incomplete splitting of the Pd_2Cl_2 bridging moiety. Once one chlorido bridge has been broken, the catalytically inactive complex forms following the double insertion of NBE molecules into the Pd–CH_3 bonds. In keeping with this hypothesis, the formation of catalytically inert monochlorido-bridged dimers following incomplete Cl removal has already been described by Nozaki et al. starting from [Pd(CH_3)(P*t*Bu$_3$)Cl].[7e]

In a similar experiment, carried out with an excess amount of $AgBF_4$, the ^{31}P NMR spectrum showed only a temperature-invariable (200–253 K) broad triplet centered at –32 ppm. Such a signal remained almost unchanged when a further 7 equivalents of NBE was added, whereas ^1H NMR spectroscopic analysis showed the formation of norbornene oligomers. The signal at –32 ppm may therefore

be confidently attributed to a catalytically active cationic mononuclear Pd complex still containing the PH_2CH_2Fc ligand and resulting from NBE insertion into the (methyl)-Pd bond with the remaining coordination sites occupied by NBE. Accordingly, neither ^1H NMR signals attributable to free NBE nor $^{31}P\{^1H\}$ NMR signals in the region of the free phosphane ($\delta_P \approx -130$ ppm) were detected at 200 K in the spectrum of the reaction mixture prepared by using a NBE/Pd ratio of 3.

Copolymerization CO/NBE

The isomeric mixture of complexes **3a**,**b** is catalytically active also for the CO/NBE copolymerization at 253 K. Although a very low yield of copolymer (polyCO/NBE1) was obtained when the reaction was carried out under 1 bar CO and by using an NBE/Pd molar ratio of 400 [T_d = 217 °C, M_n = 1862 Da, M_w/M_n = 1.55, (g polymer)/(g Pd) = 9.2], raising the CO pressure to 37 bar and decreasing the NBE/Pd molar ratio down to 50[40] increased the yield to 39%, producing a pale-yellow-colored copolymer (polyCO/NBE2). Although elemental analysis confirms that the product contains both CO and NBE, GPC measurements revealed that a low-molecular-weight oligomer [M_n = 600 Da, M_w/M_n = 1.22, (g polymer)/(g Pd) = 149] was produced. The carbonyl IR stretching band was found at 1696 cm^{-1} (accompanied by a weaker 1774 cm^{-1} band ascribable to the γ-lactone with exocyclic double bond of the terminal unit),[41] whereas the ^{13}C signals of the quaternary carbon atoms ranged from 208 to 213 ppm. The TGA curve of polyCO/NBE2 showed a decomposition temperature of 287 °C, a value similar to that found for CO/NBE copolymers obtained with other Pd catalysts.[42]

Conclusions

The reactivity of primary phosphane-ligated methylpalladium complexes $[Pd(PH_2CH_2Fc)(CH_3)(\mu\text{-}Cl)]_2$ **3a**,**b** resembles that of the corresponding tertiary phosphane analogs. Thus, the reaction of **3a**,**b** with PH_2CH_2Fc afforded *trans*-$[Pd(PH_2CH_2Fc)_2(CH_3)Cl]$ (**2**), whereas the carbonylation of **3a**,**b** and **2** resulted in the formation of the chlorido-bridged acetylpalladium(II) complex **6** and *trans*-$[Pd(PH_2CH_2Fc)_2(COCH_3)Cl]$ (**5**), respectively.

The carbonylation of **3a**,**b** was shown to pass through the formation of three intermediates bearing acetyl groups without fragmentation of the dinuclear core. The reaction of **6** with strained alkenes, such as norbornadiene and norbornene, produced *cis* addition of Pd–$C(O)CH_3$ to the *exo* face of the alkene and formation of the *exo* stable products $[Pd(\kappa^2C,O\text{-}C_7H_8C(O)CH_3)(Cl)(PH_2CH_2Fc)]$ (**7**) and $[Pd(\kappa^2C,O\text{-}C_7H_{10}C(O)CH_3)(Cl)(PH_2CH_2Fc)]$ (**8**).

After chloride abstraction, complexes **3a**,**b** were active for the vinyl addition polymerization of norbornene and for the copolymerization CO/norbornene, yielding high-molecular-weight polynorbornene and alternate co-oligomers, respectively. NMR monitoring of homopolymerization experiments showed that the primary phosphane ligand remains bound to palladium during the chain-growing process, possibly influencing the polymer architecture.

