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Carbonylation studies of Pd-methyl complexes modified with 1,4-C_s-symmetrical diphosphine ligands

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Abstract

Neutral palladium methyl chloride **2a–d** [$PdCH_3$(P^P′)Cl] and cationic palladium methyl acetonitrile mono-triflate **3a–d** [$PdCH_3$(P^P′)(CH_3CN)][CF_3SO_3) complexes were synthesized and fully characterized (P^P′ = **1a–d**). All the neutral and cationic complexes containing a C_s-symmetric diphosphine exist in solution as a mixture of geometric isomers. The carbonylation at atmospheric pressure of the neutral and cationic complexes revealed that migratory insertion of carbon monoxide is not stereospecific in these systems. The neutral and cationic acyl complexes were formed *in situ* as mixtures of stereoisomers, which were characterized by means of NMR spectroscopy.

The crystal structures of [Pd(**1a**)Cl]$_2$(OTf)$_2$ and **2d** are described.

Keywords: Carbonylation; Palladium methyl complexes; Neutral; Cationic; 1,4-C_s-Symmetrical diphosphine ligands; Copolymerization

1. Introduction

Carbon monoxide migratory insertion in transition metal alkyl carbonyl complexes is a key step of the olefin carbonylation and of the olefin-CO copolymerization reaction. Several studies on CO migratory insertion into a transition metal–carbon σ bond appeared for complexes containing monodentate and bidentate C_2-symmetrical ligands [1,2].

Few examples of CO migratory insertion into palladium(II) alkyl complexes of non-symmetrical diphosphines were reported. The CO migratory insertion was investigated in palladium(II) and platinum(II) complexes modified with 1-diphenylphosphino-2-*tert*-butyl-3-dicyclohexylphosphinoprop-1-ene. It was shown that the insertion process of CO into metal-to-carbon σ-bonds involves a migration of the alkyl group to the CO ligand [3]. More recently [4] the carbonylation reaction was investigated in palladium(II) methyl complexes of C_1-symmetrical *Josiphos* derivatives. In this series of ligands, the fragment PCy_2 was kept constant (Cy = *cyclo*-hexyl), while the other PAr_2 fragment was systematically varied. The coordination of the acyl group *trans* to the PAr_2 moiety was favored. The selectivity for the *trans* location of the acyl group to the PAr_2 moiety was higher with the increase of the π-acidity of the aryl fragment. Nozaki and co-workers investigated the elementary steps (CO and olefin insertion) of the copolymerization reaction on the cationic complex [$PdCH_3${(*R*,*S*)-BINAPHOS}-($NCCD_3$)][BAr_4) (Ar = 3,5-bis(trifluoromethyl)phenyl); {(*R*,*S*)-BINAPHOS = (*R*,*S*)-2-(diphenylphosphino)-1,1′-binaphthalen-2′-yl-1,1′-binaphthalene-2,2′-diylphosphite [5]. ^{13}CO insertion (1 atm) into complex **1**, which was present as a single species (methyl group *trans* to the PPh_2 moiety), afforded the corresponding acyl complex [$Pd^{13}C$(O)-CH_3(P^OP)($NCCD_3$)][BAr_4) (P^OP = (*R*,*S*)-BINAPHOS) as a single species, in which the acyl group was located

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trans to the PPh_2 moiety. The same selectivity was found in the next steps of the investigation, in which intermediates relevant to the copolymerization reaction were obtained upon successive propene and carbon monoxide migratory insertion reactions. Supported by theoretical studies and crystallographic data, Nozaki proposed a higher thermodynamic stability for the isomers bringing alkyl or acyl groups *trans* to the phosphine moiety. This was found in contrast with the *trans* influence concept, according to which the phosphine is ranked at higher level compared to phosphite [6,7].

In this paper the carbonylation at atmospheric pressure of palladium methyl-chloride and methyl-solvento complexes containing non-symmetrical diphosphines is described. The isomer distribution following the CO migratory insertion is explained on the basis of the non-equivalent electronic properties of the ligand dentates.

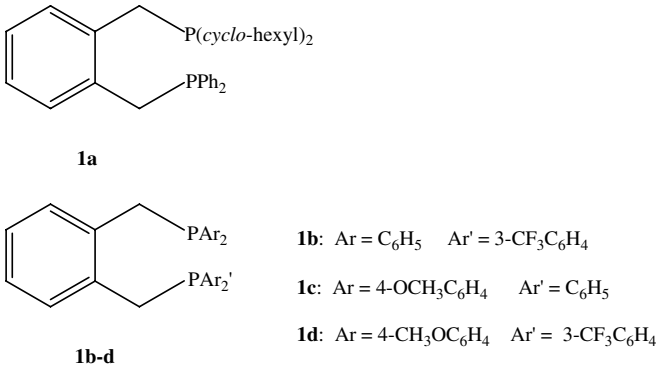


Fig. 1. C_s-symmetric 1,4-diphosphine ligands **1a–d** reacted with [$PdCH_3$(COD)Cl].

2. Results

2.1. Synthesis of the model complexes

The monocationic methyl solvento complexes were synthesized according to the procedure illustrated in Scheme 1. The palladium methyl chloride complexes were obtained from [$PdCH_3$(COD)Cl] by displacement of COD with the diphosphine **1a–d** (Fig. 1) [8,9]. Treatment of 1 equivalent of the neutral palladium methyl chloride complexes with 1.1 equivalents of AgOTf in the presence of acetonitrile afforded the corresponding methyl acetonitrile complex by scavenging the halide with the silver salt. Neutral methyl chloride palladium complexes [$PdCH_3$(P^P′)Cl] and cationic methyl acetonitrile complexes [$PdCH_3$(P^P′)-CH_3CN](OTf), containing C_s-symmetric 1,4-diphosphines, were present as a mixture of geometric isomers.

2.2. Neutral methyl chloro complexes *2a–d*

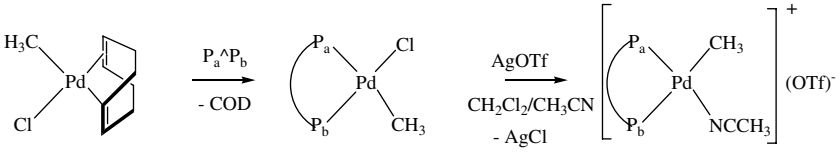
The Pd-methyl chloro complexes **2a–d** (**2a** = [$PdCH_3$(**1a**)Cl]; **2b** = [$PdCH_3$(**1b**)Cl]; **2c** = [$PdCH_3$(**1c**)Cl]; **2d** = [$PdCH_3$(**1d**)Cl]) were isolated in high yield. All the complexes were fully characterized by means of NMR spectroscopy. Together with ^1H, $^{31}P\{^1H\}$ NMR and ^1H–$^{31}P\{^1H\}$-correlation, ^1H-TOCSY and ^1H-NOESY correlation experiments were necessary to achieve an unambiguous identification of the resonances observed in the spectra. The neutral complexes **2a–d** exist in solution as a mixture of two geometric isomers, indicated as M (major) and m (minor) (Table 1). The C_s-symmetric nature of the ligand implies that the methyl group can be *cis* or *trans* with respect to each phosphorus moiety (Fig. 2).

In the ^1H NMR all the complexes **2a–d** showed the characteristic Pd–CH_3 resonance as a doublet of doublets (dd), due to the $^3J_{H-P}$ coupling with the two non-equivalent phosphorus atoms of the ligands. The Pd–CH_3 shifts are in the range 0.50–0.85 ppm. As far as the P–H coupling is concerned, values around 7.5 Hz were found for the $^3J_{H-P(trans)}$, while the $^3J_{H-P(cis)}$ ranged between 3.2 and 4.3 Hz. These values are in agreement with those reported for palladium methyl chloro complexes containing the C_{2v}-symmetrical diphosphines dppe, dppp, dppb [1].

The $^{31}P\{^1H\}$ NMR showed two pairs of doublets. Each P is coupled through a $^2J_{P-P}$ with the other P of the diphosphine ligand. The resonances of the two phosphorus atoms are separated by an interval of *ca.* 30 ppm. In each isomer, the P signal observed downfield (*i.e.*, around 30 ppm) corresponded to P_{cis} to the alkyl group, while the one upfield (*i.e.*, around 0 ppm) to P_{trans}. This assignment was supported by similar observations for the complexes [$PdCH_3$(P^P)Cl] (where P^P = dppe, dppp, dppb, dppf [1]) and by the assignment in analogous Pt complexes, in which the phosphine with the lower frequency was identified as that *trans* to the R group [10].

2.3. Cationic methyl solvento complexes *3a–d*

The complexes **3a–d** (**3a** = [$PdCH_3$(**1a**)CH_3CN](OTf); **3b** = [$PdCH_3$(**1b**)CH_3CN](OTf); **3c** = [$PdCH_3$(**1c**)CH_3CN]-(OTf); **3d** = [$PdCH_3$(**1d**)CH_3CN](OTf)) were obtained as a mixture of isomers in solution (Table 1). As in the case of the neutral complexes [$PdCH_3$(P^P′)Cl] **2a–d**



Scheme 1. Synthetic pathway to neutral methyl chloro and to monocationic methyl acetonitrile palladium complexes. Only one of the two geometric isomers is indicated in both cases. The stereochemistry has been arbitrarily assigned.

