Palladacyclopentadiene Complexes with Mono- and Didentate Imidato Ligands: Synthesis, Hemilabile Behaviour and Catalytic Application in the Stille Reaction

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The binuclear hydroxo complex $[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2]$ (**1**) has been prepared by addition of two equivalents of NBu_4OH to polymeric $[Pd\{C_4(COOMe)_4\}]_n$. Complex **1** has been successfully employed as a precursor to three novel binuclear imidate-bridged complexes $[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-imidate})_2]$ [imidate = succinimidate (suc) **2**, phthalimidate (pht) **3** or maleimidate (mal) **4**] in which the imidate group displays a bidentate *N*,*O*-coordination mode. The hemilabile behaviour of the imidate ligands has been investigated by reaction with a variety of P, N and S ligands, affording the corresponding mononuclear derivatives $[NBu_4][Pd\{C_4(COOMe)_4\}(imidate)L]$ [L = PPh_3 (**2a**, **3a** or **4a**), $P(p\text{-}C_6H_4F)_3$ (**2b**, **3b** or **4b**), PBu_3 (**2c**, **3c** or **4c**), py (**2d**, **3d** or **4d**), $p\text{-}MeC_6H_4NH_2$ (**2e**, **3e** or **4e**), tetrahydrothiophene (**2f**, **3f** or **4f**)] with terminal *N*-bonded imidate ligands. The characterization of the new complexes involved spectroscopic methods (IR, FAB, ^1H, ^{13}C, ^{19}F and ^{31}P NMR) and X-ray crystallographic analysis for **1**, **4b** and **4e**. The mononuclear derivatives are shown to catalyse the Stille cross-coupling of benzyl bromide **7** with ethyl *Z*-vinylstannyl carboxylate (**8**) in high yields. Yields and reaction times are dependent on the presence and type of imidate ligand, which suggests an important role for it in the catalytic cycle.

Introduction

Over the last twenty five years great advances in the development of palladium-catalysed carbon−carbon and carbon−heteroatom bond-forming processes have been observed.[1] Palladium-catalysed reactions, such as Stille[2] and Suzuki coupling, have made significant contributions to synthetic chemistry, not least in the synthesis of important natural products and materials.[3] For this reason, highly active, efficient and selective Pd catalysts are continually been sought after. The scope of the Suzuki and Stille reactions — the reaction of organohalides with organoboronic acids or organostannanes, respectively — has been substantially expanded upon in recent years. The design of electron-rich palladium species possessing strong σ-donor ligands that mediate mild cross-coupling reactions of activated and deactivated organohalide substrates with appropriate nucleophiles has contributed to this effort.[4] To date, however, palladacyclopentadiene complexes have not been used in classic carbon−carbon bond-forming processes, although they have been implicated in a number of other catalytic processes.[5]

In this paper, we wish to describe the synthesis of a new class of palladacyclopentadiene complexes that contain imidato ligands (succinimide, maleimide and phthalimide). We have studied in previous work[6] the hemilabile behaviour[7] of such ligands in complexes with a classical cyclometallated backbone. The precursors employed in this case were the well-known complexes with bridging acetate groups. However, regarding the desired palladacyclopentadiene compounds we envisaged that they could be synthesised from binuclear hydroxypalladium complexes, the chemistry of which has been studied recently,[8] by means of a simple acid-base reaction with protic electrophiles.[9] Thus, the preparation of the new organometallic di-μ-hydroxo complex **1** containing a palladacyclopentadiene backbone, its use as a precursor of binuclear di-μ-imidate palladacyclopentadiene complexes **2**−**4**, and their hemilabile behaviour towards monodentate ligands, such as acetonitrile,

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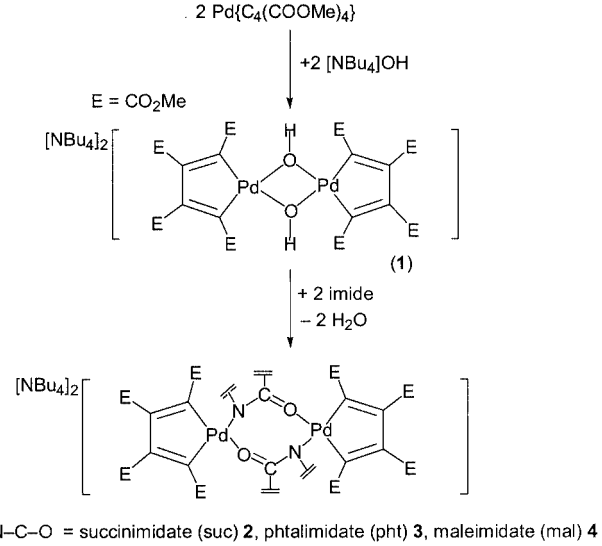
phosphanes [Ph_3P, (p-$C_6H_4F)_3P$ and nBu_3P], pyridine, p-toluidine and tetrahydrothiophene, are reported in detail herein. A comparison of the catalytic properties of the new di-μ-imidate palladacyclopentadiene complexes with [1,2,3,4-tetrakis(methoxycarbonyl)-1,3-butadiene-1,4-diyl]-palladium(II) (TCPC), [Pd($NCOC_2H_4CO$)(PPh_3)$_2$Br][10] (**5**) and [Pd($NCOC_2H_4CO$)(dppe)Br] (**6**) in the Stille reaction, is also presented. Fairlamb and Taylor[11] have recently disclosed the first application of imidato-based palladium pre-catalysts **5** and **6** in the Stille reaction,[12] where they found that allylic and benzylic substrates were coupled efficiently.[13] Here the succinimide ligand, a pseudohalide that can be viewed as a strong σ-acceptor and moderate π-donor (stronger π-donor than chlorine), plays an important role.[14] Thus, being able to compare the effect of the palladacyclopentadiene unit and the presence of an imidate ligand, is an important objective of this paper.

Results and Discussion

The novel anionic palladacyclopentadiene complex [Pd_2{C_4(COOMe)$_4$}$_2$(μ-OH)$_2$]$^{2-}$ (**1**) was conveniently prepared by reaction of the polymeric complex [Pd{C_4(COOMe)$_4$}]$_n$ (TCPC) with NBu_4OH in water (Scheme 1).[5d]



Scheme 1. Hydroxo- and imidate-bridged binuclear complexes

The analytical data for the hydroxo-bridged palladacyclopentadiene dimer **1** are consistent with the proposed formula. Negative-ion FAB mass spectrometry shows a signal at m/z = 725 due to the [Pd_2{C_4{$COOMe)_4$}{C_4{$COOMe}_3${CO}})(μ-$OH)_2$]$^-$ fragment. Evidence for the

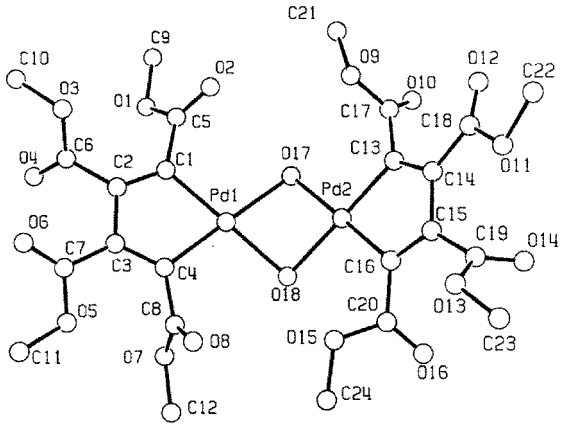
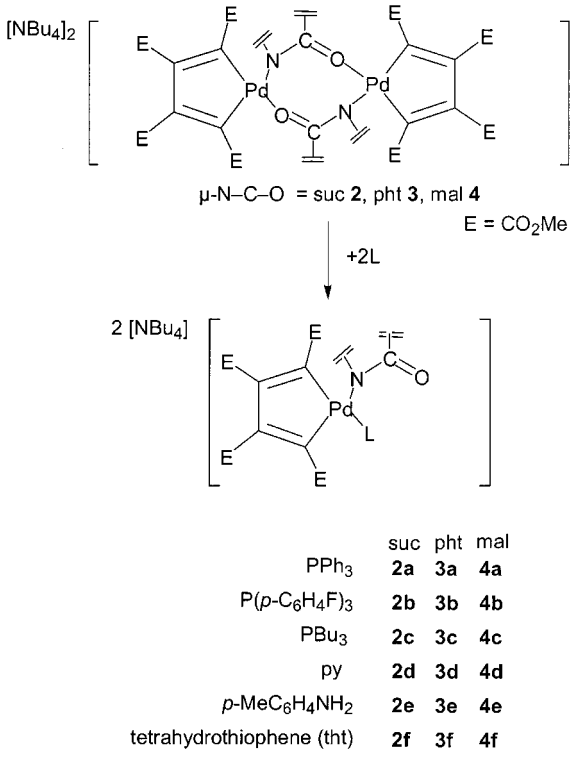


