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Synthesis and reaction chemistry of mixed ligand methylpalladium–carbene complexes[1]

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Abstract

A variety of methylpalladium carbene complexes of the type [Pd(Me)(carbene)(chelate)] [where carbene = 1,3-di-methylimidazol-2-ylidene (dmiy), chelate = acetylacetonate (acac) **1**, trifluoroacetylacetonate (tfac) **2**, hexafluoroacetylacetonate (hfac) **3**; carbene = 1,3,4,5-tetramethylimidazol-2-ylidene (tmiy), chelate = acac, **6**] have been synthesised and fully characterised. The bis-carbene complexes *trans*-[Pd(Me)(carbene)$_2$Cl] [carbene = dmiy, **7** and tmiy, **8**] have also been isolated. The unusual cationic complex {[Pd(Me)(dmiy)(cod)]$^+$ BF_4^-} **4**, in which there are three distinct Pd–carbon bonds, including *cis* alkyl/alkene coordination has been prepared and aspects of its chemistry investigated. The complex which slowly decomposes even at -20°C does not react via the expected migratory insertion of the methyl group with the coordinated cod but decomposes via a pathway involving the methyl group and the carbene ligand. Crystal structures of the bis-carbene complex **7** and the chloro-bridged dimer [Pd(Me)(tmiy)Cl]$_2$ **5** reveal square planar coordination. The carbene C_3N_2 arrays are closely planar, with the ligand planes inclined at significant angles to the coordination planes of the respective complexes. For complex **7** the interplanar dihedral angle is 70.4(3)° and for **5** the angle is 65.07(8)°. Examples of the methylpalladium monocarbene and dicarbene complexes were tested in the Heck reaction and were found to be extremely active with several having turnover frequencies (TOF's) of >20000 and total turnover numbers (TON's) of >100000.

Keywords: Palladium; Methylpalladium carbene complexes; Synthesis; Reaction chemistry; Heck reaction

1. Introduction

The role of homogeneous catalysts in the production of speciality and fine chemicals is steadily increasing [1,2]. The performance of homogeneous catalysts is generally highly dependent on the ancillary ligands coordinated to the metal centre. Important roles of ligands include stabilising reactive intermediates or transition states and governing activity and selectivity by electronic and steric influences. To this end the familiar trialkylphosphine ligands have been ubiquitous in homogeneous catalysis. Very recently however, a new approach to homogeneous catalysis has emerged, based on complexes of heterocyclic nitrogen carbene ligands [3–8]. The application of, for example, palladium carbene complexes in the Heck reaction [3–5,8] and rhodium carbene compounds in hydrosilylation [7] has opened up new opportunities in catalysis.

Recently Arduengo et al. prepared the first stable, isolable carbenes [9], heterocyclic nitrogen carbenes of the imidazole type, e.g. 1,3-di-1-adamantylimidazol-2-ylidene, prepared by deprotonation of the imidazolium chloride precursor by the use of a strong base (Reaction 1).

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[1] Dedicated to Professor Michael Bruce on the occasion of his 60th birthday and in recogition of his major international contribution to organometallic chemistry.

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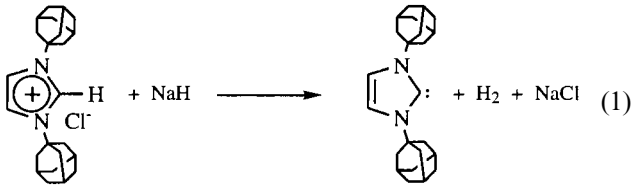
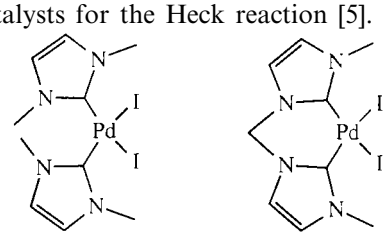


(1)

Theoretical studies showed that resonance stabilisation is not necessary and that cyclic delocalisation does not occur to any great extent [10–12]. Experimental confirmation of this came with the isolation of a saturated imidazolin-2-ylidene ([9]c) and of the first non-cyclic carbene in 1996 [13]. The theoretical studies also indicated that the stability of these carbenes is due to electron donation from the nitrogen lone pairs into the formally vacant p(π) orbital of the carbene carbon.

Heterocyclic carbene ligands in metal complexes were known long before free carbenes were isolated [14]; nonetheless since Arduengo's report of a stable carbene many different free carbenes have been isolated [7–9](c)[13,15–17], interest has been stimulated in carbene complexes and new routes for synthesis developed [18]. Complexes of heterocyclic carbenes are thought to involve only a single M–C bond. Experimental X-ray evidence shows M–C(carbene) bond lengths are virtually the same as M–C(hydrocarbyl) single bonds [5] and ab initio studies show π-back bonding is not significant with these ligands [19]. The fact that heterocyclic carbenes form stable complexes with beryllium, which has no p electrons to back donate, also supports this view [6]. The donation of electron density by the nitrogen substituents on the carbene makes the carbene carbon nucleophilic and compensates for the electron flow from the carbon to the metal. Donation from the nitrogens is such that the carbene carbon may actually become a partial π-donor [5,19]. Heterocyclic carbenes are thus pure donor ligands. They have similarities to the tertiary phosphines but appear to be stronger coordinating ligands which undergo little or no dissociation from the metal in solution [20].

Transition metal–carbene complexes have long been postulated as intermediates in some catalytic processes [14] and have extensive applications in organic synthesis [21]. In most of these cases the carbene moiety is incorporated into the organic product. In contrast, the heterocyclic carbenes act as non-participative ligands in catalytic processes and are not consumed. The first report of heterocyclic carbenes being used as ligands in active catalysts came from Herrmann et al. in 1995, where iodo palladium–carbene complexes (below) were used as catalysts for the Heck reaction [5].



The Pd–carbene complexes gave high catalyst turnovers resulting from the long term stability of the catalyst. Herrmann found that there was no deposition of palladium metal during catalysis, even when high temperatures and long reaction times were employed. It was postulated that the active species is probably Pd(0)(carbene)$_2$, in line with the generally accepted phosphine equivalent, and it is believed that the mechanism for the reaction would be essentially the same as when traditional phosphine complexes are employed. Following this initial report heterocyclic carbene complexes of rhodium were used successfully in hydrosilylation and once again showed exceptional stability [7].

In various catalytic processes hydrocarbylmetal complexes are proposed as intermediates. It was therefore of interest to prepare hydrocarbylpalladium carbene complexes as model compounds for processes catalysed by palladium carbenes or as catalysts in their own right. We had noted previously that simple alkylpalladium carbenes were rare and we therefore set out to develop general routes to synthesising a variety of such complexes. A preliminary report has been accepted for publication in this journal [22]. Herein we detail the synthesis and characterisation of a number of methylpalladium carbene complexes and we demonstrate the possibility of stabilising unusual and reactive compounds. Examples of biscarbene methylpalladium complexes have also been synthesised. Reaction pathways, including catalytic and decomposition pathways, have been investigated in detail and selected crystal structures of two important palladium carbene complexes are reported.

2. Experimental

Solvents were dried and purified by standard methods and freshly distilled under N_2 immediately prior to use. Unless otherwise stated all manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox. All other reagents were used as received. Tetramethyl tin [23], $PdCl_2$(cod) [24], PdMeCl(cod) [25] and Pd(dba)$_2$ [26] were prepared by published procedures. The 1,3-dimethylimidazolium iodide and 1,3-dimethylimidazolium chloride salts which were prepared according to literature methods, were obtained as extremely hygroscopic powders and stored and handled under N_2 [27].

Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature (21°C) unless otherwise indicated on a Varian Gemini-200 NMR spectrometer at 199.98 MHz (^{1}H) and 50.289 MHz (^{13}C); and on a Varian Unity Inova 400 WB NMR spectrometer at 100.587 MHz (^{13}C) and 376.324 MHz (^{19}F). Chemical shifts (δ) are reported in units of ppm relative to internal TMS (^{13}C, ^{1}H), or to $CFCl_3$ via external

CF_3COOD using the equation, $\delta_{CFCl_3} = \delta_{CF_3COOD} - 78.5$ ppm (^{19}F) [28]. Coupling constants (J) are given in Hz and NMR peaks are labelled as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). Elemental analyses were recorded by the Central Science Laboratory (CSL), University of Tasmania, on a Carlo Erba EA1108 elemental analyser. Gas chromatography (GC) was performed on a Hewlett-Packard 5890 series II GC fitted with a SGE 50QC3/BP1 0.5 capillary column and flame ionisation detector (FID). GC–MS and MS were carried out by the CSL, using a HP5890 GC fitted with a 25 m HP1 column (0.32 mm ID, 0.52 μm film) and a HP5970B mass selective detector, and a Kratos Concept ISQ MS by liquid secondary ion mass spectrometry (LSIMS, 10 KV cesium ions, *m*-nitrobenzyl alcohol matrix) with an accelerating voltage of 5.3 KV.