Table 1
Isomeric composition of neutral and cationic palladium methyl or palladium acetyl complexes

Neutral complexes		Cationic complexes	
Ratio M:m before carbonylation	Ratio M′:m′ after carbonylation[a]	Ratio M:m before carbonylation	Ratio M′:m′ after carbonylation
2a: 16:1[b]	**4a**: n.d.[f]	**3a**: 1.5:1[b]	**5a**: 1.8:1[b]
2b: 5.2:1[c]	**4b**: 3.1:1[c]	**3b**: 1.8:1[c]	**5b**: 2.6:1[c]
2c: 1.2:1[d]	**4c**: 1.3:1[d]	**3c**: 1.5:1[d]	**5c**: 1.8:1[d]
2d: 6.3:1[e]	**4d**: 7:1[e]	**3d**: 2.5:1[e]	**5d**: 3.2:1[e]

[a] Determined from high pressure NMR experiments.
[b] Major isomer: CH_3 or $C(O)CH_3$ *trans* to PCy_2.
[c] Major isomer: CH_3 or $C(O)CH_3$ *trans* to $P(3\text{-}CF_3C_6H_4)_2$.
[d] Major isomer: CH_3 or $C(O)CH_3$ *trans* to PPh_2.
[e] Major isomer: CH_3 or $C(O)CH_3$ *trans* to $P(3\text{-}CF_3C_6H_4)_2$.
[f] Not determined.

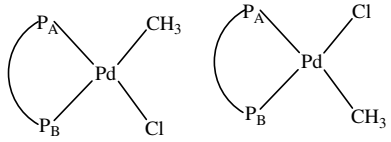


Fig. 2. Geometric isomerism in the complexes **2a**–**d**.

(P^P′ = **1a**–**d**), two Pd–CH_3 signals (dd) were observed. The coupling constants $^3J_{H-P(trans)}$ ranged from 6.5 to 7.8 Hz, while the $^3J_{H-P(cis)}$ from 2.3 to 4.3 Hz. A good agreement was observed with the values reported for palladium methyl acetonitrile complexes containing dppe, dppp, dppb [1]. The $^{31}P\{^1H\}$ NMR showed two pairs of doublets, corresponding to each geometric isomer. The dd signal arose from the coupling of each *P* with the other moiety through a $^2J_{P-P}$, which ranged between *ca.* 35.0 and 42.0 Hz [1]. The resonance of the P_{trans} to the methyl groups was detected around 0 ppm, while that of P_{cis} around 30.0 ppm. Only the *cyclo*-hexyl groups produced a shift downfield of the corresponding resonances for P_{trans} and P_{cis} in [$PdCH_3$(**1a**)- CH_3CN](OTf) at 11.0 (isomer M) and 39.5 ppm (isomer m), respectively. Apparently, the nature of the fourth ligand did not influence to a big extent the chemical shift of the P resonances in this kind of complexes. Due to the similar chemical shifts of the two non-equivalent phosphorus moieties, 2D NMR experiments were necessary for the assignment of the ^{31}P resonances, which resulted in many case overlapped.

In the cationic complexes the fourth coordination position is occupied by CH_3CN. While forming a σ bond with the metal, the CH_3 group has a higher *trans* influence than the donor ligand CH_3CN. The nature of the substituents at the phosphorus atoms as well as the nature of the other ligands influence the isomer distribution observed for the complexes **2a**–**d** and **3a**–**d** (Table 1).

The Pd–CH_3 groups gave always one signal for each isomer between 0.4 and 0.85 ppm. No exchange was detected between the Pd–CH_3 of the major and of the minor species from the ^{1}H-NOESY, in the neutral and in the cationic complexes. A broadening of the Pd–CH_3 signals was observed for **2a** when the temperature was raised to 40 °C (313 K).

The ratio M:m presented only modest variations within a range of *ca.* 80 K, when the isomer distributions M:m for the cationic complexes **3a**–**d** at 25 °C (298 K) and at −60 °C (213 K) were compared (Table 2).

The rate constant for the exchange process between the major, M, and the minor, m, isomers is related to the relaxation time of the proton T_1, which is in the magnitude of order of 1 s. When an exchange reaction is detected through a ^{1}H-NOESY experiment, the corresponding rate constant would describe an exchange rate between 0.1 and 10 s^{-1}. The absence of exchange cross peaks shows that the rate constant for the exchange M ⇌ m is slower than 0.1 s^{-1}. The ratio of the isomeric mixture for the complexes reported in Table 1 did not change over several days. Therefore, it can be assumed that for each complex the two isomers are in equilibrium, but the exchange rate between them is rather slow (the ^{1}H NMR spectrum presents sharp peaks for the Pd–CH_3 protons).

2.4. Carbonylation experiments of the neutral complexes *2a–d*

The neutral complexes **2a**–**d** were reacted with carbon monoxide and their behavior was studied *in situ* by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy, as well as with 2D NMR experiments. Insertion of carbon monoxide into palladium methyl chloro complexes was slow. Carbon monoxide was bubbled through a needle with a gentle flow (40 ml/min) for 40 min into a $CDCl_3$ 0.04 M solution of the complex. Carbonylation did not occur quantitatively, as the Pd methyl chloro could still be observed in the spectrum. Insertion of carbon monoxide is reversible, but decarbonylation occurs slowly. The solutions of the partially carbonylated neutral complexes **4a**–**d** released CO slowly upon some days. The isomer distribution M′:m′ (M′, major

Table 2
Isomeric distribution for the cationic complex **3a**–**d** at 25 and −60 °C

Ratio [$PdCH_3$(P^P′)(CH_3CN)](OTf)	**3a**	**3b**	**3c**	**3d**
$T = 25$ °C	1.5:1	1.8:1	1.5:1	2.5:1
$T = -60$ °C	1.2:1	1.3:1	1.2:1	2.6:1

insertion product, m′, minor insertion product), as of Table 1, was obtained from high pressure NMR experiments, in which complete carbonylation occurred [11]. The species **2a** was not investigated by means of high pressure NMR, so no data about the final isomer distribution after CO insertion are available. M′ should be regarded as the major species observed after bubbling CO for 40 min at room pressure.

In the ^{1}H NMR the insertion of carbon monoxide caused a shift downfield of the resonance of the methyl group; the acyl group was found in the region 1.80–2.65 ppm. The proximity of the *cyclo*-hexyl groups seemed to induce a greater shift downfield of the acyl resonance. In all the cases, no $^4J_{H-P}$ was observed in the $C(O)CH_3$ signals of the Pd acyl complexes. The ^{1}H resonance for the acyl group appeared as a broad singlet. The resonances assigned to the P_{trans} underwent a shift upfield of *ca.* 2–5 ppm upon carbonylation, while those of the P_{cis} a bigger shift, from 28–32 to 15–18 ppm for the aryl groups and from 36.5 to 27.5 ppm for the *cyclo*-hexyl groups. The coupling constants $^2J_{P-P}$ increased on going from the methyl complexes **2a–d** to the acetyl complexes **4a–d** from *ca.* 37–41 to 66–70 Hz. The values obtained for the neutral complexes are comparable with that found for [PdC(O)CH$_3$(dppb)Cl] (dppb = 1,4-bis(diphenylphosphino)butane), forming a seven-membered ring with the metal ($^2J_{P-P}$ of 39 Hz) [1].

The insertion products showed exchange peaks in the ^{1}H-NOESY (Fig. 3). This suggests that after the insertion the two isomers are in equilibrium.

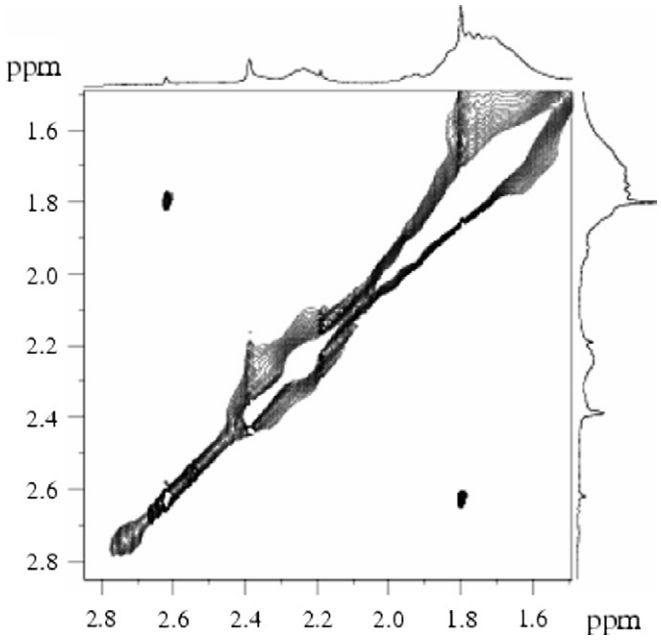


Fig. 3. ^{1}H-NOESY (δ ppm, $CDCl_3$; $T = 298$ K) for the isomeric mixture of **4a**: exchange peaks between the acyl groups of the major and minor isomers.

