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Cationic and neutral palladium(II) methyl complexes of di-N-heterocyclic carbenes †

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Cationic and neutral methyl complexes of Pd(II) incorporating di-N-heterocyclic carbenes, $^{tBu}CC^{meth}$ and $^{tBu}CC^{eth}$ (where $^{tBu}CC^{meth}$ = 1,1′-methylene-3,3′-di-*tert*-butyldiimidazol-2,2′-diylidene and $^{tBu}CC^{eth}$ = 1,2-ethylene-3,3′-di-*tert*-butyldiimidazol-2,2′-diylidene), have been prepared. The complexes [Pd($^{tBu}CC^{meth}$)Me_2] (**1**) and [Pd($^{tBu}CC^{eth}$)Me_2] (**2**) have been isolated and **2** has been characterised by single crystal X-ray diffraction. When **1** and **2** are dissolved in deuterated methanol in the presence of pyridine or bipyridine the four coordinate cations [Pd($^{tBu}CC^{meth}$)Me(py)]$^+$ (**3**), [Pd($^{tBu}CC^{eth}$)Me(py)]$^+$ (**4**), [Pd(^{tBu}C(D)-η-C^{meth})Me(η^2-bipy)]$^+$ (**5**), and [Pd(^{tBu}C(D)-η-C^{eth})Me(η^2-bipy)]$^+$ (**6**), are observed spectroscopically.

Introduction

A relatively recent development of transition metal mediated catalysis is the application of N-heterocyclic carbenes (NHC) as ancillary ligands. Particularly, C–C coupling reactions have been intensively investigated[1–12] and to a lesser extent olefin metathesis,[13–17] hydrosilylation,[18–21] C–N coupling,[22–26] olefin/CO copolymerisation[27,28] and furan ring synthesis.[29] In general, it appears that catalytic reactions that employ transition metal complexes of tertiary phosphines may also be catalysed using complexes of NHC. In comparison to tertiary phosphine ancillary ligands, many of the catalytic reactions studied to date using transition metal complexes of NHC exhibit increased thermal stability and the need for excess NHC ligands is not required.[1,2,6,30,31] In addition further interest lies in the unusual structural motif rendered at the catalytically active metal atom by NHC and in particular chelating di-NHC or hybrid C–, N–, and O–NHC ligands.[1,9–12,21,28,32–36]

Transition metal alkyl complexes of NHC are rare[5,6,12,37] however a few examples of palladium methyl complexes such as *trans*-chlorobis(1,3-dimethylimidazol-2-ylidene)methylpalladium(II) have now been prepared and it has been shown that these complexes catalyse Heck coupling reactions with higher turn-over-numbers (TON's), primarily due to a short induction period.[5,6,12] The study of NHC transition metal alkyl complexes is of inherent interest because of their relevance to catalysis. We recently reported the preparation of nickel(II) dimethyl complexes of chelating di-NHC, which are the first examples of transition metal *cis*-dialkyl complexes incorporating NHC ligands.[37] However the thermal sensitivity of these *cis*-dimethyl complexes hampered reactivity studies.

Here we report the synthesis and some reactivity of palladium(II) dimethyl complexes of the chelating di-NHC ligands $^{tBu}CC^{meth}$ and $^{tBu}CC^{eth}$ (where $^{tBu}CC^{meth}$ = 1,1′-methylene-3,3′-di-*tert*-butyldiimidazol-2,2′-diylidene and $^{tBu}CC^{eth}$ = 1,2-ethylene-3,3′-di-*tert*-butyldiimidazol-2,2′-diylidene)[34] shown in Fig. 1.

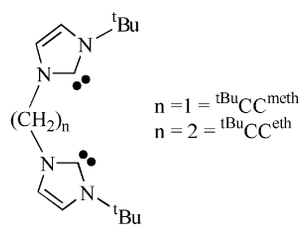


Fig. 1 Potentially chelating di-N-heterocyclic carbenes (di-NHC).