Experimental Section

Materials and Methods: All reactions were carried out under a pure dinitrogen atmosphere by using freshly distilled and oxygen-free solvents. (Ferrocenylmethyl)phosphane (**1**)[43] and the complexes $[M(cod)(CH_3)Cl]$ [M = Pd; Pt][44] were prepared by literature methods. C and H elemental analyses were carried out with a Perkin–Elmer 240B CHN Elemental Analyzer. The chloride content of the complexes was determined by argentimetric titration by using a Metrohm 716 DMS Titrino. IR spectra were recorded with a Bruker-Vector 22 spectrometer. NMR spectra were recorded with a Bruker Avance 400 spectrometer, frequencies being referenced to external Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P), and H_2PtCl_6 (^{195}Pt). Small coupling constants were obtained with COSY, HMQC, and HMBC 2D NMR experiments. The NMR features of compounds **2** and **5** were obtained by computer simulations of the experimental spectra by using DAISY software. Polymer molecular weights were determined by using a Waters 150C GPC instrument equipped with a (RI) refractive index detector, dissolving the polymer samples in chloroform. Thermogravimetric analyses (TGA) were obtained with a PerkinElmer Pyris6 TAG instrument under a N_2 flow. The value T_d indicates the temperature of 5% mass loss of the analyzed polymer. Mass spectrometry analyses (positive ion mode) were performed by using a time-of-flight mass spectrometer equipped with an electrospray ion source (Bruker microTOF-Quadruple). The sample solutions were introduced by continuous infusion with the aid of an Agilent 1100 HPLC at a flowrate of 0.2 mL min^{-1}. The instrument was operated at end plate offset –500 V and capillary –4500 V. Nebulizer pressure was 1.6 bar (N_2) and the drying gas (N_2) flow 8 L min^{-1}. Drying gas temperature was set at 200 °C. The software used for the simulations of the isotopic pattern is Bruker Daltonics Data Analysis (version 3.4).

***trans*-$[PdCl(CH_3)(PH_2CH_2Fc)_2]$ (2):** Solid **1** (175.6 mg, 0.76 mmol) was added to a CH_2Cl_2 (2 mL) solution of $[(cod)Pd(CH_3)Cl]$ (100.7 mg, 0.38 mmol) at 253 K, and the resulting yellow solution was stirred at 253 K for 30 min. Afterwards, to this solution was added cold *n*-pentane (10 mL), causing the precipitation of yellow solid **2**, which was filtered off, washed with cold *n*-pentane (3 × 5 mL), and dried under vacuum at 273 K for 30 min. Yield: 224 mg (95%). $C_{23}H_{29}ClFe_2P_2Pd$ (620.98): calcd. C 44.49, H 4.71, Cl 5.71; found C 44.79, H 4.28, Cl 5.01. IR (nujol): $\tilde{\nu}$ = 2354 (m) and 2366 (m) ν(P–H), 1277 (w), 1242 (w), 1177 (w), 1106 (m), 1079 (m), 1071 (m), 1038 (m), 1025 (m), 999 (m), 863 (s), 832 (m), 803 (m), 595 (w), 505 (m), 484 (m), 422 (w), 265 (m) ν(Pd–Cl) cm^{-1}. ^{31}P NMR (162 MHz, CD_2Cl_2, 200 K): δ = –43.3 (m, $^2J_{P,P}$ = 464 Hz, $^1J_{P,H}$ = 346 Hz, $^3J_{P,H}$ = 5 Hz) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 200 K): δ = 4.04 (m, $^1J_{P,H}$ = 346 Hz, $^3J_{P,H}$ = 5 Hz, 4 H, PH_2), 3.82–4.30 (m, 18 H, ferrocenyl protons), 2.95 (m, $^3J_{H,H}$ = 7 Hz, 4 H, CH_2), 0.27 (t, $^3J_{P,H}$ = 8 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 200 K): δ = 85.2 (s, PH_2CH_2C), 69.2 (br., Fc), 68.2 (br., Fc), 17.0 (*m*, PH_2CH_2), –8.1 (s, CH_3) ppm.