2.5. Carbonylation experiments of the cationic complexes *3a–d*

The insertion reaction was studied by bubbling CO through a metallic needle in a 0.04 M solution of the complex in $CDCl_3$ or CD_2Cl_2 at −60 or −80 °C, respectively. The reaction was completed within 5–10 min. The insertion products [PdC(O)CH$_3$(P^P′)(CH$_3$CN)](OTf) **5a–d** (**5a** = [PdC(O)CH$_3$(**1a**)(CH$_3$CN)](OTf); **5b** = [PdC(O)CH$_3$(**1b**)(CH$_3$CN)](OTf); **5c** = [PdC(O)CH$_3$(**1c**)(CH$_3$CN)](OTf); **5d** = [PdC(O)CH$_3$(**1d**)(CH$_3$CN)](OTf)) were characterized by means of 1D and 2D NMR spectroscopy. Upon carbonylation the doublet of doublets of the Pd–CH$_3$ group disappeared. A broad singlet was detected in the region 1.60–2.60 ppm, corresponding to the acyl group. As already observed in the carbonylation of the neutral complexes, the acyl group *cis* to the *cyclo*-hexyl rings in **5a** underwent a considerable shift downfield with respect to the other species with no alkyl groups at the phosphorus moieties. No $^4J_{H-P}$, describing the coupling with the non-equivalent P_{cis} and P_{trans} of the two fragments (*cis* and *trans* are referred to the position with respect to the acyl group), was observed in any of the cases investigated. The phosphorus resonances underwent a shift upfield (up to 2 ppm for the P_{trans} and 11–14 ppm for the P_{cis}). For instance, in **3c** P_{trans} was observed at 1.0 ppm and P_{cis} at 31.0 ppm for the major isomer. Upon carbonylation, for the isomer with the same stereochemistry (*i.e.*, the same moieties *cis* and *trans* to the acyl group) P_{trans} and P_{cis} were detected at 0.9 and 17.5 ppm, respectively. The coupling constants $^2J_{P-P}$ increased from *ca.* 36–42 to *ca.* 66–71 Hz. As the carbon backbone and the geometric properties of the ligands are very similar, no big differences among the values of the $^2J_{P-P}$ for the cationic palladium methyl and the acetyl complexes are expected.

3c was also treated with 1 atm of ^{13}CO; the species [Pd(^{13}C(O)CH$_3$)(**1c**)(CH$_3$CN)](OTf) was formed as a mixture of two isomers with the same distribution obtained with non-labelled CO. The $^2J_{C-P}$ coupling constants for the acetyl carbon were 103 Hz with P_{trans} and 9.6 Hz with the P_{cis}, respectively. These values are in good agreement with the data reported by Nozaki [5] for [Pd(^{13}C(O)CH$_3$)(BINAPHOS)CD$_3$CN](OTf), in which $^2J_{C-P}$ for the acetyl carbon was 94 Hz with the phosphine and 20 Hz with the phosphite. They are also comparable with those reported by Elsevier [12] for [Pd(^{13}C(O)CH$_3$)(^{13}CO){(2*S*,4*S*)-2,4-bis(diphenylphosphinopentane)}], where $^2J_{C-P}$ for the acetyl carbon was 79 Hz with the *trans* phosphorus atom and 19.8 Hz with the *cis* phosphorus atom. In [Pd(^{13}C(O)CH$_3$)(**1c**)(CH$_3$CN)](OTf) no displacement of acetonitrile by ^{13}CO was observed at 1 atm. A similar result was already found by Nozaki [5] for the complex [Pd(^{13}C(O)CH$_3$)(BINAPHOS)CD$_3$CN](OTf). However, this contrasted what observed by Elsevier [12], who reported the $^2J_{C-P}$ between phosphorus and ^{13}CO in [Pd(^{13}C(O)CH$_3$)(^{13}CO){(2*S*,4*S*)-2,4-bis(diphenylphosphinopentane)}](BF$_4$). The ligand **1c** is rather basic, as it contains the 4-CH$_3$OC$_6$H$_4$

substituents at one phosphorus moiety. The complex **3c** should then display strong affinity for the acid CO. Thermodynamic considerations may explain the stability of the palladium acyl complex **5c** without the displacement of CH_3CN. Carbonylation studies on Pd complexes modified with (*R*)-(*S*)-*Josiphos* derivatives [4] showed that the acetonitrile ligand is not replaced by carbon monoxide upon complete conversion to the palladium acyl complexes.

On the basis of what observed for the neutral complexes, the isomer distribution reported for the cationic carbonylation products should correspond to the equilibrium composition of the system.

2.6. X-ray crystallography

Efforts to obtain the cationic complex [$PdCH_3$(**1a**)CH_3-CN]OTf) resulted in the neutral dinuclear dichloride species [PdCl(**1a**)]$_2$(OTf)$_2$. The methyl group exchanged with the chloride in the chlorinated solvent $CHCl_3$ [13] and a dimerization occurred. Moreover, the non-coordinated solvent was replaced by the chloride. Four molecules of $CHCl_3$ co-crystallizes in the asymmetric unit, as well as two triflate counterions. Two molecules of the complex crystallize in the asymmetric unit. The complex crystallized in the triclinic space group $P\bar{1}$. Fig. 4 shows the molecular structure of the dinuclear complex together with the atom numbering scheme (limited to one subunit [Pd(**1a**)Cl]$^+$).

Single crystals suitable for X-ray analysis were obtained for the neutral derivative **2d** by layering a $CHCl_3$ solution of the complex with *n*-pentane. Fig. 5 shows the molecular structure of the complex with the atom numbering scheme. **2d** crystallizes in the orthorhombic space group *Pbca* as white platelets.

3. Discussion

The neutral palladium methyl chloride and cationic palladium methyl acetonitrile complexes synthesized in this work exist as a mixture of isomers in solution. The derivatives **2b–d** showed the prevalence of the geometric isomer in which the methyl group occupies the position *trans* to the more electron-withdrawing group present at the P moieties. A bigger difference in the isomer distribution is observed when a bigger differentiation between the two moieties is present, as in the case of **1b** and **1d**. Conversely, in case of **2c**, the electronic differentiation of the two phosphorus was modest and the ratio between the geometric isomers resulted close to 1. These three examples are consistent with the *trans* influence order, which is based on the following magnitude scale: $CH_3 > PCy_2 > PAr_2 >> Cl$ [14,15]. The methyl group prefers the coordination *trans* to the more electron poor fragment, which has weaker σ-inductive effect. The distribution of geometric isomers observed in the case of **2a** contradicts the "*trans* influence" concept and can rather be explained in terms of steric effects. The methyl group adopts a *trans* position to the PCy_2 fragment to minimize the steric repulsions. Apparently, this effect is remarkable, as the bigger isomer distribution in the series (16:1) is observed for **2a**. A similar trend has already been reported for chloro methyl Pt complexes modified with (*R*)-(*S*)-*Josiphos* derivatives [16]. The methyl Pd chloro complex derived by (*R*,*S*)-BINAPHOS [5] showed the prevalence of the geometric isomer with the methyl *trans* to the phosphite moiety (ratio M:m = 5:1), reflecting the less *trans* influence of the $P(OAr)_2$ group over PAr_2.

The ratio between the isomers is more similar for the cationic than for the neutral complexes. The bigger electronic differentiation between the fragments in **1b** and **1d** increases the ratio M:m. **3a** exists as a mixture of stereoiso-

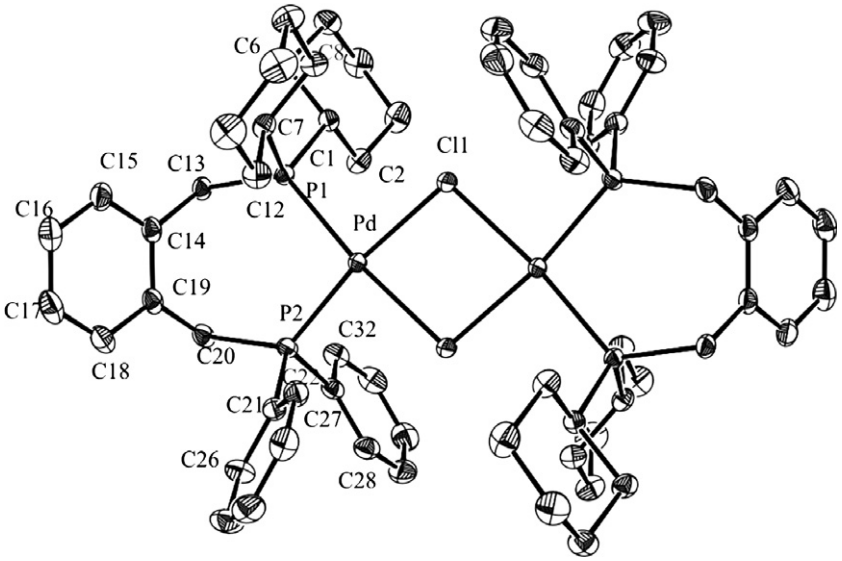


Fig. 4. ORTEP plot of the cation of [Pd(**1a**)Cl]$_2$(OTf)$_2$. Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms are omitted for clarity.