Results and discussion

In related chemistry and in common with other workers we did not have success in the preparation of *cis*-dihalide nickel(II) complexes of chelating di-NHC. These dihalide complexes were envisaged to serve as precursors to *cis*-dialkyl complexes however the target *cis*-dimethyl nickel(II) complexes were successfully prepared from [Ni(bipy)Me_2] and $^{tBu}CC^{meth}$ or $^{tBu}CC^{eth}$.[37] We therefore explored the analogous reaction between [Pd(bipy)Me_2] and the di-NHC compounds $^{tBu}CC^{meth}$ and $^{tBu}CC^{eth}$.

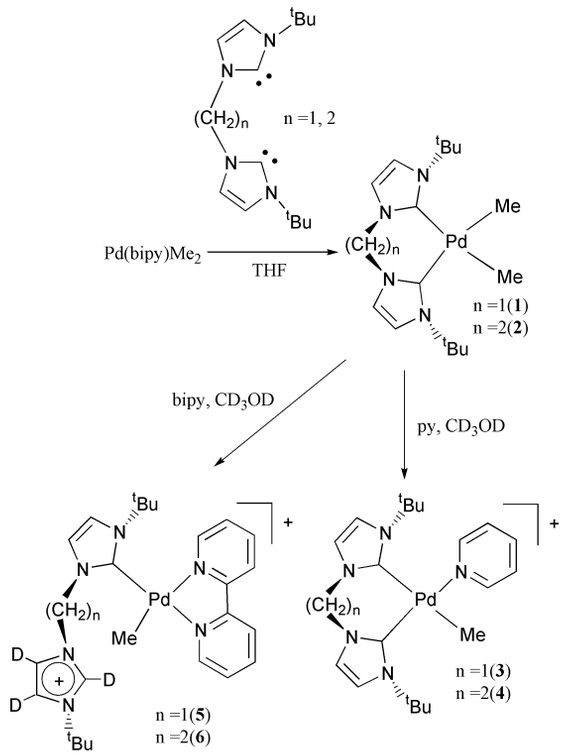
Reaction between [Pd(bipy)Me_2] and $^{tBu}CC^{meth}$ or $^{tBu}CC^{eth}$ at −78 °C gives the target compounds [Pd($^{tBu}CC^{meth}$)Me_2] (**1**) and [Pd($^{tBu}CC^{eth}$)Me_2] (**2**) as pale yellow and white microcrystalline solids respectively, as shown in Scheme 1.

In contrast to the nickel(II) analogues both compounds **1** and **2** are air stable at room temperature for days. In addition the ratio of volatile hydrocarbons on thermal decomposition of **1** and **2** favours C–C coupled products. In previous studies the nickel(II) analogues gave methane as the only detectable product by GCMS[37] whereas **1** and **2** both give an ethane : methane ratio of 4 : 1. Compounds **1** and **2** are soluble in toluene and common polar organic solvents but solutions in CH_2Cl_2 decompose within minutes. Crystallisation from Et_2O yields single crystals of **2** from which an X-ray diffraction study gave the molecular structure shown in Fig. 2. Selected bond lengths and angles are given in Table 1. The asymmetric unit contains one molecule of **2** and a molecule of diethyl ether.

The geometry at the palladium atom is essentially square planar with palladium–carbon bond lengths Pd–$C_{carbene}$ (2.070(3) and 2.089(3) Å) and Pd–C_{Me} (2.097(4) and 2.088(4) Å). In comparison, the two other related examples of

† Electronic supplementary information (ESI) available: supplementary crystal data for **2**, ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **1**–**6** and electrospray mass spectrometry of **3**–**6**. See http://www.rsc.org/suppdata/dt/b1/b110261n/

