# Migratory insertion reactions of norbornene, norbornadiene and 7-oxanorbornene derivatives into the palladium–carbon bond of heterodinuclear Fe–Pd–Acyl complexes. Substrate influence on the Pd coordination sphere and crystal structure of $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}dppa)Pd\{C_9H_9NO_3C(=O)Me\}]$

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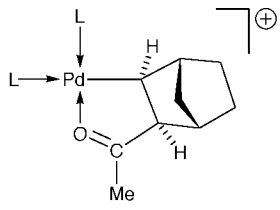
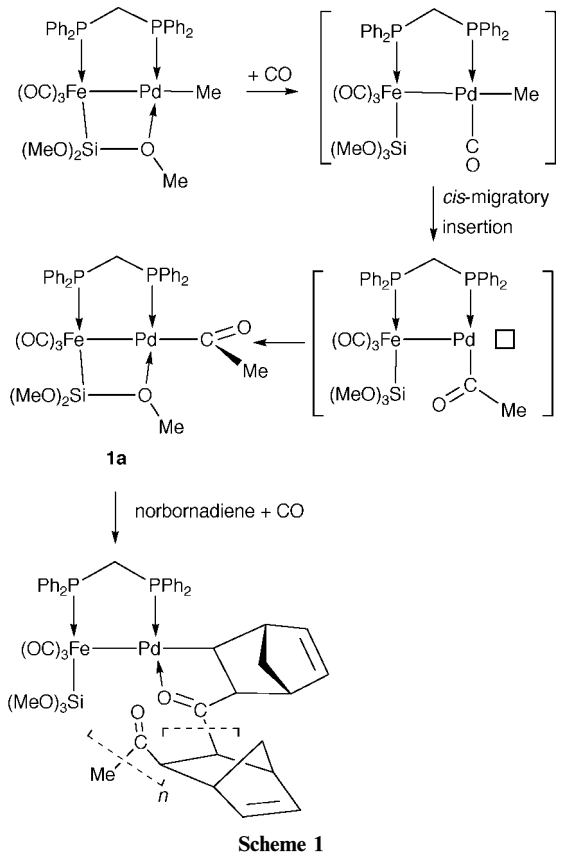
Norbornene and norbornadiene insert across the *exo*-face of their C=C bond into the Pd–acyl bond of $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}dppm)Pd\{C(=O)Me\}]$ (**1a**) (dppm = $Ph_2PCH_2PPh_2$) to afford the heterodinuclear complexes $[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-}dppm)Pd\{C_7H_{10}C(=O)Me\}]$ (**2**) and $[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-}dppm)Pd\{C_7H_8C(=O)Me\}]$ (**3**), respectively. In these insertion products, the alkoxysilyl ligand has become terminally bound whereas a dative bond between the acetyl oxygen and the metal allows the square-planar Pd centre to achieve a 16e configuration, thus resulting in a five-membered Pd–C–C–C–O ring. This chemistry was extended to chiral olefins and when the dppm and dppa complexes **1a,b** were reacted with a 9 : 1 mixture of (±)-(2-cyano-7-oxabicyclo[2.2.1]hept-5-ene-2-*endo*-yl and -2-*exo*-yl acetate (**4**,**4′**), the stable insertion products $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}Ph_2PXPPh_2)Pd\{C_9H_9NO_3C(=O)Me\}]$ (**5a**,**5a′** X = $CH_2$; **5b**,**5b′** X = NH) were isolated in high yield. A high stereo- and regioselectivity was found for these metallacarbonylations. Spectroscopic data as well as X-ray diffraction studies show that in contrast to **2** and **3**, the $\mu_2$-$\eta^2$-Si–O interaction present in the precursors **1a,b** is retained in **5a,b**. The Pd atom adopts a pseudo square-pyramidal coordination resulting from an additional weak ketonic interaction with the 5-*exo*-acetyl group of the 2-*endo*-acetoxy-2-cyano-7-oxabicyclo[2.2.1]hept-5-*exo*-yl moiety, which leads to the formation of a five-membered chelate ring. Electronic effects are invoked to account for these different structural features. Under a carbon monoxide atmosphere, CO migratory insertion into the Pd–oxanorbornyl bond of pure **5a,b** occurs and leads to the acyl complexes $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}Ph_2PXPPh_2)Pd\{C(=O)C_9H_9NO_3C(=O)Me\}]$ (**6a** X = $CH_2$; **6b** X = NH). These successive insertion reactions constitute the first elementary steps on the way to polyketone chain growth mediated by a bimetallic system.

The palladium-catalysed formation of polyketone chains represents a reaction of considerable current fundamental and applied interest.[1–22] A perfectly alternating sequence of CO/olefin units results in copolymers having unique properties.[23,24] The chain growth mechanism involves carbon monoxide migratory insertion into a metal–carbon bond, followed by olefin insertion into the resulting Pd–acyl bond. The interplay between kinetic and thermodynamic control of these elementary steps is responsible for the alternating incorporation of the monomers into the growing chain. The pioneering work of Sen *et al.* has greatly contributed to a better understanding of this important reaction.[4,25] Strained cyclic olefins like norbornene, norbornadiene and dicyclopentadiene have been used as substrates by several research groups in order to facilitate mechanistic and kinetic studies and suppress the β-elimination reaction that would lead to shorter chain oligomers (Bredt's rule).[25–34] Spectroscopic data as well as several X-ray diffraction studies performed on mononuclear Pd complexes indicate (*i*) that in all these cases olefin insertion occurs across the *exo*-face of the C=C double bond and (*ii*) that in the resulting product the organic moiety is coordinated in a chelating manner to a square-planar Pd(II) centre, thus forming a five-membered ring structure as depicted below.




L = nitrogen or phosphorus donor

We have recently expanded the scope of this insertion chemistry to heterodinuclear alkyl complexes bearing a hemilabile alkoxysilyl ligand (Scheme 1).[35,36] The latter occupies a coordination site on palladium that is easily available to an incoming substrate, such as CO or an olefin. The acyl ligand resulting from CO migratory insertion into the palladium alkyl bond occupies a position *trans* to the metal–metal bond,




**Scheme 1**

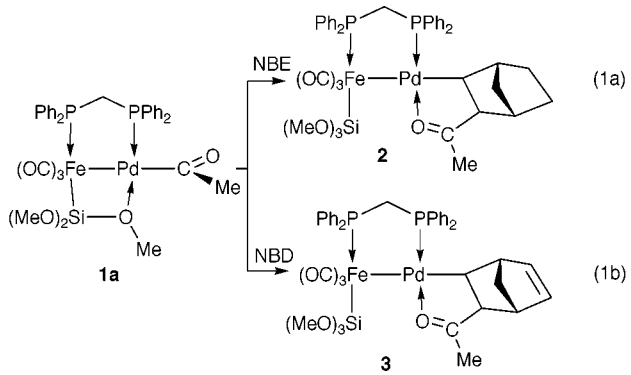
like the original alkyl ligand, as a result of rapid isomerization. This restores the $\mu_2$-$\eta^2$-Si–O bridging mode of the alkoxysilyl ligand and allows easy subsequent olefin insertion into the Pd–acyl bond. Since for thermodynamic reasons, the olefin rather than CO will insert into the Pd–acyl bond whereas CO insertion into a Pd-alkyl bond is kinetically favoured over olefin insertion, a perfect alternation of the insertion sequence leads to polyketone chain growth.[6]