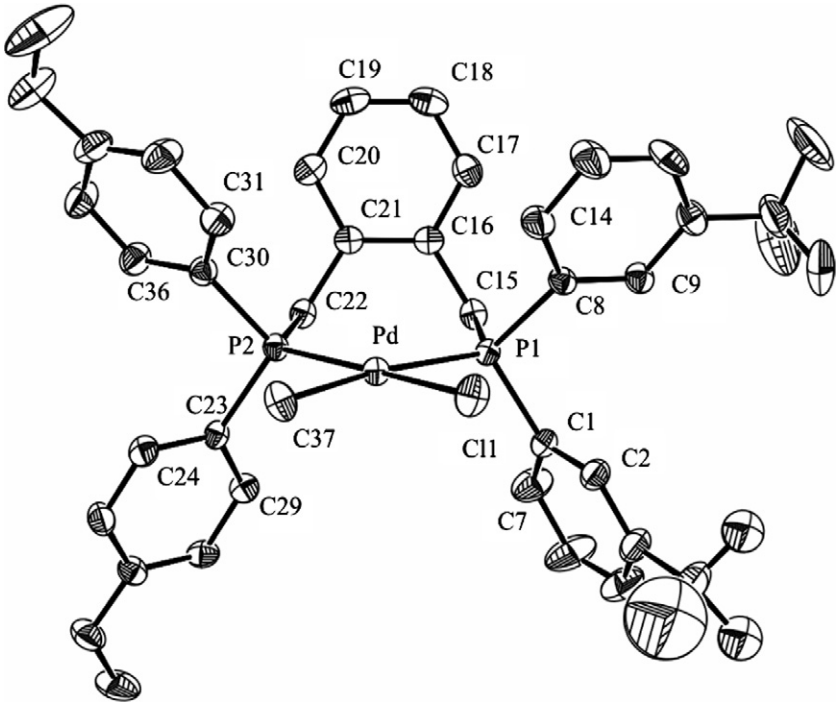


Fig. 5. ORTEP plot of **2d**. Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms and CF_3 disorder are omitted for clarity.

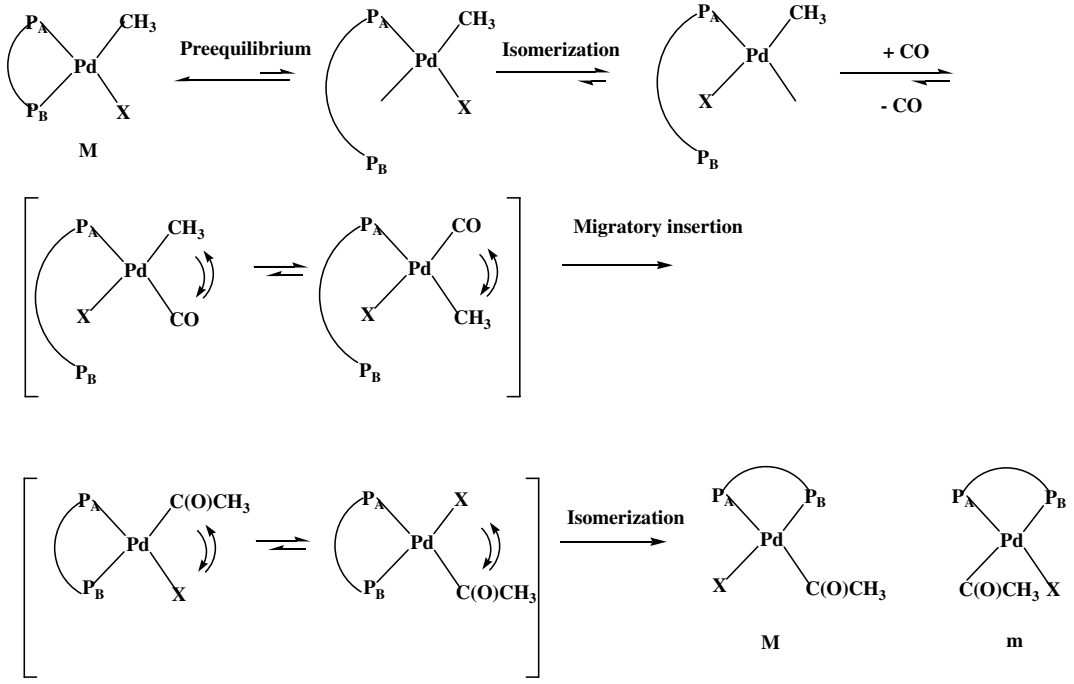
mers in the ratio 1.5:1. Steric factors may explain the location of the methyl *trans* to the *cyclo*-hexyl groups. The complex modified with **1c** was the less sensitive to variation of the fourth ligand in the coordination sphere. The isomer ratios obtained for neutral and cationic complexes were comparable.

Studies on square planar 16-electron complexes of palladium(II) and platinum(II) containing diphosphine ligands revealed that insertion of carbon monoxide occurs preferentially from a four coordinate complex, formed by substitution of a phosphine ligand by CO [9,17]. When neutral and cationic complexes of the kind $[PdCH_3(P\hat{}P)Y]^{n+}$ are considered (Y = Cl or CH_3CN; $n+ = 0$, 1), the fourth ligand of the coordination sphere, *i.e.*, chloro or acetonitrile, should play an active role in the migratory insertion. In the neutral complexes the σ-donor nature of the chloride makes its dissociation less likely than in the case of the dative weak σ-donor CH_3CN.

One can propose the pathway for the carbonylation of the neutral complexes illustrated in Scheme 2. For the minor isomer m the migratory insertion would proceed through an equivalent mechanism.

In the case of cationic palladium alkyl complexes the dissociation of acetonitrile should be more likely, since it is a weak σ-donor. The dissociation of the acetonitrile would create a vacancy that CO could readily occupy. The CO and the methyl would be *cis* to each other and the migratory insertion could occur. Alternatively, one could think about a similar mechanism as described for the neutral complexes, where one moiety of the diphosphine and not the acetonitrile dissociates from the palladium (Scheme 2). This is supported by the following observation. First, no coordination of ^{13}CO was observed in contrast to what was reported for $[Pd(CH_3)\{(S,S)\text{-BDPP}\}(S)]$ ((*S*,*S*)-BDPP = {(2*S*,4*S*)-2,4-bis(diphenylphosphinopentane)}) [12] and for $[PdCH_3(dppp)(OEt_2)](BAr'_4)$ (dppp = 1,3-bis-(diphenylphosphino)propane) [18]. The peak of the acetonitrile group could be still observed in the ^1H NMR of the carbonylated product between 2 and 2.20 ppm in all the systems investigated. As a second point, the half-life times for the CO insertion of **3b** and **3d** were much larger than the values found for more basic diphosphine investigated [11]. This may be consistent with a strong bonding of the acetonitrile to the metal in this kind of complexes, particularly enhanced in the case of ligands with electron-withdrawing substituents.

As the ratio between the major and the minor isomer is different for the reagents and the products of the migratory insertion (Table 1), an isomerization step should be taken into account. One cannot say if it occurs before or after the migratory insertion or in both cases. Before the migratory insertion, the coordinated CO and the methyl group have two possible stereochemical arrangements for the non-equivalence of the P moieties of the ligands. In a similar way, after the migratory insertion, two stereochemical alternatives, *cis* or *trans* to each P, are available for the acyl group. Two species with comparable but slightly different energy should be present in the transition state of the migratory insertion step. However, one cannot exclude that the Pd-methyl complex and the Pd-acyl complex are flipping at their own ground state between two different stereochemical arrangements (Scheme 2) according to their relative stability.



Scheme 2. Proposed mechanism for the CO insertion in the neutral complexes **2a**–**d**. The stereochemistry has been arbitrarily assigned. The arrows in brackets denote the possibility of an isomerization prior or after the CO migratory insertion (X = Cl or CH_3CN).

