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Palladium(II) complexes with the new P,N-type ligand (2-oxazoline-2-ylmethyl)di-isopropylphosphine as intermediates in CO/ethylene or CO/methyl acrylate insertion

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Abstract

The ligand (*i*-Pr)₂PCH₂(oxazoline) (**1a**), of the P,N-donor type, was reacted with [PdMeCl(COD)] to yield the square planar methylpalladium(II) complex [PdClMe(P,N)] (P,N = **1a**) (**2a**), from which the complex [PdMe(P,N)OTf] (OTf = OSO₂CF₃) (**3a**) was obtained by AgOTf-promoted chloride abstraction. The alkyl complexes [Pd{CHRCH₂C(O)Me}(P,N)]OTf (P,N = **1a**) (**5a**, R = H; **7a**, R = C(O)OMe) have been isolated from the initial CO/ethylene or CO/methyl acrylate insertion steps into the Pd–Me bond of **3a**, respectively, and spectroscopically characterized. Complexes **2a**, **3a** and **7a** have been fully characterized by single crystal X-ray diffraction. Complex **7a** is still a rare example of a structurally characterized CO/methyl acrylate stepwise insertion product. These complexes are relevant to the alternating copolymerization of olefins and carbon monoxide catalyzed by palladium complexes. In addition, the centrosymmetric dinuclear complex *trans*-[Pd(μ-Cl){(*i*-Pr)₂PCH₂(oxazoline)}]₂(OTf)₂ (**6**) has been obtained and characterized by X-ray diffraction; it appears to be the first dinuclear complex of the type [Pd(μ-Cl)(P,N)]₂ to be characterized by X-ray crystallography. **To cite this article: M. Agostinho, P. Braunstein, C. R. Chimie 10 (2007).**
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Résumé

Le ligand (*i*-Pr)₂PCH₂(oxazoline) (**1a**), de type donneur P,N, réagit avec [PdClMe(COD)] pour former le complexe plan carré méthylpalladium(II) [PdClMe(P,N)] (P,N = **1a**) (**2a**), à partir duquel le complexe [PdMe(P,N)OTf] (OTf = OSO₂CF₃) (**3a**) a été obtenu par abstraction de chlorure à l'aide de AgOTf. Les complexes alkyles [Pd{CHRCH₂C(O)Me}(P,N)]OTf (P,N = **1a**) (**5a**, R = H; **7a**, R = C(O)OMe), ont été isolés lors des premières étapes d'insertion de CO/éthylène ou de CO/acrylate de méthyle, respectivement, dans la liaison Pd–Me de **3a**, et caractérisés par méthodes spectroscopiques. Les complexes **2a**, **3a** et **7a** ont été complètement caractérisés par diffraction des rayons X sur monocristal. Le complexe **7a** est un exemple encore rare de produit d'insertion par étapes de CO/acrylate de méthyle qui ait été caractérisé structuralement. Ces complexes sont pertinents pour la copolymérisation alternée d'oléfinés et de monoxyde de carbone catalysée par les complexes du palladium. En outre, le complexe

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dinucléaire centrosymétrique *trans*-[Pd(μ -Cl){(*i*-Pr)₂PCH₂(oxazoline)}]₂(OTf)₂ (**6**) a été obtenu et caractérisé par diffraction des rayons X; il s'agit du premier complexe dinucléaire de type [Pd(μ -Cl)(P,N)]₂ à être caractérisé par diffraction des rayons X.

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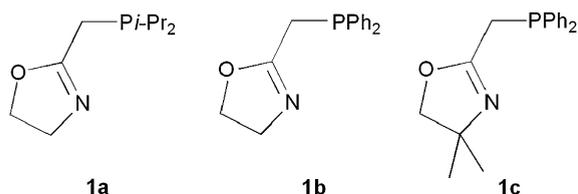
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keywords: Palladium complexes; CO/olefin insertion; Methylacrylate; Phosphinooxazoline ligands

Mots-clés : Complexes de palladium ; Insertion CO/oléfines ; Acrylate de méthyle ; Ligands phosphinooxazoline

1. Introduction

The synthesis of ligands which combine hard and soft donor functionalities is a subject of considerable current interest, in particular with respect to the development of new reactive, hemilabile metal–ligand systems and more selective homogeneous catalysts [1,2]. In particular, numerous metal complexes containing P,N type ligands are catalytically active in a wide range of reactions of both academic and industrial interest [2,3]. Various unsymmetrical P,N-type bidentate ligands have recently been applied to CO/alkene copolymerization reactions [4].



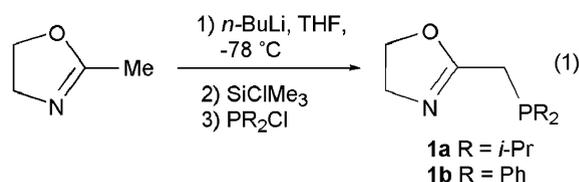
Using phosphinito- and phosphonito-oxazoline ligands as P,N chelates in Pd(II) complexes, we could recently isolate and fully characterize intermediates in the CO/ethylene stepwise insertion reaction [4a]. Cationic Pd(II) complexes containing the diphenylphosphino-P,N type ligands **1b** or **1c** have been investigated as catalysts for ethylene oligomerization [5,6] and CO/ethylene copolymerization [4h]. These ligands have allowed us to prepare and fully characterize initial intermediates in the sequential CO/ethylene or CO/methyl acrylate coupling reactions, without the need for using excess methyl acrylate [4b]. Despite the considerable interest in the alternating copolymerization of olefins with CO and with polar monomers, such as methyl acrylate [4b,7], up to date only few metal complexes featuring CO/methyl acrylate coupling have been isolated and characterized [4b,g,8–13]. Therefore, investigating the behaviour of other functional ligands bearing substituents on the phosphorus donor atom with different stereoelectronic properties

should be of particular interest for these types of reactions. We have now extended our studies with the diphenylphosphino-P,N ligands **1b,c** to the new isopropyl derivative **1a** and studied the reactivity of its Pd(II) complexes.

2. Results and discussion

2.1. Ligand synthesis

The ligand (*i*-Pr)₂PCH₂(oxazoline) (**1a**) was obtained in quantitative yield (95%) by the one-pot procedure previously used to synthesize **1b** [4h], which consists first of the deprotonation of the corresponding 2-methyl-2-oxazoline in THF at –78 °C, followed by the addition at this temperature of SiClMe₃, to form the *N*-silyl derivative, and the reaction with P(*i*-Pr)₂Cl (Eq. (1)).



In the ¹H NMR spectrum of ligand **1a**, the PCH₂ (δ = 2.35, ²J_{PH} = 1.0 Hz) and NCH₂ (δ = 3.75, ³J_{HH} = 9.3 Hz) protons appear as a broad doublet and broad triplet, respectively, indicating a small ⁵J_{HH} coupling, while the CH protons of the *i*-Pr substituents on phosphorus appear as a septet of doublets (δ = 1.75, ²J_{PH} = 1.4 Hz, ³J_{HH} = 7.1 Hz). The ³¹P{¹H} NMR spectrum contains a singlet at δ 6.4 and the characteristic ν_{CN} band for the oxazoline ring appears in the IR spectrum at 1658 cm^{–1} (Table 1). In contrast to ligand **1b**, which was obtained as a white powder, [4h] ligand **1a** is a pale yellow oil that can be exposed to air for short periods of time, but is best kept under an inert atmosphere. Comparative spectroscopic data are presented in Table 1.