These results prompted us to extend our studies to chiral olefins and investigate the stereochemical features of the insertion of functionalized non-symmetrical 7-oxanorbornene derivatives into the Pd–acyl bond of $[(OC)_3\overline{Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}Ph_2PXPPh_2)}\overline{Pd\{C(=O)Me\}}]$ (**1a** X = $CH_2$; **1b** X = NH). A substrate of particular interest appeared to be 2-cyano-7-oxabicyclo[2.2.1]hept-5-ene-2-*endo*-yl acetate **4** obtained by the $ZnI_2$-catalysed Diels–Alder reaction of furan with 1-cyanovinyl acetate.[37a] With enantiomerically pure dienophiles such as 1-cyanovinyl camphonates,[37b] 1-cyanovinyl RADO(Et)oate or SADO(Et)oate,[37c] furan generates diastereomerically pure Diels–Alder adducts ("naked sugars of the first generation"[37d]) that have become useful starting materials ("chirons") in the asymmetric organic synthesis of complicated organic systems.[37e] Any new, stereo- and regioselective functionalization of the olefinic centres of these 7-oxanorbornene derivatives enhances their synthetic potential and opens new fields for their application in asymmetric synthesis. The bicyclic alkene **4** has been employed recently for catalytic aryl- and vinylpalladation reactions and the influence of the remote substituents, CN and OC(=O)Me on the regio- and diasteroselectivity of their reaction products has been assessed.[38,39] In order to evaluate the influence of both the oxa-bridge and the electron withdrawing cyano- and OC(=O)Me groups at the C-2 carbon position on the insertion rate into the Pd–acyl bond of **1** as well as on the regio- and diasteroselectivity of the reaction products, we investigated stoichiometric CO/olefin coupling reactions with this substrate. We have found that **4** (and its isomer **4′** (2-*exo*-yl acetate)) undergo with **1a** and **1b** *exo*-face metallacarbonylations, like norbornene or norbornadiene. Most interesting, however, is the finding that these reactions are highly regioselective, the isolated products having palladium attached at C-6 whereas the acetyl moiety occupies the *exo*-5 position of the 7-oxabicyclo[2.2.1]hept-2-yl derivatives.

## Results and discussion

### Reactivity of 1a towards norbornene and norbornadiene

In a preliminary communication, some of us showed that norbornene cleanly inserts in a regioselective manner into the Pd–acyl bond of **1a** according to eqn. (1*a*) to yield quantitatively the yellow compound **2**, which is stable towards β-elimination.[35] The IR, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data



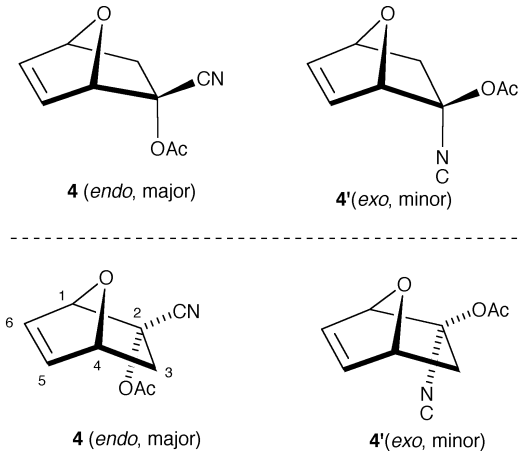

indicate that the alkoxysilyl ligand in **2** is terminally bound and that a dative bond between the keto function of the chelating organic moiety and the palladium centre is present, as documented for several mononuclear Pd complexes (see above), and allows the latter to achieve a 16e configuration. Thus, an IR vibration of medium intensity is found at 1645 $cm^{-1}$, which is characteristic for the coordination of the keto group to palladium, whereas the ν(CO) stretch for an uncoordinated ketone would be expected around 1700 $cm^{-1}$. The $^{13}C\{^1H\}$ resonance at δ 230.7 for the chelating keto group is significantly lowfield shifted compared to a non-chelating R(*C*=O)Me unit, as reported for related mononuclear complexes. The other eight resonances of the 3-acetylnorborn-2-yl ligand are close to those reported for the related mononuclear complexes $[\overline{Pd\{C_7H_{10}C(=O)Me\}}(PPh_3)_2]BF_4$ and $[\overline{Pd\{C_7H_{10}C(=O)Me\}}Cl(PPh_3)_2]$ (see Experimental).[25]

When norbornadiene was used as substrate, the insertion product **3** was isolated as a stable yellow solid in almost quantitative yield [eqn. (1*b*)]. The spectroscopic data indicate that as in **2**, the $Si(OMe)_3$ ligand is terminally bound and the ketonic dative bond between the acetyl oxygen and the Pd centre leads to a five-membered $\overline{Pd–C–C–C–O}$ chelate ring [ν(C=O) = 1642 $cm^{-1}$ in KBr].

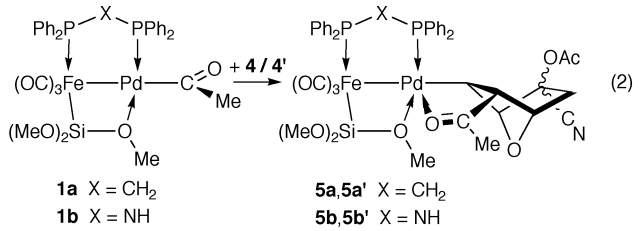
### Reactivity of 1a towards (±)-(2-cyano-7-oxabicyclo-[2.2.1]hept-5-ene-2-*endo*-yl and -2-*exo*-yl acetate (4,4′)

The 7-oxanorbornene derivatives **4** and **4′** functionalized by a cyano and an acetoxy group at the C-2 position were used as a mixture of *endo* and *exo* isomers in a *ca.* 9 : 1 ratio, with **4** being the major component.[37] Both stereoisomers, which possess a stereogenic centre at the C-2 carbon, as well as at the bridgehead positions C-1 and C-4 were employed as racemic mixtures.

Upon addition of a twofold excess of **4,4′** to a solution of **1a** in $CH_2Cl_2$ at ambient temperature, quantitative olefin inser-




tion into the Pd–acyl bond occurred within 2 h to afford yellow stable **5a,5a′**, [eqn. (2)].




*In situ* $^{31}P\{^{1}H\}$ NMR examination of the reaction mixture revealed the presence in solution of a major isomer together with a second species in a *ca.* 9 : 1 ratio. The main product displays a doublet at δ 58.8 (in $CDCl_3$) for the Fe-bound phosphorus atom and a doublet centred at δ 36.3 with a $^{2+3}J$(PP) coupling of 55 Hz assigned to the Pd-bound phosphorus. The second species also displays an AX pattern, centred at δ 58.8 (overlap with the resonances of the main species) and 34.2, respectively, with a $^{2+3}J$(PP) coupling of 56 Hz.

Recrystallization from $CH_2Cl_2$–hexane afforded an analytically pure yellow compound containing one solvent molecule per formula unit. $^{31}P\{^{1}H\}$ NMR spectroscopy revealed that only traces of the minor isomer **5a′** with the *exo*-acetoxy group remained in the product. The $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ displays three distinct doublets for the carbonyl ligands on iron at δ 216.7 [$^{2}J$(PC) = 17 Hz], 215.4 [$^{2}J$(PC) = 15 Hz] and 212.6 [$^{2}J$(PC) = 15 Hz], a singlet at δ 210.8 for the carbon of the ketonic group and a singlet at δ 168.5 for that of the ester function. By analogy with the chemical shifts reported for the free ligand (119.3 ppm), the singlet at δ 118.5 is assigned to the cyano carbon. The carbon directly attached to Pd at δ 37.1 is split into a doublet due to a small $^{2}J$(PC) *cis*-coupling of 3 Hz. The resonances of the ketonic methyl group and the acetyl methyl group are found at δ 28.1 and 20.1, respectively. The $Si(OMe)_3$ group gives rise to a singlet at δ 51.4 (owing to dynamic behaviour[36]) and the methylene carbon of the dppm ligand is split into a doublet of doublets centred at δ 47.3 with $^{1}J$(PC) couplings of 17 and 32 Hz. The resonances for the aromatic carbons are observed in the region δ 125.8–137.5.