Figure 1. X-ray single-crystal structure of **1**

μ-OH ligand comes from the IR spectrum of **1**, which shows a stretching vibration at $\tilde{\nu}$ = 3600 cm^{-1}. A high-field shielded resonance is also seen at δ = −0.85 ppm in the ^{1}H NMR spectrum, which is attributable to this ligand. Two and four signals for the metallacycle moiety are found in the ^{1}H and ^{13}C NMR spectra, respectively. These attributes are consistent with the symmetrical nature of **1**. X-ray crystallographic analysis on a poor quality crystal of **1** allowed us to unambiguously define the connectivities of the atoms in the anion complex (Figure 1), confirming the proposed molecular structure and its similarity to previously reported halide complexes.[15] It was not possible to refine the structure with acceptable R-values to obtain an adequate data set for an accurate structure determination. Complex **1** crystallized from dichloromethane/diethyl ether as yellow crystals in the monoclinic space group $P2_1/c$ with cell parameters a = 12.8481(6) Å, b = 63.7441(30), c = 16.6102(8) Å, γ = 119.9433(9)°, V = 12618.0(17) Å^3, Z = 8, D_c = 1.369 g·cm^{-3}.

In acetone, **1** reacts with succinimide, phthalimide or maleimide to give the dinuclear complexes **2**, **3** and **4**, respectively, in which the imidato ligands replace the bridging hydroxo groups (as shown in Scheme 1). The imidate complexes are air-stable yellow solids, whose IR spectra exhibit strong bands between $\tilde{\nu}$ = 1700 ± 20 cm^{-1} and 1620 ± 20 cm^{-1}, that are characteristic of the carboxylate and imidate groups, respectively. The dinuclearity of these complexes was confirmed by FAB mass spectrometry. The negative FAB mass spectra of complexes **2**−**4** show peaks corresponding to [(NBu_4)Pd_2{C_4(COOMe)$_4$}$_2$(μ-suc)$_2$]$^-$ (m/z = 1220, **2**), [(NBu_4)Pd_2{C_4(COOMe)$_4$}$_2$(μ-phthal)$_2$-2]$^-$ (m/z = 1314, **3**) and [Pd_2{C_4(COOMe)$_4$}$_2$(mal)]$^-$ (m/z = 876, **4**). The dinuclear complexes **2**−**4** undergo rapid dissociation in acetonitrile to give mononuclear species. In CD_3CN, complex **2** exhibits four singlet resonances (δ = 3.36, 3.46, 3.49 and 3.60 ppm) in the ^{1}H NMR spectrum, which are attributable to the four methoxycarbonyl groups of the asymmetric [Pd{C_4(COOMe)$_4$}(suc)(CD_3CN)]$^-$ complex. Compounds **3** and **4** behave in a similar manner (see Exp. Sect.).

We have investigated the hemilabile behaviour of the imidato-bridged compounds toward neutral ligands, such as phosphanes, amines and tetrahydrothiophene. These reactions take place in acetone under mild conditions to give the corresponding anionic square-planar complexes $[Pd\{C_4\{COOMe)_4\}(N\text{-imidate})(L)]^-$ (**2a**−**f**, **3a**−**f**, **4a**−**f**, Scheme 2), which are air-stable pale-yellow solids. The IR spectra show bands characteristic of the palladacyclopentadiene backbone and imidate ligands (see Exp. Sect.).



	suc	pht	mal
PPh_3	**2a**	**3a**	**4a**
$P(p\text{-}C_6H_4F)_3$	**2b**	**3b**	**4b**
PBu_3	**2c**	**3c**	**4c**
py	**2d**	**3d**	**4d**
$p\text{-}MeC_6H_4NH_2$	**2e**	**3e**	**4e**
tetrahydrothiophene (tht)	**2f**	**3f**	**4f**

Scheme 2. Mononuclear *N*-imidate complexes

With regard to the ^1H NMR spectra, the expected resonances of the palladacyclopentadiene, imidate and neutral ligands are seen. The resonances of the methoxycarbonyl groups on the carbons *trans* to the imidate units appear between $\delta = 3.25$ and 3.58 ppm, whilst the resonances of the methoxycarbonyl groups on the carbons *trans* to the neutral ligands occur at higher field, particularly in complexes containing PPh_3 and $P(p\text{-}C_6H_4F)_3$ ligands (between $\delta = 2.50$ and 2.62 ppm for complexes **2a**,**b**, **3a**,**b** and **4a**,**b**). The $^{31}P\{^1H\}$ NMR spectra of the phosphane complexes show a single resonance in the usual range for palladium(II) complexes (for PPh_3 (**2a**, **3a**, **4a**), $\delta = 28.1-28.7$ ppm; $P(4\text{-}F\text{-}C_6H_4)_3$ (**2b**, **3b**, **4b**), $\delta = 26.4-26.8$ ppm; $PnBu_3$ (**2c**, **3c**, **4c**), $\delta = 2.5-3.6$ ppm). The molecular structures of **4b** and **4e** were confirmed by X-ray single crystal diffraction (Figure 2 and 3, respectively; data collection and refinement information is given in the Exp. Sect.).

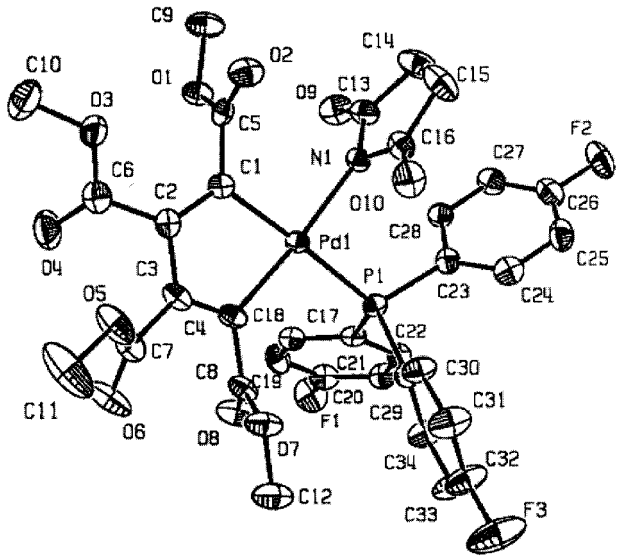


Figure 2. X-ray single crystal structure of **4b**

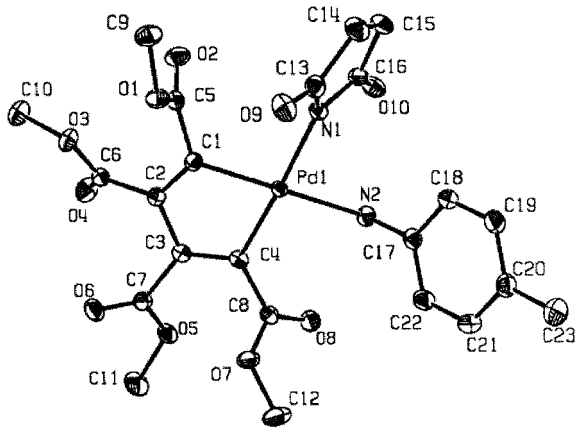


Figure 3. X-ray single crystal structure of **4e**

The X-ray data represent the first description of crystal structures in which the maleimidate ligand appears coordinated to a metal centre in a *N*-monodentate mode (η^2-alkene coordination is common for maleimide ligands).[16] Selected bond lengths and angles are given in Table 1.