Table 1
Selected IR and NMR data for the ligands and complexes

	IR		NMR ^c	
	ν_{CN}	ν_{CO}	¹ H	³¹ P
1a	1658 ^a (s)			6.4
1b	1660 ^a (s)			–15.8
2a	1639 ^b (s)		0.51 Pd–CH ₃ (d, ³ J _{PH} = 2.3)	57.3
2b	1647 ^a (s)		0.55 Pd–CH ₃ (d, ³ J _{PH} = 2.7)	33.1
3a	1642 ^b (m)		0.51 Pd–CH ₃ (s)	63.4
3b	1633 ^b (s)		0.60 Pd–CH ₃ (s)	37.4
4a	1642 ^a (m)	1697 ^a (m)		54.4
4b	1644 ^a (s)	1704 ^a (s)		22.0
	$\nu_{\text{CN/CO}}$	$\nu_{\text{C(O)OMe}}$		
5a	1635 ^b (s)		2.45 C(O)CH ₃ (s)	62.3
5b	1634 ^b (s)		2.45 C(O)CH ₃ (s)	34.4
7a	1639 ^b (s)	1679 ^b (s)	2.55 C(O)CH ₃ (s)	59.5
7b	1633 ^b (s)	1683 ^b (s)	2.52 C(O)CH ₃ (s)	32.8

^a In CH₂Cl₂.

^b In KBr, cm^{–1}.

^c In CDCl₃, ppm, *J* in Hz.

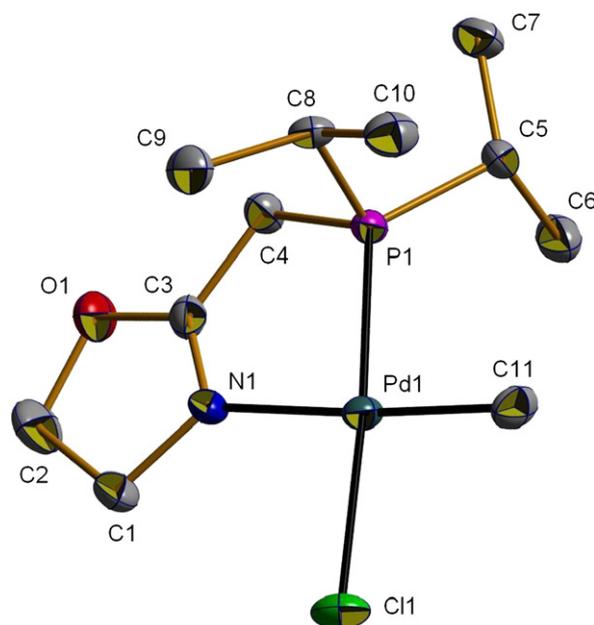


Fig. 1. ORTEP view of the structure of complex **2a** (H atoms omitted). Displacement ellipsoids are drawn at 50% probability level.

2.2. Synthesis of the complex [PdClMe(P,N)] (**2a**)

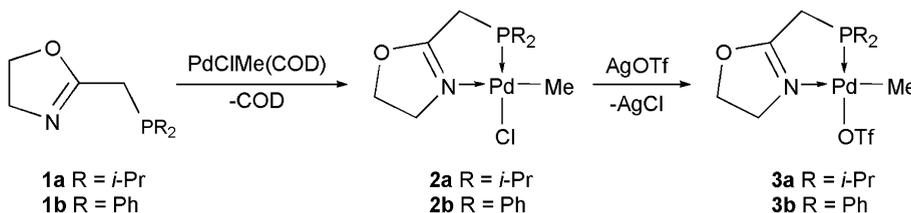
Reaction of **1a** with 0.8 equiv of [PdClMe(COD)] (COD = cycloocta-1,5-diene) afforded [PdClMe(P,N)] (P,N = **1a**) (**2a**) in quantitative yield (Scheme 1).

Coordination of the ligand resulted in a shift of the ν_{CN} absorption to 1639 cm^{–1} (Table 1). The presence of a single peak in the ³¹P{¹H} NMR spectrum of **2a** suggests the formation of a single isomer. In the ¹H NMR spectrum, the Pd–Me resonance of **2a** appears as a doublet at δ 0.51, of which the magnitude of the coupling constant (³J_{PH} = 2.3 Hz) indicates a *cis* relationship between the two groups with the largest *trans* influence, namely the phosphorus atom and the methyl group. The PCH₂ protons appear as a doublet of triplets (δ 2.51, ²J_{PH} = 8.8, ⁵J_{HH} = 2.0 Hz) owing to a ⁵J_{HH} coupling between the PCH₂ and NCH₂ protons. A similar ⁵J_{HH} coupling has been observed for **2b** and related palladium complexes stabilized by the ligand **1b** [4b,h]. The CH protons of the *i*-Pr substituents of the phosphorus appear as a doublet of septets (δ = 2.19, ²J_{PH} = 8.6,

³J_{HH} = 7.1 Hz). Other characterizing data are given in Section 3. Single crystals of **2a** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH₂Cl₂ solution of the complex. A view of its molecular structure is shown in Fig. 1 and selected distances and angles are given in Table 2.

As observed for **2b** [4b], the coordination geometry around the palladium centre in **2a** is very close to square planar. As expected, the Me group is positioned *cis* to the phosphorus donor atom, which is consistent with the fact that the groups with the largest *trans* influence avoid being mutually *trans* to one another [4b,14,15]. The P,N-chelate bite angle [82.68(6)°] is close to that reported for **2b** [82.2(3)°] [4b], and is consistent with that in other five-membered ring complexes of the type [PdClMe(P,N)] [4f,g,15,16].

Although no classical intermolecular hydrogen bonds were detected in **2a**, a non-conventional C–



Scheme 1. Synthesis of complexes **2a,b** and **3a,b**. All reactions were performed at room temperature in CH₂Cl₂.