Considering that we used a 9 : 1 mixture of the stereoisomers **4**/**4′** in excess, the observation of a nearly 9 : 1 mixture of product complexes in the reaction of eqn. (2) indicates that both isomers have similar reactivity. Comparison of the spectroscopic data with those obtained in the case of norbornene or norbornadiene indicates an overall similar behaviour but with two significant differences: (*i*) the highfield $^{13}C$ NMR shift of the ketonic group at δ 210.8 contrasts with the typical values found in both mononuclear complexes containing this moiety and in **2** or **3** (*ca.* 230–235 ppm) but does not rule out coordination to palladium; (*ii*) the $^{2+3}J$(PP) coupling of 56 Hz is smaller than that found for **2** and **3** (62 Hz). Previous studies have shown that $^{2+3}J$(PP) couplings in the range 52–56 Hz are very diagnostic for Fe–Pd systems of the type $[(OC)_3\overline{Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}Ph_2PXPPh_2)PdR}]$ (R = halide, $SnR_3$, alkyl, aryl) containing a $\mu_2$-$\eta^2$-Si–O interaction with the Pd centre, whereas in Fe–Pd complexes possessing a terminal $Si(OR)_3$ ligand, the $^{2+3}J$(PP) coupling is larger than 60 Hz.[36] These spectroscopic findings suggest a different coordination mode for the silyl group and the organic moiety compared to the norbornene and norbornadiene insertion products **2** and **3**. In order to unambiguously establish the arrangement of the ligands in **5a**, an X-ray diffraction study was performed. Unfortunately, due to the poor quality of the crystals and several disorder problems, only a partial structure solution was possible but it clearly revealed the molecular geometry, which is similar to that of the analogous dppa complex **5b** (see below). The most salient features are (*i*) that olefin insertion occurred, as expected, across the *exo*-face of the C=C double bond (the Pd–C7 and the C8–C15 bonds having an *exo*-position); (*ii*) the acetoxy group occupies the *endo*-position corresponding to the major isomer present in the reagent **4**; (*iii*) the existence of a four-membered $\overline{Fe\text{–}Si\text{–}O\text{–}Pd}$ ring, and (*iv*) the orientation of the ketonic oxygen O10 towards the Pd centre.

The IR spectrum of **5a** in the solid state (KBr) is consistent with the NMR data and contains three distinct, very strong ν(C≡O) bands at 1945, 1877 and 1852 $cm^{-1}$ due to a meridional arrangement of the ligands around iron, two ν(C=O) absorptions of medium intensity, at 1749 $cm^{-1}$ assigned to the ester function and at 1647 $cm^{-1}$ for the palladium-coordinated ketonic function. In addition, a weak absorption is observed at 2239 $cm^{-1}$ for the nitrile group. In $CH_2Cl_2$ solution, the corresponding ν(C≡O) vibrations are found at 1960, 1897 and 1874 $cm^{-1}$ and the two medium intensity ν(C=O) absorptions at 1755 and 1658 $cm^{-1}$. An additional absorption at 1712 $cm^{-1}$ is observed with approximately the same intensity as the ketonic band at 1658 $cm^{-1}$, which suggests coexistence in solution of isomers with coordinated and non-coordinated acyl groups.

**Reactivity of 1b towards 4,4′**

In order to examine the influence of the bridging diphosphine backbone on the rate and stereoselectivity of the olefin insertion, we also reacted the bimetallic acyl derivative **1b**, in which the metal–metal bond is spanned by the weaker electron donating bis(diphenylphosphino)amine ligand (dppa), with **4,4′**. Olefin insertion occurred again quantitatively within 2 h at ambient temperature to yield a mixture of yellow **5b,5b′** in a *ca.* 9 : 1 ratio, as evidenced by examination of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture. The major isomer **5b** gives rise to two doublets at δ 110.5 and 79.6. The minor isomer **5b′** displays a somewhat highfield shifted doublet for the dppa phosphorus on palladium, the resonance for the iron-bound phosphorus being masked by the doublet due to **5b**. For both isomers, a $^{2+3}J$(PP) coupling of 55 Hz was observed, again indicative of the existence of a four-membered $\overline{Fe\text{–}Si\text{–}O\text{–}Pd}$ cycle, as encountered in **1a,b** and **5a**. This derivative can be handled in air for several hours without decomposition. In solution, no sign of β-elimination was observed, however in chlorinated solvents cleavage of the Pd–carbon bond gradually occurred, affording the known chloro complex $[(OC)_3\overline{Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppa})PdCl}]$.[40] This cleavage reaction, combined with a lower solubility of **5b** compared to **5a**, prevented the recording of a good quality $^{13}C$ NMR spectrum. The lower basicity of the dppa ligand compared to dppm manifests itself in the IR spectrum where the three ν(CO) bands of the iron carbonyl fragment are noticably shifted to higher frequencies compared to those of **5a**. The molecular structure of **5b** was determined by X-ray diffraction and established the stereochemical features of the complex.

### Crystal structure of $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}dppa)Pd\{C_9H_9NO_3C(=O)Me\}]\cdot 2CH_2Cl_2$

The molecular structure of the dppa-bridged derivative **5b**$\cdot 2CH_2Cl_2$ is shown in Fig. 1, which includes the atom numbering scheme.

Suitable crystals were obtained by slow diffusion of hexane into a saturated dichloromethane solution of **5b**. The iron and palladium centres are linked by a dppa bridge and a metal–metal bond. The Fe–Pd separation of 2.660(9) Å is almost identical with that observed in the $SnPh_3$ derivative $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}dppm)PdSnPh_3]$ [2.665(5) Å].[41] The coordination geometry around the Fe atom may be viewed as distorted octahedral, consistent with a formal $Fe(d^7)$–$Pd(d^9)$ situation. The alkoxysilyl ligand, which is situated *trans* to P1 [Si–Fe–P1 169.58(6)°] is at a distance of 2.263(2) Å from Fe, typical for heterometallic systems having a $\mu\text{-}\eta^2\text{-}Si(OMe)_3$ unit. For example, a Fe–Si bond length of 2.258(1) Å has been found in $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}pdppm)PdSnPh_3]$.[41] Three meridional carbonyl ligands complete the environment of the iron centre. The square-pyramidal coordination geometry around the palladium involves the Fe atom, a phosphorus atom [Pd–P2 2.170(1) Å], the O6 atom of the $\mu_2\text{-}\eta^2$-alkoxysilyl ligand and the C7 atom of the organic moiety. The root mean-square deviation from the basal plane passing through Fe, P2, O6 and C7 amounts to 0.063 Å. The dative Pd–O6 bond distance of 2.240(3) Å is significantly longer than those in $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}dppm)PdSnPh_3]$ [2.165(2) Å] and $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}dppm)PdCl]$ [2.100(4) Å].[42] This elongation is probably due to the influence of the O10 atom of the chelating keto function, which occupies the apical site of the square-based pyramid shown in Fig. 2. The rather long separation of 2.769(5) Å between Pd and O10 suggests a weaker ketonic interaction compared to that in $[Pd\{C_7H_{10}C(=O)Me\}(PPh_3)_2]BF_4$ [25] and other related mononuclear complexes where Pd–O distances have been found in the range 2.026–2.114 Å.[21,26,28] A pseudo-pentacoordinate Pd complex has very recently been obtained by Cavell *et al.* by insertion of ethylene into the Pd–acyl bond of $[Pd\{C(=O)Me\}(NC_5H_4CO_2Me\text{-}2)(PPh_3)_2]BF_4$.[43] In the resulting insertion product $[Pd\{CH_2CH_2C(=O)Me\}(NC_5H_4CO_2Me\text{-}2)(PPh_3)_2]BF_4$, the former acyl ligand is now coordinated to Pd [2.16(2) Å] to form a five-membered chelate ring, whereas the oxygen atom [Pd–O 2.78(1) Å] from a $NC_5H_4CO_2Me$-2 ligand occupies an apical position above the palladium coordination plane.[43] Compared with the C=O bond distances in $[Pd\{C_7H_{10}C(=O)Me\}(PPh_3)_2]BF_4$ [1.240(10) Å] and $[Pd\{C_7H_{10}C(=O)Me\}(bipy)_2]CF_3SO_3$ [1.235(5) Å],[28] the C15–O10 double bond of 1.215(7) Å is slightly shorter and compares well with that of an average uncoordinated C=O double bond in organic molecules (1.23 Å).[44] The Pd atom and the C(=O)Me unit are bound in an *exo*-position to the 7-oxanorbornyl unit, as well as the cyano group attached to C10. The Pd, C7, C8, C15 and O10 atoms form a five-membered ring and the palladium deviates from the mean plane passing through these five atoms by 0.137 Å, the torsion angle O10–Pd–C7–C8 being 17.21(3)°.