The Pd(1)−N(1) distance and the C(1)−Pd(1)−C(4) angle are similar in both compounds and lie close to those determined for related structures.[5n] A slight tetrahedral distortion of the planar palladium environment is observed in **4b**, with torsion angles of −2.13° for P(1)−C(4)−C(1)−Pd(1) and −6.19° for N(1)−C(1)−C(4)−Pd(1).[17] In complex **4e** the coordination around the metal centre is characterised by a plane defined by the C(1)−C(4)−N(1)−Pd(1) atoms, with N(2) out of the plane [torsion angles of −0.30° for N(1)−C(1)−C(4)−Pd(1) and −9.40° for N(2)−C(4)−C(1)−Pd(1)]. Following the recent classification put forward by Dance and Scudder[18] for PPh_3, the conformation of the $Pd-P(p\text{-}C_6H_4F)_3$ group can be de-

Table 1. Selected bond lengths (Å) and angles (°) for complexes **4b** and **4e**

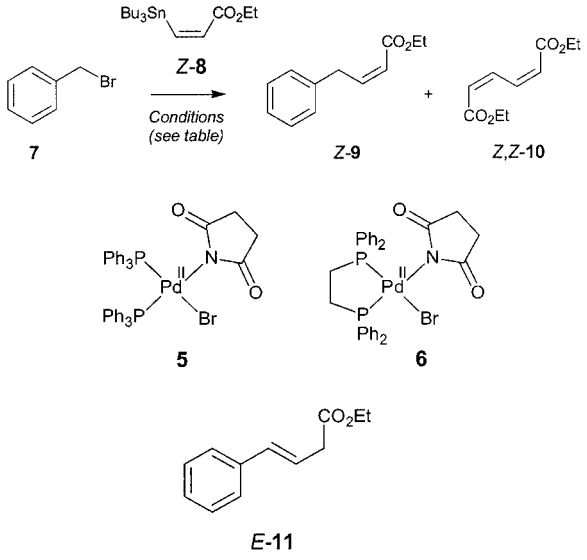
	4b	**4e**
Pd(1)−C(1)	2.066(4)	2.0154(19)
Pd(1)−C(4)	2.036(4)	2.0095(18)
Pd(1)−N(1)	2.077(3)	2.0900(15)
Pd(1)−P(1)[a]	2.3339(12)	2.1789(16)
N(1)−C(13)	1.378(5)	1.390(2)
N(1)−C(16)	1.357(5)	1.362(2)
C(13)−O(9)	1.213(5)	1.216(2)
C(16)−O(10)	1.224(5)	1.232(2)
C(13)−C(14)	1.521(7)	1.507(3)
C(14)−C(15)	1.308(7)	1.319(3)
C(15)−C(16)	1.511(6)	1.506(3)
C(1)−Pd(1)−C(4)	80.05(17)	79.73(8)
C(1)−Pd(1)−N(1)	167.52(15)	177.16(7)
C(4)−Pd(1)−N(1)	91.05(15)	97.47(7)
C(1)−Pd(1)−P(1)[a]	97.74(13)	94.26(7)
C(4)−Pd(1)−P(1)[a]	176.28(12)	165.48(7)
N(1)−Pd(1)−P(1)[a]	91.58(10)	88.57(6)

[a] N(2) in compound (**4e**)

scribed as a *good rotor* for **4b** (T_1 = 16.96°; T_2 = 36.35°; T_3 = 69.46°), based on the M−P−C_{ipso}−C torsion angle.

Catalytic Properties of the Mononuclear Imidate Complexes

The mononuclear palladacyclopentadiene complexes **2a**, **2d**, **2f**, **3a**−**3f**, **4a**, **4d** and **4f** were evaluated in the Stille coupling of benzyl bromide (**7**) with ethyl *Z*-vinylstannyl carboxylate (**8**) in dry toluene at 60 °C under an atmosphere of nitrogen (Table 2).



This was achieved under identical reactant concentrations and catalyst loadings to that reported in the successful Stille coupling using **5** and **6** as catalysts.[11] All of the mononuclear complexes were shown to catalyse the cross-coupling reaction. The particular type of imidate (succinimide, maleimide, phthalimide) and the neighbouring ligand attenuated the catalyst activity and overall yields of *Z*-**9**. The tetrahydrothiophene (tht) ligand proved to be the best for all of the imidate complexes, indicating that ligand dissociation is probably important (entries 5, 11 and 14). Credibility for this suggestion is gained by comparing the

Table 2. Palladacyclopentadiene screening against Stille cross-coupling[a]

Entry	Catalyst[b]	Imidate	Time (h)	Yield of (*Z*)-**9** (%)	Yield of (*Z*,*Z*)-**10** (%)
1	[Pd(NCOC$_2$H$_4$CO)(PPh$_3$)$_2$Br] (**5**)	Suc	3	98	–
2	]Pd(NCOC$_2$H$_4$CO)(dppe)Br] (**6**)	Suc	24	90[c]	–
3	**2a** (PPh$_3$)	Suc	22	82[d]	0
4	**2d** (Py)	Suc	1.3	86[e]	4
5	**2f** (tht)	Suc	1.5	95	4
6	**3a** (PPh$_3$)	Pht	3.75	72[f]	0
7	**3b** [P(*p*-C$_6$H$_4$F)$_3$]	Pht	6	99[g]	0
8	**3c** (P*n*Bu$_3$)	Pht	20	80	0
9	**3d** (Py)	Pht	2.75	63	3
10	**3e** (*p*-MeC$_6$H$_4$NH$_2$)	Pht	5.75	84	0
11	**3f** (tht)	Pht	1	81	0
12	**4a** (PPh$_3$)	Mal	21	53	0
13	**4d** (Py)	Mal	20	32	1
14	**4f** (tht)	Mal	3	70[h]	0
15	TCPC	–	15[i]	68	0
16	Pd/P(*t*Bu)$_3$[j]	–	1.5	71	0

[a] Reaction conditions: **7** (0.5 mmol), (*Z*)-**8** (0.6 mmol), $C_6H_5CH_3$ (5 mL) at 60 °C, under an inert atmosphere of N_2. Isolated yields are given after column chromatography in all cases. All reactions were closely monitored by TLC using 5% ethyl acetate/petroleum ether as eluent. The reaction time given is representative of complete reaction, as adjudged by complete disappearance of **7**. [b] 5 mol % [Pd] unless stated otherwise. [c] Isomer ratio [(*E*)-**9**:(*Z*)-**9**, 1:29]. [d] Isomer ratio [(*E*)-**9**:(*Z*)-**9**, 1:3.7]. The *E*-regioisomer **11** was also observed (2%). [e] Isomer ratio [(*E*)-**9**:(*Z*)-**9**, 1:14.3]. [f] Isomer ratio (*E*:*Z*, 1:23). [g] Isomer ratio (*E*:*Z*, 1:2.5). The *E*-regioisomer **11** was also observed (8%). [h] Isomer ratio (*E*:*Z*, 1:12.2). The *E*-regioisomer **11**was also observed (4%). [i] The reaction had to be conducted at 100 °C. Very slow conversion into *Z*-**9** was seen at 60 °C. [j] [Pd$_2$dba$_3$] (2.5 mol %), P(*t*Bu)$_3$ (5.5 mol %), $C_6H_5CH_3$, 60 °C.