$[Pd(\mu\text{-}Cl)(CH_3)(PH_2CH_2Fc)]_2$ (3): Solid **1** (88.5 mg, 0.38 mmol) was added to a CH_2Cl_2 (2 mL) solution of $[(cod)Pd(CH_3)Cl]$ (100.7 mg, 0.38 mmol) at 253 K, and the resulting yellow suspension was stirred at 253 K for 30 min. Then, to this suspension was added cold Et_2O (10 mL), and the yellow solid obtained was filtered off, washed with cold *n*-hexane (3 × 5 mL), and dried under vacuum at 253 K for 30 min. Yield: 136 mg (92%). Elemental and

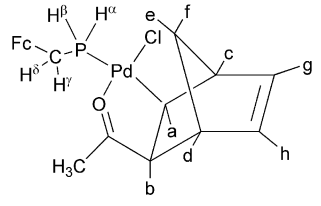
ESI-MS analyses were not performed on **3** as a result of its instability at room temperature. IR (nujol): $\tilde{\nu}$ = 2384 (w), 2356 (w) and 2334 ν(P–H), 1263 (w), 1241 (w), 1210 (m), 1104 (s), 1074 (s), 1022 (s), 933 (m), 924 (m), 899 (s), 841 (m), 827 (m), 814 (m), 731 (m), 527 (w), 520 (w), 502 (m), 491 (m), 484 (m), 465 (m), 429 (m), 382 (w), 320 (w), 303 (w), 252 (m) ν(Pd–Cl), 246 (w) ν(Pd–Cl) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 200 K): δ = –35.8 (s, **3a**), –36.4 (s, **3b**) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 200 K): δ = 4.08 (m, $^1J_{P,H}$ = 375 Hz, 4 H, PH_2), 3.90–4.20 (m, 18 H, ferrocenyl protons), 2.91 (m, 8 H, CH_2), 0.63 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 200 K): δ = 84.0 (s, PH_2CH_2C), 69.3 (br., Fc), 68.5 (br., Fc), 68.2 (br., Fc), 19.1 (d, $^1J_{P,C}$ = 26 Hz, PH_2CH_2), –0.91 (s, CH_3) ppm.

[PtCl(CH$_3$)(PH$_2$CH$_2$Fc)$_2$] (4): Solid **1** (65.2 mg, 0.28 mmol) was added to a CH_2Cl_2 (2 mL) solution of [(cod)Pt(CH_3)Cl] (50.0 mg, 0.14 mmol) at 273 K, and the resulting yellow solution was stirred at 273 K for 30 min. Then, to this solution was added cold Et_2O (10 mL), causing the precipitation of yellow solid **4**, which was filtered off, washed with *n*-hexane (3 × 2.5 mL), and dried under vacuum at 273 K for 2 h. Yield: 81.5 mg (82%). At room temperature, the complex was stable in the solid state but slowly decomposed in solution. $C_{23}H_{29}ClFe_2P_2Pt$ (709.67): calcd. C 38.93, H 4.12, Cl 5.00; found C 39.38, H 3.92, Cl 5.01. MS (ESI): *m*/*z* = 709.8 $[M]^+$. IR (nujol): $\tilde{\nu}$ = 2350 (w) and 2339 [w, ν(P–H)], 1262 (w), 1238 (w), 1203 (w), 1106 (m), 1038 (m), 1023 (m), 1000 (m), 923 (m), 878 (m), 819 (m), 596 (w), 480 and 483 (s) ν(Pt–P), 439 (w), 393 (w), 298 (m) ν(Pt–Cl), 276 (m) ν(Pt–Cl) cm^{-1}. Data for **4a**: $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 200 K): δ = –47.5 (d, $^1J_{P,Pt}$ = 1497 Hz, $^2J_{P,P}$ = 12 Hz, $P_{trans\text{-}CH_3}$), –52.5 (d, $^1J_{P,Pt}$ = 3956 Hz, $^2J_{P,P}$ = 12 Hz, $P_{trans\text{-}Cl}$) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.25 (m, $^1J_{P,H}$ = 390 Hz, $^2J_{H,Pt}$ = 55 Hz, $^3J_{H,P}$ = 12 Hz, $^3J_{H,H}$ = 6 Hz, 2 H, $H_2P_{trans\text{-}Cl}$), 4.05 (dt, $^1J_{P,H}$ = 342 Hz, $^2J_{H,Pt}$ = 18 Hz, $^3J_{H,H}$ = 7 Hz, 2 H, $H_2P_{trans\text{-}CH_3}$), 3.96–4.40 (m, 18 H, ferrocenyl protons), 2.91 (m, $^2J_{P,H}$ = 13 Hz, $^3J_{H,H}$ = 7 Hz, 2 H, FcCH_2H$_2$P$_{trans\text{-}CH_3}$), 2.85 (m, $^2J_{P,H}$ = 16 Hz, $^3J_{H,H}$ = 6 Hz, 2 H, FcCH_2H$_2$P$_{trans\text{-}Cl}$), 0.67 (m, $^3J_{P,H}$ = 7 Hz, $^2J_{H,Pt}$ = 56 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 273 K): δ = 84.3 (s, PH_2CH_2C), 77.7 (s, PH_2CH_2C), 68.1–69.2 (m, Fc), 19.8 (m, $CH_2H_2P_{trans\text{-}Cl}$), 17.3 (m, $CH_2H_2P_{trans\text{-}CH_3}$), 4.5 (s, CH_3) ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, CD_2Cl_2, 273 K): δ = –4541 (dd, $^1J_{Pt,P\,trans\text{-}CH_3}$ = 1497 Hz, $^1J_{Pt,P\,trans\text{-}Cl}$ = 3956 Hz) ppm. Data for **4b**: $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 200 K): δ = –40.1 (s, $^1J_{P,Pt}$ = 2948 Hz, $^2J_{P,P}$ = 530 Hz) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.5 (m, $^1J_{P,H}$ = 360 Hz, $^2J_{H,Pt}$ = 48 Hz, 4 H, PH_2), 3.8–4.3 (m, 18 H, ferrocenyl protons), 3.1 (m, $^2J_{P,H}$ = 13 Hz, 4 H, CH_2), 0.4 (m, $^3J_{P,H}$ = 9 Hz, $^2J_{Pt,H}$ = 80 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 273 K): δ = 83.0 (s, PH_2CH_2C), 68.0–70.3 (m, Fc), 17.6 (m, PH_2CH_2), –22.5 (s, CH_3) ppm. $^{195}Pt\{^1H\}$ NMR (86 MHz, CD_2Cl_2, 273 K): δ = –4458 (t, $^1J_{Pt,P}$ = 2940 Hz) ppm.