 DOI: 10.1039/b110261n



Scheme 1

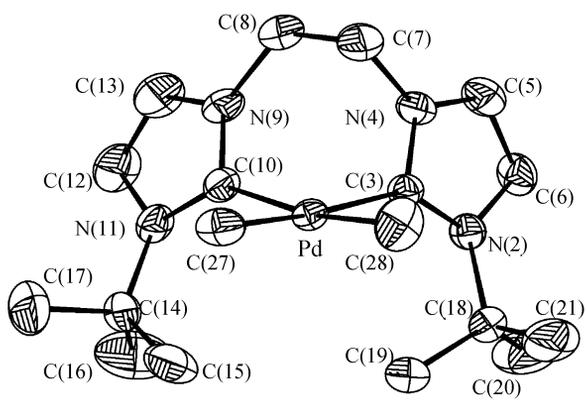


Fig. 2 Molecular structure of **2**. Hydrogen atoms have been omitted for clarity.

structurally characterised methyl palladium(II) complexes of bis-NHC *trans*-PdMeCl(timy)$_2$ (timy = 1,3,4,5-tetramethylimidazolin-2-ylidene)[12] (Pd–C_{Me} = 1.98(1) and Pd–C_{timy} = 2.033(3) Å) and *trans*-PdMeCl(dimy)$_2$ (dimy = 1,3-dimethylimidazolin-2-ylidene)[5] (Pd–C_{Me} = 2.117(8) and Pd–C_{dimy} = 1.999(7) and 2.009(8) Å) exhibit Pd–C bond lengths similar to **2**. The dicarbene bite angle C(3)–Pd–C(10) of 88.12(13)° is also comparable to those observed for the two other structurally characterised ethylene bridged dicarbene complexes [Ni(^{tBu}CC^{eth})Cl(PMe$_3$)][BPh$_4$] (88.4(4)°)[34] and [Ni(^{tBu}CC^{eth})Me$_2$] (88.9(2)°).[37]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** and **2** are consistent with C_s symmetry. The ^{1}H NMR spectrum of **1** shows two doublet resonances at δ 4.65 and 6.54 that are attributed to the diastereotopic methylene protons. The resonance at δ 4.65 is significantly upfield from that observed for the parent free carbene (δ 6.22) and is tentatively assigned to the *endo*-proton that is in closer spatial proximity to the metal atom. The signal of the palladium bound methyl protons of compound **1** is observed at δ 0.89 in comparison to 0.66 for compound **2**. Two resonances at δ 3.26 (*endo*) and 5.48 (*exo*) exhibit coupling indicative of an AA′XX′ spin system and are assigned

Table 1 Selected bond lengths (Å) and angles (°) for compound **2**

Pd–C(3)	2.070(3)
Pd–C(10)	2.089(3)
Pd–C(27)	2.097(4)
Pd–C(28)	2.088(4)
N(2)–C(3)	1.356(4)
C(3)–N(4)	1.350(4)
N(9)–C(10)	1.361(4)
C(10)–N(11)	1.364(4)
N(4)–C(7)	1.459(5)
C(7)–C(8)	1.394(8)
C(8)–N(9)	1.475(6)
C(5)–C(6)	1.343(6)
C(12)–C(13)	1.320(7)
N(2)–C(6)	1.395(4)
N(4)–C(5)	1.376(5)
N(9)–C(13)	1.364(5)
N(11)–C(12)	1.396(5)
C(3)–Pd–C(10)	88.12(13)
C(3)–Pd–C(27)	172.52(15)
C(3)–Pd–C(28)	91.21(16)
C(10)–Pd–C(27)	95.78(16)
C(10)–Pd–C(28)	171.13(16)
C(27)–Pd–C(28)	83.94(19)
N(2)–C(3)–N(4)	103.7(3)
N(9)–C(10)–N(11)	103.4(3)
Pd–C(3)–N(4)	115.8(2)
C(3)–N(4)–C(7)	120.6(3)
N(4)–C(7)–C(8)	116.2(4)
C(7)–C(8)–N(9)	123.0(4)
C(8)–N(9)–C(10)	130.3(4)
Pd–C(10)–N(9)	119.0(2)
Ring twist$_{C(3)}$ [a]	69.6(2)
Ring twist$_{C(10)}$ [a]	59.8(3)

[a] The angle between the coordination plane defined by palladium and carbene carbon atoms and the heterocyclic ring containing C(*n*).

collectively to the four ethylene protons of compound **2**. The ^{13}C{^{1}H} NMR spectra of compounds **1** and **2** are similar except for the resonances of the bridging methylene and ethylene groups that are at δ 64.0 and 48.9 respectively. Characteristic signals at δ 195.3 for compound **1** and 193.2 for compound **2** are observed for the carbene carbon atoms.