Regardless to the details of the mechanism, each complex has two non-equivalent fragments with different stability and different reactivity with respect to CO. Van Leeuwen reported that both [$PdCH_3$(P^P′)(solvent)](OTf) and [PdC-(O)CH_3(P^P′)(solvent)](OTf) are in rapid equilibrium between their *cis*/*trans* isomers (P^P′ = 1-diphenylphosphino-2-*tert*-butyl-3-dicyclohexylphosphinoprop-1-ene) [3]. Nozaki proposed a similar *cis*/*trans* isomerization for the Pd-(*R*, *S*)-BINAPHOS system, although it was not directly observed [5]. Supported by some evidences for Pt complexes, it was proposed that the methyl group in [$PdCH_3$(CO){(*R*, *S*)-BINAPHOS}](BAr_4), which exists as a single isomer, migrates from *trans* to the phosphine to *cis* to the phosphine prior to the migration to the coordinated CO. With this isomerization, the methyl group may become more activated in *trans* to the phosphite than at the original position. In this way, the migration to the coordinated CO should be accelerated to give the acyl complex [19,20]. In the present work such high degree of stereospecificity is not observed, probably because the two moieties were not as electronically different as in the case of (*R*, *S*)-BINAPHOS. One may assume that the activation mechanism proposed by Nozaki occurs also for the present systems [5]. When the single complex is considered, the major isomer M has the methyl group occupying the position *trans* to the more acid moiety, with the exception of systems derived from **1a**. This isomer is the more thermodynamically stable (Table 1). In the conditions of the experiment the intermediate [$PdCH_3CO$(P^P′)](OTf) cannot be observed. One may assume that the methyl group migrates [5] from *trans* to *cis* to the more acid dentate of the ligand prior to the migration of the coordinated CO. This isomerization has the effect of activating the methyl group. The migration of the alkyl to the coordinated CO should be accelerated to give the major final insertion product M′ (acyl group *trans* to the acid moiety, see Table 1). At the same time, the other isomer exists, where the methyl group is *trans* to the more basic moiety. These two intermediates should have different energy and reactivity. The intermediate [$PdCH_3CO$(P^P′)] originating from the minor isomer, where the methyl is *trans* to the more basic moiety, might insert CO directly without isomerization, following Nozaki's assumptions [5]. A similar isomerization of an alkyl platinum complex prior to the migration of the alkyl group to the coordinated CO is well known in monodentate phosphine complexes [21,22].

Effects on the reactivity of two different isomeric species have been recently reported [23]. The rate of reductive elimination for palladium aryl amido complexes was measured. The work suggested that ground state effects, the "*trans* influence" effects, dominate the control of the rate. The determination of the half-life times for these complexes [11] suggests that there are differences in reactivity not only in the series **3b**–**d**, due to overall donating properties of the ligands, but also within the same species for the non-equivalence of the dentates (the major, M, and minor, m, isomers insert CO with unlike rate).

4. Conclusions

Insertion of carbon monoxide into Pd methyl complexes modified with 1,4-C_s-symmetric diphosphines is not stereospecific. The entire synthetic pathway for the generation of these complexes, from the neutral methyl chloride to the

cationic methyl acetonitrile palladium complexes to the acyl palladium complexes shows that thermodynamic and kinetic factors are affecting the isomer distribution at every step.

Complexes $[Pd(P\hat{}P')(H_2O)_2](OTf)_2$ were used as catalyst precursors for the CO propene copolymerization, affording materials with high degree of regio- and stereoregularity. Complexes $[Pd(P\hat{}P')(H_2O)_2](OTf)_2$ (P^P′ = **1a**–**c**) showed good activity, while $[Pd(\mathbf{1d})(H_2O)_2](OTf)_2$ achieved a quite unsatisfactory performance [24]. However, the stereo- and regiocontrol was high in all the cases considered. The catalytic behavior may be related to the different reactivity of these complexes with carbon monoxide. According to the model study described in this paper, the carbon monoxide insertion is never stereospecific. The ratio between the stereoisomers depends on the ligand. Considerations related to electronic factors may suggest that the single fragments have different reactivity, not only with respect to the CO insertion but also relatively to the following steps of the copolymerization reaction.

The olefin insertion seems to be the rate-determining step of the copolymerization [25]. With achiral C_s-symmetric ligands, the enantioface selection should be chain-end controlled. Highly isotactic copolymers imply a high enantioface control in the coordination and then in the insertion of the olefin. The insertion of carbon monoxide creates two isomers that can lead to four Pd-alkyl complexes after the insertion of the olefin. These considerations show that a big number of pathways are potentially available. However, among them, one should be working effectively in transmitting the stereochemical information in the copolymerization process. Even though some polymerization pathways may start, some of the intermediates are probably ''sleeping'' in the further steps of the catalytic cycle. Alternatively, an isomerization process should probably take place during the growth of the polymer chain, which develops eventually at the more reactive/stable moiety. This is reasonable, as the Pd has unsymmetrical electron contributions from the two different dentates. At the stage of the CO insertion one cannot suggest which the more reactive moiety is, as this reaction is not stereospecific in all the cases examined. These differences probably remain in the catalytic cycle.

5. Experimental part

5.1. General remarks

All manipulations with air- or moisture-sensitive compounds were carried out under nitrogen or argon using standard Schlenk techniques or a glove box. *Trans*-$[PdCl_2(NCPh)_2]$ [26], $[Pd(COD)Cl_2]$ [8] and $[PdCH_3(COD)Cl]$ [27] were prepared according to published procedures. The synthesis of the ligands **1a**–**d** has been previously published [24]. $PdCl_2$ was purchased from Johnson Matthey, benzonitrile, COD and $Sn(CH_3)_4$ were purchased from Fluka, and were all used as received. Silver trifluoromethansulfonate was purchased from Fluka. Dichloromethane, and acetonitrile used for the synthesis were of ''puriss.'' grade, dried over molecular sieves (''crown cap'') and were purchased from Fluka. All the solvents used for recrystallization were of ''puriss.'' quality, purchased from Fluka or J.T. Baker and purified according to standard procedures. $CDCl_3$ was purchased from Merck and was used without further purification. Elemental analysis (EA) was performed by the service of ''Laboratorium für Organische Chemie'' of the ETH Zurich.

5.2. NMR spectroscopy

The ^1H, $^{31}P\{^1H\}$ and the 2D spectra were recorded on a Bruker Avance 500 (frequency in MHz: ^1H, 500.13; ^{31}P, 202.45). $^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker Avance 200 (frequency in MHz: ^{19}F, 188.31). Chemical shifts are given in parts per million (ppm) relative to TMS (internal standard) or to the solvent residual peak for ^1H NMR, and relative to 85% H_3PO_4 (external standard) for $^{31}P\{^1H\}$ NMR. ^{19}F NMR spectra are calibrated to CCl_3F as the internal standard.

The coupling constants J are given in hertz. The multiplicity is denoted by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; sx, sextet; sp, septet; m, multiplet; dd, doublet of doublets; dq, doublet of quartets; br, broad.

NMR probe temperature was measured by means of a thermocouple. Standard pulse sequences were employed for ^{31}P–^1H, ^1H-COSY, ^1H-TOCSY and ^1H-NOESY correlation studies. ^1H-TOCSY spectra were recorded using a 0.2 s mixing time. ^1H-NOESY spectra were recorded using a 0.8 s mixing time.

5.3. X-ray crystallography

X-ray structures were measured on a Bruker CCD diffractometer (Bruker SMART PLATFORM, with CCD detector, graphite monocromator, Mo Kα radiation). The program SMART served for the data collection. Integration was performed with SAINT. The structure solution and refinement on F^2 were accomplished with SHELXTL 97. Model plots were made with ORTEP32. All non-hydrogen atoms were refined freely with anisotropic displacements. The hydrogen atoms were refined at calculated positions riding on their carrier atoms. Weights are optimized in the final refinement cycles. Table 3 gives the crystallographic data for the compounds $[Pd(\mathbf{1a})Cl]_2(OTf)_2$ and **2d**.

5.4. Synthesis of palladium methyl chloro complexes *2a–d*

5.4.1. General procedure

To a solution of $[PdCH_3(COD)Cl]$ (1 equivalent) in CH_2Cl_2 the diphosphine ligand **1a**–**d** (1.1–1.2 equivalents) in CH_2Cl_2 was added. The mixture was stirred for 3 h at

Table 3
Crystal data, measurement and refinement parameters for $[Pd(\mathbf{1a})Cl]_2(OTf)_2$ and **2d**

Identification code	$[Pd(\mathbf{1a})Cl]_2(OTf)_2$	**2d**
Empirical formula	$C_{34.75}H_{41}Cl_7F_3O_3P_2PdS$	$C_{37}H_{33}ClF_6O_2P_2Pd$
Formula weight	1012.23	827.42
Temperature (K)	200(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbca*
Unit cell dimensions		
a (Å)	14.4236(10)	18.002(2)
b (Å)	14.5509(10)	15.1104(17)
c (Å)	21.6669(15)	26.847(3)
α (°)	82.2550(10)	90
β (°)	84.8970(10)	90
γ (°)	72.1660(10)	90
Volume (Å^3)	4283.9(5)	7302.6(14)
Z	4	8
Density (calc.) (mg cm^{-3})	1.569	1.505
Absorption coefficient (mm^{-1})	1.040	0.732
F(000)	2046	3344
Crystal size (mm)	$1.00 \times 0.46 \times 0.31$	$0.40 \times 0.20 \times 0.13$
Θ range for data collection (°)	1.67–26.37	1.52–24.71
Limiting indices	$-18 \leqslant h \leqslant 17$, $-18 \leqslant k \leqslant 18$, $-27 \leqslant l \leqslant 27$	$-21 \leqslant h \leqslant 21$, $-17 \leqslant k \leqslant 17$, $-26 \leqslant l \leqslant 31$
Reflections collected	38968	39894
Independent reflections (R_{int})	17452 (0.0178)	6224 (0.0472)
Completeness to θ	26.37° 99.6%	24.71° 100.0%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restrains/parameters	17452/18/993	6224/24/494
Goodness-of-fit on F^2	1.052	1.290
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0424$	$R_1 = 0.0703$
	$wR_2 = 0.1182$	$wR_2 = 0.1344$
R indices (all data)	$R_1 = 0.0500$	$R_1 = 0.0775$
	$wR_2 = 0.1248$	$wR_2 = 0.1375$
Largest diff. peak and hole (e Å^{-3})	1.606 and −1.097	0.681 and −1.070

room temperature. The solution was then evaporated to *ca.* 0.5 ml of CH_2Cl_2 and the product was precipitated by adding *n*-pentane, washed with *n*-pentane and dried under HV.