pyridine and triphenylphosphane ligands (entries 3, 4, 6, 9, 12 and 13). The presence of a pyridine ligand in combination with a succinimide or phthalimide provides higher reaction rates than those catalysts containing phosphane ligands (entries 4 and 9). The reaction employing the maleimide-based complex **4d** was surprisingly sluggish and the overall yield was low (entry 13). With the exception of the phthalimide/triphenylphosphane derivative **3a** (entry 6), triphenylphosphane retards the reaction rate (entries 3 and 12). For a number of examples, regio- and/or stereoisomerisation was observed (entries 2−4, 6, 7 and 14) which is a common problem observed with this type of product.[11] We generally found that isomerisation occurs during the latter stages of the reaction (as judged by ^{1}H NMR spectroscopy and TLC analysis). In terms of isolated yields, **3b** is the best catalyst, providing *Z*-**9**/*E*-**11** in 99% combined yield, although extensive isomerisation was observed, which might be related to its high activity. The succinimido catalyst **2f** provided the product *Z*-**9** in 95% yield and no isomerisation was observed (entry 5). This catalyst reduces the reaction time by half in comparison to precatalyst **5** (entries 1 and 5) and is the catalyst of choice. As a control experiment, the TCPC complex was screened for catalytic activity (entry 15). Higher temperatures (100 °C) were required to facilitate the reaction, with the coupling product isolated in 68% yield after 15 h. The requirement for a higher temperature is presumably associated with the polymeric form of TCPC. Against a state-of-the-art catalyst system developed by Fu et al., namely the Pd/P(*t*Bu)$_3$ system,[19] our results compare well (entries 4, 5, 11). Employing an identical catalyst loading to that used in our studies (5 mol % Pd), the product *Z*-**9** was isolated in 71% yield after 1.5 h (entry 16). For catalyst **2f**, containing the tht ligand, lowering the catalyst concentration to 0.5 mol % gives the cross-coupled product in a 93% yield after only 3.25 h. Future studies will be focussed on assessing the effect and impact of catalyst loading on the reaction rates and yields of these reactions.

Generally, the results indicate that a phosphane ligand is *not* a prerequisite (it is usually required to promote the oxidative addition process). The type of imidate seems to affect the yields and reaction times, suggesting that it too plays an important role within the catalytic cycle. The substantially lower activity of TCPC in this reaction also suggests that the imidate and other ligands are important for catalysis. In consideration of the classic catalytic cycle, where a Pd^0/Pd^{II} or related anionic cycle is considered,[20] the palladacyclopentadiene unit would be reduced. However, we have yet to isolate any side-products related to the organic diene fragment of the palladacyclopentadiene unit. In the absence of phosphane ligand, reduction would be expected to release metallic palladium black, particularly towards the latter stages of the reaction when substrate concentration is low. In several reactions (entries 4, 5, 9 and 13, Table 2) small quantities of the homocoupled (self-coupled) product *Z*,*Z*-**10**, derived from the organotin reagent, *Z*-**8**, were isolated. The exact quantity of *Z*,*Z*-**10** varies, but it should be emphasised that we only begin to detect this during the latter stages of the reaction (by TLC).

Conclusion

The new di-μ hydroxo complex $[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2]$ (**1**) has been synthesised and characterised. Its validity as a precursor in acid-base reactions has been demonstrated by preparation of new imidate-bridged complexes in which an *N*,*O*-bidentate coordination mode is exhibited. Bridge splitting with neutral ligands affords mononuclear *N*-bonded imidate complexes. Two *N*-bonded maleimidate complexes have been described and represent the first such examples where the maleimidate is *N*-bonded to a metal centre. These mononuclear complexes demonstrate very good catalytic properties in the Stille reaction and represent the first uses of anionic palladacyclopentadiene complexes in classical carbon−carbon bond-forming reactions. We intend to extend their use to other important reactions in synthesis, such as the Suzuki and Heck reactions. A number of complexes are more active than the previously described succinimido catalyst **5**. Complexes **2d**, **2f** and **3f** were the most efficient in this respect. Further studies are being carried out to probe whether these catalysts operate by classical or non-classical catalytic pathways, whether the palladacyclopentadiene unit is stable under the catalytic conditions, and which Pd complex is observed after catalysis. These results will be reported in due course.

Experimental Section

General Remarks: C, H, N and S analyses were carried out with a Carlo Erba model 1108 microanalyser. IR spectra were recorded on a Perkin−Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. NMR spectroscopic data were recorded on a Bruker AC 200E or a Varian Unity 300 spectrometer. Mass spectrometric analyses were performed on a Fisons VG Autospec double-focusing spectrometer, operating in the negative mode. Ions were produced by fast-atom bombardment (FAB) with a beam of 25-KeV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000. The palladacyclopentadiene precursor (TCPC) was prepared by a published method.[4] Dry CH_2Cl_2 and toluene were distilled from calcium hydride. THF was distilled from sodium-benzophenone ketyl. Reagents were purchased from commercial sources and used directly unless stated otherwise in the text.

Catalysis: Nitrogen gas was oxygen-free and was dried immediately prior to use by passing over sodium hydroxide pellets. All TLC analysis was performed using Merck 5554 aluminium-backed silica plates. Compounds were visualised using UV light (254 nm) and either an acidic aqueous solution of vanillin, a basic aqueous solution of potassium permanganate, acidic DNP or iodine silica. Column chromatography was performed with Fisons matrix silica using the eluent specified in the text. The inorganic solutions used were either saturated (NaCl, KF) or of the approximate concentration indicated in the text. PE refers to petroleum ether 40−60 °C.

^{1}H and ^{13}C NMR spectra were recorded on a Jeol EX270 spectrometer operating at 270 and 67.9 MHz, respectively, on a Bruker AMX 500 at 500 and 125 MHz, respectively, or a Jeol EX400 spectrometer operating at 400 and 100 MHz. The solutions were prepared in suitable deuterated solvents. The spectra were referenced

to either TMS or residual protonated solvent. Proton assignments were based on coupling constants, integration and correlation tables. Carbon spectral assignments were aided using DEPT studies and correlation tables. All melting points were recorded on an Electrothermal IA9000 digital melting point apparatus and are uncorrected. Low- and high-field resolution electron ionisation (EI) and chemical ionisation (CI) mass spectrometry were performed by Dr. T. A. Dransfield and Mr. B. R. Glennie, using a Fisons analytical (VG) Autospec instrument. All values are reported in accordance with convention and high resolution molecular ions given are within ±5 ppm of the required molecular mass. Infrared spectroscopic data were obtained using an ATI Mattson Genesis FT-IR spectrometer. Samples were prepared for analysis as either neat films between NaCl plates, nujol mulls or solutions.

$[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2]$ (1): $[NBu_4]OH$ (aq) (7.68 mL of 1 M solution, 7.68 mmol) was added to a suspension of $[Pd\{C_4\{COOMe)_4\}]_n$ (1.5 g, 3.84 mmol) in water (15 mL), with constant stirring for 30 min. The solvent was partly evaporated under reduced pressure until a yellow solid began to precipitate. The mixture was then stored overnight at ca. 4 °C and the solid was filtered off, washed with diethyl ether and air-dried. The compound was recrystallised from acetone/diethyl ether. Yield (1.972 g, 79%). M.p. 155 °C (dec.). $C_{56}H_{98}N_2O_{18}Pd_2$ (1300.2): calcd. C 51.7, H 7.6, N 2.1; found C 52.0, H 7.8, N 1.9. IR (nujol): $\tilde{\nu}$ = 3602m (νOH), 1686s (νCO), 1546s (νCO) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = −0.85 (s, 2 H, OH), 3.60 (s, 12 H, COOMe), 3.66 (s, 12 H, COOMe) ppm. $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 50.5 (COO*Me*), 50.8 (COO*Me*), 50.8 (COO*Me*), 51.0 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 784 $[Pd_2\{C_4(COOMe)_4\}\{C_4(COOMe)_3(CO)\}(\mu\text{-}OH)_2]^-$, 725 $[Pd_2\{C_4(COOMe)_4\}\{C_4(COOMe)_2(CO)\}(\mu\text{-}OH)_2]^-$, 407 $[Pd\{C_4(COOMe)_4O]^-$.