2.1. Structure determinations

Unique room temperature (r.t.) diffractometer data sets (T ca. 295 K; monochromatic Mo–K_α radiation, $\lambda = 0.71073$ Å; $2\theta/\theta$ scan mode; $2\theta\max = 56°$(complex **7**), 60°(complex **5**) were measured, yielding N independent reflections, N_o with $I > 3\sigma(I)$ (complex **7**), $I > 2\sigma(I)$ (complex **5**), being considered 'observed' and used in the full-matrix least squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-H atoms, (x, y, z, $U_{iso})_H$ being constrained at estimated values. Conventional residuals on $|F|$ at convergence R, Rw are quoted; statistical weights were derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma4(I_{diff})$. Neutral atom complex scattering factors were employed, with computation using the XTAL 3.2 program system implemented by Hall [29]. Pertinent results are given in the figures and tables. Tables of structure factor amplitudes, thermal and H atom parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

2.1.1. Crystal/refinement data

Complex **7**. $[Pd(methyl)(dmiy)_2(Cl)] = C_{11}H_{19}ClN_4Pd$, $M = 349.17$. Monoclinic, space group $P2_1/c$, $a = 7.490(5)$, $b = 13.814(5)$, $c = 14.276(4)$ Å, $\beta = 99.18(4)°$, $V = 1458(1)$ Å^3, $D_{calc.}$ $(Z = 4) = 1.590$ g cm^{-3}; $F(000) = 704$. μMo $= 14.4$ cm^{-1}; specimen: $0.32 \times 0.14 \times 0.10$ mm^3; A^*(min, max) $= 1.14, 1.53$. $N = 3508$, $N_o = 1847$; $R = 0.046$; $R_w = 0.060$; $n_v = 154$.

Complex **5**. $[Pd(methyl)(tmiy)(Cl)]_2 = C_{16}H_{30}Cl_2N_4Pd_2$, $M = 562.19$. Monoclinic, space group $P2_1/c$, $a = 8.132(2)$, $b = 15.753(4)$, $c = 8.380(2)$ Å, $\beta = 93.66(2)°$, $V = 1071.2(5)$ Å^3, $D_{calc.}$ $(Z = 2) = 1.743$ g cm^{-3}; $F(000) = 560$. μMo $= 19.3$ cm^{-1}; specimen: $0.51 \times 0.20 \times 0.70$ mm^3; A^*(min, max) $= 1.51, 2.48$. $N = 3116$ (derived from a hemisphere of data, $R_{int} = 0.022$), $N_o = 2780$; $R = 0.029$; $R_w = 0.044$; $n_v = 110$.

2.2. Synthesis of carbene ligands

The heterocyclic carbenes were prepared by two methods: 1,3-dimethylimidazol-2-ylidene was prepared according to the method of Arduengo et al. ([9]b) and used immediately. 1,3,4,5-Tetramethylimidazol-2-ylidene was prepared by the method of Kuhn and Kratz [15], with minor changes. The thione was refluxed for 3–10 h. The solution was then left to settle overnight, filtered through Celite and the solvent removed in vacuo to yield an oily orange solid. This was washed with hexane to leave a pale yellow extremely air sensitive powder in an overall yield of 50%.

2.3. Synthesis of precursor carbene complexes

$Pd(dmiy)_2I_2$ was prepared according to the method of Herrmann with minor modifications [5]. After refluxing, the resultant yellow solution was removed from the fine black residue and centrifuged to remove last traces of the solid. The solvent was then removed in vacuo and the solid washed twice with ether and once with $MeOH/H_2O$. Drying in vacuo at 60°C afforded a yellow solid in ca. 60% yield.

$[PdMe(dmiy)(\mu\text{-}Cl)]_2$ was prepared in 50% yield by the method of Green et al. [22].

2.4. Synthesis of mixed ligand palladium carbene complexes

2.4.1. [Pd(Me)(1,3-dimethylimidazol-2-ylidene)(acac)] **1**

At −20°C Na(acac) (57 mg, 0.47 mmol) was washed (20 ml of CH_2Cl_2) into a suspension of $[Pd(Me)(dmiy)(\mu\text{-}Cl)]_2$ (97 mg, 0.19 mmol) in 20 ml of CH_2Cl_2. The temperature was immediately raised to −10°C and the mixture stirred for ca. 30 h. The solution was filtered through Celite and the solvent removed in vacuo to yield a white solid. Yield: 100%. Anal. Calc. for $C_{11}H_{18}O_2N_2Pd$: C, 41.72; H, 5.73; N, 8.85%. Found: C, 41.64; H, 5.60; N, 8.58%. MS (LSIMS) m/z: 317, $[MH]^+$ (38%); 301, $[M - Me]^+$ (88%); 217, $[M - (acac)]^+$ (100%); 202, $[M - Me(acac)]^+$ (98%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.88 (s, 2H, NC*H*), 5.28 (s, 1H, acac CC*H*), 3.95 (s, 6H, NCH_3), 1.98 [s, 3H, acac CCH_3 (*trans* to ylidene)], 1.86 [s, 3H, acac CCH_3 (*cis* to ylidene)], 0.26 (s, 3H, Pd–CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 187.2, 186.4 (O*C*), 172.0 (N*C*N), 121.8 (*C*=*C*), 99.4 (OC*C*H), 37.9 (NCH_3), 28.2, 28.1 (CCH_3), −11.9 (Pd*C*H$_3$).

2.4.2. [Pd(Me)(1,3-dimethylimidazol-2-ylidene)(tfac)] **2**

The complex was prepared in the same manner described for **1**. The CH_2Cl_2 was removed to yield a yellow oil. This was triturated with 5 ml of hexane and the resulting foamy white solid dried in vacuo. Yield 100%. Anal. Calc. for $C_{11}H_{15}O_2N_2F_3Pd$: C, 35.64; H,

4.08; N, 7.56%. Found: C, 35.79; H, 4.03; N, 7.55%. MS (LSIMS) m/z: 370, $[M]^+$(62%); 355, $[M-Me]^+$ (94%); 217, $[M-(tfac)]^+$(94%); 202, $[M-Me(tfac)]^+$ (100%). ^{1}H-NMR (200 MHz, $CDCl_3$): Two isomers in ca. 1:1.4 ratio, the major one being the CF_3 *cis* ylidene isomer; δ 6.91 (s, 2H, NCH_{min}), 6.88 (s, 2H, NCH_{maj}), 5.63 (s, (1H, CCH_{maj} + 1H, CCHmin)), 3.95 (s, 6H, $NCH_{3\,min}$), 3.91 (s, 6H, $NCH_{3\,maj}$), 2.09 (s, 3H, $CCH_{3\,maj}$), 1.98 (s, 3H, $CCH_{3\,min}$), 0.39 (s, 3H, $PdCH_{3\,maj}$), 0.35 (s, 3H, $PdCH_{3\,min}$). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 193.83, 193.77 (min + maj, $OCCH_3$), 170.0 (min, NCN), 169.3 (maj, NCN), 168.1 (maj, q, $^2J_{CF}$ = 31 Hz, $OCCF_3$), 167.1 (min, q, $^2J_{CF}$ = 31 Hz, $OCCF_3$), 121.9 (min + maj coincident, $C{=}C$), 119.0 (min + maj coincident, q, J_{CF} = 286 Hz, CF_3), 94.4 (min, $OCCH$), 93.9 (maj, $OCCH$), 37.5 (maj, NCH_3), 37.3, (min, NCH_3), 29.1 (min + maj coincident, CCH_3), − 11.3 (maj, $PdCH_3$), − 11.7 (min, $PdCH_3$). ^{19}F-NMR (376 MHz, toluene-d_8): two isomers; δ − 74.1 (min), − 74.4 (max).

2.4.3. [Pd(Me)(1,3-dimethylimidazol-2-ylidene)(hfac)] **3**

The complex was prepared in the same manner described for **2** to give a white foamy solid. Yield: 100%. Anal. Calc. for $C_{11}H_{12}O_2N_2F_6Pd$: C, 31.11; H, 2.85; N, 6.60%. Found: C, 31.14; H, 2.86; N, 6.42%. MS (LSIMS) m/z: 424, $[M]^+$(8%); 409, $[M-Me]^+$(51%); 370, $[M-CH_4F_2]^+$(46%); 217, $[M-(hfac)]^+$(78%); 202, $[M-Me(hfac)]^+$(100%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.93 (s, 2H, NCH), 5.97 (s, 1H, CCH), 3.94 (s, 6H, NCH_3), 0.51 (s, 3H, $PdCH_3$). ^{13}C-NMR (MHz, $CDCl_3$): δ 175.9 (*cis* or *trans*, q, $^2J_{CF}$ = 33 Hz, OC), 175.4 (*cis* or *trans*, q, $^2J_{CF}$ = 33 Hz), 169.4 (NCN), 123.4 ($C{=}C$), 119.1 (*cis*/*trans* coincident, q, J_{CF} = 286 Hz, CF_3), 90.0 ($OCCH$), 39.0 (NCH_3), − 10.0 ($PdCH_3$). ^{19}F-NMR (376 MHz, toluene-d_8): δ 69.8, 70.1.