***trans*-[PdCl(COCH$_3$)(PH$_2$CH$_2$Fc)$_2$] (5):** Solid **1** (177.0 mg, 0.76 mmol) was added to a CH_2Cl_2 (2 mL) solution of [(cod)Pd(CH_3)Cl] (100.0 mg, 0.38 mmol) at 253 K, and the resulting yellow solution was stirred at 253 K for 30 min. Then, the reaction mixture was put under an atmosphere of carbon monoxide and left whilst stirring at 273 K for a further 30 min. Afterwards, the yellow solution was concentrated to ca. 1 mL and *n*-pentane (10 mL) was added, causing the precipitation of yellow solid **5**, which was filtered off, washed with *n*-pentane (3 × 5 mL), and dried under vacuum at room temperature. Yield: 227 mg (92%). $C_{24}H_{29}ClFe_2OP_2Pd$ (648.99): calcd. C 44.42, H 4.50, Cl 5.46; found C 43.82, H 3.87, Cl 5.90. MS (ESI): *m*/*z* = 647.8 $[M]^+$. IR (nujol): $\tilde{\nu}$ = 2347 (w) ν(P–H), 1683 (s) ν(C–O), 1105 (s), 1070 (s), 1042 (w), 1027 (w), 1001 (w), 921 (w), 847 (s), 574 (w), 484 (s), 245 (m) ν(Pd–Cl) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 200 K): δ = –64.2 (m, $^2J_{P,P}$ = 317 Hz, $^1J_{P,H}$ = 339 Hz, $^3J_{P,H}$ = 4 Hz) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.14 (m, $^1J_{P,H}$ = 339 Hz, $^3J_{P,H}$ = 4 Hz, 4 H, PH_2), 3.92–4.30 (m, 18 H, ferrocenyl protons), 3.01 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, CH_2), 2.15 (br. s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 273 K): δ = 228.8 (s, $COCH_3$), 84.4 (s, PH_2CH_2C), 69.0 (br., Fc), 68.2 (br., Fc), 43.1 (s, COCH_3), 17.1 (s, PH_2CH_2) ppm.