Table 2
Selected bond lengths [Å] and angles [°] in complexes **2a**, **3a**, **6** and **7a**

	2a	3a	6	7a
Pd1–N1	2.138(2)	2.135(2)	2.008(5)	2.076(6)
Pd1–P1	2.2058(7)	2.1817(7)	2.2140(14)	2.222(2)
Pd1–C11	2.042(3)	2.031(3)		2.049(7)
Pd1–O2		2.177(2)		2.112(5)
Pd1–Cl1	2.3724(7)		2.3220(14)	
Pd1–Cl1 ^{iv}			2.4357(13)	
N1–C3	1.276(3)	1.274(4)	1.284(7)	1.278(10)
C3–C4	1.488(4)	1.488(4)	1.475(7)	1.480(12)
C4–P1	1.852(3)	1.839(3)	1.833(5)	1.845(8)
O2–C13				1.232(10)
C13–C12				1.506(14)
C12–C11				1.538(13)
N1–Pd1–P1	82.68(6)	83.63(6)	83.18(14)	84.1(2)
N1–Pd1–C11	175.32(10)	174.2(1)		174.7(3)
N1–Pd1–O2		96.73(8)		94.3(2)
N1–Pd1–Cl1	94.19(6)		176.71(14)	
N1–Pd1–Cl1 ^{iv}			94.09(14)	
P1–Pd1–O2		177.76(6)		174.3(2)
P1–Pd1–C11	92.99(8)	91.55(10)		100.1(2)
P1–Pd1–Cl1	175.80(3)		93.54(5)	
P1–Pd1–Cl1 ^{iv}			176.93(5)	
C11–Pd1–O2		88.2(1)		81.8(3)
C11–Pd1–Cl1	90.22(8)			
C11–Pd1–Cl1 ^{iv}			89.19(5)	
Pd1–Cl1–Pd1 ^{iv}			88.22(5)	

Symmetry code: (iv) 1 – x, y, 3/2 – z.

H···Cl hydrogen interaction is present, which involves the Cl atom bound to palladium and the unique PC–H atom of an isopropyl group of a neighbouring molecule (C8–H···Cl1, Table 3). This results in an infinite, one-dimensional wavelike chain structure (Fig. 2). Interactions of this type have been recently reported for related complexes [PdClMe(P,N)] and [PdCl₂(P,N)] (P,N = 2-(2,6-dimethylphenyl)-6-(diphenylphosphino-methyl)pyridine) [15].

2.3. Synthesis of the complex [PdMe(P,N)OTf] (**3a**)

The complex [PdMe(P,N)OTf] (P,N = **1a**, OTf = OSO₂CF₃) (**3a**) was prepared similarly to **3b** [4h] by treatment of a dichloromethane solution of **2a** with AgOTf (Scheme 1). After filtration through Celite to

Table 3
Hydrogen-bonding parameters (Å, deg) for compounds **2a** and **3a**

Complex	D–H···A	D–H	H···A	D···A	D–H···A
2a	C8–H···Cl1 ⁱ	1.00	2.77	3.610(3)	142
3a	C4 ⁱⁱⁱ –H···O4	0.99	2.26	3.215(4)	160

Symmetry codes: (i) x, 0.5 – y, 0.5 + z; (iii) x, 1 + y, z.

remove the AgCl formed, the solvent was evaporated under reduced pressure and the desired complex was obtained as a solid and washed with diethylether and pentane. Selected IR and NMR data are reported in Table 1. As for **2a**, the singlet resonance at δ 0.51 for the Pd–Me protons is characteristic of the coordination geometry in **3a**. The absence of ³J_{PH} coupling constant (or too small value to be detected) indicates a *cis* relationship between the phosphorus atom and the methyl group. There was no spectroscopic indication of a coordinated solvent molecule, consistent with the triflate anion being a better donor than CH₂Cl₂ and remaining coordinated to the metal in solution. Note, however, that the ¹⁹F{¹H} NMR signal for **3a** in CDCl₃ is very similar to that in **5a** and **7a**. As expected, the formation of cationic Pd(II) complexes is observed in solvents such as MeCN [4h]. When compared to the ³¹P{¹H} NMR data of its less electrophilic but also neutral analogue **2a**, the downfield shift observed ($\Delta\delta$ = 6.1 ppm) is larger than when going from **2b** to **3b** ($\Delta\delta$ = 4.3 ppm) (Table 1).

X-ray quality single crystals of **3a** were grown by slow diffusion of hexane into a dichloromethane solution of the complex; its molecular structure is represented in Fig. 3 and selected bond lengths and angles are given in Table 2. It confirmed that the triflate anion is directly bonded to Pd, with a Pd–O2 distance of 2.177(2) Å. The geometry around Pd is square planar, as shown by the values of the P1–Pd1–O2 and N1–Pd1–C11 angles of 177.76(6)° and 174.20(11)°, respectively. The bond lengths and angles involving the P,N chelate are similar to those found in **3b** [4b].

Examination of the crystal packing of complex **3a** reveals an intermolecular C4–H···O4 hydrogen-bonding interaction involving a triflate oxygen and a PC4–H hydrogen atom of an adjacent molecule [C4···O4 = 3.215 (4) Å, Table 3], which leads to a one-dimensional chain arrangement in the solid state (Fig. 4).

2.4. CO/ethylene or CO/methyl acrylate insertion reactions

The reaction of complex **3a** with CO in CH₂Cl₂ at room temperature was monitored by ³¹P{¹H} NMR spectroscopy. CO insertion into its palladium methyl bond produced in less than 1 h the acyl derivative [Pd{C(O)Me}(P,N)(OTf)] (P,N = **1a**) (**4a**) (Scheme 2), which was only observed in solution and characterized by the large high-field shift of its ³¹P{¹H} NMR resonance ($\Delta\delta$ = –9.0, Table 1) and by infrared spectroscopy. The IR absorption band due to the CO

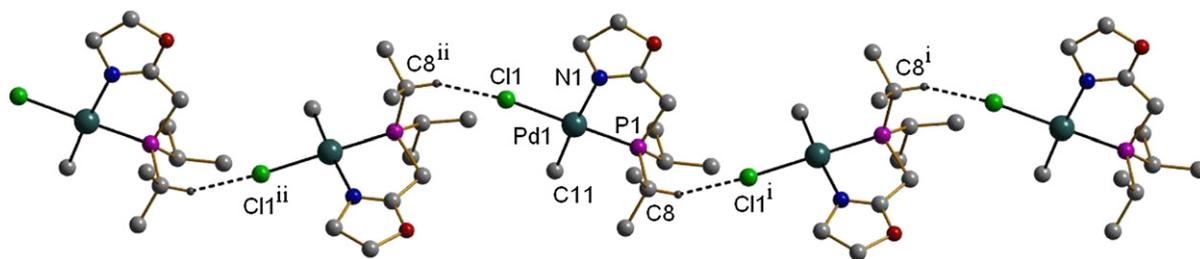


Fig. 2. View of the crystal structure of complex **2a** showing the PC8–H···Cl1 interactions. Symmetry codes: (i) $x, 0.5 - y, 0.5 + z$; (ii) $x, 0.5 - y, -0.5 + z$.

stretching appears at 1697 cm^{-1} , which is typical for such acyl complexes [4b,e,g]. Previous efforts to isolate the analogous complex **4b** have not been successful because of the instability of the complex, and no satisfactory elemental analyses could be obtained [4h]. Therefore, no attempt was made to isolate **4a**. In a previous study with ligands **1b** and **1c**, we have demonstrated the existence of a temperature-dependent equilibrium between the triflate, acyl complex, $[\text{Pd}\{\text{C}(\text{O})\text{Me}\}(\text{P},\text{N})\text{OTf}]$ (P,N = **1c**), and a cationic carbonyl, acyl Pd(II) complex $[\text{Pd}\{\text{C}(\text{O})\text{Me}\}(\text{P},\text{N})(\text{CO})\text{OTf}]$ [4b], and

a similar equilibrium is expected to occur in the case of **4a**, i.e. at room temperature the triflate anion coordinates to the palladium centre.