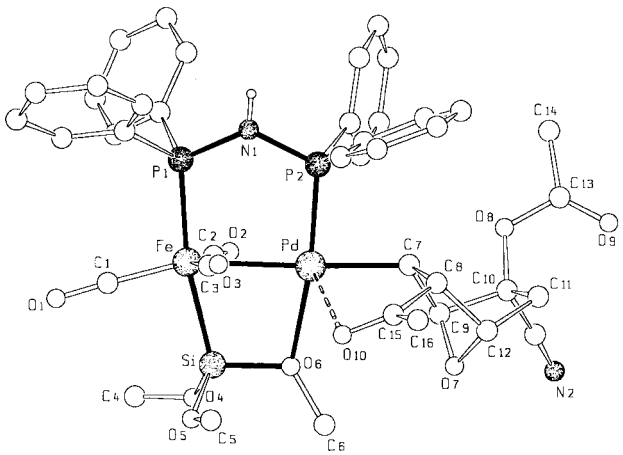



**Fig. 1** View of the crystal structure of $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}dppa)Pd\{C_9H_9NO_3C(=O)Me\}]$ **5b** with the atom numbering scheme.

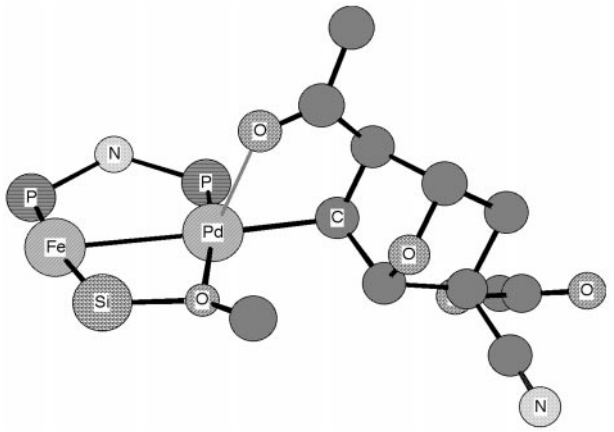
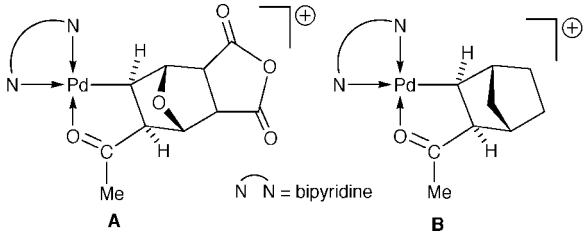



**Fig. 2** Perspective view of the core structure of **5b**. The phenyl groups and carbonyl ligands are omitted for clarity.

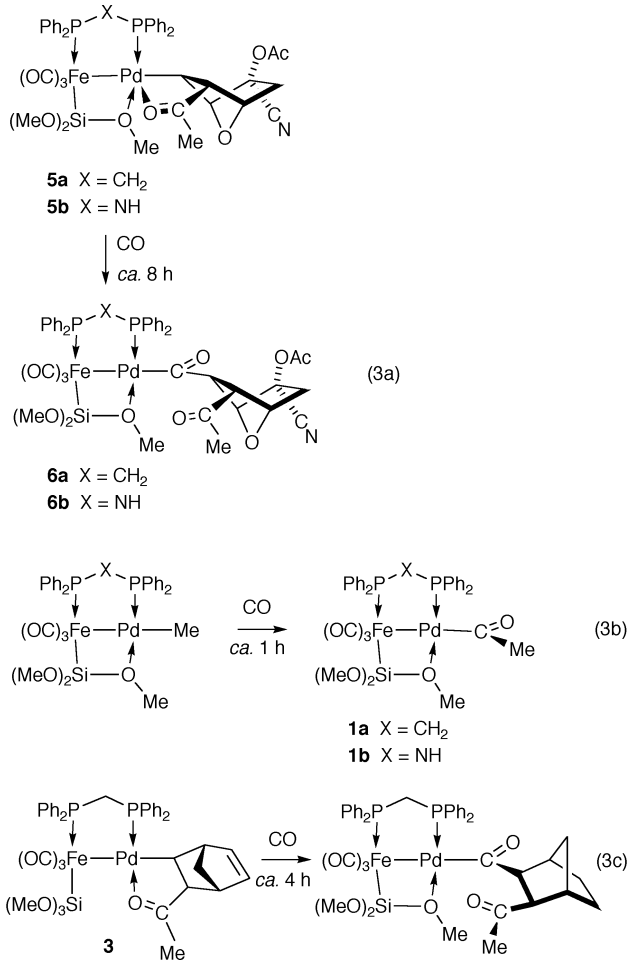
In order to verify whether the crystals used for the X-ray determination of **5b** corresponded to the major species observed in solution by $^{31}P$ NMR analysis of the isomeric mixture of **5b/5b′**, some crystals were redissolved in $CDCl_3$. The chemical shifts recorded for the pure isomer corresponded indeed to the major species, thus confirming our assignment. An obvious question relates to the origin of the different coordination geometries observed around the palladium centre in **2**,**3** and **5a**,**b**. We can safely rule out steric effects and assume that in **5a**,**b** the presence of an oxa bridge and of cyano and acetoxy groups renders the chelating keto function less basic owing to their electron withdrawing character compared to the norbornyl or norbornadienyl units of **2** and **3**, respectively. Therefore, an additional coordination of a methoxy oxygen from the $Si(OMe)_3$ moiety is made more favourable in the case of **5**, resulting in a pentacoordination around palladium. Note that in the mononuclear complex **A** obtained by insertion of 7-oxa-5-norbornene-*exo*-2,3-dicarboxylic anhydride into the Pd–acyl bond of $[Pd\{C(=O)Me\}(bipy)(NCMe)]^+$, the stereochemistry observed was the same as in the norbornene insertion product **B**. A comparison of the ketonic ν(CO) frequencies indicates that in **A** (1612 $cm^{-1}$) the interaction with palladium is indeed slightly weaker than in **B** (1601 $cm^{-1}$).[26]




### CO insertion reactions

For comparison with reactions performed with norbornadiene, we investigated the reactivity of **5a**,**b** towards

further CO insertion. Upon purging a $CH_2Cl_2$ solution of pure **5a** with a gentle stream of CO for 8 h, the acyl complex **6a** {$^{31}P\{^1H\}$ NMR: δ 60.6 [d, P(Fe), $^{2+3}J(PP)$ = 54 Hz], 27.0 [d, P(Pd)]} was obtained in quantitative spectroscopic yield [eqn. (3*a*)]. In addition to the three ν(CO) stretches of the iron carbonyls, this complex exhibits three further carbonyl vibrations at 1760 (m) 1705 (w) and 1666 $cm^{-1}$ due to the acetate group, the uncoordinated keto function and the acyl group, respectively. Unfortunately, during recrystallization attempts partial decomposition of **6a** occurred, so that satisfactory elemental analyses could not be obtained.