2.4.4. [Pd(Me)(1,3-dimethylimidazol-2-ylidene)(cod)]BF_4 (**4**)

This cationic complex was prepared by a variation of the method used to prepare the analogous bipy and dppe complexes, but lower temperatures were necessary [22]. To a suspension of [Pd(Me)(dmiy)(μ-Cl)]$_2$ (117 mg, 0.46 mmol) in 10 ml of DCM at − 15°C was added cyclooctadiene (57 ml, 0.46 mmol) and the solution was stirred for 10 min. After this time the solution was added to a suspension of $AgBF_4$ (95 mg, 0.49 mmol) in 4 ml of DCM at − 20°C. The mixture was maintained at this temperature for 1 h before filtering cold through Celite and removing the solvent in vacuo (at − 15 to − 20°C). A white powder was obtained. The complex rapidly turned grey at r.t. and overnight at − 20°C. Yield: 100%. Anal. Calc. for $C_{14}H_{23}N_2BF_4Pd$: C, 40.76; H, 5.62; N, 6.79%. Found: C, 40.59; H, 5.44; N, 7.03%. MS (LSIMS) m/z: 325, $[M]^+$(100%). ^{1}H-NMR (200 MHz, $CDCl_3$, − 20°C): δ 7.19 (s, 2H, NCH), 5.82, 5.65 (br, s, 4H, $HC{=}CH_{cod}$), 3.89 (s, 6H, NCH_3), 2.9–2.6 (br, m, 8H, $CH_{2\,cod}$), 0.62 (s, 3H, $PdCH_3$). ^{13}C-NMR (50 MHz, $CDCl_3$, − 20°C): δ 168.4 (NCN), 123.6 ($C{=}C_{dmiy}$), 118.3, 116.3 ($C{=}C_{cod}$), 37.8 (NCH_3), 29.3, 28.8 (CH_2), 1.8 ($PdCH_3$).

2.4.5. [Pd(Me)(1,3,4,5-tetramethylimidazol-2-ylidene)(μ-Cl)]$_2$ (**5**)

This complex was prepared in the same manner described for the dmiy dimer [22]. The free carbene was isolated before use. At 0°C a solution of tmiy (0.347 g, 2.79 mmol) in 15 ml of THF was added to a suspension of PdMeCl(cod) (0.700 g, 2.6 mmol) in 5 ml of THF and the solvent removed in vacuo. The yellow solid was taken up in DCM (45 ml) at 0°C, filtered through Celite and the DCM removed in vacuo. The solid was washed three times with DCM/THF (2 ml/5 ml) to leave an off-white chalky solid. A crystal suitable for an X-ray structural determination was grown by vapour diffusion of ether into a DCM solution of the complex at − 20°C. Yield: 54%. Anal. Calc. for $C_{16}H_{30}N_4Cl_2Pd_2$: C, 34.18; H, 5.38; N, 9.97%. Found: C, 34.01; H, 5.28; N, 9.77%. MS (LSIMS) m/z: 527, $[M-Cl]^+$(27%); 230, $[Pd(tmiy)]^+$(100%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 3.90 (br, s, 12H, NCH_3), 2.08 (br, s, 12H, CCH_3), 0.26 (br, s, 6H, $PdCH_3$). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 168.9 (NCN), 125.3 ($C{=}C$), 35.6 (NCH_3), 9.4 (CCH_3), − 9.5 ($PdCH_3$).

2.4.6. [Pd(Me)(1,3,4,5-tetramethylimi-dazol-2-ylidene)(acac)] **6**

Complex **6** was prepared in the same way as that described for complex **2**, yielding a pale yellow solid. Yield: 80%. Anal. Calc. for $C_{13}H_{21}N_2O_2Pd\cdot 0.1CH_2Cl_2$ (Presence of DCM verified by ^{1}H-NMR): C, 44.54; H, 6.33; N, 7.93%. Found: C, 43.76; H, 6.34; N, 8.06%. MS (LSIMS) m/z: 345, $[MH]^+$(23%); 329, $[M-CH_3]^+$ (60%); 230, $[Pd(tmiy)]^+$(100%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 5.27 (s, 1H, CCH), 3.85 (s, 6H, NCH_3), 2.08 (s, 6H, $C{=}CCH_3$), 1.98 [s, 3H, CCH_3 (*trans* to ylidene)], 1.86 [s, 3H, CCH_3 (*cis* to ylidene)], 0.25 (s, 3H, $PdCH_3$). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 187.2, 186.5 (OC), 168.5 (NCN), 124.9 ($C{=}C$), 99.4 ($OCCH$), 35.2 (NCH_3), 28.3, 28.2 (CCH_3), 9.2 ($C{=}CCH_3$), − 12.0 ($PdCH_3$).

2.4.7. [Pd(Me)(1,3-dimethylimidazol-2-ylidene)$_2$Cl] **7**

A solution of dmiy (10.5 mmol of dimethylimidazolium chloride) in 30 ml of THF was filtered into a suspension of [PdMeCl(cod)] (0.95g, 3.6 mmol) in 10 ml of THF. The solvent was removed in vacuo and the resulting solid taken up in 90 ml of DCM and filtered through Celite. The DCM was removed in vacuo. The solid was washed twice with DCM/THF (5 ml/10 ml) to

yield a white powder. Crystals suitable for X-ray diffraction were grown by vapour diffusion of ether into a DCM solution of the complex at −20°C. Yield: 80%. Anal. Calc. for **7**: C, 37.84; H, 5.48; N, 16.05%. Found: C, 37.78; H, 5.42; N, 16.02%. MS (LSIMS) m/z: 335, $[M-CH_3]^+$(18%); 313, $[M-Cl]^+$(100%); 298, $[M-CH_3Cl]^+$(51%); 217, $[PdMe(dmiy)]^+$(10%); 202, $[Pd(dmiy)]^+$(29%). ^{1}H-NMR (200 MHz, CD_2Cl_2): δ 6.88 (s, 4H, NC*H*), 4.00 (s, 12H, NCH_3), −0.16 (s, 3H, PdCH_3). ^{13}C-NMR (50 MHz, CD_2Cl_2): δ 186.0 (N*C*N), 121.5 (*C*=*C*), 37.8 (N*C*H_3), −17.2 (Pd*C*H_3).

2.4.8. [Pd(Me)(1,3,4,5-tetramethylimi-dazol-2-ylidene)$_2$Cl] **8**

A solution of tmiy (0.22 g, 1.8 mmol) in 8 ml of THF was added to a suspension of [PdMeCl(cod)] (0.22 g, 0.83 mmol) in 3 ml of THF. The solvent was removed in vacuo, the solid taken up in DCM (20 ml, 0°C) and filtered through Celite. The DCM was then removed. The solid was washed twice with DCM/THF (0.7 ml/3 ml) followed by THF (2 × 2 ml) to yield a very pale yellow powder. Yield: 72%. Anal. Calc. for **8**: C, 44.45; H, 6.71; N, 13.82%. Found: C, 44.39; H, 6.74: N, 13.59%. MS (LSIMS) m/z: 389, $[M-CH_3]^+$(29%); 369, $[M-Cl]^+$(100%); 354, $[M-CH_3Cl]^+$(69%), 245, $[PdMe(tmiy)]^+$(21%); 230, $[Pd(tmiy)]^+$(47%). ^{1}H-NMR (200 MHz, CD_2Cl_2): δ 3.90 (s, 12H, NCH_3), 2.10 (s, 12H, CCH_3), −0.19 (s, 3H, PdCH_3). ^{13}C-NMR (50 MHz, CD_2Cl_2): δ 180.4 (N*C*N), 121.9 (*C*=*C*), 32.6 (N*C*H_3), 8.8 (C*C*H_3), −19.2 (Pd*C*H_3).