As previously observed for **4b** [4b], ethylene insertion into the palladium–acyl bond of **4a** to the five-membered C,O chelate complex $[\text{Pd}\{\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}\}(\text{P},\text{N})\text{OTf}]$ (**5a**) was completed in less than 1 h ($^{31}\text{P}\{^1\text{H}\}$ monitoring). The IR spectrum shows only one absorption band at 1635 cm^{-1} , corresponding to the CN and CO stretching vibrations ($\nu_{\text{CN/CO}}$, Table 1), which represents a shift for the CO band of 62 cm^{-1} to a lower wave number with respect to that for **4a**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5a** contains a singlet at $\delta 62.3$ which is shifted to low field relative to that of **4a** ($\delta 54.4$, Table 1). In the ^1H NMR spectrum of **5a**, the Pd–CH₂ protons give rise to a well-resolved triplet ($\delta 1.65$, $^3J_{\text{HH}} = 6.2$, $^3J_{\text{PH}} = 1.6\text{ Hz}$), whereas the CH₂CO protons appear as a broad triplet ($\delta 3.09$, $^3J_{\text{HH}} = 6.2\text{ Hz}$), indicating a smaller J_{PH} coupling constant.

Attempts to crystallize **5a** by layering a CH₂Cl₂ solution with hexane were unsuccessful. Nevertheless, this procedure afforded a crystalline material suitable for X-ray crystallography, which subsequently revealed to be the dinuclear palladium complex *trans*- $[\text{Pd}(\mu\text{-Cl})\{(i\text{-Pr})_2\text{PCH}_2(\text{oxazoline})\}_2(\text{OTf})_2]$ (**6**) containing a di- μ -chloro bridge and two equivalent five-membered P,N-chelate rings. A view of the centrosymmetric dinuclear cationic complex in **6** is shown in Fig. 5, and selected bond distances and angles are given in Table 2. According to the Cambridge Structure Database, **6** is the first dinuclear complex of the type $[\text{Pd}(\mu\text{-Cl})(\text{P},\text{N})_2]$, and only the second of the type $[\text{Pd}(\mu\text{-X})(\text{P},\text{N})_2]$ (X = halide) to be characterized by X-ray crystallography [16]. The coordination geometry around the palladium atoms in **6** is close to square planar with the nitrogen donor atoms in *transoid* relationship with respect to the Pd–Pd axis, and is essentially similar to those of cyclopalladated species containing a five-membered chelate ring [16,17]. The

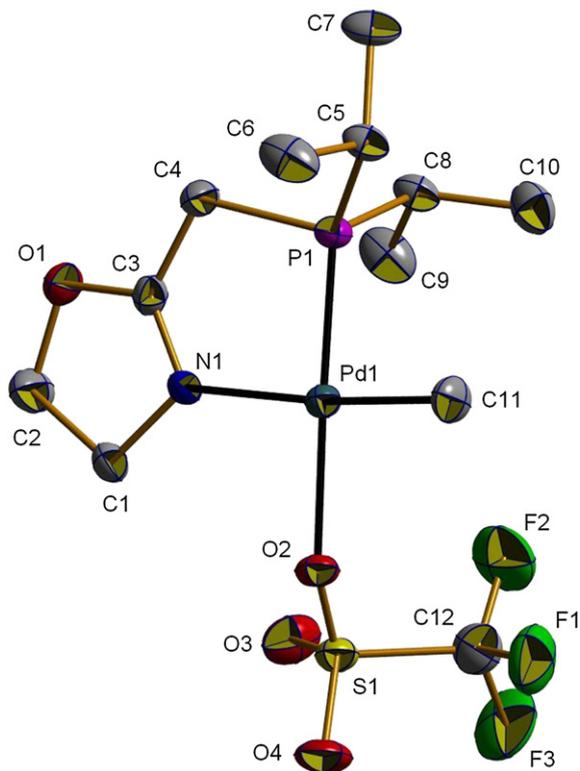


Fig. 3. ORTEP view of the structure of complex **3a** (H atoms omitted). Displacement ellipsoids are drawn at the 50% probability level.

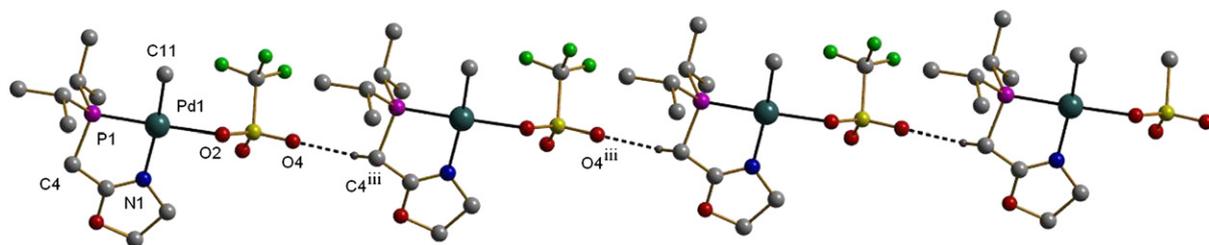


Fig. 4. View of the crystal structure of complex **3a** showing the $C4^{iii}-H \cdots O4$ interaction. Only one of the H atoms at C4 is shown. Symmetry code: (iii) $x, 1 + y, z$.

coordination planes (mean planes passing through C11, C11^{iv}, N1, P1 and through C11, C11^{iv}, N1^{iv}, P1^{iv}) form an angle of $25.47(1)^\circ$ and the distance between two palladium atoms is $3.3126(5) \text{ \AA}$, which excludes the presence of metal–metal bonding. The length of the Pd–Cl bond *trans* to P [$2.4357(13) \text{ \AA}$] is longer than that *trans* to N [$2.3220(14) \text{ \AA}$], which parallels the different *trans* influences exerted by the phosphorus and the nitrogen atoms [14,15,18].