Complexes $[NBu_4]_2[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-imidate})_2]$ [imidate = succinimidate (suc) (2), phthalimidate (pht) (3) or maleimidate (mal) (4): These dinuclear complexes were obtained according to the following general method. A stoichiometric amount of imide (0.46 mmol) was added to an acetone solution of hydroxo complex **1** (0.3 g, 0.23 mmol). The solution was stirred at room temperature for 30 min and the solvent was partly evaporated under reduced pressure. Addition of a mixture of diethyl ether and hexane (1:1) caused the formation of yellow-orange solids, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from acetone/diethyl ether.

$[NBu_4]_2[Pd(C_4\{COOMe\}_4(\mu\text{-suc})]_2$ (2): Yield: 0.239 g (71%), m.p. 95 °C (dec.). $C_{64}H_{104}N_4O_{20}Pd_2$ (1462.4): calcd. C 52.6, H 7.2, N 3.8; found C 52.4, H 7.5, N 3.9. IR (nujol): $\tilde{\nu}$ = 1704 s (νCO), 1598 s (νCO). ^1H NMR (200 MHz, CD_3CN): δ = 2.27 (s, 4 H, suc), 3.36 (s, 3 H, COOMe), 3.46 (s, 3 H, COOMe), 3.49 (s, 3 H, COOMe), 3.60 (s, 3 H, COOMe) ppm. FAB-MS (negative mode): *m*/*z* = 1220 $[(NBu_4)Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-suc})_2]^-$, 880 $[Pd_2\{C_4(COOMe)_4\}_2(suc)]^-$, 488 $[Pd\{C_4(COOMe)_4\}(suc)]^-$.

$[NBu_4]_2[Pd\{C_4(COOMe)_4\}(\mu\text{-pht})]_2$ (3): Yield: 0.229 g (64%), m.p. 147 °C (dec.). $C_{72}H_{104}N_4O_{20}Pd_2$ (1558.5): calcd. C 55.5, H 6.7, N 3.6; found C 55.6, H 6.9, N 3.9. IR (nujol): $\tilde{\nu}$ = 1698 s (νCO), 1634 s (νCO). ^1H NMR (200 MHz, CD_3CN): δ = 3.01 (s, 3 H, COOMe), 3.45 (s, 3 H, COOMe), 3.51 (s, 3 H, COOMe), 3.62 (s, 3 H, COOMe), 7.46 (m, 4 H, pht) ppm. FAB-MS (negative mode): *m*/*z* = 1314 $[(NBu_4)Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-pht})_2 - 2]^-$, 930 $[Pd_2\{C_4(COOMe)_4\}_2(pht) + 1]^-$, 536 $[Pd\{C_4(COOMe)_4\}(pht)]^-$.

$[NBu_4]_2[Pd(C_4\{COOMe\}_4(\mu\text{-mal})]_2$ (4): Yield: 0.208 g (62%), m.p. 79 °C (dec.). $C_{64}H_{100}N_4O_{20}Pd_2$ (1458.6): calcd. C 52.7, H 6.9, N 3.8; found C 52.4, H 7.1, N 3.9. IR (nujol): $\tilde{\nu}$ = 1714 s (νCO), 1626 (νCO). ^1H NMR (200 MHz, CD_3CN): δ = 3.27 (s, 3 H, COOMe), 3.45 (s, 3 H, COOMe), 3.49 (s, 3 H, COOMe), 3.60 (s, 3 H, COOMe), 6.34 (s, 2 H, mal) ppm. FAB-MS (negative mode): *m*/*z* = 876 $[Pd_2\{C_4(COOMe)_4\}_2(mal)]^-$, 486 $[Pd\{C_4(COOMe)_4\}(mal)]^-$.

Complexes $[NBu_4][Pd\{C_4(COOMe)_4\}(suc)L]$ [L = PPh_3 (2a), P(*p*-$C_6H_4F)_3$ (2b), PBu_3 (2c), py (2d), *p*-$MeC_6H_4NH_2$ (2e), tetrahydrothiophene (2f)]: A stoichiometric amount of ligand (0.068 mmol) was added to a solution of the dinuclear complex $[NBu_4]_2[Pd(C_4\{COOMe\}_4(\mu\text{-suc})]_2$ (**2**; 0.05 g, 0.034 mmol) in acetone. The solution was stirred at room temperature for 30 min, and then the solvent was partly evaporated under reduced pressure to approximately one-third of the initial volume. The addition of diethyl ether caused the formation of yellow or pale-yellow solids, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

$[NBu_4][Pd\{C_4(COOMe)_4\}(suc)(PPh_3)]$ (2a): Yield: 0.046 g (69%). M.p. 103 °C (dec.). $C_{50}H_{67}N_2O_{10}PPd$ (993.48): calcd. C 60.4, H 6.8, N 2.8; found C 60.2, H 7.0, N 3.1. IR (nujol): $\tilde{\nu}$ = 1694 s (νCO), 1614 s (νCO). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.60 (m, 2 H, suc), 2.04 (m, 2 H, suc), 2.50 (s, 3 H, COOMe), 3.49 (s, 3 H, COOMe), 3.51 (s, 3 H, COOMe), 3.56 (s, 3 H, COOMe), 7.30 (m, 9 H, PPh_3), 7.61 (m, 6 H, PPh_3) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 28.7 (s) ppm. FAB-MS (negative mode): *m*/*z* = 749 $[Pd\{C_4(COOMe)_4\}(suc)(PPh_3) - 1]^-$, 488 $[Pd\{C_4(COOMe)_4\}(suc)]^-$.

$[NBu_4][Pd\{C_4(COOMe)_4\}(suc)\{P(p\text{-}C_6H_4F)_3\}]$ (2b): Yield: 0.057 g (80%). M.p. 164 °C (dec.). $C_{50}H_{64}F_3N_2O_{10}PPd$ (1047.5): calcd. C 57.3, H 6.2, N 2.7 found C 57.0, H 6.5, N 2.5. IR (nujol): $\tilde{\nu}$ = 1698 s (νCO), 1614 s (νCO). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.67 (m, 2 H, suc), 2.04 (m, 2 H, suc), 2.62 (s, 3 H, COOMe), 3.52 (s, 3 H, COOMe), 3.53 (s, 3 H, COOMe), 3.57 (s, 3 H, COOMe), 7.02 [m, 6 H, P(*p*-$C_6H_4F)_3$], 7.62 [m, 6 H, P(*p*-$C_6H_4F)_3$] ppm. $^{19}F\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = −110.9 (td, ^3J = 5.6, ^5J = 1.9 Hz) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 26.8 (s) ppm. FAB-MS (negative mode): *m*/*z* = 804 $[Pd\{C_4\{COOMe)_4\}(suc)\{P(p\text{-}C_6H_4F)_3\}]^-$, 488 $[Pd\{C_4(COOMe)_4\}(suc)]^-$.

$[NBu_4][Pd\{C_4(COOMe)_4\}(suc)(PBu_3)]$ (2c): Yield: 0.039 g (62%). M.p. 102 °C (dec.). $C_{44}H_{79}N_2O_{10}PPd$ (933.51): calcd. C 56.6, H 8.5, N 3.0; found C 56.5, H 8.8, N 3.2. IR (nujol): $\tilde{\nu}$ = 1694 s (νCO), 1622 s (νCO). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, J = 3.6 Hz, 9 H, PBu_3), 1.32 (m, 6 H, PBu_3), 1.48 (m, 12 H, PBu_3), 2.44 (m, 4 H, suc), 3.53 (s, 3 H, COOMe), 3.57 (s, 3 H, COOMe), 3.60 (s, 3 H, COOMe), 3.63 (s, 3 H, COOMe) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 2.5 (s) ppm. FAB-MS (negative mode): *m*/*z* = 690 $[Pd\{C_4\{COOMe)_4\}(suc)(PBu_3)]^-$, 488 $[Pd\{C_4\{COOMe)_4\}(suc)]^-$.