In the labeling of the carbon backbone protons (H_α, H_β, H_γ, H_δ) *syn* and *anti* are referred to the position with respect to each non-equivalent moiety of the ligand. P_{trans} and P_{cis} are referred to the position with respect to the methyl group.

5.4.2. Synthesis of [PdCH$_3$(**1a**)Cl] (**2a**)

Yield: 98%, white solid. The compound exists as a mixture of two isomers in solution (M, major isomer, and m, minor isomer). M:m = 16:1.

5.4.2.1. Major isomer, CH_3 trans to PCy_2. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.48 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.16$ Hz; $^3J_{H-P(cis)} = 3.77$ Hz), 1.18–1.44 (m, 11H, Cy, overl. with isomer m), 1.58–1.90 (m, 11H, Cy, overl. with isomer m), 3.24 (br, 2H, CH_2PCy_2), 3.69 (br, 2H, CH_2PPh_2), 6.03 (m, 1H, H_δ *syn* to PPh_2), 6.82 (m, 1H, H_γ), 7.11 (m, 1H, H_β), 7.26 (m, 1H, H_α *syn* to PCy_2), 7.40–7.55 (m, 5H, Ph, overl. with isomer m), 7.66–7.80 (m, 5H, Ph, overl. with isomer m).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 9.6 (d, PCy_2; $^2J_{P-P} = 38.5$ Hz), 29 (d, PPh_2; $^2J_{P-P} = 39.3$ Hz).

5.4.2.2. Minor isomer, CH_3 trans to PPh_2. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.84 (dd, 3 H, CH_3, $^3J_{H-P(trans)} = 7.16$ Hz; $^3J_{H-P(cis)} = 3.77$ Hz), 1.18–1.44 (m, 11H, Cy, overl. with isomer M), 1.58–1.90 (m, 11H, Cy, overl. with isomer M), 2.52 (br, 2H, CH_2PCy_2), 3.42 (br, 2H, CH_2PPh_2), 6.10 (m, 1H, H_δ *syn* to PPh_2), 6.85 (m, 1H, H_γ), 7.10 (m, 1H, H_β), 7.17 (m, 1H, H_α *syn* to PCy_2), 7.40–7.55 (m, 5H, Ph, overl. with isomer M), 7.66–7.80 (m, 5H, Ph, overl. with isomer M).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 0.6 (d, PPh_2; $^2J_{P-P} = 37.0$ Hz), 36.5 (d, PCy_2; $^2J_{P-P} = 36.3$ Hz).

Anal. Calc. for $C_{33}H_{43}P_2ClPd$ (643.52): C, 61.59; H, 6.73. Found: C, 61.98; H, 6.81.

5.4.3. Synthesis of [PdCH$_3$(**1b**)Cl] (**2b**)

Yield: 83%, light-brown solid. The compound exists as a mixture of two isomers in solution (M, major isomer, and m, minor isomer). M:m = 5.2:1

5.4.3.1. Major isomer, CH_3 trans to P(3-$CF_3C_6H_4$)$_2$. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.72 (dd, 3 H, CH_3, $^3J_{H-P(trans)} = 7.80$ Hz; $^3J_{H-P(cis)} = 4.05$ Hz), 3.79–3.91 (br, 4H, $CH_2P(3\text{-}CF_3C_6H_4)_2$ and CH_2PPh_2), 6.04 (m, 1H, C_6H_4, H_δ *syn* to $P(3\text{-}CF_3C_6H_4)_2$), 6.14 (m, 1H, C_6H_4, H_α *syn* to PPh_2), 6.79–6.83 (m, 2H, C_6H_4, H_β and H_γ, overl.

with isomer m), 7.45–7.55 (m, 6H, Ph), 7.55–7.59 (m, 2H, 3-$CF_3C_6H_4$), 7.70–7.84 (m, 4H, Ph, overl. with isomer m), 7.89–7.97 (br, 4H, 3-$CF_3C_6H_4$, overl. with isomer m), 8.03–8.13 (br, 2H, 3-$CF_3C_6H_4$ overl. with isomer m).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 1.9 (d, P(3-$CF_3C_6H_4)_2$; $^2J_{P-P} = 38.5$ Hz), 30.9 (d, PPh_2; $^2J_{P-P} = 38.5$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ 62.5 (s, CF_3).

5.4.3.2. Minor isomer, CH_3 trans to PPh_2. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.62 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.50$ Hz; $^3J_{H-P(cis)} = 4.30$ Hz), 3.72–3.82 (br, 4H, $CH_2P(3\text{-}CF_3C_6H_4)_2$ and CH_2PPh_2), 6.10 (m, 1H, C_6H_4, H_δ *syn* to P(3-$CF_3C_6H_4)_2$), 6.22 (m, 1H, C_6H_4, H_α *syn* to PPh_2), 6.79–6.83 (m, 2H, C_6H_4, H_β and H_γ, overl. with isomer M), 7.43–7.49 (m, 6H, Ph), 7.65–7.69 (m, 2H, 3-$CF_3C_6H_4$), 7.80–7.85 (m, 4H, Ph, overl. with isomer M), 7.89–7.97 (br, 4H, 3-$CF_3C_6H_4$, overl. with isomer M), 8.03–8.13 (br, 2H, 3-$CF_3C_6H_4$ overl. with isomer M).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 0.6 (d, PPh_2, $^2J_{P-P} = 39.3$ Hz), 31.5 (d, P(3-$CF_3C_6H_4)_2$, $^2J_{P-P} = 39.3$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ 62.6 (s, CF_3).

Anal. Calc. for $C_{35}H_{29}F_6P_2ClPd$ (767.42): C, 54.78; H, 3.81. Found: C, 54.85; H, 3.86.

*5.4.4. Synthesis of [PdCH$_3$(**1c**)Cl] (**2c**)*

Yield: 88%, white solid. The compound exists as a mixture of two isomers in solution (M, major isomer, and m, minor isomer). M:m = 1.2:1.

5.4.4.1. Major isomer, CH_3 trans to PPh_2. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.61 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.60$ Hz; $^3J_{H-P(cis)} = 3.80$ Hz), 3.69 (s, 2H, CH_2PPh_2), 3.76 (d, 2H, $CH_2P(4\text{-}OCH_3C_6H_4)_2$; $^2J_{H-P} = 12.70$ Hz), 3.90 (s, 6H, OCH_3), 6.15 (m, 1H, C_6H_4, H_δ *syn* to PPh_2), 6.20 (m, 1H, C_6H_4, H_α *syn* to P(4-OCH_3-$C_6H_4)_2$), 6.84–6.89 (m, 2H, C_6H_4, H_β and H_γ, overl. with isomer m), 6.98–7.02 (m, 4H, 4-$OCH_3C_6H_4$), 7.41–7.47 (m, 6H, Ph), 7.68–7.74 (m, 4H, 4-$OCH_3C_6H_4$), 7.80–7.87 (m, 4H, Ph).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ −1.4 (d, PPh_2, $^2J_{P-P} = 39.3$ Hz), 31.5 (d, P(4-$OCH_3C_6H_4)_2$, $^2J_{P-P} = 39.3$ Hz).

5.4.4.2. Minor isomer, CH_3 trans to P(4-$OCH_3C_6H_4)_2$. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.64 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.60$ Hz; $^3J_{H-P(cis)} = 3.80$ Hz), 3.67 (s, 2H, $CH_2P(4\text{-}CH_3OC_6H_4)_2$), 3.82 (d, 2H, CH_2PPh_2; $^2J_{H-P} = 10.73$ Hz), 3.86 (s, 6H, OCH_3), 6.10–6.14 (m, 1H, C_6H_4, H_δ *syn* to PPh_2), 6.21–6.25 (m, 1H, C_6H_4, H_α *syn* to P(4-$OCH_3C_6H_4)_2$), 6.78–6.84 (m, 1H, C_6H_4, H_β), 6.84–6.88 (m, 1H, C_6H_4, H_γ, overl. with isomer M), 6.95–6.98 (m, 4H, 4-$OCH_3C_6H_4$), 7.47–7.56 (m, 6H, Ph), 7.71–7.78 (m, 4H, 4-$OCH_3C_6H_4$), 7.75–7.81 (m, 4H, Ph).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 1.1 (d, P(4-$OCH_3C_6H_4)_2$, $^2J_{P-P} = 39.0$ Hz), 28.9 (d, PPh_2, $^2J_{P-P} = 39.0$ Hz).

Anal. Calc. for $C_{35}H_{35}O_2P_2ClPd$ (691.48): C, 60.79; H, 5.10. Found: C, 61.23; H, 5.26.