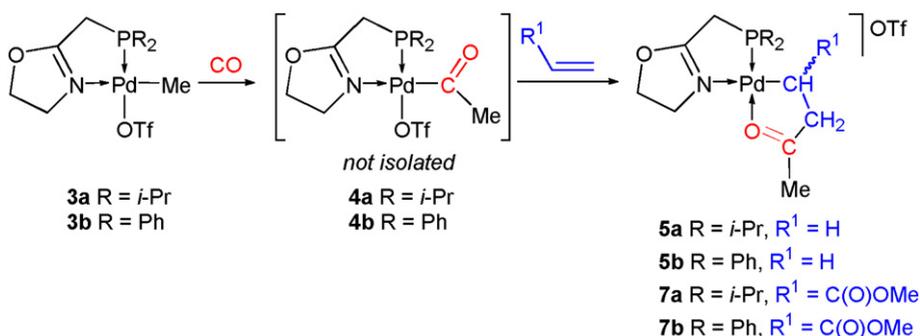
In order to determine the fate of the growing polymer chain upon formation of **6**, the ^{13}C -labeled isotopomer of **5a** was prepared by bubbling ^{13}CO into a solution of $[\text{PdMe}(\text{P,N})\text{OTf}]$ (**3a**), which was subsequently treated with ethylene according to the described procedure. In the ^1H NMR spectrum of the ^{13}C -labeled isotopomer of **5a**, the methyl group [$^{13}\text{C}(\text{O})\text{CH}_3$] appears as a doublet due to coupling of the protons with the ^{13}C of the labeled ^{13}CO , with a coupling constant ($^2J_{\text{HC}} = 5.8 \text{ Hz}$) which is in agreement with values reported in a related study with ^{13}CO and propene [19]. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays $^1J_{\text{CC}}$ of 40.3 and 40.1 Hz for the [$^{13}\text{C}(\text{O})\text{CH}_3$] and [$\text{CH}_2^{13}\text{C}(\text{O})\text{CH}_3$], respectively, in agreement with values reported for a ^{13}C -labeled isotopomer of a CO/methyl acrylate insertion product [8].

Complex **5a** is stable in the solid state for several weeks; however, it decomposes progressively in

solution by β -hydrogen elimination. Keeping a CDCl_3 solution of the ^{13}C -labeled isotopomer of **5a** in a NMR tube over a period of 10 days at room temperature affords a few crystals of complex **6**, which deposit along with some palladium metal. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the remaining solution shows only one singlet at $\delta 56.4$, indicating that the only P-containing species in solution is the dinuclear complex **6**. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the disappearance of the signal for the ^{13}C -labeled **5a** is accompanied by the appearance of a new singlet at $\delta 199.0$ corresponding to methyl vinyl ketone resulting from β -hydrogen elimination from complex **5a** (Scheme 3).

Further confirmation came from GC–MS analysis of the solution after trap-to-trap distillation. The fragmentation pattern found for $\text{Me}^{13}\text{C}(\text{O})\text{CH}=\text{CH}_2$ corresponds perfectly, plus one unit, to that for $\text{MeC}(\text{O})\text{CH}=\text{CH}_2$.

Palladium hydride complexes resulting from CO–ethylene copolymerization termination reactions usually decompose into dicationic complexes of the type $[\text{Pd}(\text{L})_2]$ (L = bidentate ligand) [4e,20]. However, Consiglio recently reported the structure of a dinuclear complex of the type $[\text{Pd}(\mu\text{-Cl})(\text{L})_2](\text{OTf})_2$ (L = diphosphine ligand) obtained by replacement of a CH_3 group with a chloride from CHCl_3 [21].



Scheme 2. All reactions were performed at room temperature in CH_2Cl_2 .

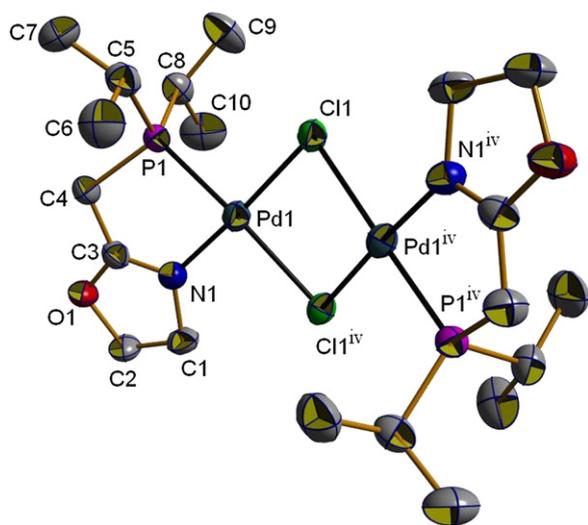


Fig. 5. View of the structure of the dicationic complex in **6** (H atoms and triflate anions omitted). Displacement ellipsoids are drawn at 50% probability level. Symmetry code: (iv) $1 - x, y, 3/2 - z$.

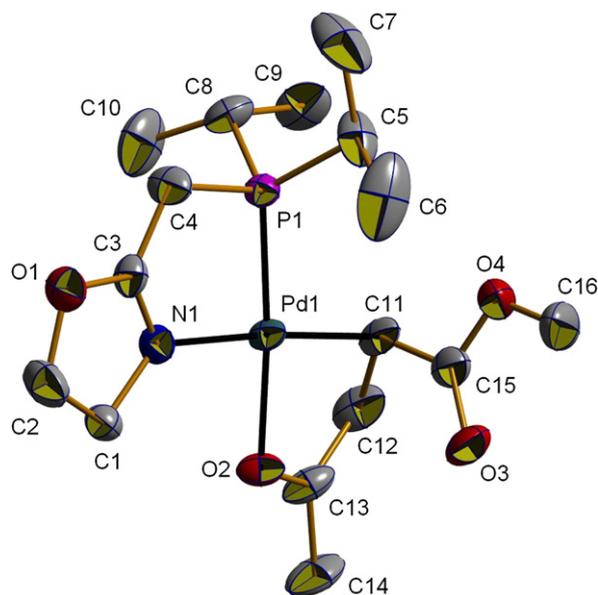
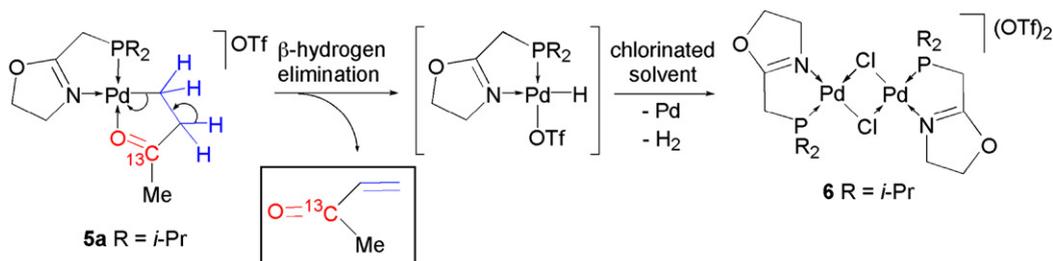


Fig. 6. View of the structure of the cation in **7a** (H atoms omitted). Displacement ellipsoids are drawn at 50% probability level.

The insertion of methyl acrylate into the palladium acyl bond of **4a** was regioselective (2,1-insertion) and afforded $[\text{Pd}\{\text{CH}[\text{C}(\text{O})\text{OMe}]\text{CH}_2\text{C}(\text{O})\text{Me}\}(\text{P},\text{N})]\text{OTf}$ (**7a**) within 1 h ($^{31}\text{P}\{^1\text{H}\}$ monitoring). The low-field shift in the $^{31}\text{P}\{^1\text{H}\}$ resonance of **7a** relative to that of **4a** ($\Delta\delta = 5.1$, Table 1) is smaller than when considering **7b** and **4b** ($\Delta\delta = 10.8$, Table 1) [4b]. The ^1H NMR spectrum of **7a** contains methyl signals for the inserted methyl acrylate at $\delta = 2.55$ [C(O)Me] and 3.63 [C(O)OMe], the CH and CH_2 protons were identified by means of 2D (COSY and HSQC) NMR experiments and resonate at $\delta = 2.55$ and 3.07, respectively (see Section 3). The latter resonance appears, surprisingly, as a slightly broadened singlet. Complex **7a** is stable in the solid state for several weeks, and in contrast to **5a**, no significant decomposition is observed in a CDCl_3 solution over a period of 10 days.