$[NBu_4][Pd(C_4\{COOMe\}_4(suc)(py)]$ (2d): Yield: 0.038 g (69%). M.p. 160 °C (dec.). $C_{37}H_{57}N_3O_{10}Pd$ (810.30) calcd. C 54.8, H 7.1, N 5.2; found C 54.5, H 7.4, N 5.2. IR (nujol): $\tilde{\nu}$ = 1692 s (νCO), 1624 s (νCO). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.37 (m, 4 H, suc), 3.14 (s, 3 H, COOMe), 3.56 (s, 3 H, COOMe), 3.57 (s, 3 H, COOMe), 3.58 (s, 3 H, COOMe), 7.21 (m, 2 H, py), 7.63 (m, 1 H, py), 8.73 (d, J = 2.4 Hz, 2 H, py) ppm. $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 32.1 (suc), 50.0 (COO*Me*), 50.7 (COO*Me*), 50.8 (COO*Me*), 51.0 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 567 $[Pd(C_4\{COOMe\}_4(suc)(py)]^-$, 488 $[Pd(C_4\{COOMe\}_4(suc)]^-$.

$[NBu_4][Pd\{C_4(COOMe)_4\}(suc)(p\text{-}MeC_6H_4NH_2)]$ (2e): Yield: 0.038 g (66%). M.p. 155 °C (dec.). $C_{39}H_{61}N_3O_{10}Pd$ (838.35): calcd. C 55.9, H 7.3, N, 5.0; found C 55.6, H 7.6, N 5.2. IR (nujol): $\tilde{\nu}$ =

1720 s (νCO), 1602 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, *Me*C_6H_4), 2.33 (m, 4 H, suc), 3.54 (s, 3 H, COOMe), 3.55 (s, 3 H, COOMe), 3.66 (s, 3 H, COOMe), 3.68 (s, 3 H, COOMe), 5.18 (br., 2 H, NH_2), 6.75 (d, J = 8.2 Hz, 2 H, C_6H_4), 6.91 (d, J = 8.2 Hz, 2 H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 20.6 (*Me*C_6H_4), 31.8 (suc), 50.8 (COO*Me*), 51.1 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 595 [Pd{C_4(COOMe)$_4$}(suc)(*p*-Me$C_6H_4NH_2$)]$^-$, 488 [Pd{C_4(COOMe)$_4$}(suc)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(suc)(tht)] (2f): Yield: 0.044 g (79%). M.p. 185 °C (dec.). $C_{36}H_{60}N_2O_{10}PdS$ (819.36): calcd. C 52.8, H 7.4, N 3.4, S 3.9; found C 53.0, H 7.6, N 3.2, S 4.2. IR (nujol): $\tilde{\nu}$ = 1698 s (νCO), 1620 s (νCO). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86 (m, 4 H, tht), 2.47 (m, 4 H, suc), 2.93 (m, 4 H, tht), 3.54 (s, 3 H, COOMe), 3.56 (s, 3 H, COOMe), 3.60 (s, 3 H, COOMe), 3.67 (s, 3 H, COOMe) ppm. ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$): δ = 30.2 (tht), 32.4 (suc), 35.1 (tht), 50.6 (COO*Me*), 50.8 (COO*Me*), 50.9 (COO*Me*), 51.0 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 595 [Pd{C_4(COOMe)$_4$}(suc)(*p*-Me$C_6H_4NH_2$)]$^-$, 488 [Pd{C_4(COOMe)$_4$} (suc)]$^-$.

Complexes [NBu$_4$][Pd(C_4{COOMe}$_4$(pht)L] [L = PPh$_3$ (3a), P(*p*-C_6H_4F)$_3$ (3b), PBu$_3$ (3c), py (3d), *p*-Me$C_6H_4NH_2$ (3e), tetrahydrothiophene (3f)]: A stoichiometric amount of ligand (0.064 mmol) was added to a solution of complex **3** (0.05 g, 0.032 mmol) in acetone. The solution was stirred at room temperature for 30 min and the solvent was then partly evaporated under reduced pressure to approximately one-third of the initial volume. The addition of diethyl ether caused the formation of yellow or pale-yellow solids, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallized from dichloromethane/diethyl ether.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(pht)(PPh$_3$)] (3a): Yield: 0.051 g (77%). M.p. 95 °C. $C_{54}H_{67}N_2O_{10}PPd$ (1041.5): calcd. C 62.3, H 6.5, N 2.7; found C 62.0, H 6.8, N 3.1 IR (nujol): $\tilde{\nu}$ = 1694 s (νCO), 1640 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.51 (s, 3 H, COOMe), 3.25 (s, 3 H, COOMe), 3.51 (s, 3 H, COOMe), 3.55 (s, 3 H, COOMe), 7.57 (m, 13 H, pht + PPh$_3$), 7.60 (m, 6 H, PPh$_3$) ppm. ^{31}P{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 28.3 (s) ppm. FAB-MS (negative mode): *m*/*z* = 798 [Pd{C_4(COOMe)$_4$}(pht)(PPh$_3$)]$^-$, 536 [Pd{C_4(COOMe)$_4$}(pht)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(pht)(P{*p*-C_6H_4F}$_3$)] (3b): Yield: 0.057 g (81%). M.p. 165 °C (dec.). $C_{54}H_{64}F_3N_2O_{10}PPd$ (1095.5): calcd. C 59.2, H 5.9, N 2.6; found C 59.0, H 6.1, N 2.9. IR (nujol): $\tilde{\nu}$ = 1694 s (νCO), 1640 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.61 (s, 3 H, COOMe), 3.26 (s, 3 H, COOMe), 3.52 (s, 3 H, COOMe), 3.55 (s, 3 H, COOMe), 6.86 [m, 6 H, P(*p*-C_6H_4F)$_3$], 7.27 [m, 4 H, pht + P(*p*-C_6H_4F)$_3$], 7.57 [m, 6 H, pht + P(*p*-C_6H_4F)$_3$] ppm. ^{19}F{^{1}H} NMR (200 MHz, $CDCl_3$): δ = −111.2 (td, ^3J = 5.6, ^5J = 3.8 Hz, 3 F) ppm. ^{31}P{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 26.5 (s) ppm. FAB-MS (negative mode): *m*/*z* = 852 [Pd{C_4(COOMe)$_4$}(pht){P(*p*-C_6H_4F)$_3$}]$^-$, 536 [Pd{C_4(COOMe)$_4$}(pht)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(pht)(PBu$_3$)] (3c): Yield: 0.038 g (60%). M.p. 132 °C (dec.). $C_{48}H_{79}N_2O_{10}PPd$ (981.56): calcd. C 58.7, H 8.1, N 2.8; found C 58.5, H 8.4, N 2.7. IR (nujol): $\tilde{\nu}$ = 1692 s (νCO), 1646 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.75 (t, J = 7.2 Hz, 9 H, PBu$_3$), 1.19 (m, 6 H, PBu$_3$), 1.46 (m, 12 H, PBu$_3$), 3.07 (s, 3 H, COOMe), 3.45 (s, 3 H, COOMe), 3.57 (s, 3 H, COOMe), 3.60 (s, 3 H, COOMe), 7.40 (m, 2 H, pht), 7.54 (m, 2 H, pht) ppm. ^{31}P{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 3.2 (s) ppm. FAB-MS (negative mode): *m*/*z* = 738 [Pd{C_4(COOMe)$_4$}(pht)(PBu$_3$)]$^-$, 536 [Pd{C_4(COOMe)$_4$}(pht)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(pht)(py)] (3d): Yield: 0.042 g (76%). M.p. 168 °C (dec.). $C_{41}H_{57}N_3O_{10}Pd$ (858.34): calcd. C 57.4, H 6.7, N 4.9; found C 57.1, H 7.0, N 5.0. IR (nujol): $\tilde{\nu}$ = 1698 s (νCO), 1644 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.16 (s, 3 H, COOMe), 3.25 (s, 3 H, COOMe), 3.55 (s, 3 H, COOMe), 3.59 (s, 3 H, COOMe), 7.19 (m, 2 H, py), 7.37 (m, 2 H, pht), 7.50 (m, 2 H, pht), 7.59 (m, 1 H, py), 8.74 (m, 2 H, py) ppm. ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$): δ = 50.1 (COO*Me*), 50.7 (COO*Me*), 50.8 (COO*Me*), 50.9 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 928 [Pd$_2${C_4(COOMe)$_4$}$_2$(suc)]$^-$, 536 [Pd(C_4{COOMe}$_4$(pht)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(pht)(*p*-Me$C_6H_4NH_2$)] (3e): Yield: 0.037 g (65%). M.p. 93 °C (dec.). $C_{43}H_{61}N_3O_{10}Pd$ (886.40): calcd. C 58.3; H 6.9, N 4.7; found C 58.6, H 7.1, N 5.0. IR (nujol): $\tilde{\nu}$ = 1698 s (νCO), 1646 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.11 (s, 3 H, *Me*C_6H_4), 3.24 (s, 3 H, COOMe), 3.52 (s, 3 H, COOMe), 3.66 (s, 3 H, COOMe), 3.71 (s, 3 H, COOMe), 5.34 (br., 2 H, NH_2), 6.75 (m, 4 H, C_6H_4), 7.44 (m, 2 H, pht), 7.56 (m, 2 H, pht) ppm. ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 20.5 (*Me*C_6H_4), 50.7 (COO*Me*), 50.8 (COO*Me*), 51.1 (COO*Me*), 51.2 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 536 [Pd{C_4(COOMe)$_4$}(pht)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(pht)(tht)] (3f): Yield: 0.036 g (65%). M.p. 180 °C (dec.). $C_{40}H_{60}N_2O_{10}PdS$ (867.41): calcd. C 55.4, H 7.0, N 3.2, S 3.7; found C 55.6, H 7.3, N 3.4, S 4.0. IR (nujol): $\tilde{\nu}$ = 1698 s (νCO), 1644 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.82 (m, 4 H, tht), 2.98 (m, 4 H, tht), 3.10 (s, 3 H, COOMe), 3.58 (s, 3 H, COOMe), 3.62 (s, 3 H, COOMe), 3.71 (s, 3 H, COOMe), 7.45 (m, 2 H, pht), 7.58 (m, 2 H, pht) ppm. ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 30.1 (tht), 35.0 (tht), 50.6 (COO*Me*), 50.7 (COO*Me*), 50.9 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 536 [Pd{C_4(COOMe)$_4$}(pht)]$^-$.