Cationic palladium(II) methyl complexes of ^{tBu}CC^{meth} and ^{tBu}CC^{eth}

Cationic transition metal methyl compounds incorporating NHC have received some attention due to their relevance to catalysis in particular C–C coupling and carbonylation reactions.[5,38] It has been reported that one of the primary decomposition pathways is the elimination of methyl imidazolium cations and a recent report has also examined aspects of this potential catalyst deactivation route in detail.[39] However all studies to date have centred on mono-NHC complexes and we were interested in investigating the preparation of cationic palladium(II) methyl complexes incorporating chelating di-NHC.

Addition of d^4-methanol to a mixture of **1** and 1 equivalent of pyridine in air gave a colourless solution with concomitant evolution of a gas (presumably CH_3D). ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and electrospray mass spectrometry of the solution indicate that protonation of **1** occurs to yield quantitatively the cation [Pd(^{tBu}CC^{meth})Me(py)]$^+$ (**3**) and presumably [CD_3O]$^-$ as the counter anion as shown in Scheme 1. Similarly addition of d^4-methanol to a mixture of **2** and 1 equivalent of pyridine gave [Pd(^{tBu}CC^{eth})Me(py)]$^+$ (**4**). ^{1}H and ^{13}C{^{1}H} NMR spectra of solutions of **3** and **4** remain unchanged for days. Integration of the ^{1}H NMR spectrum of **3** is consistent with the formulation and that the two NHC moieties are magnetically inequivalent. Two ^{t}Bu group and four imidazole proton resonances are observed in addition to two doublets at δ 6.20 and 6.92 assigned to the methylene bridge protons. Signals

attributable to coordinated pyridine are distinct from those of uncoordinated pyridine present in the solution due to the addition of slightly greater than 1 equivalent. The $^{13}C\{^{1}H\}$ NMR spectrum is characterised by the two carbene carbon resonances at δ 172.0 and 184.9 that are shifted upfield with respect to **1** and are characteristic of cationic palladium(II) complexes of NHC. In addition to the signals attributable to coordinated pyridine and magnetically inequivalent NHC moieties a characteristic methyl carbon signal is observed at δ −1.1. Compound **4** exhibits similar ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra to **3** except that the ^{1}H NMR spectrum displays four signals for the diastereotopic ethylene bridge protons and two signals are observed for the ethylene bridge carbons in the $^{13}C\{^{1}H\}$ NMR spectrum.