The solid-state structure of **7a** was unambiguously established by single-crystal X-ray diffraction (Fig. 6)

and it represents, to the best of our knowledge, only the fourth methyl acrylate–acyl coupling product to be structurally characterized [4b,g]. This structural determination confirms the formation of a five-membered (C,O) chelated product, which makes β -hydrogen elimination more difficult [4b,22]. The Pd–C distance in **7a** of 2.049(7) Å (Table 2) is close that in **7b** [2.046(4) Å] [4b], the most significant difference between these two structures being the value of the Pd1–P1 bond length, which is longer in **7a** than in **7b** by about 0.02 Å. Although it has not yet been possible to insert a CO molecule into the Pd–C11 bond of **7a** or **7b** (1 atm, 25 °C), our results provide further insight into the comparative reactivity of ethylene and methylacrylate into a Pd–carbon bond, and the stability of the corresponding insertion products. Although (partial) dissociation in solution of the triflate ligand of **3a** and **4a** cannot be completely ruled out, which would render the



Scheme 3. β -hydrogen elimination from complex **5a** with formation of methylvinylketone and the dinuclear complex **6**.

complexes more electrophilic (see above), we assume that it remains coordinated to the Pd(II) centre. This obviously does not prevent insertion reactions to take place because the triflate ligand can be displaced by CO or the olefin. In all cases, ethylene or methylacrylate insertion occurred into the Pd–C(O)Me and not into the Pd–Me bond. The increased basicity of the P(*i*-Pr)₂ group compared to PPh₂ did not translate into significant reactivity differences [4a,b].

3. Experimental section

The ¹H, ¹³C{¹H}, ³¹P{¹H} and ¹⁹F{¹H} NMR spectra were recorded at 300.13, 75.48, 121.49 and 282.38 MHz, respectively, on FT Bruker AC300, Avance 300, unless otherwise stated. IR spectra in the range 4000–400 cm⁻¹ were recorded on a Bruker IFS66FT and a Perkin Elmer 1600 Series FTIR. Elemental analyses were performed by the ‘Service de microanalyse, universit  Louis-Pasteur (Strasbourg, France)’. All reactions were carried out under purified N₂, using Schlenk techniques, and the solvents were freshly distilled under nitrogen prior to use. [PdClMe(COD)] (COD = 1,5-cyclooctadiene, C₈H₁₂) was prepared according to literature procedures [23].

3.1. Preparation and spectroscopic data for **1a**

To a THF solution (75 mL) of 2-methyl-2-oxazoline (0.5 mL, 5.87 mmol) in a 250-mL flask at –78 °C, was added dropwise a solution of *n*-butyllithium in hexane (3.67 mL, 1.6 M, 5.87 mmol). The mixture was stirred for 1 h and degassed SiClMe₃ (0.75 mL, 5.87 mmol) was added. The mixture was further stirred for 1 h at –78 °C and P(*i*-Pr)₂Cl (0.95 mL, 5.87 mmol) was added. The solution was stirred until it reached room temperature. After evaporation of the solvent under reduced pressure, the oily residue was dissolved in toluene (60 mL) and the solution was filtered through Celite. After evaporation of the toluene under vacuum, **1a** was obtained as a pale yellow oil (1.12 g, 95%). IR (CH₂Cl₂): 1658 (s, ν_{CN}) cm⁻¹. ¹H NMR (300.13 MHz, CDCl₃, room temp.): δ 1.02 [d, ³J_{HH} = 7.1 Hz, 6H, (CH(CH₃)(CH₃)₂)], 1.06 [dd, ³J_{PH} = 2.3 Hz, ³J_{HH} = 7.1 Hz, 6H, (CH(CH₃)(CH₃)₂)], 1.75 [septd, ²J_{PH} = 1.4 Hz, ³J_{HH} = 7.1 Hz, 2H, (CH(CH₃)₂)], 2.35 (br d, ²J_{PH} = 1.0 Hz, 2H, PCH₂), 3.75 (br t, ³J_{HH} = 9.3 Hz, 2H, NCH₂), 4.18 (t, ³J_{HH} = 9.3 Hz, 2H, OCH₂). ¹³C{¹H} (75.48 MHz, CDCl₃, room temp.): δ 18.6 [d, ²J_{PC} = 10.1 Hz, (CH(CH₃)(CH₃)₂)], 19.6 [d, ²J_{PC} = 15.8 Hz, (CH(CH₃)(CH₃)₂)], 21.4 (d, ¹J_{PC} = 25.6 Hz,

PCH₂), 23.6 [d, ¹J_{PC} = 13.9 Hz, (CH(CH₃)₂)], 54.5 (s, NCH₂), 67.5 (s, OCH₂), 167.3 (d, ²J_{PC} = 7.5 Hz, CN). ³¹P{¹H} NMR (121.49 MHz, CDCl₃, room temp.): δ 6.4 (s).

3.2. Preparation and spectroscopic data for [PdClMe(P,N)] (**2a**)

To a solution of ligand **1a** (0.48 g, 2.38 mmol) in CH₂Cl₂ (20 mL) was added solid [PdClMe(COD)] (0.50 g, 1.90 mmol, 0.8 equiv) at room temperature and the resulting mixture was stirred overnight. The solvent was then evaporated under reduced pressure. The resulting white residue was washed with diethylether (10 mL) and pentane (2 × 10 mL) and dried under vacuum to give a white powder (0.61 g, 89%). IR (KBr): 1639 (s, ν_{CN}) cm⁻¹. ¹H NMR (300.13 MHz, CDCl₃, room temp.): δ 0.51 (d, ³J_{PH} = 2.3 Hz, 3H, PdCH₃), 1.20 [dd, ³J_{PH} = 16.2 Hz, ³J_{HH} = 7.1 Hz, 6H, (CH(CH₃)(CH₃)₂)], 1.26 [dd, ³J_{PH} = 19.0 Hz, ³J_{HH} = 7.1 Hz, 6H, (CH(CH₃)(CH₃)₂)], 2.19 [dsept, ²J_{PH} = 8.6 Hz, ³J_{HH} = 7.1 Hz, 2H, (CH(CH₃)₂)], 2.51 (dt, ²J_{PH} = 8.8 Hz, ⁵J_{HH} = 2.0 Hz, 2H, PCH₂), 3.96 (tt, ³J_{HH} = 9.7 Hz, ⁵J_{HH} = 2.0 Hz, 2H, NCH₂), 4.54 (t, ³J_{HH} = 9.7 Hz, 2H, OCH₂). ¹³C{¹H} (75.48 MHz, CDCl₃, room temp.): δ –10.9 (d, ²J_{PC} = 2.9 Hz, PdCH₃), 17.6 [s, (CH(CH₃)(CH₃)₂)], 18.3 [d, ²J_{PC} = 4.6 Hz, (CH(CH₃)(CH₃)₂)], 21.5 (d, ¹J_{PC} = 23.6 Hz, PCH₂), 23.9 [d, ¹J_{PC} = 26.0 Hz, (CH(CH₃)₂)], 52.0 (s, NCH₂), 72.0 (s, OCH₂), 171.8 (d, ²J_{PC} = 15.4 Hz, CN). ³¹P{¹H} NMR (121.49 MHz, CDCl₃, room temp.): δ 57.3 (s). Anal. Calcd for C₁₁H₂₃ClNOPPd: C, 36.89; H, 6.47; N, 3.91. Found: C, 36.84; H, 6.30; N, 3.72.