2.4.9. [Pd(tmiy)$_2$(4-acetophenonyl)Br] **9**

A solution of tmiy (53 mg, 0.43 mmol) in 10 ml of toluene was added to $Pd(dba)_2$ (107 mg, 0.186 mmol) dissolved in 20 ml of toluene. After 2 h 4-bromoacetophenone (42.2 mg, 0.212 mmol) in 3 ml of THF was added and the solution refluxed for 40 min. After cooling the solution was filtered through Celite, the solvent removed in vacuo until ca. 15 ml remained and layered with 15 ml of hexane. After sitting at −20°C overnight the precipitate was triturated with hexane and dried in vacuo to yield a light yellow to orange solid. The complex was contaminated with unreacted $Pd(dba)_2$ which could not be completely removed and consequently microanalyses were unsatisfactory. However the complex was characterised spectroscopically. MS (LSIMS) m/z: 555, $[MH]^+$(1%); 473, $[M-Br]^+$ (7%); 243, $[C_{15}H_{19}N_2O]^+$ (tmiy + acetophenonyl) (100%); 125, $[C_7H_{13}N_2]^+$ (tmiyH] (76%). ^{1}H-NMR (200 MHz, DMSO-d$_6$): δ 7.41 (d, $J=8$ Hz, 2H, arom*H*), 7.32 (d, $J=8$ Hz, 2H, arom*H*), 3.87 (s, 12H, NCH_3), 2.37 (s, 3H, COCH_3), 2.04 (s, 12H, CCH_3). ^{13}C-NMR (50 MHz, DMSO-d$_6$): δ 197.9 (*C*=O), 177.8 (N*C*N), 137.0, 129.3, 129.0, 125.4 (arom*C*), 124.4 (*C*=*C*), 34.7 (N*C*H_3), 25.4 (CO*C*H_3), 8.7 (C*C*H_3).

2.5. Decomposition reaction of **4**

Approximately 50 mg of **4** was dissolved in DCM (20 ml) and decomposed with gentle heating. The solution was then filtered through Celite to remove Pd(0) and the DCM was removed in vacuo. The resulting solid was recrystallised twice from DCM/ether and dried in vacuo with gentle heating to afford a pale grey powder, 1,2,3-trimethylimidazolium tetrafluoroborate. Anal. Calc. for $C_6H_{11}N_2BF_4 \cdot 0.1CH_2Cl_2$ (DCM indicated by ^{1}H-NMR): C, 35.49; H, 5.47; N, 13.57%. Found: C, 35.63; H, 5.55; N, 13.44%. MS (LSIMS) m/z: 111.1 $[M]^+$. ^{1}H-NMR (DMSO-d$_6$, 200 MHz): δ 7.58 (s, 2H, *H*CC*H*), 3.76 (s, 6H, NCH_3), 2.56 (s, 3H, CCH_3). ^{13}C-NMR (50 MHz, DMSO-d$_6$): δ 145.0 (N*C*N), 122.2 (H*CC*H), 34.9 (N*C*H_3), 9.3 (C*C*H_3).

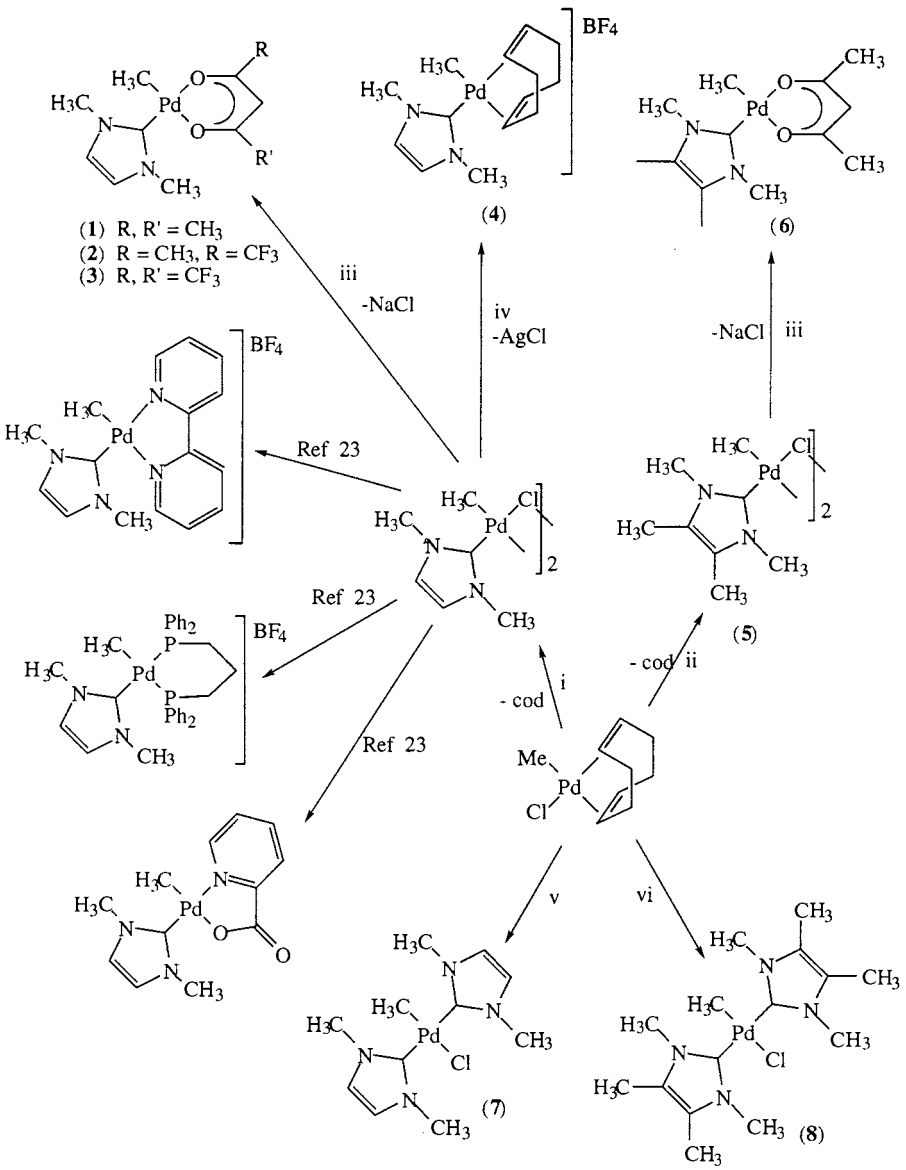
2.6. Catalytic Heck coupling of n-butyl acrylate and 4-bromoacetophenone

In a typical run, a 100 ml two-necked flask fitted with an air cooled condenser and a septum was charged with 4-bromoacetophenone (9.96 g, 50 mmol) and anhydrous sodium acetate (4.58 g, 56 mmol) and degassed by successive vacuum-nitrogen cycles. *N*,*N*-Dimethylacetamide (50 ml), *n*-butyl acrylate (10 ml, 55 mmol) and nonane (GC internal standard, 900 ml) were then injected and the mixture heated to 120°C by means of an oil bath. A solution of the catalyst dissolved in *N*,*N*-dimethylacetamide was then injected. Samples of the solution (500 μl) were taken at regular intervals, washed with 5% HCl (5.00 ml) and extracted with 2.50 ml of CH_2Cl_2. The CH_2Cl_2 extracts were analysed by gas chromatography using the following temperature program: 35°C for 20 min followed by a ramp of 10°C min^{-1} up to 220°C. When samples could not be analysed immediately they were stored at −20°C in sealed sample vials until GC could be done. The peak at $R_t = 52$ min that emerges as the reaction proceeds was positively identified by GC–MS and ^{1}H-NMR to be the expected product, *n*-butyl-(*E*)-4-formylcinnamate.

3. Results and discussion

3.1. Preparation and characterisation of methylpalladium carbene complexes

The *N*-heterocyclic carbene ligands, 1,3-dimethylimidazol-2-ylidene (dmiy) and 1,3,4,5-tetramethylimidazol-2-ylidene (tmiy) were synthesised and used in the synthesis of new hydrocarbylpalladium complexes. The ligand dmiy was prepared by the method of Arduengo et al. ([9]b), by deprotonation of the imidazolium chloride precursor with sodium hydride in the presence of



Scheme 1. Reagents and conditions: (i) dmiy, THF, 0°C; (ii) tmiy, THF, 0°C; (iii) Na(O ^ O), DCM, −20→ −10°C, 30 h; (iv) cod, $AgBF_4$, DCM, −20°C, 1 h; (v) dmiy, THF, 0°C and (vi) tmiy, THF, 0°C.

catalytic amounts of potassium *t*-butoxide. The free carbene was not isolated, but was used immediately. The approach taken for preparation of tmiy was that of Kuhn and Kratz [15], which involves the condensation of 3-hydroxy-2-butanone and dimethylthiourea to give the thione, which is then reduced with potassium to give the free carbene. This carbene could be stored under nitrogen without decomposition.

The general route used for the synthesis of carbene complexes (Scheme 1) involved treatment of PdMeCl(cod) with one equivalent of free carbene to give a methylpalladium carbene dimer, which could then be used to prepare a large range of neutral and cationic complexes by reaction with Na(chelate) or $AgBF_4$/chelate respectively [22]. Treatment of PdMeCl(cod) with two equivalents of carbene affords the monomeric bis(carbene) complexes. Complexes were obtained in high yields.