Preparation of the Complexes [NBu$_4$][Pd{C_4(COOMe)$_4$}(mal)L] [L = PPh$_3$ (4a), P(*p*-C_6H_4F)$_3$ (4b), PBu$_3$ (4c), py (4d), *p*-Me$C_6H_4NH_2$ (4e), tetrahydrothiophene (4f)]: A stoichiometric amount of ligand (0.068 mmol) was added to a solution of the dinuclear complex [NBu$_4$]$_2$[Pd(C_4{COOMe}$_4$(μ-mal)]$_2$ (**4**; 0.05 g, 0.034 mmol) in acetone. The solution was stirred at room temperature for 30 min, and then the solvent was partly evaporated under reduced pressure to approximately one-third of the initial volume. The addition of diethyl ether caused the formation of yellow or pale-yellow solids, which were filtered off, washed with diethyl ether and air-dried. The compounds were recrystallised from dichloromethane/diethyl ether.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(mal)(PPh$_3$)] (4a): Yield: 0.043 g (64%). M.p. 140 °C (dec.). $C_{50}H_{65}N_2O_{10}PPd$ (991.47): calcd. C 60.6, H 6.6, N 2.8; found C 60.4, H 6.9, N 3.0. IR (nujol): $\tilde{\nu}$ = 1698 s (νCO), 1636 s (νCO. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50 (s, 3 H, COOMe), 3.43 (s, 3 H, COOMe), 3.49 (s, 3 H, COOMe), 3.55 (s, 3 H, COOMe), 5.91 (s, 2 H, mal), 7.27 (m, 9 H, PPh$_3$), 7.60 (m, 6 H, PPh$_3$) ppm. ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): δ = 28.1 (s) ppm. FAB-MS (negative mode): *m*/*z* = 748 [Pd{C_4(COOMe)$_4$}(mal)(PPh$_3$)]$^-$, 486 [Pd{C_4(COOMe)$_4$}(mal)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(mal)(P{*p*-C_6H_4F)$_3$]] (4b): Yield: 0.047 g (66%). M.p. 160 °C (dec.). $C_{50}H_{62}F_3N_2O_{10}PPd$ (1045.4): calcd. C 57.4, H 6.0, N 2.7; found C 57.2, H 6.3, N 2.9. IR (nujol): $\tilde{\nu}$ = 1694 s (νCO), 1632 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.60 (s, 3 H, COOMe), 3.43 (s, 3 H, COOMe), 3.51 (s, 3 H, COOMe), 3.55 (s, 3 H, COOMe), 5.99 (s, 2 H, mal), 6.97 [m, 6 H, P(*p*-C_6H_4F)$_3$], 7.56 [m, 6 H, P(*p*-C_6H_4F)$_3$] ppm. ^{19}F{^{1}H} NMR (200 MHz, $CDCl_3$): δ = −111.1 (td, ^3J = 5.6, ^5J = 3.8 Hz, 3 F) ppm. ^{31}P{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 26.4 (s) ppm. FAB-

MS (negative mode): *m*/*z* = 802 [Pd{C_4(COOMe)$_4$}(mal){P(*p*-$C_6H_4F)_3$}]$^-$, 486 [Pd{C_4(COOMe)$_4$}(mal)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(mal)(PBu$_3$)] (4c): Yield: 0.034 g (54%). M.p. 90 °C (dec.). $C_{44}H_{77}N_2O_{10}PPd$ (931.50): calcd. C 56.7, H 8.3, N 3.0; found C 56.4, H 8.4, N 3.3. IR (nujol): $\tilde{\nu}$ = 1694 s (νCO), 1638 s (νCO). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 9 H, J = 4.8 Hz, PBu_3), 1.30 (m, 6 H, PBu_3), 1.48 (m, 12 H, PBu_3), 3.46 (s, 3 H, COOMe), 3.51 (s, 3 H, COOMe), 3.59 (s, 3 H, COOMe), 3.62 (s, 3 H, COOMe), 6.42 (s, 2 H, mal) ppm. ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): δ = 3.6 (s) ppm. FAB-MS (negative mode): *m*/*z* = 688 [Pd{C_4(COOMe)$_4$}(mal)(PBu$_3$)]$^-$, 486 [Pd{C_4-(COOMe)$_4$}(mal)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(mal)(py)] (4d): Yield: 0.042 g (76%). M.p. 158 °C (dec.). $C_{37}H_{55}N_3O_{10}Pd$ (808.28): calcd. C 55.0, H 6.9, N 5.2; found C 54.7, H 7.2, N 5.3. IR (nujol): $\tilde{\nu}$ = 1692 s (νCO), 1638 s (νCO). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.15 (s, 3 H, COOMe), 3.49 (s, 3 H, COOMe), 3.55 (s, 3 H, COOMe), 3.57 (s, 3 H, COOMe), 6.39 (s, 2 H, mal), 7.20 (m, 2 H, py), 7.61 (m, 1 H, py), 8.66 (m, 2 H, py) ppm. ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$): δ = 50.1 (COO*Me*), 50.8 (COO*Me*), 50.9 (COO*Me*), 51.1 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 486 [Pd{C_4(COOMe)$_4$}(mal)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(mal)(*p*-MeC$_6$H$_4$NH$_2$)] (4e): Yield: 0.032 g (56%). M.p. 135 °C (dec.). $C_{39}H_{59}N_3O_{10}Pd$ (836.34): calcd. C 56.0, H 7.1, N 5.0; found C 55.9, H 7.3, N 5.2. IR (nujol): $\tilde{\nu}$ = 1720 s (νCO), 1634 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, *Me*C$_6$H$_4$), 3.47 (s, 3 H, COOMe), 3.54 (s, 3 H, COOMe), 3.66 (s, 3 H, COOMe), 3.69 (s, 3 H, COOMe), 5.23 (br., 2 H, NH$_2$), 6.42 (s, 2 H, mal), 6.70 (d, J = 8.0 Hz, 2 H, C$_6$H$_4$), 6.87 (d, J = 8.0 Hz, 2 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 23.9 (*Me*C$_6$H$_4$), 50.9 (COO*Me*), 51.1 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 486 [Pd{C_4(COOMe)$_4$}(mal)]$^-$.