In analogous experiments addition of d^4-methanol to a mixture of **1** and 1 equivalent of bipyridine in air again gave a colourless solution with concomitant evolution of a gas (presumably CH_3D). However, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy and electrospray mass spectrometry of the solution indicate that in effect double protonation of **1** occurs to yield quantitatively the cation $[Pd(^{tBu}C(D)\text{-}\eta\text{-}C^{meth})Me(\eta^2\text{-bipy})]^+$ (**5**) and presumably $[CD_3O]^-$ as the counter anion as shown in Scheme 1. Similarly addition of d^4-methanol to a mixture of **2** and 1 equivalent of bipyridine gave $[Pd(^{tBu}C(D)\text{-}\eta\text{-}C^{eth})Me(\eta^2\text{-bipy})]^+$ (**6**). ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of solutions of **5** and **6** remain unchanged for days. This class of compound incorporating a transition metal complex of a NHC with a pendant imidazolium salt has recently been reported and a representative example is the cation [1,1′-di-*tert*-butyl-3,3′-methylene-(imidazolin-2-ylidene)imidazolium]palladium(II)acetate dibromide.[40] The ^{1}H NMR spectrum of **5** shows that the two imidazole moieties are inequivalent, two ^{t}Bu group resonances being observed at δ 1.41 and 1.82. In addition the methyl group protons are assigned to the signal at δ 0.43 and eight resonances between the range δ 7.55 and 8.77 are observed for the protons of the coordinated bipyridine ligand. The $^{13}C\{^{1}H\}$ NMR spectrum displays signals that are also consistent with the formulation, in particular the presence of a lone carbene carbon resonance at δ 173.3 and a broadened signal at δ 135.9 that is typical of an N*C*N imidazolium carbon atom. An apparent anomaly in the NMR spectra is the fact that only two doublet signals with relative integration 1H attributable to the imidazole rings can be discerned in the ^{1}H NMR spectrum. It was anticipated that deuteration of the N*C*N carbon atom of the imidazolium moiety would occur, the deuterium atom originating from the solvent. However it appears that hydrogen/deuterium exchange has also occurred at the two remaining C*H* positions of the imidazolium ring. Hydrogen/deuterium exchange of all the hydrogen atoms on the imidazolium ring would account for the observed ^{1}H NMR spectrum. It has been reported that hydrogen/deuterium exchange occurs for all three C*H* positions in imidazolium salts dissolved in D_2O and the rate of exchange is significantly increased in basic solution.[41,42] In previous studies we have not observed hydrogen/deuterium exchange of the two C(*H*)C(*H*) protons of imidazolium salts in CD_3OH therefore the presence of the anion $[CD_3O]^-$ presumably catalyses the rapid hydrogen/deuterium C*H* exchange of the imidazolium moiety of **5**. The corresponding reaction of **2** to yield **6** is similarly interpreted based on ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy and electrospray mass spectrometry.

Attempts to isolate cations **3**–**6** as their $[CD_3O]^-$ salts or by the addition of other anions (PF_6^- and BPh_4^-) were not successful. ^{1}H NMR analysis of the resulting yellow oils did not allow identification of the products, however there did not appear to be any indication of the presence of methyl substituted NC(C*H*$_3$)N imidazolium salts that typically display a characteristic signal in the range δ 2.3–2.8 in the ^{1}H NMR spectrum.[5,39]

In a previous study[37] and here we have shown that stable *cis*-dimethyl compounds of Ni(II) and Pd(II) of chelating di-NHC can be prepared. Thermal decomposition of the Ni(II) compounds does not proceed *via* reductive elimination of an alkyl imidazolium moiety and the results presented here, particularly in the case of the cationic complexes **4**–**6** indicate that chelating di-NHC may reduce the rate of this potential catalyst deactivation pathway. The presence of bulky ^{t}Bu group substituents and the geometry enforced by chelation of the di-NHC may prevent the requisite overlap of the relevant molecular orbitals that have been implicated[39] in the reductive elimination of alkyl imidazolium salts from transition metal alkyl complexes of NHC. Using chelating bulky di-NHC ligands may therefore be one potentially useful strategy to prevent deactivation by reductive elimination of alkyl imidazolium salts from this class of complex.

Experimental

General procedures

All manipulations were performed under nitrogen in a drybox or using standard Schlenk techniques. All solvents were dried over the appropriate drying agent and distilled under dinitrogen.[43]

$^{tBu}CC^{meth}$,[34] $^{tBu}CC^{eth}$,[34] and $Pd(bipy)Me_2$[44] were prepared according to published procedures. ^{1}H, $^{13}C\{^{1}H\}$ and ^{31}P NMR spectra were recorded at 500, 125.7 and 202.4 MHz respectively at probe temperature on a Varian Unity 500 spectrometer. Proton spectra were referenced internally to the residual solvent proton resonance relative to tetramethylsilane. Carbon spectra were referenced internally to the ^{13}C resonance of the solvent relative to tetramethylsilane. Electrospray mass spectra were recorded using a LC TOF electrospray ionisation mass spectrometer (Micromass, UK). Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory, Oxford.