Slow CO insertion into the Pd–alkyl bond of pure **5b** was also observed, but after purging with CO for 4 h, only *ca.* 40% conversion to the acyl derivative **6b** was observed. For comparison, the synthesis of the acyl complexes $[(OC)_3\overline{Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}Ph_2PXPPh_2)}\overline{Pd\{C(=O)Me\}}]$ **1a,b** requires approximately 1 h for quantitative CO insertion to occur under similar conditions [eqn. (3*b*)].[40]

In the case of renewed CO insertion into the Pd–C bond of $[(OC)_3\{(MeO)_3Si\}\overline{Fe(\mu\text{-dppm})Pd\{C_7H_8C(=O)Me\}}]$ **3**, completion of the reaction took *ca.* 4 h [eqn. (3*c*)], which may be related to the strength of the five-membered ring chelate.[35] However, quantitative formation of **6b** was achieved within 2 h in an autoclave under a CO pressure of 40 bar at ambient temperature. The spectroscopic data for this stable orange-red product as well as the elemental analyses are in agreement with the structure shown in eqn. (3*a*). Since the CO insertion affording **6a,b** is irreversible, thermodynamic reasons for the slow insertion rate under atmospheric pressure can be excluded. Note that reversible CO insertion/deinsertion reactions are well established in organopalladium and -platinum chemistry.[45–48] We assume that the lower rate of CO insertion observed for **5a,b** is due to the (incipient) pentacoordination around the Pd centre in combination with the presence of electron withdrawing groups on the organic ligand. Occupation by the keto group of the apical coordination site of the approximately square-based pyramid around the Pd would make more difficult the approach of a CO molecule on the Pd centre. Studies on square-planar Pd and Pt alkyls have established that pentacoordinate species with a CO ligand may be formed as intermediates (associative mechanism), which are subsequently converted to the corresponding acyl complexes (dissociative pathways are also known).[48–53] Assuming that CO insertion into the Pd alkyl bond of **5a,b** also follows an associative pathway, the incoming CO molecule has first to compete with the keto group for a coordination site on palladium, thus explaining the acceleration of the insertion rate under higher CO pressure. It is furthermore well established that migratory insertion reactions are favoured by electron donating substituents on the migrating organic group.[47] This is consistent with the observation that CO insertion into a Pd–norbornadienyl bond is faster compared to that in a Pd–oxanorbornyl moiety bearing electron withdrawing cyano and acetoxy groups.

## Conclusion

This study has shown that there is a general pattern for olefin insertion into the palladium–acyl bond of diphosphine-bridged heterodinuclear Fe–Pd complexes that applies to norbornene, norbornadiene and 7-oxanorbornenes. Whereas chiral ligands on palladium have been used to control the stereoselective alternating copolymerization of carbon monoxide and prochiral alkenes,[21*b*] we have reported here the use of chiral olefins and shown that the insertion reaction occurs with high stereo- and regioselectivity. No significant chemical differences were observed between the systems containing dppm or dppa as bridging ligands. The complexes are generally stable, which is particularly noteworthy since many related mononuclear palladium complexes are of limited stability. The observation that CO insertion is again possible after olefin insertion into the Pd–acyl bond opens the way to the sequential growth of polyketones containing chiral centres. Preliminary studies have shown that other 7-oxanorbornene derivatives such as 7-oxabicyclo[2.2.1]hept-5-ene-2-one,[37] which possess a keto group at the C-2 position, insert in a less regioselective manner into the Pd–acyl bond of **1a**. Further developments should also include the use of enantiomerically pure olefins as substrates.

## Experimental

All reactions were performed in Schlenk tubes under purified nitrogen. Solvents were dried and distilled under nitrogen before use, toluene and hexane over sodium, dichloromethane from $P_4O_{10}$. Nitrogen was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen or water. Norbornene and norbornadiene were obtained from Aldrich and used as received. Elemental C, H and N analyses were performed on a Leco Elemental Analyser CHN 900. The $^1H$, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 200.13, 81.01 and 50.32 MHz, respectively, on a Bruker ACP 200 instrument. Phosphorus chemical shifts were referenced to 85% $H_3PO_4$ in $H_2O$ with downfield shifts reported as positive. NMR spectra were recorded in pure $CDCl_3$, unless otherwise stated. The presence and amount of $CH_2Cl_2$ of solvation in **3**, **5a** and **6b** has been determined from the $^1H$ NMR spectra. The reactions were generally monitored by IR spectroscopy in the ν(CO) region.

### Reactions

**$[(OC)_3\{(MeO)_3Si\}\overline{Fe(\mu\text{-dppm})Pd\{C_7H_{10}C(=O)Me\}}]$ (2).** Norbornene (0.6 mmol) was added to a stirred solution of **1a** (159 mg, 0.2 mmol) in $CH_2Cl_2$ (6 mL). After the reaction

**Table 1** Selected bond lengths (Å) and angles (°) of **5b**

| | | | |
|---|---|---|---|
| Fe–Si | 2.263(2) | Si-O6 | 1.685(4) |
| Pd–Fe | 2.660(9) | O1–C1 | 1.161(7) |
| Pd–O6 | 2.240(3) | O2–C2 | 1.161(7) |
| Pd–O10 | 2.769(5) | O3–C3 | 1.167(7) |
| Pd–C7 | 2.118(5) | O7–C9 | 1.430(6) |
| Fe–P1 | 2.190(1) | O7–C12 | 1.454(6) |
| Pd–P2 | 2.170(1) | O9–C13 | 1.191(7) |
| Fe–C1 | 1.759(6) | O10–C15 | 1.215(7) |
| Fe–C2 | 1.770(6) | P1–N1 | 1.692(4) |
| Fe–C3 | 1.765(6) | P2–N1 | 1.685(4) |
| Si–O4 | 1.646(4) | C17–N2 | 1.137(7) |
| Si–O5 | 1.644(4) | | |
| Pd–Fe–Si | 75.05(4) | C7–Pd–O6 | 102.6(2) |
| P1–Fe–Si | 169.58(6) | Si–O6–Pd | 99.4(2) |
| P1–Fe–Pd | 94.83(4) | Pd–C7–C8 | 116.1(3) |
| C7–Pd–Fe | 177.26(14) | C8–C15–O10 | 122.9(5) |
| P2–Pd–Fe | 92.81(4) | C15–O10–Pd | 103.45(5) |
| P2–Pd–C7 | 84.96(14) | C1–Fe–C3 | 108.8(6) |
| P2–Pd–O6 | 169.41(10) | C1–Fe–C2 | 142.7(5) |
| O6–Pd–Fe | 79.68(9) | C3–Fe–C2 | 106.5(6) |
| C7–Pd–Fe | 170.0(3) | P1–N1–P2 | 121.8(3) |