***anti*-[Pd(μ-Cl)(COCH$_3$)(PH$_2$CH$_2$Fc)]$_2$ (6):** Solid **1** (64.7 mg, 0.278 mmol) was added to a CH_2Cl_2 (2 mL) solution of [(cod)Pd(CH_3)Cl] (73.7 mg, 0.278 mmol) at 253 K, and the resulting yellow suspension was stirred at 253 K for 30 min. Then, the reaction mixture was put under an atmosphere of carbon monoxide and left whilst stirring at 0 °C, until the suspension turned into an orange solution (≈30 min). The solution was concentrated under vacuum to ca. 1 mL and Et_2O (5 mL) was added, causing the precipitation of yellowish-orange solid **6**, which was filtered off, washed with *n*-pentane (3 × 5 mL), and dried under vacuum at room temperature. Yield: 103 mg (89%). $C_{26}H_{32}Cl_2Fe_2O_2P_2Pd_2$ (833.89): calcd. C 37.37, H 3.86, Cl 8.49; found C 37.44, H 3.65, Cl 9.06. MS (ESI): *m*/*z* = 831.7 $[M]^+$. IR (nujol): $\tilde{\nu}$ = 2393 (w) and 2339 (w) ν(P–H), 1717 (s) ν(C–O), 1326 (w), 1241 (w), 1104 (m), 1070 (s), 1039 (m), 1023 (m), 999 (w), 921 (m), 881 (s), 836 (m), 814 (m), 579 (m), 484 (m), 427 (m), 253 ν(Pd–Cl) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 200 K): δ = –55.4 (s) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.05–4.20 (m, ferrocenyl protons, 18 H), 4.00 (dt, $^1J_{P,H}$ = 358 Hz, $^3J_{H,H}$ = 7 Hz, 4 H, PH_2), 2.92 (m, $^2J_{P,H}$ = 7 Hz, $^3J_{H,H}$ = 7 Hz, 4 H, CH_2), 2.36 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 273 K): δ = 218.1 (s, $COCH_3$), 83.8 (s, PH_2CH_2C), 69.1 (br., Fc), 68.3 (br., Fc), 67.9 (br., Fc), 38.5 (d, $^3J_{P,C}$ = 30 Hz, COCH_3), 18.2 (d, $^1J_{P,C}$ = 26 Hz, PH_2CH_2) ppm.

[PdCl(C$_7$H$_8$COMe)(PH$_2$CH$_2$Fc)] (7): 2,5-Norbornadiene (31.28 mg, 0.340 mmol) was added to a thf solution (5 mL) of **6** (141.83 mg, 0.170 mmol) at 273 K and, after a few minutes stirring, yellow solid **7** began to precipitate from the yellow solution. The reaction mixture was left whilst stirring for 6 h at 273 K, and afterwards the solvent was evaporated under vacuum to ca. 2 mL at room temperature. The reaction mixture was treated with *n*-pentane (10 mL). Resulting yellow solid **7** was filtered off and washed with *n*-pentane (3 × 5 mL) before being dried under vacuum. Yield: 162 mg (94%). $C_{20}H_{24}ClFeOPPd$ (509.08): calcd. C 47.18, H 4.75, Cl 6.96; found C 47.08, H 4.63, Cl 6.97. MS (ESI): *m*/*z* = 473.0 $[M – Cl]^+$. IR (nujol): $\tilde{\nu}$ = 2360 (s) and 2343 (s) ν(P–H), 1623 (m), 1623 ν(C–O), 1276 (w), 1222 (w), 1198 (w), 1106 (w), 1071 (w), 1022 (w), 932 (m), 922 (m), 874 (w), 801 (w), 668 (m), 494 (m), 486 (m), 477 (m), 289 (w) ν(Pd–Cl) cm^{-1}.



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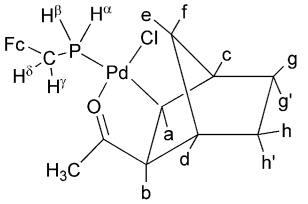
$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 200 K): δ = –36.0 (s) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 6.01 (dd, $^3J_{H^h,H^g}$ = 6 Hz, $^3J_{H^h,H^d}$ = 3 Hz, 1 H, H^h), 5.96 (dd, $^3J_{H^g,H^h}$ = 6 Hz, $^3J_{H^g,H^c}$ = 3 Hz, 1 H, H^g), 4.23 (d, $^1J_{P,H^\alpha}$ = 366 Hz, 1 H, H^α), 4.14 (d, $^1J_{P,H^\beta}$ = 366 Hz, 1 H, H^β), 4.02–4.20 (m, 9 H, ferrocenyl protons), 3.12 (m, 2 H, H^γ and H^δ), 3.01 (s, 1 H, H^d), 2.57 (d, $^3J_{H^a,H^b}$ = 6.2 Hz, 1 H, H^b), 2.49 /d, $^4J_{P,H^c}$ = 5.0 Hz, 1 H, H^c), 2.40 (s, 3 H, CH_3), 1.78