3.3. Preparation and spectroscopic data for [PdMe(P,N)OTf] (**3a**)

To a solution of complex **2a** (0.51 g, 1.42 mmol) in CH₂Cl₂ (20 mL) was added AgOTf (0.44 g, 1.71 mmol, 1.2 equiv). The reaction mixture was protected from room light with an aluminum foil and stirred for 2 h at room temperature. The solution was then filtered through dry Celite and the solvent was evaporated under reduced pressure. The residue was washed with diethylether (10 mL), pentane (2 × 10 mL) and dried under vacuum overnight. Complex **3a** was obtained as a light beige powder (0.65 g, 97%). IR (KBr): 1642 (m, ν_{CN}) cm⁻¹. ¹H NMR (300.13 MHz, CDCl₃, room temp.): δ 0.51 (s, 3H, PdCH₃), 1.23 [dd, ³J_{PH} = 16.2 Hz, ³J_{HH} = 7.0 Hz, 6H, (CH(CH₃)(CH₃)₂)], 1.29 [dd, ³J_{PH} = 18.6 Hz, ³J_{HH} = 7.0 Hz, 6H, (CH(CH₃)(CH₃)₂)], 2.20 [dsept, ²J_{PH} = 8.8 Hz, ³J_{HH} = 7.0 Hz, 4H,

(CH(CH₃)₂)₂], 2.58 (dt, ²J_{PH} = 9.1 Hz, ⁵J_{HH} = 2.0 Hz, 2H, PCH₂), 4.00 (tt, ³J_{HH} = 9.7 Hz, ⁵J_{HH} = 2.0 Hz, 2H, NCH₂), 4.57 (t, ³J_{HH} = 9.7 Hz, 2H, OCH₂). ¹³C{¹H} (75.48 MHz, CDCl₃, room temp.): δ -7.4 (d, ²J_{PC} = 3.0 Hz, PdCH₃), 17.6 [s, (CH(CH₃)(CH₃)₂)], 18.3 [d, ²J_{PC} = 3.4 Hz, (CH(CH₃)(CH₃)₂)], 21.8 (d, ¹J_{PC} = 27.0 Hz, PCH₂), 24.4 [d, ¹J_{PC} = 29.3 Hz, (CH(CH₃)₂)], 52.3 (s, NCH₂), 72.1 (s, OCH₂), 171.5 (d, ²J_{PC} = 12.8 Hz, CN). ³¹P{¹H} NMR (121.49 MHz, CDCl₃, room temp.): δ 63.4 (s). ¹⁹F{¹H} NMR (282.4 MHz, CDCl₃): δ -78.1 (s). Anal. Calcd for C₁₂H₂₃F₃NO₄PPdS: C, 30.55; H, 4.91; N, 2.97. Found: C, 30.30; H, 4.67; N, 2.74.

3.4. Preparation and spectroscopic data for [Pd{CH₂CH₂C(O)Me}(P,N)]OTf (**5a**)

A solution of **3a** (0.17 g, 0.36 mmol) in CH₂Cl₂ (25 mL) was stirred under 1 atm CO at room temperature for 1 h, the CO was then replaced by 1 atm ethylene and the solution was further stirred for 1 h. The workup was as described for **2a**, and afforded **5a** as an orange powder (0.13 g, 68% yield). IR (KBr): 1635 (m, ν_{CN} and ν_{CO}) cm⁻¹. ¹H NMR (300.13 MHz, CDCl₃, room temp.): δ 1.25 [dd, ³J_{PH} = 16.6 Hz, ³J_{HH} = 7.0 Hz, 6H, (CH(CH₃)(CH₃)₂)], 1.27 [dd, ³J_{PH} = 18.9 Hz, ³J_{HH} = 7.0 Hz, 6H, (CH(CH₃)(CH₃)₂)], 1.65 (td, ³J_{HH} = 6.2, ³J_{PH} = 1.6 Hz, 2H, PdCH₂), 2.23 [dsept, ²J_{PH} = 8.8 Hz, ³J_{HH} = 7.0 Hz, 2H, (CH(CH₃)₂)], 2.45 [s, 3H, C(O)CH₃], 2.85 (dt, ²J_{PH} = 9.4 Hz, ⁵J_{HH} = 1.9 Hz, 2H, PCH₂), 3.09 (br t, ³J_{HH} = 6.2 Hz, 2H, PdCH₂CH₂), 3.98 (tt, ³J_{HH} = 9.7 Hz, ⁵J_{HH} = 1.9 Hz, 2H, NCH₂), 4.72 (t, ³J_{HH} = 9.7 Hz, 2H, OCH₂). ¹³C{¹H} (75.48 MHz, CDCl₃, room temp.): δ 11.9 (s, PdCH₂), 17.7 [s, (CH(CH₃)(CH₃)₂)], 18.3 [d, ²J_{PC} = 3.1 Hz, (CH(CH₃)(CH₃)₂)], 21.3 (d, ¹J_{PC} = 28.3 Hz, PCH₂), 24.5 [d, ¹J_{PC} = 28.7 Hz, (CH(CH₃)₂)], 27.9 [d, ⁴⁺⁵J_{PC} = 1.4 Hz, CH₂C(O)CH₃], 50.7 (s, PdCH₂CH₂), 52.3 (s, NCH₂), 72.2 (s, OCH₂), 173.9 (d, ²J_{PC} = 13.1 Hz, CN), 233.7 [d, ³⁺⁴J_{PC} = 0.7 Hz, CH₂C(O)CH₃]. ³¹P{¹H} NMR (121.49 MHz, CDCl₃, room temp.): δ 62.3 (s). ¹⁹F{¹H} NMR (282.4 MHz, CDCl₃): δ -78.6 (s). Anal. Calcd for C₁₅H₂₇F₃NO₅PPdS: C, 34.13; H, 5.16; N, 2.65. Found: C, 34.04; H, 4.93; N, 2.41.