mixture was stirred for 3 h, all volatiles were removed under reduced pressure. The yellow residue was rinsed with pentane (5 mL) to remove any remaining free olefin and dried under vacuum for 2 h. Yield: (167 mg, 94%). Anal. found: C, 54.32; H, 5.28. Calcd. for $C_{40}H_{44}FeO_7P_2PdSi$ ($M$ = 889.09): C, 54.04; H, 4.99%. IR ($CH_2Cl_2$, $cm^{-1}$) ν(CO): 1944 s, 1872 s, 1845 vs, 1645 m. $^1H$ NMR: δ 0.18 (br, m, 1H), 0.95–1.10 (m, 2H, overlap), 1.31 (br, s, 1H), 1.51 (br, t, 1H), 1.59 (ddd, 1H, $J$ = 2.1, 8.4, 9.0 Hz), 1.79, (d, 1H, $J$ = 10.3 Hz), 1.97 (br, s, 1H), 2.39 [s, 3H, C(=O)Me], 2.41 (d, 1H, $J$ = 3.6 Hz), 2.69 (d, 1H, $J$ = 6.6 Hz), 3.68 (s, 9H, $OCH_3$), 3.79 (m, 2H, $PCH_2P$), 7.11–7.72 (m, 20H, phenyl). $^{13}C\{^1H\}$ NMR: δ 230.7 [s, *C*(=O)Me], 216.4 [vbr, s, FeCO, $^2J$(PC) not resolved], 214.8 (vbr, s, FeCO), 213.1 (vbr, s, FeCO), 126.6–137.9 (phenyl), 71.3 (s, C-norb), 62.6 [d, C-norb, $J$(PC) = 9 Hz], 50.2 (s, SiOMe), 44.4 [dd, PCP, $^1J$(PC) = 16 and 32 Hz], 43.4 (s, C-norb), 43.2 (s, C-norb), 31.1 [d, C-norb, $^2J$(PC) = 7 Hz], 29.2 [s, C(=O)*C*H$_3$], 26.7 (s, C-norb). $^{31}P\{^1H\}$ NMR: δ 61.1 [d, $P^1$(Fe), $^{2+3}J(P^1P^2)$ = 62 Hz], 33.8 [d, $P^2$(Pd)].

**[(OC)$_3${(MeO)$_3$Si}Fe(μ-dppm)Pd{C$_7$H$_8$C(=O)Me}] (3).** Norbornadiene (0.6 mmol) was added to a stirred solution of **1a** (159 mg, 0.2 mmol) in $CH_2Cl_2$ (6 mL). After the reaction mixture was stirred for 2 h, all volatiles were removed under reduced pressure. The yellow residue was rinsed with pentane (5 mL) to remove any remaining free olefin and dried under vacuum for 1 h. Yield: (176 mg, 95%). Anal. found: C, 52.44; H, 4.40. Calcd. for $C_{40}H_{42}FeO_7P_2PdSi \cdot 0.5CH_2Cl_2$ ($M$ = 887.07 + 42.46): C, 52.33; H, 4.66%. IR ($CH_2Cl_2$, $cm^{-1}$) ν(CO): 1945 s, 1873 s, 1845 vs, 1642 m. $^1H$ NMR: δ 1.15 (m, 2H), 1.70 (d, 1H, $J$ = 8.9 Hz), 1.97 (br, s, 1H), 2.43 (d, 1H, $J$ = 8.9 Hz), 2.45 [s, 3H, C(=O)Me], 2.98 (br, s, 1H), 3.65 (s, 9H, $OCH_3$), 3.78 (m, 2H, $PCH_2P$), 5.21 (dd, 1H, olefinic, $J$ = 5.2, 3.0 Hz), 5.73 (dd, 1H, olefinic, $J$ = 5.2, 3.0 Hz), 7.10–7.77 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR: δ 228.8 [s, *C*(=O)Me], 217.6 [vbr, m, 3FeCO. $^2J$(PC) not resolved], 138.3 (s, olefinic C), 137.1 (s, olefinic C), 127.6–136.3 (aromatic), 71.3 (s, C-norb), 63.9 (s, C-norb), 55.4 [d, C-norb, $J$(PC) = 8 Hz), 50.4 (s, SiOMe), 47.9 (s, C-norb.), 44.6 (s, C-norb.), 44.5 [dd, PCP, $^1J$(PC) = 19 and 29 Hz], 26.8 [s, C(=O)*C*H$_3$]. $^{31}P\{^1H\}$ NMR: δ 62.0 [d, $P^1$(Fe), $^{2+3}J(P^1P^2)$ = 62 Hz], 34.3 [d, $P^2$(Pd)].

**[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppm)Pd{C$_9$H$_9$NO$_3$C(=O)Me}] (5a).** The oxanorbornene **4** (0.4 mmol) was added as a 9 : 1 mixture of *exo* : *endo* isomers to a stirred solution of **1a** (159 mg, 0.2 mmol) in $CH_2Cl_2$ (6 mL). After 3 h, all volatiles were removed under reduced pressure. The yellow residue was rinsed with hexane (5 mL) to remove remaining free olefin and dried under vacuum for 2 h. Yield: (202 mg, 95%). The yellow powder was recrystallized from $CH_2Cl_2$–hexane to separate **5a** from **5a′**. Anal. found: C, 48.28; H, 4.40; N, 1.41. Calcd. for $C_{42}H_{43}FeNO_{10}P_2PdSi \cdot CH_2Cl_2$ ($M$ = 974.11 + 84.95): C, 48.76; H, 4.28; N, 1.32%. IR (KBr, $cm^{-1}$) ν(CN): 2239 w; ν(CO): 1945 s, 1877 s, 1852 vs, 1749 s, 1647 m; ($CH_2Cl_2$) ν(CO): 1960 s, 1897 s, 1874 vs, 1755 m, 1712 w, 1658 w. $^1H$ NMR: δ 1.18 (d, 1H, H-C$_6$, $J$ = 14 Hz), 1.51 [s, 3H, C(=O)Me], 1.56 (d, 1H, H$_{endo}$-C$_3$, $J$ = 9.2 Hz), 2.00, (br t, 1H, H$_{exo}$-C$_3$, $J$ = 9.4 Hz), 2.12 [s, 3H, C(=O)Me], 2.57 (dd, 1H, H-C$_5$, $J$ = 5.8 and 14.0 Hz), 3.55–3.81 (m, 2H, $PCH_2P$), 3.74 (s, 9H, $OCH_3$), 4.56 (d, 1H, H-C$_4$, $J$ = 5.8 Hz), 4.56 (d, 1H, H-C$_1$, $J$ = 4.0 Hz), 7.13–7.92 (m, 20H, phenyl). $^{13}C\{^1H\}$ NMR: δ 216.7 [d, FeCO, $^2J$(PC) = 17 Hz], 215.4 [d, FeCO, $^2J$(PC) = 15 Hz], 212.6 [d, FeCO, $^2J$(PC) = 15 Hz], 210.8 [s, *C*(=O)Me], 168.5 [s, *C*(=O)O], 118.5 (s, CN), 125.8–137.5 (phenyl), 85.8 (s, C-oxanorb), 83.3 (s, C-oxanorb), 74.6 (s, C-oxanorb), 64.1 (s, C-oxanorb), 51.4 (s, SiOMe), 47.3 [dd, PCP, $^1J$(PC) = 17 and 32 Hz], 43.0 (s, C-oxanorb), 37.1 [d, C-oxanorb, $^2J$(PC) = 3 Hz], 28.1 [s, C(=O)*Me*], 20.1 (s, $CO_2$*Me*). $^{31}P\{^1H\}$ NMR: δ 58.8 [d, $P^1$(Fe), $^{2+3}J(P^1P^2)$ = 55 Hz], 36.3 [d, $P^2$(Pd)].