(ddd, $^3J_{H^a,P}$ = 11.0 Hz, $^3J_{H^a,H^b}$ = 6.2 Hz, $^4J_{H^a,H^f}$ = 2.2 Hz, 1 H, H^a), 1.62 (d, $^2J_{H^e,H^f}$ = 9.0 Hz, 1 H, H^e), 1.27 (d, $^2J_{H^e,H^f}$ = 9.0 Hz, 1 H, H^f) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 273 K): δ = 233.0 (s, COCH$_3$), 137.5 (d, $^4J_{P,C}$ = 6 Hz, CH^g), 133.6 (s, CH^h), 83.9 (s, PH_2CH_2C), 69.0 (br., Fc) 68.2 (br., Fc), 68.3 (br., Fc), 64.8 (s, CH^b), 48.2 (s, CH^c and CH^d), 45.9 (s, CH^eH^f), 41.5 (s, CH^a), 27.2 (s, COCH_3), 19.2 (d, $^1J_{P,C}$ = 30 Hz, PH_2CH_2) ppm.

[PdCl(C_7H_{10}COMe)(PH_2CH_2Fc)] (8): Norbornene (49.46 mg, 0.509 mmol) was added to a thf solution (5 mL) of **6** (141.83 mg, 0.170 mmol) at 273 K and, after 30 min stirring, yellow solid **8** began to precipitate from the yellow solution. The reaction mixture was left whilst stirring for 6 h at 273 K, afterwards the solvent was evaporated under vacuum to ca. 2 mL at room temperature. The reaction mixture was treated with *n*-pentane (10 mL). Resulting yellow solid **8** was filtered off and washed with *n*-pentane (3 × 5 mL) before being dried under vacuum. Yield: 152 mg (87%). $C_{20}H_{26}ClFeOPPd$ (511.10): calcd. C 47.00, H 5.13, Cl 6.94; found C 46.84, H 4.92, Cl 6.70. MS (ESI): *m*/*z* = 475.0 $[M - Cl]^+$ IR (nujol): $\tilde{\nu}$ = 2363 (w) and 2350 (w) ν(P–H), 1627 (s) ν(C–O), 1307 (m), 1297 (m), 1261 (w), 1208 (w), 1193 (w), 1170 (w), 1112 (w), 1105 (m), 1090 (w), 1075 (w), 1036 (w), 1022 (m), 933 (m), 922 (m), 875 (m), 862 (m), 799 (m), 619 (w), 590 (w), 513 (w), 496 (m), 488 (m), 480 (m), 415 (w), 376 (w), 294 (w) ν(Pd–Cl) cm^{-1}.



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$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 200 K): δ = –35.26 (s) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.15 (m, $^1J_{P,H^\alpha}$ = 365 Hz, 1 H, H^α), 4.07 (m, $^1J_{P,H^\beta}$ = 366 Hz, 1 H, H^β), 4.07–4.18 (m, 9 H, ferrocenyl protons), 3.10 (m, 2 H, H^γ and H^δ), 2.80 (d, $^3J_{H^a,H^b}$ = 6.5 Hz, 1 H, H^b), 2.45 (d, $^3J_{H^d,H^h}$ = 4.5 Hz, 1 H, H^d), 2.31 (s, CH_3, 3 H), 2.18 (ddd, $^3J_{H^a,H^b}$ = 6.5 Hz, $^3J_{P,H^a}$ = 10.2 Hz, $^4J_{H^a,H^f}$ = 2.1 Hz, 1 H, H^a), 1.89 (dd, $^4J_{P,H^e}$ = 9.2 Hz, $^3J_{H^e,H^g}$ = 3.7 Hz, 1 H, H^e), 1.70 (dt, $^2J_{H^e,H^f}$ = 10.2 Hz, $^3J_{H^e,H^d}$ = 1.9 Hz, $^3J_{H^e,H^c}$ = 1.9 Hz, 1 H H^e), 1.52 (tt, $^2J_{H^h,H^{h'}}$ = 12.1 Hz, $^3J_{H^h,H^g}$ = 4.5 Hz, $^3J_{H^h,H^d}$ = 4.5 Hz, $^3J_{H^h,H^{g'}}$ = 12.1 Hz, 1 H, H^h), 1.35 (m, $^2J_{H^g,H^{g'}}$ = 12.2 Hz, $^3J_{H^g,H^{h'}}$ = 12.2 Hz, $^3J_{H^g,H^c}$ = 4.2 Hz, $^3J_{H^g,H^h}$ = 4.2 Hz, $^5J_{P,H^g}$ = 2.2 Hz, 1 H, H^g), 1.13 (d, $^2J_{H^e,H^f}$ = 10.2 Hz, 1 H, H^f), 1.05 (m, 1 H, $H^{g'}$), 1.23 (m, 1 H, $H^{h'}$) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 273 K): δ = 234.8 (s, COCH$_3$), 84.0 (s, PH_2CH_2C), 72.0 (s, CH^b), 69.1 (br., Fc), 68.2 (br., Fc), 48.7 (s, CH^a), 43.6 (d, $^3J_{P,C}$ = 4 Hz, CH^c), 42.9 (s, CH^d), 36.8 (s, CH^eH^f), 30.4 (d, $^4J_{P,C}$ = 8 Hz, $CH^gH^{g'}$), 29.7 (s, $CH^hH^{h'}$), 27.2 (s, COCH_3), 19.5 (d, $^1J_{P,C}$ = 30 Hz, PH_2CH_2) ppm.