3.5. Preparation and spectroscopic data for [Pd{CH[C(O)OMe]CH₂C(O)Me}(P,N)]OTf (**7a**)

A solution of **3b** (0.15 g, 0.32 mmol) in CH₂Cl₂ (20 mL) was stirred under 1 atm CO at room temperature for 1 h, after this period the CO atmosphere was

replaced with nitrogen and methyl acrylate (29 μL, 1 equiv) was added and the solution was further stirred for 1 h. The workup was as described for **2a**, and afforded **7a** as a beige powder (0.16 g, 85% yield). IR (KBr): 1639 (m, ν_{CN} and ν_{CO}), 1679 (m, ν_{CO}) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃, room temp.): 2D (COSY and HSQC) and ³¹P decoupled NMR experiments were used to determine chemical shifts and coupling constants; δ 1.18–1.47 [complex m, 12H, (CH(CH₃)₂)], 2.36 [dsept, ²J_{PH} = 1.8 Hz, ³J_{HH} = 7.0 Hz, (CH(CH₃)₂)(CH(CH₃)₂)], 2.55 [s, 3H, C(O)CH₃], 2.57 [sept, ³J_{HH} = 7.1 Hz, 1H, (CH(CH₃)₂)(CH(CH₃)₂)], overlapping with the C(O)CH₃ signal], ABMN spin system (A = B = M = N = H, X = P, δ_A 2.88, δ_B 3.07, ²J_{AB} = 18.8, ²J_{AX} = 9.5, ²J_{BX} = 9.4, ⁵J_{AH} = 1.6, ⁵J_{BH} = 1.9 Hz, 2H, PCH₂), 3.07 [appearance of br s, 2H, CH₂C(O)CH₃, overlapping with PCH₂ signal], 3.63 [s, 3H, C(O)OCH₃], 3.92 (m, 1H, NCHH), 4.05 (m, 1H, NCHH), ABMN spin system (A = B = M = N = H, δ_A 4.70, δ_B 4.81, ²J_{AB} = 10.7, ³J_{AH} = 8.4, ³J_{BH} = 8.7 Hz, 2H, OCH₂), although it was not possible to clearly observe the signal of the PdCH proton, COSY and HSQC experiments indicate that it resonates at 2.55 ppm, thus overlapping with the signals for the C(O)CH₃ and (CH(CH₃)₂)(CH(CH₃)₂) protons. ¹³C{¹H} (75.48 MHz, CDCl₃, room temp.): δ 16.2 [d, ²J_{PC} = 5.6 Hz, CH(CH₃)], 17.7 [d, ²J_{PC} = 1.0 Hz, CH(CH₃)], 18.8 [d, ²J_{PC} = 2.3 Hz, CH(CH₃)], 18.9 [s, CH(CH₃)], 21.2 (d, ¹J_{PC} = 29.9 Hz, PCH₂), 23.1 [d, ¹J_{PC} = 26.4 Hz, (CH(CH₃)₂)(CH(CH₃)₂)], 25.5 [d, ¹J_{PC} = 29.2 Hz, (CH(CH₃)₂)(CH(CH₃)₂)], 27.0 (d, ²J_{PC} = 2.3 Hz, PdCH), 28.2 [d, ⁴⁺⁵J_{PC} = 2.4 Hz, CH₂C(O)CH₃], 50.7 [s, CH₂C(O)CH₃], 51.6 [s, C(O)OCH₃], 51.9 (s, NCH₂), 72.6 (s, OCH₂), 174.8 (d, ²J_{PC} = 13.8 Hz, CN), 177.7 [s, C(O)OCH₃], 233.2 [d, ³⁺⁴J_{PC} = 2.2 Hz, CH₂C(O)CH₃]. ³¹P{¹H} NMR (121.49 MHz, CDCl₃, room temp.): δ 59.5 (s). ¹⁹F{¹H} NMR (282.4 MHz, CDCl₃): δ -78.6 (s). Anal. Calcd for C₁₇H₂₉F₃NO₇PPdS: C, 34.85; H, 4.99; N, 2.39. Found: C, 34.59; H, 4.83; N, 2.14.

3.6. Crystal structure determinations

Crystals of **2a**, **3a** and **7a** suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a CH₂Cl₂ solution of the respective complex at 5 °C. Crystals of **6** were obtained by slow diffusion of hexane into a CH₂Cl₂ solution of complex **5a** at 5 °C or, alternatively, by slow evaporation of a CDCl₃ solution at room temperature. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)

Table 4
X-ray diffraction data for the structural determination of complexes **2a**, **3a**, **6** and **7a**

	2a	3a	6	7a
Formula	C ₁₁ H ₂₃ ClNOPPd	C ₁₂ H ₂₃ NOPPd·CF ₃ SO ₃	C ₂₀ H ₄₀ Cl ₂ N ₂ O ₂ P ₂ Pd ₂ ·2(CF ₃ SO ₃)	C ₁₆ H ₂₉ NO ₄ PPd·CF ₃ SO ₃
<i>M_r</i>	358.12	471.74	984.32	585.84
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> ₂ / <i>c</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> [Å]	8.3170(2)	8.3800(2)	24.6530(7)	9.4210(2)
<i>b</i> [Å]	10.6290(3)	10.2020(3)	8.6270(3)	25.2850(4)
<i>c</i> [Å]	16.6060(4)	11.3650(4)	18.9330(7)	9.9140(2)
α [°]		86.1340(8)		
β [°]	95.509(2)	80.6550(8)	116.4510(14)	96.68(5)
γ [°]		73.1650(17)		
<i>V</i> [Å ³]	1461.21	917.43(5)	3605.2(2)	2345.6(3)
<i>Z</i>	4	2	4	4
<i>D</i> _{calc} [kg m ⁻³]	1.628	1.708	1.814	1.659
μ [mm ⁻¹]	1.544	1.255	1.425	1.009
<i>T</i> [K]	173(2)	173(2)	173(2)	173(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
θ_{\max} [°]	30.03	30.06	29.14	30.01
Data set [<i>h</i> , <i>k</i> , <i>l</i>]	–11/11, –14/14, –23/23	–11/11, –11/14, –14/16	–33/33, –10/11, –25/25	–11/13, –35/32, –13/13
Tot., unique data, <i>R</i> (int)	7268, 4255, 0.0305	7018, 5346, 0.0218	7943, 4829, 0.0374	19315, 6815, 0.0672
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	3151	4298	3192	5607
No. reflns, No. params	4255, 145	5346, 208	4829, 202	6815, 250
<i>R</i> ₁ , <i>wR</i> ₂ , GOF	0.0373, 0.0921, 1.058	0.0382, 0.0918, 1.076	0.0609, 0.1671, 1.068	0.0992, 0.2525, 1.128

(Table 4). Data were collected using phi-scans and the structures were solved by direct methods using the SHELXL 97 software [24,25], and the refinement was performed by full-matrix least squares on *F*². No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors (*d*_{C–H} = 0.95 Å, *U*₁₁ = 0.04).

The crystallographic material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material CCDC 630553–630556 and can be obtained by contacting the CCDC (quoting the article details and the corresponding SUP number). See <http://www.ccdc.cam.ac.uk/deposit> for crystallographic files in .cif format.

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