**[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppa)Pd{C$_9$H$_9$NO$_3$C(=O)Me}] (5b).** This derivative was prepared from **1b** and purified as described for **5a**. Under vacuum, crystalline **5b** · 2 $CH_2Cl_2$ rapidly lost the solvated $CH_2Cl_2$ molecule. Anal. found: C, 49.76; H, 4.33; N, 2.84. Calcd. for $C_{41}H_{42}FeN_2O_{10}P_2PdSi$ ($M$ = 975.01): C, 50.50; H, 4.34; N, 2.88%. IR (KBr, $cm^{-1}$) ν(CN): 2237 w; ν(CO): 1964 s, 1885 vs, br, 1757 m, 1707 w, 1653 m; ($CH_2Cl_2$) ν(CO): 1960 s, 1897 s, 1874 vs, 1755 m, 1712 w, 1658 w. $^1H$ NMR: δ 0.89 (m, 1H, H-C$_6$), 1.56 [s, 3H, C(=O)Me], 1.90 (d, 1H, H$_{endo}$-C$_3$, $J$ = 8.7 Hz), 2.05 [s, 3H, C(=O)Me], 2.21 (br t, 1H, H$_{exo}$-C$_3$, $J$ = 9.9 Hz), 2.61 (dd, 1H, H-C$_5$, $J$ = 5.9 and 13.9 Hz), 3.74 (s, 9H, $OCH_3$), 4.23 (m, 1H, N-H), 4.61 (d, 1H, H-C$_4$, $J$ = 5.98 Hz), 4.87 (d, 1H, H-C$_1$, $J$ = 3.6 Hz), 7.14–7.95 (m, 20H, phenyl). $^{31}P\{^1H\}$ NMR: δ 110.5 [d, $P^1$(Fe), $^{2+3}J(P^1P^2)$ = 55 Hz], 79.6 [d, $P^2$(Pd)].

**[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppa)Pd{C(=O)C$_9$H$_9$NO$_3$C(=O)Me}] (6b).** Complex **5b** (206 mg, 0.2 mmol) was dissolved in $CH_2Cl_2$ (10 mL) and transferred into a steel autoclave. After stirring for 2 h at ambient temperature under a CO pressure of 40 bar, the pressure was released and the clear orange-yellow solution was concentrated to *ca.* 5 mL. $^{31}P\{^1H\}$ NMR monitoring revealed quantitative conversion to **6b**. Upon layering the solution with hexane, **6b** readily crys-

**Table 2** Summary of crystal data, intensity measurements and refinement of **5b**

| | |
|---|---|
| Empirical formula | $C_{41}H_{42}FeN_2O_{10}P_2PdSi \cdot 2CH_2Cl_2$ |
| Formula mass/g mol$^{-1}$ | 1144.90 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $\mu$/mm$^{-1}$ | 1.020 |
| $R_1$ [a] $[I > 2\sigma(I)]$ | 0.0576 |
| $wR_2$ [b] (all data) | 0.0822 |
| $a$/Å | 11.057(2) |
| $b$/Å | 26.977(5) |
| $c$/Å | 17.087(3) |
| $\beta$/deg | 104.63(3)° |
| $U$/Å$^3$ | 4931.5(15) |
| $T$/K | 173(2) |
| $Z$ | 4 |
| No. of reflns collected | 38 039 |
| No. of indep. reflns | 9637 |
| No. of obs. reflns $[I > 2\sigma(I)]$ | 3833 |
| Goodness-of-fit | 1.006 |

[a] $R_1 = \sum \| F_o| - |F_c \| / \sum |F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{0.5}$.

tallized in the form of orange-yellow needles. The moderate solubility of **6b** in chlorinated solvents prevented the recording of a good quality $^{13}C$ NMR spectrum. Anal. found: C, 49.03; H, 4.27; N, 2.69. Calcd. for $C_{42}H_{42}FeN_2O_{11}P_2PdSi \cdot 0.5CH_2Cl_2$ ($M$ = 1003.10 + 42.46): C, 48.82; H, 4.14; N, 2.69%. IR (KBr, cm$^{-1}$) ν(CN): 2246 w; ν(CO): 1967 s, 1900 s, 1883 vs, 1759 m, 1691 m, 1663 m; ($CH_2Cl_2$) ν(CO): 1972 s, 1910 s, 1887 vs, 1758 m, 1696 m, 1671 m. $^1H$ NMR: δ 1.52 (d, 1H, $H_{endo}$-$C_3$, $J$ = 10.9 Hz), 1.99 [s, 3H, C(=O)Me], 2.03 [s, 1H, $H_{exo}$-$C_3$, partial overlap with C(=O)Me], 2.14 [s, 3H, C(=O)Me], 2.59 (dd, 1H, H-$C_5$, $J$ = 5.8 and 13.9 Hz), 3.72 (s, 9H, $OCH_3$), 3.98 (d, 1H, H-$C_6$, $J$ = 9.1 Hz), 4.11 (m, 1H, N-H), 4.47, (br s, 1H, H-$C_1$), 4.73 (d, 1H, H-$C_4$, $J$ = 5.4 Hz), 7.19–7.82 (m, 20H, phenyl). $^{31}P\{^1H\}$ NMR: δ 113.8 [d, $P^1$(Fe), $^{2+3}J(P^1P^2)$ = 56 Hz], 71.1 [d, $P^2$(Pd)].

### X-Ray structure determination of 5a and 5b

For **5a**, the poor quality of the crystals prevented the determination of an accurate structure, see text (experimental conditions as for **5b**). The following cell parameters have been determined: monoclinic, space group $P2_1/n$, $a$ = 11.262(2), $b$ = 19.050(4), $c$ = 19.538(4) Å, $\alpha = \gamma = 90.00°$, $\beta$ = 99.56(3)°, $U$ = 4133.5(14) Å$^3$, $Z$ = 4.

For **5b**, yellow-orange crystals were grown from $CH_2Cl_2$–hexane. Data were collected on a Stoe IPDS diffractometer using Mo-$K_\alpha$ graphite monochromated radiation (λ = 0.71073 Å). The structure was solved using direct methods and refined by full-matrix least-squares methods (based on $F_0^2$, SHELXL-93[54a]). Anisotropic thermal parameters for all non-H atoms were used in the final cycles. The hydrogen atoms were calculated and fixed in idealized positions using a riding model. SHELXS-86[54b] and SHELXL-93[54a] computer programs were used. Selected bond distances and angles are given in Table 1 and crystallographic details in Table 2.

CCDC reference number 440/152. See http://www.rsc.org/suppdata/nj/1999/1215/ for crystallographic files in .cif format.