General Procedure for Norbornene Polymerization: For the synthesis of PolyNBE1, solid $AgBF_4$ (44.1 mg, 0.22 mmol) was added to a CH_2Cl_2 (2.0 mL) suspension of **3a**,**b** (74.1 mg, 0.095 mmol) at 253 K, and the resulting dark-green suspension was stirred at 253 K for 1 h.

For the synthesis of the other homopolymers, solid **1** (44.2 mg, 0.19 mmol for PolyNBE2 and PolyNBE3; 88.4 mg, 0.38 mmol for PolyNBE4) was added to a CH_2Cl_2 (2.0 mL) solution of [(cod)Pd(CH_3)Cl] (50.3 mg, 0.19 mmol) at 253 K, and the resulting yellow suspension was stirred at 253 K for 30 min. Solid $AgBF_4$ (44.1 mg, 0.22 mmol) was then added to the CH_2Cl_2 suspension at 253 K, and the resulting dark-green suspension was stirred at 253 K for 1 h.

To the dark-green catalytic suspension was added NBE in the desired NBE/Pd molar ratio (NBE/Pd = 400, polyNBE1, polyNBE2, and polyNBE4; NBE/Pd = 50, polyNBE3), causing a change of color to orange and provoking the precipitation of white polynorbornene after 1 h stirring. At this time, the reaction solution was again green. The mixture was kept whilst stirring for a further 11 h to ensure complete conversion before the reaction was terminated. At the end of the reactions palladium metal was present in the vessel. The resulting orange brown suspension was poured into acidified methanol, causing the precipitation of a white solid, which was separated by filtration, washed with methanol several times, and dried overnight under vacuum at 343 K. PolyNBE1, PolyNBE2, and polyNBE4 were insoluble in all common solvents (including ethers, chloroform, dichloromethane, 1,2-dichloroethane, chlorobenzene, toluene) even at high temperature (hot 1,2-dichlorobenzene, hot 1,2,4-trichlorobenzene), though their lighter fractions were soluble enough in $CDCl_3$ at 295 K to obtain ^1H NMR spectra (see Supporting Information). PolyNBE3 was very soluble in chlorinated solvents and insoluble in methanol.

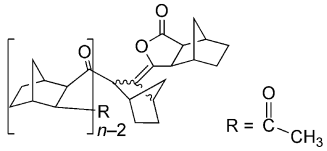
PolyNBE1: Yield: 5.2 g (73%). ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 0.5–2.7 (br. m, CH, CH_2, CH_3) ppm. T_d = 409 °C.

PolyNBE2: Yield: 5.0 g (70%). ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 0.5–2.7 (br. m, CH, CH_2, CH_3) ppm. T_d = 410 °C.

PolyNBE3: Yield: 644.0 g (72%). ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 0.5–2.7 (br. m, CH, CH_2, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 295 K): δ = 35–56 (br. m, CH), 27–38 (br. m, CH$_2$) ppm. T_d = 409 °C. M_w = 6078 Da; M_n = 4303 Da.

PolyNBE4: Yield: 4.2 g (59%). ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 0.5–2.7 (br. m, CH, CH_2, CH_3) ppm. T_d = 389 °C.