Complexes **1**–**5**, which contain only one carbene ligand, are air sensitive and thermally unstable to varying degrees. Substituents on the acac ligand in complexes **1**–**3** have a pronounced effect on stability, and the complexes become less stable as the number of CF_3 groups is increased. Complex **1** is stable for several days at r.t. under N_2, and for one day in solution, while **2** undergoes decomposition after several hours in solution. A solution of complex **3** deposits Pd(0) in <1 h at r.t. The complexes can be stored in the solid state under N_2 for long periods at −20°C.

The cationic complex **4**, which contains the weakly bonding cod ligand, is extremely unstable. The solid complex darkens in <1 h at r.t. and more slowly at -20°C. In solution decomposition is immediate at r.t. and synthesis requires rapid work up at -20°C. In DMSO-d_6 solution, in which no Pd precipitation is observed after several hours, the cod ligand is displaced by DMSO. ^{1}H-NMR shows the presence of free cod only. The complex, $[PdMe(dmiy)(DMSO)_2]^+$ is considerably more stable than its cod counterpart. The chemistry of this interesting new complex is now being investigated in detail. Placing weakly electron donating methyl groups in the 4 and 5 positions of the imidazol ring has a small stabilising influence on the complexes. A much greater increase in complex stability occurs when a second carbene ligand is introduced. Both **7** and **8** are quite stable at r.t., and a solution of **8** shows no signs of decomposition even when exposed to air.

Full characterisation of complexes **1**–**8** was accomplished by MS, microanalysis, ^{1}H-, ^{13}C- and ^{19}F-NMR where appropriate. Selected NMR spectral data are shown in Table 1. In the free carbene ^{13}C peaks appear at δ 215 (dmiy) and 214 ppm (tmiy) ([9]b). The very low field chemical shift of the free carbene carbons is ascribed to the large chemical shielding anisotropy of singlet carbenes [30], which effect is reduced by coordination to the palladium centre. Interestingly, the chemical shifts of the carbene signals remain nearly constant for the monocarbene complexes, regardless of the other ligands bound to the complex. Only when a second carbene ligand is introduced (in a *trans* arrangement) is there a significant change in the chemical shift of this carbon.

Clear trends in the positions of the Pd–methyl signals are observed for these complexes. In complexes **1**–**3**, the ^{1}H- and ^{13}C-NMR signals shift to lower fields as the O–O ligand changes from acac to tfac to hfac. This can be related to changes in the donor ability of the ligands, caused by the electron withdrawing effects of the fluorine substituents. A stronger donor ligand increases the electron density on the Pd and a more shielding environment results. This effect is even more pronounced when a second carbene ligand is coordinated to the metal centre. For biscarbene complexes **7** and **8** a significant upfield shift is observed for the Pd–methyl signals (ca. 0.4 ppm in ^{1}H-NMR and 5–7 ppm in ^{13}C-NMR, relative to complex **6**), consistent with the strong donor properties of heterocyclic carbenes. The downfield chemical shift of the Pd–methyl resonance in the cationic complex, **4**, is also consistent with this premise.

The asymmetry of the tfac ligand means **2** can exist as two isomers, described as *cis* and *trans* on the basis of the position of the carbene ligand with respect to the CF_3 group. NMR indicates that both isomers are present in solution. On the basis of NOE measurements on complexes **1** and **6**, it was deduced that the *cis* isomer is the more abundant. The exact ratio of the isomers is effected by the solvent. In $CDCl_3$ (^{1}H-NMR) the proportion of the *cis* isomer is ca. 60% from peak integrals, but in toluene-d_8 it is increased to ca. 70%.

To establish the relative lability of the acac ligand in complexes **1** and **2**, variable temperature NMR studies were undertaken. Complex **1** shows two acac methyl resonances which remain fixed and sharp even when the temperature of a toluene-d_8 solution was raised to 373 K. The tfac ligand in complex **2** however, is somewhat more labile, and the isomer peaks start to converge at around 353 K, coalescing at 393 K. The lability of the acac ligand increases as a result of the weaker bonding caused by the electron withdrawing CF_3 group. The solvent also has a large effect on ligand dissociation. In the coordinating solvent, DMSO-d_6, the acac methyl peaks of **1** appear as two broad peaks which almost coalesce at r.t. As expected, the weak cod ligand in complex **4** also appears to be quite labile. At 233 K in the ^{1}H-NMR spectrum the broad peaks of the olefinic protons are separated by 0.18 ppm, but converge as the temperature is raised. Above 303 K decomposition is so rapid that further NMR measurements are not possible, and the peaks give way to a singlet due to free cod.

The ^{1}H-NMR of the dimer **5**, consists of three broad peaks at ambient temperature, but on cooling each of these peaks splits into two singlets. This has been observed previously for the dmiy and phosphine equivalents, and is due to *cis–trans* isomerisation which is very fast at r.t. [22,31].

Table 1
Selected NMR data for complexes (**1**)–(**8**)

Complex	^{1}H $PdCH_3$	^{13}C $PdCH_3$	^{13}C C(carbene)
(1)[a]	0.26	−11.9	172.0
(2)[a]	0.35, 0.39	−11.3, −11.7	170.0, 169.3
(3)[a]	0.51	−10.0	169.4
(4)[a]	0.62	1.8	168.4
(5)[a]	0.26	−9.5	168.9
(6)[b]	0.25	−12.0	168.5
(7)[b]	−0.16	−17.2	186.0
(8)[b]	−0.19	−19.2	180.4
dmiy[c]	—	—	215
tmiy[c]	—	—	214

[a] NMR in CD_2Cl_2. [b] In $CDCl_3$. [c] Free ligands, in THF-d_8.

3.2. Crystal structures of the complexes $[Pd(Me)(tmiy)Cl]_2$ and $[Pd(Me)(dmiy)_2Cl]$

Crystal structure determinations were undertaken for complexes **5** and **7**. Selected bond distances and angles are provided in Table 2 together with comparative data for [Pd(Me)(pyca)(dmiy)] [22]. Projections oblique (complex **5**) and normal (complex **7**) to the coordination planes are shown in Figs. 1 and 2.

Table 2
Coordination geometry (distance in Å, angles in °) for the complexes [Pd(Me)(dmiy)(μ-Cl)]2 (**5**), [Pd(Me)(Cl)(dmiy)2] (**7**) and [Pd(Me)(pyca)(dmiy)] [22] for comparison

(5)		**(7)**		[Pd(Me)(pyca)(dmiy)]	
Pd–C(0)	2.011(3)	Pd–C(0)	2.117(8)	Pd–C(methyl)	2.019(4)
Pd–C(1)	1.973(2)	Pd–C(11)	1.999(7)	Pd–C(carbene)	1.971(2)
Pd–Cl	2.3996(9)	Pd–C(21)	2.009(8)	Pd–N(pyca)	2.092(2)
Pd–Cl′	2.4827(9)	Pd–Cl	2.455(2)	Pd–O(pyca)	2.140(2)
C(1)–N(2)	1.349(3)	C(n1)–N(n2)	1.36(1), 1.36(1)	C–N(carbene)	1.347(3)
C(1)–N(5)	1.347(3)	C(n1)–N(n5)	1.369(9), 1.345(9)	C–N(carbene)	1.348(3)
Cl–Pd–C(0)	90.2(1)	Cl–Pd–C(0)	178.8(2)	C(Me)–Pd–N(pyca)	97.4(1)
Cl–Pd–C(1)	175.80(8)	Cl–Pd–C(11)	91.3(2)	C(Me)–Pd–O(pyca)	174.5(1)
Cl–Pd–Cl′	86.68(2)	Cl–Pd–C(21)	91.1(2)	C(Me)–Pd–C(carb)	88.3(1)
C(0)–Pd–C(1)	86.4(1)	C(0)–Pd–C(11)	89.4(3)	N(pyca)–Pd–O(pyca)	78.67(8)
C(0)–Pd–Cl′	174.4(1)	C(0)–Pd–C(21)	88.2(3)	N(pyca)–Pd–C(carb)	174.21(8)
Cl–Pd–Cl′	96.84(7)	C(11)–Pd–C(21)	177.2(3)	O(pyca)–Pd–C(carb)	95.61(8)
Planes					
I: C(1), N(2), C(3), C(4), N(5)		I: C(n1),N(n2),C(n3),C(n4),N(n5)			
II: Pd, Cl, Pd′, Cl′		II: C(0), C(11), Cl, C(21)			
Interplanar angle I/II (°)					
65.07(8)		70.4(3), 73.1(3)			

[a] pyca, pyridine carboxylate.