Syntheses

$[Pd(^{tBu}CC^{meth})Me_2]$ (1). To an orange toluene suspension (20 mL) of $Pd(bipy)Me_2$ (1.460 g, 4.99 mmol) at −78 °C was added a cooled (−78 °C) THF solution (20 mL) of $^{tBu}CC^{meth}$ (1.300 g, 4.99 mmol). The orange suspension was allowed to warm to room temperature over 2 h and stirred for a further 12 h to give a dark orange suspension. The volume was reduced to 10 mL under reduced pressure and diethyl ether (100 mL) added to give a beige precipitate and an orange supernatant. The supernatant was isolated by filtration and cooled to −78 °C for 20 h giving a beige microcrystalline solid (**1**). The solid was isolated by filtration, washed with 40–60 petroleum ether (3 × 15 mL) and the residual volatiles removed under reduced pressure. Yield: 0.581 g, 29%. A second crop of **1** was obtained by adding 40–60 petroleum ether (50 mL) to the mother liquor and cooling to −78 °C for 20 h. Yield: 0.663 g. Combined yield: 1.244 g, 63%. ^{1}H NMR (C_6D_6, 500 MHz): δ 0.88 (6H, s, $Pd(CH_3)_2$), 1.59 (18H, s, $C(CH_3)_3$), 4.65 (1H, d, $^{2}J_{HH}$ = 13 Hz, CH_2), 6.25 (2H, d, $^{3}J_{HH}$ = 2 Hz, C*H*), 6.41 (2H, d, $^{3}J_{HH}$ = 2 Hz, C*H*), 6.54 (1H, d, $^{2}J_{HH}$ = 13 Hz, CH_2). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125.7 MHz): δ −3.0 ($Pd(CH_3)_2$), 31.5 ($C(CH_3)_3$), 57.8 ($C(CH_3)_3$), 64.0 (CH_2), 116.6 (*C*H), 118.3 (*C*H), 195.3 (N*C*N). Elemental analysis found (calc.) C, 51.4 (51.5); H, 7.6 (7.6); N, 14.0 (14.1%).

$[Pd(^{tBu}CC^{eth})Me_2]$ (2). To an orange THF suspension (20 mL) of $Pd(bipy)Me_2$ (3.200 g, 10.93 mmol) at −78 °C was added a cooled (−78 °C) THF solution (20 mL) of $^{tBu}CC^{eth}$ (3.000 g, 10.93 mmol). The orange suspension was allowed to warm to room temperature over 2 h and stirred for a further 12 h to give a dark orange suspension. The solvent volume was reduced to 20 mL under reduced pressure and diethyl ether (100 mL) added to give a white precipitate and an orange supernatant. The supernatant was isolated by filtration and cooled to −78 °C for 20 h to give a white microcrystalline solid (**2**). The solid was

isolated by filtration, washed with 40–60 petroleum ether (3 × 15 mL) and residual volatiles removed under reduced pressure. Yield: 2.870 g, 64%. ^{1}H NMR (C_6D_6, 500 MHz): δ 0.66 (6H, s, Pd(CH_3)$_2$), 1.66 (18H, s, C(CH_3)$_3$), 3.26 (2H, m, CH_2), 5.48 (2H, m, CH_2), 6.04 (2H, d, $^3J_{HH}$ = 2 Hz, CH), 6.37 (2H, d, $^3J_{HH}$ = 2 Hz, CH). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz): δ −4.8 (Pd(*C*H$_3$)$_2$), 31.8 (C(*C*H$_3$)$_3$), 48.9 (N(*C*$_2$H$_4$)N), 57.5 (*C*(CH$_3$)$_3$), 117.2 (*C*H), 119.5 (*C*H), 193.2 (N*C*N). Elemental analysis found (calc.) C, 52.2 (52.6); H, 8.2 (7.8); N, 13.3 (13.6%).