General Procedure for Copolymerization of Norbornene with CO: The isomeric mixture **3a**,**b** (9.7 mg, 0.0125 mmol in the case of PolyCO/NBE1; 77.9 mg, 0.10 mmol in the case of PolyCO/NBE2) and $AgBF_4$ (5.8 mg, 0.03 mmol in the case of PolyCO/NBE1; 46.1 mg, 0.24 mmol in the case of PolyCO/NBE2) was dissolved in CH_2Cl_2 (2.0 mL). The resulting green mixture was stirred at 253 K for 30 min and then placed in a 50-mL steel autoclave purged with CO. The autoclave was then charged with norbornene (1.00 g, 10 mmol) and pressurized with CO (1 atm for PolyCO/NBE1, 37 atm for PolyCO/NBE2). The autoclave was cooled to 265 K and stirred for 12 h. After reaction, the remaining carbon monoxide was vented off, and the crude product was subjected to flash chromatography on silica gel (petroleum ether/ethyl acetate, 10:1; and then CH_2Cl_2) to obtain a yellow solid in 2% yield (24.5 mg, PolyCO/NBE1) and 32% yield (395.2 mg, PolyCO/NBE2).



PolyCO/NBE1: ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 0.5–4.0 (br. m, CH, CH_2, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 295 K): δ = 14–35 (br. m, CH$_2$), 40–60 (br. m, CH), 174.6 (m, = CHO-CO-), 210.2 (m, -CO-) ppm. T_d = 217 °C. M_w = 2896 Da; M_n = 1862 Da. $(C_8H_{10}O)_n$: calcd. C 78.65, H 8.25; found C 78.1, H 8.14.

PolyCO/NBE2: ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ = 0.5–3.6 (br. m, CH, CH_2, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$,

295 K): δ = 24–31 (br. m, *C*H_2, *C*H_3), 35–60 (br. m, *C*H), 175.7 (m, =CHO-*C*O-), 210.2 (m, -*C*O-) ppm. IR (KBr): $\tilde{\nu}$ = 1775 (s, =CHO–*CO*–), 1732 (s, =H*CO*–CO–), 1699 (s, –*CO*–) cm^{-1}. T_d = 287 °C. M_w = 732 Da; M_n = 600 Da. $(C_8H_{10}O)_n$: calcd. C 78.65, H 8.25; found C 78.2, H 8.18.

Supporting Information (see footnote on the first page of this article): $^{31}P\{^1H\}$ and ^{31}P NMR spectra of **3a**,**b**; $^{31}P\{^1H\}$, ^{31}P, ^{195}Pt, and ^1H–^{195}Pt HMQC NMR spectra of **4a**,**b**; ^{31}P and $^{13}C\{^1H\}$ NMR spectra of **5**; $^{13}C\{^1H\}$ and ^1H–^{13}C HMBC NMR spectra of **6**; $^{13}C\{^1H\}$ APT spectrum of the reaction mixture: **3a**,**b** + ^{13}CO; ^1H NMR, $^{13}C\{^1H\}$ APT, ^1H COSY, and ^1H–^{13}C HMQC spectra of **7** and **8**; ^1H NMR spectrum of the soluble fraction of polyNBE1; ^1H and $^{13}C\{^1H\}$ NMR spectra of polyNBE3; ^1H and $^{13}C\{^1H\}$ APT NMR spectra of polyCO/NBE2; hypothesis about the stereochemistry of the enchainment of polyNBE3; MS (ESI+) spectra of **4a**, **4b**, and **5**–**8**.

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[12] Under the same conditions, corresponding (methyl)Pt complexes **4a**,**b** did not insert carbon monoxide. This difference in reactivity is not unexpected and can be ascribed to the difference in the M–CH_3, M–CO, and M–$COCH_3$ bond strengths between the Pd and Pt complexes; those in the Pt complexes are stronger than those in the Pd complexes: a) N. Koga, K. Morokuma, *J. Am. Chem. Soc.* **1986**, *108*, 6136–6144; b) Y. Kayaki, H. Tsukamoto, M. Kaneko, I. Shimizu, A. Yamamoto, M. Tachikawa, T. Nakajima, *J. Organomet. Chem.* **2001**, *622*, 199–209.

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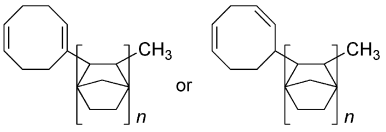

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