In the solid state, complex **5** has a *trans* arrangement of the carbene ligands and a distorted square planar core geometry is displayed (Fig. 1). The imidazol-2-ylidene ring is planar and twisted by 65.07(8)° relative to the $PdCl_2Pd$ plane. The ability to relieve steric congestion by rotation from the coordination plane is a characteristic feature of carbene complexes [5]. The Pd–C(carbene) bond length in **5** [1.973(2) Å] is slightly shorter than in typical Pd carbene complexes [1.990(3)–2.137(5) Å] [32,6]. This difference is only small and may simply reflect the low *trans* influence of the Cl^- ligand. There is a significant difference (Δr ca. 0.08 Å) between the two Pd–Cl bond lengths in **5**. Fig. 1 suggests that steric interactions between the $N–CH_3$ group and the Pd–Cl′ bond are probably not important. Therefore, in the absence of steric congestion, the difference may be attributed to the differing *trans* influences of the methyl and carbene ligands, with the methyl group having a higher *trans* influence.

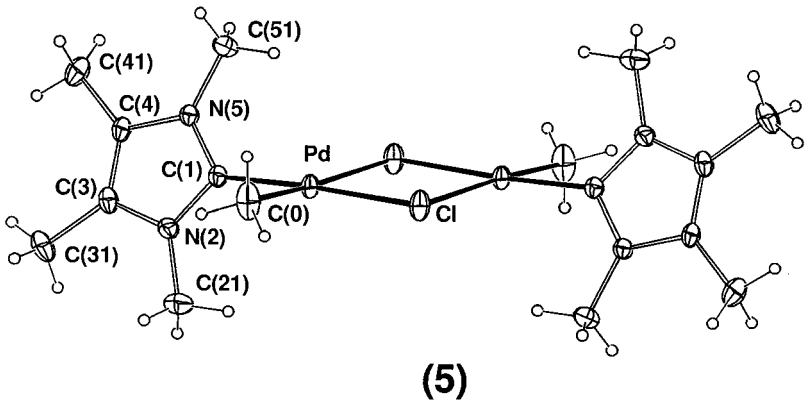
A *trans* arrangement of carbene ligands in **7** is verified by the crystal structure (Fig. 2, Table 2). A slightly distorted square planar geometry is revealed and the highly planar carbene ligands are rotated by 70.4(3) and 73.1(3)° relative to the coordination plane; the dihedral angle between the two substantially parallel ligand planes is 3.5(3)°. The Pd–C(carbene) bond lengths are the same within experimental error [1.999(8) and 2.009(8) Å] and are rather longer than in **5**.

The $Pd–CH_3$ bond in **7** [2.117(8) Å] is quite long considering the low *trans* influence usually attributed to Cl^-. This may be due to the high electron density induced on palladium by two carbene ligands, reducing the σ-donor ability of the methyl group. The Pd–C(carbene) bond lengths in **7** lie at the low end of the range for normal Pd–C(sp^2, sp^3) bonds (1.981(no estimated S.D. given)–2.130(8) Å) [33,34] indicating that, in accord with previous studies [6,19], metal–ligand π backbonding is probably not significant for heterocyclic carbene ligands. The C(carbene)–N bond lengths in the complexes are in the range 1.345(9)–1.369(9) Å. This is significantly shorter than the other C–N bond lengths present in the complexes which, for instance, in **5** range from 1.383(3)–1.461(4) Å, and is possibly indicative of greater partial double bond character in these C(carbene)–N bonds due to partial electron donation by nitrogen to the carbene carbon.

3.3. Fundamental reaction chemistry

3.3.1. Decomposition of complexes *4* and *7*

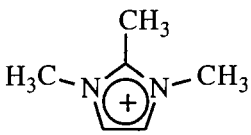
It is interesting to note that the cationic complex **4** contains three modes of Pd–carbon bonding; σ-methyl–, π-alkene– and a carbene–Pd bond. Complexes containing both a π-olefin ligand and a carbene have been considered as intermediates in olefin metathesis [35] and complexes with an olefin coordinated *cis* to an alkyl group may be considered to be intermediates in olefin migratory insertion reactions. Therefore, complex **4** can be envisaged as reacting/decomposing via two possible pathways; via metathesis of the carbene and alkene or via migratory insertion. The decomposition of **4** was monitored by ^{1}H-NMR in DMSO-d_6 and in $CDCl_3$. In both solvents the $Pd–CH_3$ peak disappears and a new peak at 2.56 ppm (DMSO-d_6), 2.64 ($CDCl_3$) emerges, and in $CDCl_3$ peaks due to coordinated cod are replaced by peaks for free cod. The methyl peak and the carbene



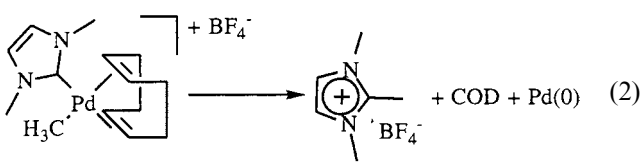
(5)

Fig. 1. Projection of **5** (centrosymmetric), oblique to the Pd(μ-Cl)$_2$Pd plane. Thermal ellipsoids (20%) are shown for the non-H atoms, H atoms having arbitrary radii of 0.1 Å.

HC=C*H* and N–C*H*$_3$ peaks, are consistent with the formation of the 1,2,3-trimethylimidazolium ion:

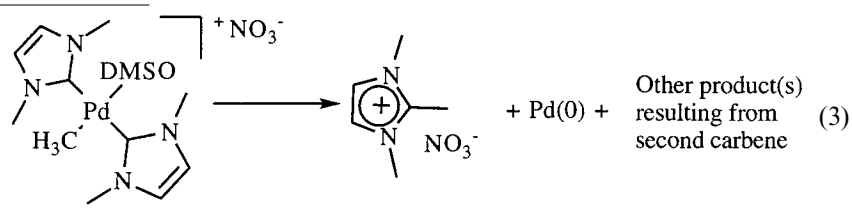


In $CDCl_3$, the product gradually crystallises out (long needle-like crystals form as the decomposition proceeds). Mass spectroscopic and elemental analyses of the crystalline product verify the formation of the tetrafluoroborate salt of the 1,2,3-trimethylimidazolium ion. The decomposition therefore, is not one of the expected routes but instead follows a pathway comprising elimination of methylimidazolium ion to yield metallic Pd and free cod (Reaction 2). The mode of elimination is unclear. Migratory insertion of the methyl group into the metal carbene bond is not likely. Migratory insertion of the carbene ligand into a carbon–metal bond is noted for Fischer and Schrock type carbene but has not been cited for these heterocyclic carbenes. This is an important and interesting aspect of the reaction and further investigation is necessary to elucidate the detail.



(2)

The decomposition of complex **7** was also studied. When **7** is heated at 120°C in DMSO-d_6 it slowly decomposes to Pd(0) and a complex mix of unidentified organic products. However, when the complex is first treated with $AgNO_3$ only slight shifts in the signals are observed. These changes are due to Cl^- abstraction and subsequent formation of the cationic complex [PdMe(dmiy)$_2$(DMSO-d_6)]NO_3. When the cationic complex is heated to 60°C it decomposes rapidly to yield the 1,2,3-trimethylimidazolium ion and Pd(0). Four other peaks also appear which are due to the second carbene ligand, the exact identity of which is still unclear (Reaction 3).



(3)

Elimination of methyl–carbene groups appears to be the favoured decomposition route for the cationic methylpalladium carbene complexes. Decomposition of the cationic complexes is also considerably more facile compared to decomposition from neutral complexes, as judged by the much lower temperature and greater rate with which it occurs. This is an important result, as it shows that under appropriate conditions there exists a reasonably facile mode of Pd–C(carbene) bond cleavage for heterocyclic carbene complexes.

3.3.2. Intermediates in the Heck reaction catalysed by Pd–carbene complexes

With Herrmann's application of Pd–carbene complexes in the Heck reaction, it has generally been assumed that the complexes catalyse the reaction in the same way as traditional phosphine containing complexes. To gain further information on this point we have investigated separate steps in the catalytic cycle of the Heck reaction: (i) in situ synthesis of a dicarbene–Pd(0) complex, (ii) oxidative addition to the Pd(0)–carbene complex and (iii) olefin insertion into the Pd-C bond of the hydrocarbylpalladium–carbene complex.