*5.4.5. Synthesis of [PdCH$_3$(1d)Cl] (**2d**)*

Yield: 91%, light-brown solid. The compound exists as a mixture of two isomers in solution (M, major isomer, and m, minor isomer). M:m = 6.3:1

5.4.5.1. Major isomer, CH_3 trans to P(3-$CF_3C_6H_4)_2$. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.71 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.50$ Hz; $^3J_{H-P(cis)} = 3.50$ Hz), 3.71 (br, 2H, $CH_2P(3\text{-}CF_3C_6H_4)_2$ overl. with isomer m), 3.79 (br, 2H, $CH_2P(4\text{-}OCH_3C_6H_4)_2$), 3.90 (s, 6H, OCH_3), 6.06 (m, 1H, C_6H_4, H_δ *syn* to P(3-$CF_3C_6H_4)_2$), 6.25 (m, 1H, C_6H_4, H_α *syn* to P(4-$OCH_3C_6H_4)_2$), 6.80–6.92 (m, 2H, C_6H_4, H_β and H_γ, overl. with isomer m), 6.99–7.04 (m, 4H, 4-$OCH_3C_6H_4$), 7.55–7.62 (m, 2H, 3-$CF_3C_6H_4$), 7.66–7.73 (m, 4H, 4-$OCH_3C_6H_4$, overl. with isomer m), 7.73–7.79 (m 2H, 3-$CF_3C_6H_4$), 7.90–8.00 (br, 2H, 3-$CF_3C_6H_4$, overl. with isomer m), 8.05–8.16 (br, 2H, 3-$CF_3C_6H_4$, overl. with isomer m).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 2.2 (d, P(3-$CF_3C_6H_4)_2$; $^2J_{P-P} = 38.7$ Hz), 28.5 (d, P(4-$OCH_3C_6H_4)_2$; $^2J_{P-P} = 38.7$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ 62.5 (s, CF_3).

5.4.5.2. Minor isomer, CH_3 trans to P(4-$OCH_3C_6H_4)_2$. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.58 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.50$ Hz; $^3J_{H-P(cis)} = 3.50$ Hz), 3.66 (s, 2H, $CH_2P(4\text{-}OCH_3C_6H_4)_2$), 3.70 (br, 2H, $CH_2P(3\text{-}CF_3C_6H_4)_2$, overl. with isomer M), 3.89 (s, 6H, OCH_3), 6.10 (m, 1H, C_6H_4, H_δ *syn* to P(3-$CF_3C_6H_4)_2$), 6.29 (m, 1H, C_6H_4, H_α *syn* to P(4-$OCH_3C_6H_4)_2$), 6.80–6.92 (m, 2H, C_6H_4, H_β and H_γ, overl. with isomer M), 6.94–6.99 (m, 4H, 4-$OCH_3C_6H_4$), 7.66–7.73 (m, 4H, 4-$OCH_3C_6H_4$, overl. with isomer M), 7.82–7.86 (m, 2H, 3-$CF_3C_6H_4$), 7.90–8.00 (br, 4H, 3-$CF_3C_6H_4$, overl. with isomer M), 8.05–8.16 (br, 2H, 3-$CF_3C_6H_4$, overl. with isomer M).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ −1.6 (d, P(4-$OCH_3C_6H_4)_2$; $^2J_{P-P} = 40.7$ Hz), 31.6 (d, P(3-CF_3-$C_6H_4)_2$; $^2J_{P-P} = 40.7$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ 62.6 (s, CF_3).

Anal. Calc. for $C_{37}H_{33}O_2F_6P_2ClPd$ (827.48): C, 53.71; H, 4.02. Found: C, 53.92; H, 4.15.

5.5. Synthesis of palladium methyl acetonitrile complexes

5.5.1. General procedure [1]

To a solution of **2a**–**d** (1 equivalent) in CH_2Cl_2 AgOTf (1.1 equivalents) in a mixture of CH_2Cl_2 and CH_3CN (v/v *ca.* 20:1) was added. The solution was stirred at room temperature for 2 h and then filtered through Celite to remove AgCl. The filtrate was concentrated under reduced

pressure to *ca.* 0.5 ml and then collected in 30 ml of cold (0 °C) pentane with rapid stirring. The complex was recovered by filtration, washed with cold pentane and dried under vacuum.

*5.5.2. Synthesis of [PdCH$_3$(**1a**)(CH$_3$CN)](OTf) (**3a**)*

Quantitative yield of a yellow powder. The compound exists as a mixture of two isomers in solution (M, major isomer, and m, minor isomer). M:m = 1.5:1.

5.5.2.1. Major isomer, CH$_3$ trans to PCy$_2$. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.44 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 6.50$ Hz; $^3J_{H-P(cis)} = 2.50$ Hz), 1.08–1.96 (m, 22H, Cy overl. with isomer m), 2.55 (br, 3H, CH_3CN), 3.32 (d, 2H, CH_2PCy_2; $^2J_{H-P} = 10.40$ Hz), 3.68 (br, 2H, CH_2PPh_2), 6.00 (m, 1H, C_6H_4, H_δ *syn* to PPh_2), 6.86 (m, 1H, C_6H_4, H_γ), 7.12–7.20 (m, 1H, C_6H_4, H_β, overl. with isomer m), 7.25 (m, 1H, C_6H_4, H_α *syn* to PCy_2), 7.36–7.86 (m, 10H, Ph, overl. with isomer m).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 11.0 (d, PCy_2; $^2J_{P-P} = 40.0$ Hz), 32.4 (d, PPh_2; $^2J_{P-P} = 40.0$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.7 (free triflate).

5.5.2.2. Minor isomer, CH$_3$ trans to PPh$_2$. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.68 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 6.50$ Hz; $^3J_{H-P(cis)} = 2.50$ Hz), 1.08–1.96 (m, 22H, Cy overl. with isomer M), 2.15 (br, 3H, CH_3CN), 3.39 (br, 2H, CH_2PCy_2), 3.49 (br, 2H, CH_2PPh_2), 6.39 (m, 1H, C_6H_4, H_δ *syn* to PPh_2), 6.96 (m, 1H, C_6H_4, H_γ), 7.12–7.20 (m, 1H, C_6H_4, H_β overl. with isomer M), 7.30 (m, 1H, C_6H_4, H_α *syn* to PCy_2), 7.36–7.86 (m, 10H, Ph, overl. with isomer M).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ −1.0 (d, PPh_2; $^2J_{P-P} = 35.7$ Hz), 39.5 (d, PCy_2; $^2J_{P-P} = 35.7$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.7 (free triflate).

Anal. Calc. for $C_{36}H_{46}NO_3F_3P_2SPd$ (798.20): C, 54.17; H, 5.81. Found: C, 54.68; H, 6.02.

*5.5.3. Synthesis of [PdCH$_3$(**1b**)(CH$_3$CN)](OTf) (**3b**)*

Yield: 88%, light-brown powder. The compound exists as a mixture of two isomers in solution (M, major isomer, and m, minor isomer). M:m = 1.8:1.

5.5.3.1. Major isomer, CH$_3$ trans to P(3-CF$_3$C$_6$H$_4$)$_2$. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.72 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.80$ Hz; $^3J_{H-P(cis)} = 4.00$ Hz), 1.90–2.10 (br, 3H, CH_3CN, overl. with isomer m), 4.07 (br, 2H, CH_2PPh_2), 4.12 (br, 2H, $CH_2P(3\text{-}CF_3C_6H_4)_2$), 6.08 (m, 1H, C_6H_4, H_δ *syn* to $P(3\text{-}CF_3C_6H_4)_2$), 6.23 (m, 1H, C_6H_4, H_α *syn* to PPh_2), 6.75–6.83 (m, 2H, C_6H_4, H_β and H_γ), 7.53–7.68 (m, 6H, Ph, overl. with isomer m), 7.69–7.82 (m, 4H, Ph, overl. with isomer m), 7.73 (m, 2H, 3-$CF_3C_6H_4$), 7.83–7.84 (m, 4H, 3-$CF_3C_6H_4$, overl. with isomer m), 8.03–8.11 (br, 2H, 3-$CF_3C_6H_4$, overl. with isomer m).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 1.9 (d, $P(3\text{-}CF_3C_6H_4)_2$; $^2J_{P-P} = 38.5$ Hz), 30.9 (d, PPh_2; $^2J_{P-P} = 38.5$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.7 (free triflate), 62.5 (s, CF_3).