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## References

1 U. Klabunde and S. D. Ittel, *J. Mol. Catal.*, 1987, **41**, 123.
2 A. X. Zhao and J. C. W. Chien, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 2735.
3 S. Bronco, G. Consiglio, R. Hutter, A. Batistini and U. W. Suter, *Macromolecules*, 1994, **27**, 4436.
4 A. Sen, *Acc. Chem. Res.*, 1993, **26**, 303.
5 E. Drent, J. A. M. van Broekhoven and M. J. Doyle, *J. Organomet. Chem.*, 1992, **417**, 235.
6 E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663.
7 W. Keim and H. Maas, *J. Organomet. Chem.*, 1996, **514**, 271.
8 M. Brookhart, F. C. Rix, J. M. DeSimone and J. C. Barborak, *J. Am. Chem. Soc.*, 1992, **114**, 5894.
9 F. C. Rix, M. Brookhart and P. S. White, *J. Am. Chem. Soc.*, 1996, **118**, 4746.
10 A. Batistini and G. Consiglio, *Organometallics*, 1992, **11**, 1766.
11 A. Aeby and G. Consiglio, *J. Chem. Soc., Dalton Trans.*, 1999, 655.
12 B. Milani, L. Vicentini, A. Sommazzi, F. Garbassi, E. Chiarparin, E. Zangrando and G. Mestroni, *J. Chem. Soc., Dalton Trans.*, 1996, 3139.
13 B. Milani, E. Alessio, G. Mestroni, E. Zangrando, L. Randaccio and G. Consiglio, *J. Chem. Soc., Dalton Trans.*, 1996, 1021.
14 K. Nozaki, N. Sato and H. Takaya, *J. Am. Chem. Soc.*, 1995, **117**, 9911.
15 B. Domhöver, W. Kläui, A. Kremer–Aach, R. Bell and D. Mootz, *Angew. Chem., Int. Ed.*, 1998, **37**, 3050.
16 M. A. Zuideveld, P. C. J. Kamer, P. W. N. M. van Leeuven, P. A. A. Klusener, H. A. Stil and C. F. Roobeck, *J. Am. Chem. Soc.*, 1998, **120**, 7977.
17 D.-J. Liaw and B.-F. Lay, *Polym. J.*, 1996, **28**, 266.
18 E. Lindner, R. Schreiber, T. Schneller, P. Wegner, H. A. Mayer, W. Göpel and C. Ziegler, *Inorg. Chem.*, 1996, **35**, 514.
19 G. J. P. Britovsek, K. J. Cavell, M. J. Green, F. Gerhards, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1997, **533**, 201.
20 M. J. Green, G. J. P. Britovsek, K. J. Cavell, F. Gerhards, B. F. Yates, K. Frankcombe, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, 1137.
21 (*a*) K. Nozaki, N. Sato, Y. Tonomura, M. Yasutomi, H. Takaya, T. Hiyama, T. Matsubara and N. Koga, *J. Am. Chem. Soc.*, 1997, **119**, 12779. (*b*) K. Nozaki and T. Hiyama, *J. Organomet. Chem.*, 1999, **576**, 248 and references cited.
22 M. Svensson, T. Matsubara and K. Morokuma, *Organometallics*, 1996, **15**, 5568.
23 C. E. Ash, *Int. J. Polym. Mater.*, 1995, **30**, 1.
24 A. Gray, *Chem. Brit.*, 1998, 44.
25 J. S. Brumbaugh, R. R. Whittle, M. Parvez and A. Sen, *Organometallics*, 1990, **9**, 1735.
26 B. A. Markies, D. Kruis, M. H. P. Rietveld, K. A. N. Verkerk, J. Boersma, H. Kooijman, M. T. Lakin, A. L. Spek and G. van Koten, *J. Am. Chem. Soc.*, 1995, **117**, 5263.
27 B. A. Markies, K. A. N. Verkerk, M. H. P. Rietveld, J. Boersma, H. Kooijman, A. L. Spek and G. van Koten, *J. Chem. Soc., Chem. Commun.*, 1993, 1317.
28 A. L. Spek, B. A. Markies, D. Kruis, J. Boersma and G. van Koten, *Acta Crystallogr, Sect. C*, 1995, **51**, 1535.
29 G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen and C. F. Roobeek, *J. Organomet. Chem.*, 1992, **430**, 357.
30 R. van Asselt, E. E. C. G. Gielens, R. E. Rülke, K. Vrieze and C. J. Elsevier, *J. Am. Chem. Soc.*, 1994, **116**, 977.
31 J. H. Groen, C. J. Elsevier, K. Vrieze, W. J. J. Smeets and A. L. Spek, *Organometallics*, 1996, **15**, 3445.
32 J. H. Groen, J. G. P. Delis, P. W. N. M. van Leeuwen and K. Vrieze, *Organometallics*, 1997, **16**, 68.
33 G. A. Luinstra and P. H. P. Brinkmann, *Organometallics*, 1998, **17**, 5160.
34 P. H. P. Brinkmann and G. A. Luinstra, *J. Organomet. Chem.*, 1999, **572**, 193.
35 P. Braunstein, M. Knorr and T. Stährfeldt, *J. Chem. Soc., Chem. Commun.*, 1994, 1913.
36 P. Braunstein, M. Knorr and C. Stern, *Coord. Chem. Rev.*, 1998, **178–180**, 903.
37 (*a*) E. Vieira and P. Vogel, *Helv. Chim. Acta*, 1982, **65**, 1700. (*b*) E. Vieira and P. Vogel, *Helv. Chim. Acta*, 1983, **66**, 1865. (*c*) J.-L. Reymond and P. Vogel, *Tetrahedron: Asymmetry*, 1990, **1**, 729. (*d*) A. Warm and P. Vogel, *J. Org. Chem.*, 1986, **51**, 5348; P. Vogel, D. Fattoni, F. Gasparini and C. Le Drian, *Synlett*, 1990, 173. (*e*) Y. Cheu and P. Vogel, *J. Org. Chem.*, 1994, **59**, 2487; J. Cossy, J.-L. Ranaivosata, V. Bellasta, J. Ancerewicz, P. Ferritto and P. Vogel, *ibid.*, 1995, **60**, 8351; F. Emery and P. Vogel, *ibid.*, 1995, **60**, 5843; C. Marquis, S. Picasso and P. Vogel, *Synthesis*, 1999, 1441.

38 C. Montalbetti, M. Savignac, J.-P. Genêt, J.-M. Roulet and P. Vogel, *Tetrahedron Lett*., 1996, **37**, 2033.
39 P. Vogel, *Chimie Organique, Méthodes et Modèles*, DeBoeck Université, Bruxelles, 1998, p. 1333.
40 P. Braunstein, J. Durand, G. Kickelbick, M. Knorr, X. Morise, R. Pugin, A. Tiripicchio and F. Ugozolli, *J*, *Chem. Soc*., *Dalton Trans*., 1999, 4175.
41 P. Braunstein, M. Knorr, H. Piana and U. Schubert, *Organometallics*, 1991, **10**, 828.
42 P. Braunstein, M. Knorr, A. Tiripicchio and M. Tiripicchio–Camellini, *Angew. Chem*., *Int. Ed. Engl*., 1989, **28**, 1361.
43 M. J. Green, G. J. P. Britovsek, K. J. Cavell, B. W. Skelton and A. H. White, *J. Chem. Soc*., *Chem. Commun*., 1996, 1563.
44 *CRC Handbook of Chemistry and Physics*, eds. R. C. Weast, M. J. Astle and W. H. Beyer, CRC Press, Boca Raton, FL, 1988, p. F-166.
45 B. A. Markies, P. Wijkens, J. Boersma, A. L. Spek and G. van Koten, *Recl. Trav. Chim. Pay-Bas*, 1991, **110**, 133.
46 I. Tóth and C. J. Elsevier, *J. Am. Chem. Soc*., 1993, **115**, 10388.
47 H. Jin and K. J. Cavell, *J. Chem. Soc*., *Dalton Trans*., 1994, 415.
48 V. De Felice, V. G. Albano, C. Castellari, M. E. Cucciolito and A. De Renzi, *J. Organomet. Chem*., 1991, **403**, 269.
49 P. E. Garrou and R. F. Heck, *J. Am. Chem. Soc*., 1976, **98**, 4115.
50 G. K. Anderson and R. J. Cross, *Acc. Chem. Res*., 1984, **17**, 67.
51 F. Calderazzo, *Angew. Chem*., *Int. Ed. Engl*., 1977, **16**, 299.
52 K. E. Frankcombe, K. J. Cavell, B. F. Yates and R. B. Knott, *Organometallics*, 1997, **16**, 3199.
53 V. De Felice, M. L. Ferrara, F. Giordano and F. Ruffo, *Gazz. Chim. Ital*., 1994, **124**, 117.
54 (*a*) G. M. Sheldrick, *SHELXL-93*, Universität Göttingen, Göttingen, Germany, 1993; (*b*) G. M. Sheldrick, *SHELXS-86*, Universität Göttingen, Göttingen, Germany, 1986.

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