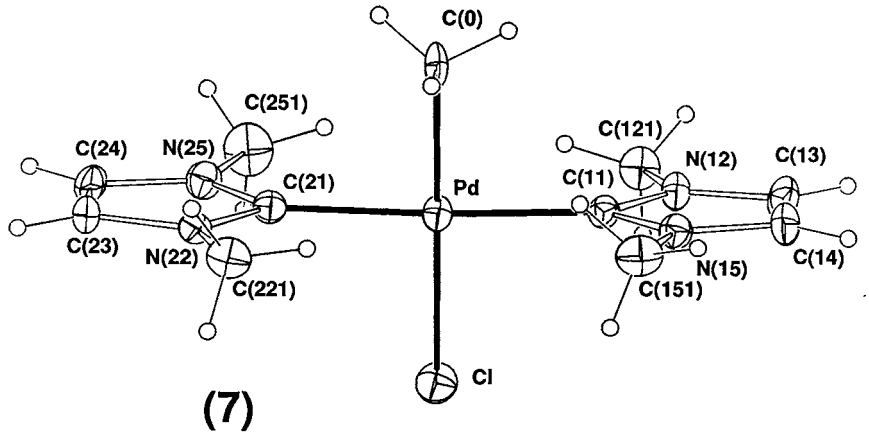


Fig. 2. Projection of **7**, normal to the coordination plane. Thermal ellipsoids (20%) are shown for the non-H atoms, H atoms having arbitrary radii of 0.1 Å.

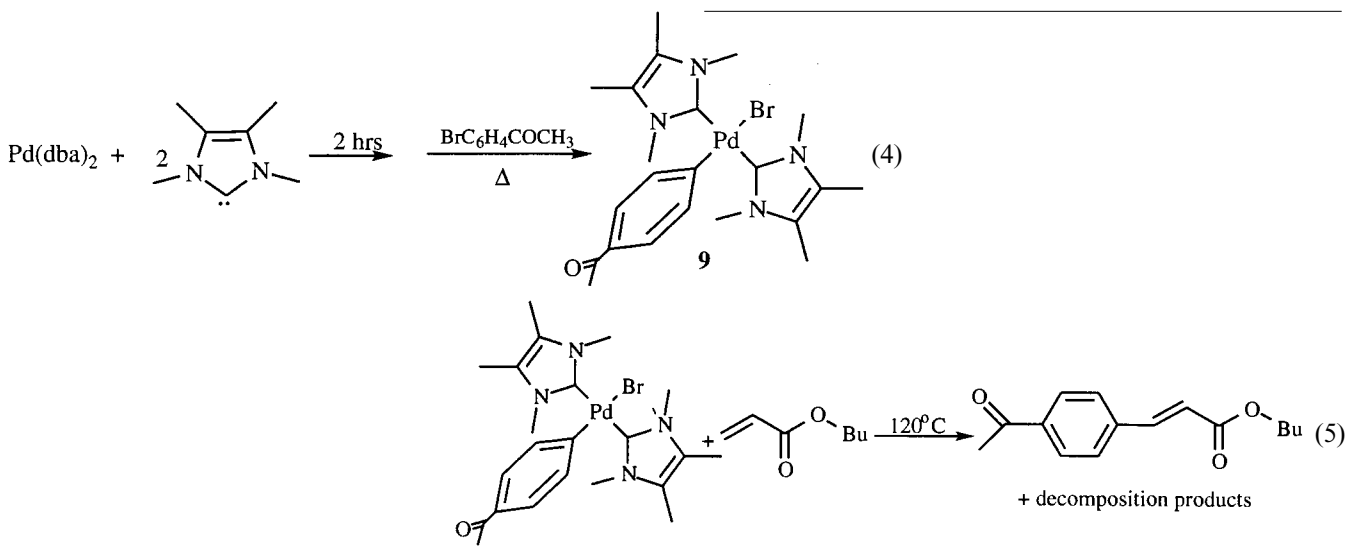
The study was complicated somewhat by the observation that tmiy rapidly reacts with free dba in solution to give a dark red extremely fine solid. The addition of carbenes across activated double bonds is an established reaction in organic chemistry [18].

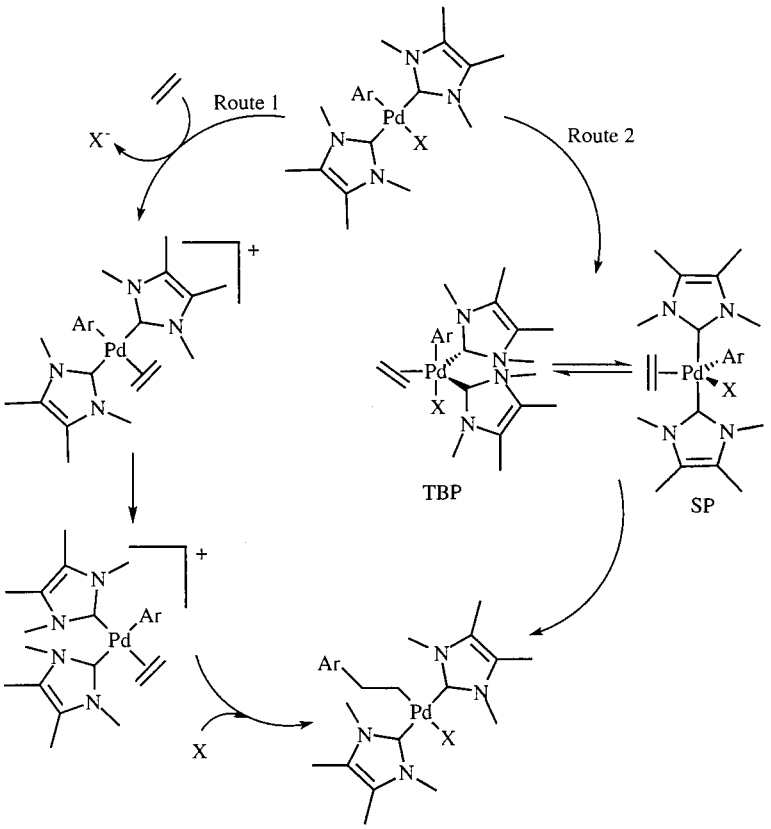
3.3.3. Oxidative addition to Pd(0) carbene complexes

It is thought that the Heck reaction proceeds via oxidative addition of a hydrocarbyl halide to the active species, a Pd(0) complex. This is followed by coordination and migratory insertion of a substituted olefin. The aryl halide, 4-bromoacetophenone, was used for catalytic testing in the Heck reaction and was therefore studied in the oxidative addition reaction with palladium carbenes. Treatment of $Pd(dba)_2$ with two equivalents of tmiy followed by refluxing with 4-bromoacetophenone yielded complex **9** as a light yellow–orange product (Reaction 4) which was characterised spectroscopically.

The NMR spectra of complex **9** indicate a *trans* arrangement of the carbene ligands, as the imidazol methyl groups give rise to only one singlet resonance in both the ^{1}H- [3.87 (NCH_3), 2.04 (CCH_3) ppm] and ^{13}C-NMR [34.7 (NCH_3), 8.9 (CCH_3) ppm]. The simple A_2B_2 pattern of the aromatic protons ($J = 8$ Hz) also indicates a *trans* arrangement. The aromatic protons are shifted ca. 0.5 ppm upfield compared to free 4-bromoacetophenone, reflecting the shift of electron density onto the aromatic group when the halogen is replaced with Pd. Complex **9** slowly decomposes in solution.

Insertion of butylacrylate (H_2C=CHCOOBu) into the Pd–C(aryl) bond of **9** was studied in DMSO-d_6 solution. On heating a solution of **9** and butylacrylate at 120°C for 1 h, complete decomposition occurred and Pd(0) was deposited. The ^{1}H-NMR spectrum of the resulting solution was too complex for ready interpretation. Analysis of the solution by GC however, showed unambiguously that the insertion/β-hydride elimination product (*n*-butyl-(*E*)-4-formylcinnamate) had formed (Reaction 5) in high yield. Other organic products from the carbene residues were also present.



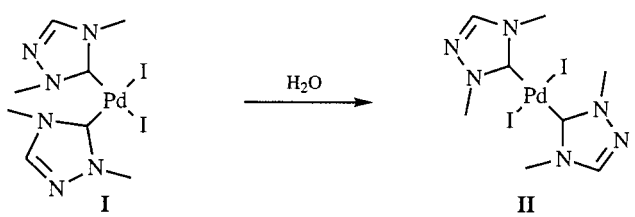


Scheme 2. Possible migratory insertion pathways; four coordinate (dissociative) mechanism (Route 1); five coordinate (associative) mechanism (Route 2).

3.4. Mechanistic aspects

The above results show that a Pd(0)–Pd(II) oxidation is a probable step in the catalytic cycle of the Heck reaction with carbene based complexes. It is also evident that the generally proposed migratory insertion step for the reaction between the olefin and the coordinated aryl group is a feasible pathway. However, the exact nature of the migratory insertion step is unclear. Insertion from the generally proposed four coordinate intermediate would require the dissociation of a ligand, most likely the Br rather than one of the strongly bonding heterocyclic carbenes. Furthermore, the high reactivity of free carbenes with activated olefins (of the type used for Heck coupling), as demonstrated previously, indicates that if carbene dissociation were to occur it would react immediately, leading to rapid catalyst deactivation. A possible dissociative route is shown in Route 1 of Scheme 2.