5.5.3.2. Minor isomer, CH$_3$ trans to PPh$_2$. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.62 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.50$ Hz; $^3J_{H-P(cis)} = 4.30$ Hz), 1.90–2.10 (br, 3H, CH_3CN overl. with isomer M), 4.00 (br, 2H, CH_2PPh_2), 4.03 (br, 2H, $CH_2P(3\text{-}CF_3C_6H_4)_2$), 6.04 (m, 1H, C_6H_4, H_δ *syn* to $P(3\text{-}CF_3C_6H_4)_2$), 6.53 (m, 1H, C_6H_4, H_α *syn* to PPh_2), 6.83–6.88 (m, 1H, C_6H_4, H_γ), 6.94–6.99 (m, 1H, C_6H_4, H_β), 7.53–7.68 (m, 6H, Ph overl. with isomer M), 7.69–7.82 (m, 4H, Ph overl. with isomer M), 7.83–7.84 (m, 4H, 3-$CF_3C_6H_4$ overl. with isomer M), 7.89 (m, 2H, 3-$CF_3C_6H_4$), 8.03–8.11 (m, 2H, 3-$CF_3C_6H_4$ overl. with isomer M).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 0.6 (d, PPh_2; $^2J_{P-P} = 40.0$ Hz), 30.9 (d, $P(3\text{-}CF_3C_6H_4)_2$; $^2J_{P-P} = 40.0$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.7 (free triflate), 62.6 (s, CF_3).

Anal. Calc. for $C_{38}H_{32}NO_3F_9P_2SPd$ (922.09): C, 49.50; H, 3.50. Found: C, 49.82; H, 3.59.

*5.5.4. Synthesis of [PdCH$_3$(**1c**)(CH$_3$CN)](OTf) (**3c**)*

Yield: 88%, yellow powder. The compound exists as a mixture of two isomers in solution (M, major isomer, and m, minor isomer). M:m = 1.5:1.

5.5.4.1. Major isomer, CH$_3$ trans to PPh$_2$. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.45 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 6.90$ Hz; $^3J_{H-P(cis)} = 2.30$ Hz), 2.14 (br, 3H, CH_3CN, overl. with isomer m), 3.75 (br, 2H, $CH_2P(4\text{-}OCH_3C_6H_4)_2$), 3.84 (br, 2H, CH_2PPh_2), 3.89 (s, 6H, OCH_3), 6.13 (m, 1H, C_6H_4, H_α *syn* to $P(4\text{-}OCH_3C_6H_4)_2$), 6.52 (m, 1H, C_6H_4, H_δ *syn* to PPh_2), 6.86–6.91 (m, 1H, C_6H_4, H_γ), 6.92–6.99 (m, 1H, C_6H_4, H_β), 7.01–7.10 (m, 4H, 4-$OCH_3C_6H_4$, overl. with isomer m), 7.48–7.62 (m, 4H, 4-$OCH_3C_6H_4$, overl. with isomer m), 7.55–7.62 (m, 8H, Ph, overl. with isomer m), 7.65–7.71 (m, 2H, Ph, overl. with isomer m).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 1.0 (d, PPh_2; $^2J_{P-P} = 39.3$ Hz), 31.0 (d, $P(4\text{-}OCH_3C_6H_4)_2$; $^2J_{P-P} = 39.3$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.7 (free triflate).

5.5.4.2. Minor isomer, CH$_3$ trans to P(4-OCH$_3$C$_6$H$_4$)$_2$. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.41 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 6.90$ Hz; $^3J_{H-P(cis)} = 2.30$ Hz), 2.15 (br, 3H, CH_3CN, overl. with isomer M), 3.77 (br, 2H, $CH_2P(4\text{-}OCH_3C_6H_4)_2$), 3.82 (br, 2H, CH_2PPh_2), 3.88 (s, 6H, OCH_3), 6.04 (m, 1H, C_6H_4, H_δ *syn* to PPh_2), 6.48 (m, 1H, C_6H_4, H_α *syn* to P(4-OCH_3-

$C_6H_4)_2$), 6.79-6.84 (m, 1H, C_6H_4, H_β), 6.92–6.99 (m, 1H, C_6H_4, H_γ), 7.01–7.10 (m, 4H, 4-$OCH_3C_6H_4$, overl. with isomer M), 7.48–7.62 (m, 4H, 4-$OCH_3C_6H_4$, overl. with isomer M), 7.55–7.62 (m, 8H, Ph, overl. with isomer M), 7.65–7.71 (m, 2H, Ph, overl. with isomer M).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ −1.0 (d, P(4-$OCH_3C_6H_4)_2$; $^2J_{P-P} = 40.7$ Hz), 33.7 (d, PPh_2; $^2J_{P-P} =$ 40.7 Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.7 (free triflate).

Anal. Calc. for $C_{38}H_{38}NO_5F_3P_2SPd$ (846.15): C, 53.94; H, 4.53. Found: C, 54.50; H, 4.95.

5.5.5. Synthesis of [PdCH$_3$(**1d**)(CH$_3$CN)](OTf) (**3d**)

Yield: 81%, light-brown powder. The compound exists as a mixture of two isomers in solution (M, major isomer, and m, minor isomer). M:m = 2.5:1.

5.5.5.1. Major isomer, CH_3 trans to P(3-$CF_3C_6H_4)_2$. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.61 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 7.10$ Hz; $^3J_{H-P(cis)} = 2.30$ Hz), 2.13-2.25 (br, 3H, CH_3CN, overl. with isomer m), 3.90 (s, 6H, OCH_3, overl. with $CH_2P(4\text{-}OCH_3C_6H_4)_2$ of isomer m), 3.91 (br, 2H, $CH_2P(4\text{-}OCH_3C_6H_4)_2$), 4.03 (br, 2H, $CH_2P(3\text{-}CF_3\text{-}C_6H_4)_2$, overl. with isomer m), 6.16 (m, 1H, C_6H_4, H_α *syn* to P(4-$OCH_3C_6H_4)_2$), 6.27 (m, 1H, C_6H_4, H_δ *syn* to P(3-$CF_3C_6H_4)_2$), 6.81–6.88 (m, 2H, C_6H_4, H_β and H_γ, overl. with isomer m), 7.02–7.10 (m, 4H, 4-$OCH_3C_6H_4$, overl. with isomer m), 7.62–7.69 (m, 4H, 4-$OCH_3C_6H_4$, overl. with isomer m), 7.69–7.74 (m, 2H, 3-$CF_3C_6H_4$), 7.78–7.86 (m, 4H, 3-$CF_3C_6H_4$, overl. with isomer m), 7.96–8.00 (br, 2H, 3-$CF_3C_6H_4$, overl. with isomer m).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ 2.9 (d, P(3-$CF_3C_6H_4)_2$; $^2J_{P-P} = 40.6$ Hz), 30.5 (d, P(4-$OCH_3C_6H_4)_2$; $^2J_{P-P} = 40.6$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.7 (free triflate), 62.5 (s, CF_3).

5.5.5.2. Minor isomer, CH_3 trans to P(3-$CF_3C_6H_4)_2$. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.47 (dd, 3H, CH_3, $^3J_{H-P(trans)} = 6.90$ Hz; $^3J_{H-P(cis)} = 2.90$ Hz), 2.13–2.25 (br, 3H, CH_3CN, overl. with isomer M), 3.89 (s, 6H, OCH_3), 3.90 (br, 2H, $CH_2P(4\text{-}OCH_3C_6H_4)_2$ overl. with OCH_3 group of isomer M), 4.03 (br, 2H, $CH_2P(3\text{-}CF_3C_6H_4)_2$, overl. with isomer M), 6.03 (m, 1H, C_6H_4, H_δ *sin* to P(3-$CF_3C_6H_4)_2$), 6.50 (m, 1H, C_6H_4, H_α *syn* to P(4-$OCH_3C_6H_4)_2$), 6.81–6.88 (m, 1H, C_6H_4, H_γ, overl. with isomer M), 6.95–7.00 (m, 1H, C_6H_4, H_β), 7.02–7.10 (m, 4H, 4-$OCH_3C_6H_4$ overl. with isomer M), 7.50–7.60 (m, 4H, 4-$OCH_3C_6H_4$), 7.78–7.86 (m, 4H, 3-$CF_3C_6H_4$ overl. with isomer M), 7.88 (m, 2H, 3-$CF_3C_6H_4$), 7.96–8.00 (br, 2H, 3-$CF_3C_6H_4$ overl. with isomer M).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ −0.8 (d, P(4-$OCH_3C_6H_4)_2$; $^2J_{P-P} = 41.8$ Hz), 34.4 (d, P(3-$CF_3C_6H_4)_2$; $^2J_{P-P} = 41.8$ Hz).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.7 (free triflate), 62.6 (s, CF_3).

Anal. Calc. for $C_{40}H_{36}NO_5F_9P_2SPd$ (982.17): C, 48.92; H, 3.69. Found: C, 49.10; H, 3.88.

5.6. Carbonylation of the neutral complexes **2a–d**

CO was bubbled (*ca.* 40 ml/min) through a metallic needle into a solution of 20–25 mg of the complex in 5 ml of $CDCl_3$ for *ca.* 40 min. The sample was then introduced into the probe and the first spectrum acquired after 5 min.

5.7. Carbonylation of the cationic complexes **3a–d**

The complex (20–25 mg) was dissolved in 0.5 ml of $CDCl_3$ and the solution cooled down to −60 °C. CO was bubbled for 5–10 min through a metallic needle. The sample was then introduced into the precooled (−60 °C) probe and the first spectrum recorded after 5 min.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 281609 (**2d**) and 281610 ([Pd(**1a**)Cl]$_2$-(OTf)$_2$). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing to data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.038.

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