[NBu$_4$][Pd{C_4(COOMe)$_4$}(mal)(tht)] (4f): Yield: 0.032 g (57%). M.p. 170 °C (dec.). $C_{36}H_{58}N_2O_{10}PdS$ (817.35): calcd. C 52.9, H 7.1, N 3.4, S 3.9: found C 53.1, H 7.3, N 3.6, S 4.0. IR (nujol): $\tilde{\nu}$ = 1704 s (νCO), 1640 s (νCO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.84 (m, 4 H, tht), 2.91 (m, 4 H, tht), 3.47 (s, 3 H, COOMe), 3.54 (s, 3 H, COOMe), 3.61 (s, 3 H, COOMe), 3.69 (s, 3 H, COOMe), 6.47 (s, 2 H, mal) ppm. ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 30.1 (tht), 34.9 (tht), 50.5 (COO*Me*), 50.7 (COO*Me*), 50.9 (COO*Me*) ppm. FAB-MS (negative mode): *m*/*z* = 486 [Pd{C_4(COOMe)$_4$}(suc)]$^-$.

Preparation of Ethyl (*Z*)-3-(Tributylstannyl)propenoates (8): AIBN (0.073 g (0.4 mmol) was added to a neat mixture of ethyl propiolate (1.74 g, 17.7 mmol) and tributyltin hydride (5 mL, 18.6 mmol) and the mixture heated to 60 °C for 24 h. It was then allowed to cool to ambient temperature and purified by column chromatography using PE/EtOAc (95:5, v/v) as the eluent. This gave the *Z* isomer (2.72 g, 39%) and the *E* isomer (3.89 g, 56%), both as colourless oils. R_f = 0.70, PE/EtOAc (9:1, v/v). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.85−0.99 (m, 18 H, 4 × CH_3 and 3 × CH_2), 1.24−1.32 (m, 6 H, 3 × CH_2), 1.43−1.56 (m, 6 H, 3 × CH_2), 4.21 (q, ^3J = 7.0 Hz, 2 H, CH_2), 6.72 (d, ^3J = 13.0 Hz, 1 H, *CH*), 7.15 (d, ^3J = 13.0 Hz, 1 H, *CH*) ppm. These data are consistent with those previously published.[21]

General Procedure for Stille Cross-Coupling: The specified catalyst (5 mol %) was added to a solution of benzyl bromide (0.5 mmol) and the stannane (0.6 mmol) in dry toluene (5 mL) and heated to 60 °C in the dark, under N_2 atmosphere, for the specified time. The reaction was allowed to cool to ambient temperature, then saturated aq. KF (5 mL) was added and the mixture stirred vigorously for 1 h. The mixture was filtered through Celite, washed with saturated aq. NaCl (2 × 5 mL) and dried ($MgSO_4$). Concentration in vacuo and subsequent purification by column chromatography using ethyl acetate/hexane mixtures (1:20 to 1:9, v/v) afforded the desired product along with some minor side-products.

Preparation of Ethyl (2*Z*)-4-Phenyl-2-butenoate (9): Obtained as a colourless oil. R_f = 0.51, PE/EtOAc (9:1, v/v). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.32 (t, ^3J = 7.0 Hz, 3 H, CH_3), 4.03 (dd, ^3J = 7.5, 1.5, 2 H, CH_2), 4.22 (q, ^3J = 7.0 Hz, 2 H, CH_2), 5.86 (dt, ^3J = 11.5, ^4J = 1.5 Hz, 1 H, *CH*), 6.36 (dt, ^3J = 11.5, 7.5, 1 H, *CH*), 7.22−7.34 (m, 5 H, *Ph-H*) ppm. ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$): δ = 14.2 (CH_3), 35.1 (CH_2), 59.9 (CH_2), 119.9 (CH), 126.3 (CH), 128.7 (CH), 139.4 (C), 147.9 (CH), 166.3 (C) (*ipso* CH) ppm. These data are consistent with those previously published.[22]

Preparation of Ethyl (2*E*)-4-Phenyl-2-butenoate (9′): Obtained as a colourless oil. R_f = 0.30, PE/EtOAc (9:1, v/v). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.27 (t, ^3J = 7.5 Hz, 3 H, CH_3), 3.52 (dd, ^3J = 7.0, 1.0, 2 H, CH_2) 4.18 (q, ^3J = 7.5 Hz, 2 H, CH_2), 5.81 (dt, ^3J = 15.5, ^4J = 1.0 Hz, 1 H, *CH*), 7.10 (dt, ^3J = 15.5, 7.0, 1 H, *CH*), 7.13−7.19 (m, 5 H, *Ph-H*) ppm. ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$): δ = 14.3 (CH_3), 38.6 (CH_2), 60.4 (CH_2), 122.5 (CH), 126.8 (CH), 128.8 (CH), 128.9 (CH), 137.8 (C), 147.4 (CH), 166.6 (C) ppm. These data are consistent with those previously published.[23]

Preparation of Diethyl (2*Z*,4*Z*)-2,4-Hexadienedioate (10): Obtained as a white solid. R_f = 0.10, PE/EtOAc (9:1 v/v). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.30 (t, ^3J = 7.0 Hz, 6 H, CH_3), 4.21 (q, ^3J = 7.0 Hz, 4 H, CH_2), 5.52 (m, 2 H, *CH*), 7.89 (m, 2 H, *CH*) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3), 61.0 (CH_2), 128.5 (CH), 140.9 (CH), 166.0 (C) ppm. These data are consistent with those previously published.[24]

Preparation of Diethyl (2*E*,4*E*)-2,4-Hexadienedioate (10′): Obtained as a white solid. R_f = 0.09, PE/EtOAc (9:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, ^3J = 7.0 Hz, 6 H, CH_3), 4.24 (q, ^3J = 7.0 Hz, 4 H, CH_2), 6.19 (m, 2 H, *CH*), 7.31 (m, 2 H, *CH*) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3), 61.0 (CH_2), 128.5 (CH), 140.9 (CH), 166.0 (C) ppm. These data are consistent with those previously published.[25]

X-ray Crystallography: Crystals of **4b** and **4e** suitable for a diffraction study were grown from acetone/diethyl ether. Data collection for **4e** was performed at −173 °C on a Bruker Smart CCD diffractometer with a nominal crystal to detector distance of 4.5 cm. Diffraction data were collected based on a ω scan run. A total of 1371 frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package[26] and corrected for absorption with SADABS.[27] Data collection for **4b** was performed at −100 °C on a Siemens P4 diffractometer. The structures were solved by the Patterson (**4b**) or direct (**4e**) methods[28] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms[28] (Table 3). Hydrogen atoms were introduced in calculated positions and refined during the last stages of the refinement.

CCDC-218969 (**4b**) and -218971 (**4e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structure refinement for compounds **4b** and **4e**

	4b·$C_4H_{10}O$	**4e**
Formula	$C_{54}H_{72}F_3N_2O_{11}PPd$	$C_{39}H_{59}N_3O_{10}Pd$
Molecular mass	1119.51	836.29
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	11.4262(17)	33.3156(15)
b (Å)	27.753(3)	9.0527(4)
c (Å)	17.5419(17)	27.4288(13)
β (°)	96.140(10)	92.6040(10)
V (Å^3)	5330.9(11)	8263.9(7)
Z	4	8
T (K)	173(2)	100(2)
Reflections collected	10318	25058
μ (mm^{-1})	0.433	0.506
Independent reflections	9724 [R(int) = 0.0410]	9196 [R(int) = 0.0213]
Final $R1$	$R1$ = 0.0451	$R1$ = 0.0315
$wR2$ [$I > 2\sigma(I)$]	$wR2$ = 0.0980	$wR2$ = 0.0785
R indices (all data)	$R1$ = 0.0833	$R1$ = 0.0362
	$wR2$ = 0.1079	$wR2$ = 0.0848

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