That the reaction occurs via a dissociative pathway is far from certain. A *cis* arrangement of the alkyl group and the olefin is required for migratory insertion to occur, but dissociation of the bromide ligand followed by coordination of the alkene would lead to a *trans* arrangement (Reaction 5). Molecular rearrangement must therefore occur before insertion can proceed. Herrmann et al. [36] have reported isomerisation of the *cis* triazolylidene complex **I** to give the *trans* isomer **II** (Reaction 6). Herrmann notes that isomerisation proceeds without ligand dissociation, but gives no indication of how the process may occur. More troubling is that dissociation of a halide ligand would give a cationic species. We have shown that cationic carbene complexes are considerably more susceptible to decomposition, and at relatively low temperatures, than neutral complexes. In this context it is particularly noteworthy that **4** underwent decomposition by methylcarbene elimination rather than olefin insertion into the $Pd–CH_3$ bond.



I **II** (6)

The alternative mechanism of insertion from a five coordinate intermediate does not require dissociation of the halide ligand, thus a cationic intermediate is

Table 3
Heck coupling of 4-bromoacetophenone with butylacrylate

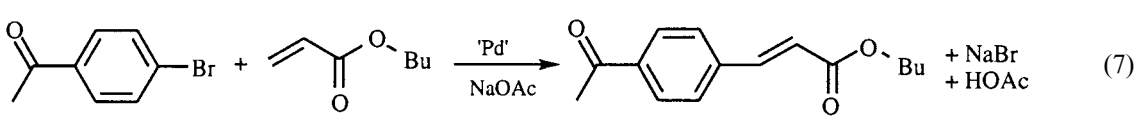
Experiment	Complex	Mol%	Time	Conversion	TOF	TON
1	**2**	0.60	<20 min	100	[a]	[b]
2	**1**	0.24	25 min	100	2500	[b]
3	**1**	4.0×10^{-4}	7.5 h	29	24 000	74 500
4	**3**	4.6×10^{-4}	11.7 h	50	10 400	109 000
5	**7**	4.0×10^{-4}	8.5 h	40	24 000	100 500

[a] Reaction proceeded too rapidly to obtain TOF.
[b] Reagents consumed in minutes so TON is not meaningful.

avoided. Coordination of the alkene would yield a square pyrimidal (SP) complex in the first instance, in which the required *cis* arrangement of the alkene and hydrocarbyl groups is present. Rearrangement to give a trigonal bypyramidal (TBP) intermediate, from which insertion should occur more readily [37], may also occur via a Berry pseudorotation pathway (Route 2, Scheme 2).

3.5. Catalysis: the Heck reaction

The coupling of 4-bromoacetophenone and *n*-butylacrylate to form *n*-butyl-(*E*)-4-formylcinnamate (Reaction 7) was investigated with complexes **1**–**3** and **8**. Herrmann et al. have demonstrated the high efficiency of palladium carbene complexes in this reaction [5] and Herrmann's catalysts did not contain a hydrocarbyl group. In this investigation we wished to examine the effect that the methyl group has on catalyst performance and to study the effect of varying the number of carbene ligands. The results of catalytic testing are given in Table 3.



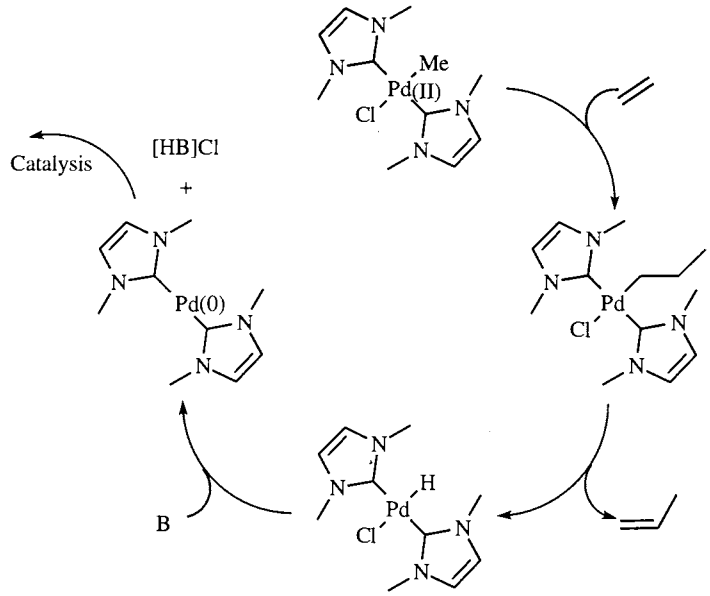
(7)

All complexes tested were excellent catalysts for Heck coupling. Both total turnover numbers (TON's) and initial turnover frequencies (TOF's) are significantly higher than values obtained for traditional phosphine based catalysts. In terms of initial rates of conversion, the new complexes have activities comparable to the particularly active palladacycles of Herrmann et al. ([1]b). In only one case (experiment 1, Table 3) was the formation of palladium metal observed, and this occurred sometime after the reaction had gone to completion. However, in experiments 3, 4 and 5 (Table 3) it is doubtful whether Pd(0) would be observed in the event of decomposition.

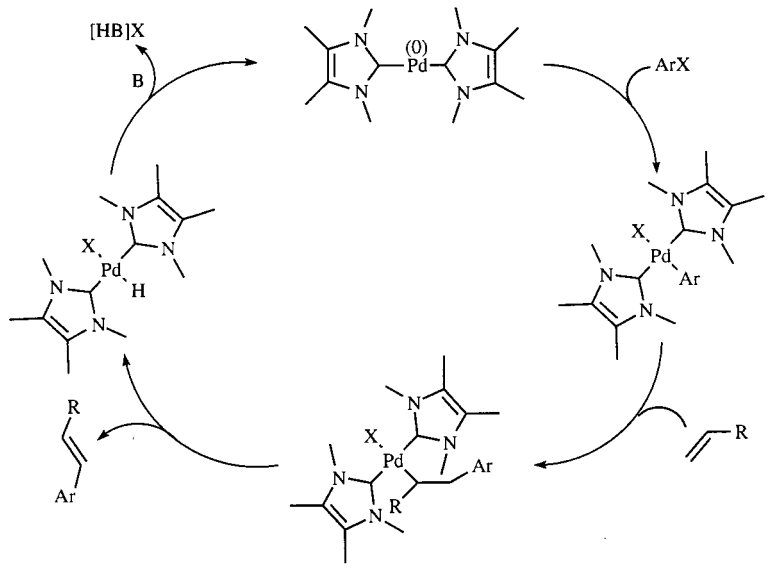
In the monocarbene complexes, the active species is presumably a Pd(0) complex such as Pd(0)(carbene)L, where L is a ligand such as the solvent (DMA) that takes the place of a second carbene ligand. L would be expected to be weakly coordinated. In agreement with this proposition a comparison of experiments 3 and 5 (Table 3) demonstrates the increased stability generated by the presence of a second carbene ligand. The initial activities are identical for the two catalysts, however the dicarbene catalyst continues to operate for a longer period giving significantly higher overall TON's.

The presence of the methyl group in these complexes gives rise to highly active catalysts with little or no induction period, as demonstrated by the very high initial TOF's, and hence the need for a reducing agent to generate Pd(0) is removed. This is in contrast to the results of Herrmann [5] with $Pd(dmiy)_2I_2$, which in the absence of an added reducing agent showed a very long induction period. Only with the addition of a reducing agent does the activity increase significantly. Thus, it seems that replacing a halide ligand with a methyl group provides a facile pathway for formation of the Pd(0) active species. A proposed pathway for catalyst generation from the methylpalladium carbene precurser is provided in Scheme 3. The Pd(0) active species may be formed by olefin insertion into the Pd–CH_3 bond, followed by β-hydride elimination and reductive elimination in the presence of the base (NaOAc).

An overall mechanism for the Heck reaction catalysed by these complexes may be proposed (Scheme 4). The first step in the catalytic cycle is thought to consist of oxidative addition of the aryl halide to a zero valent active species (formed in situ) yielding a Pd(II)–aryl complex. Coordination and insertion of the olefin into the Pd–C bond could then occur, followed by β-hydride elimination to generate a short lived Pd(II)–hydride complex. Reductive elimination in the presence of a base could then regenerate the active Pd(0) species allowing the cycle to proceed again. This mechanism is essentially the same as the Pd–phosphine catalysed Heck reaction.



Scheme 3. Role of the methyl group in generation of the Pd(0) active species.



Scheme 4. Proposed mechanism for Heck coupling with dicarbene–Pd complexes.

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