[Pd(^{tBu}CC^{meth})Me(py)]$^+$ (3). To a mixture of Pd(^{tBu}CC^{meth})Me$_2$ (**1**) (0.060 g, 0.15 mmol) and pyridine (0.012 g, 0.15 mmol) in air was added *d*^{4}-methanol (1 mL) to give a colourless solution with concomitant evolution of a gas. ^{1}H NMR (CD$_3$OD, 500 MHz): δ 0.04 (3H, s, Pd(CH_3)), 1.31 (9H, s, C(CH_3)$_3$), 1.80 (9H, s, C(CH_3)$_3$), 6.20 (1H, d, $^2J_{HH}$ = 14 Hz, CH_2), 6.92 (1H, d, $^2J_{HH}$ = 14 Hz, CH_2), 7.28 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.42 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.46 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.50 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.53 (2H, m, Pd(NC$_5H_5$)), 7.95 (1H, m, Pd(NC$_5H_5$)), 8.70 (2H, m, Pd(NC$_5H_5$)). ^{13}C{^{1}H} NMR (CD$_3$OD, 125.7 MHz): δ −1.1 (Pd*C*H$_3$), 31.1 (C(*C*H$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 59.1 (*C*(CH$_3$)$_3$), 60.0 (*C*(CH$_3$)$_3$), 66.0 (*C*H$_2$), 119.5 (N*C*H), 121.0 (N*C*H), 121.5 (N*C*H), 121.9 (N*C*H), 127.0 (Pd(N*C*$_5$H$_5$)), 139.4 (Pd(N*C*$_5$H$_5$)), 153.4 (Pd(N*C*$_5$H$_5$)), 172.0 (N*C*N), 184.9 (N*C*N). MS (electrospray; *m*/*z* (%)): 460 (100) [M$^+$].

[Pd(^{tBu}CC^{eth})Me(py)]$^+$ (4). To a mixture of Pd(^{tBu}CC^{eth})Me$_2$ (**2**) (0.075 g, 0.18 mmol) and pyridine (0.014 g, 0.18 mmol) in air was added *d*^{4}-methanol (1 mL) to give a colourless solution with concomitant evolution of a gas. ^{1}H NMR (CD$_3$OD, 500 MHz): δ −0.10 (3H, s, Pd(CH_3)), 1.44 (9H, s, C(CH_3)$_3$), 1.81 (9H, s, C(CH_3)$_3$), 4.54 (1H, m, CH_2), 4.63 (1H, m, CH_2), 5.44 (1H, m, CH_2), 6.22 (1H, m, CH_2), 7.26 (1H, d, $^2J_{HH}$ = 14 Hz, CH_2), 7.35 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.37 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.43 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.50 (2H, m, Pd(NC$_5H_5$)), 7.94 (1H, m, Pd(NC$_5H_5$)), 8.59 (2H, m, Pd(NC$_5H_5$)). ^{13}C{^{1}H} NMR (CD$_3$OD, 125.7 MHz): δ −2.2 (Pd*C*H$_3$), 31.7 (C(*C*H$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 50.2 (*C*H$_2$), 50.3 (*C*H$_2$), 59.1 (*C*(CH$_3$)$_3$), 59.5 (*C*(CH$_3$)$_3$), 120.5 (N*C*H), 121.7 (N*C*H), 122.3 (N*C*H), 124.0 (N*C*H), 126.8 (Pd(N*C*$_5$H$_5$)), 139.2 (Pd(N*C*$_5$H$_5$)), 153.3 (Pd(N*C*$_5$H$_5$)), 169.0 (N*C*N), 181.3 (N*C*N). MS (electrospray; *m*/*z* (%)): 475(90) [M$^+$], 396(10) [M$^+$ − py].

[Pd(^{tBu}C(D)-η-C^{meth})Me(η^2-bipy)]$^+$ (5). To a mixture of Pd(^{tBu}CC^{meth})Me$_2$ (**1**) (0.060 g, 0.15 mmol) and 2,2′-bipyridyl (0.023 g, 0.15 mmol) in air was added *d*^{4}-methanol (1 mL) to give a colourless solution with concomitant evolution of a gas. ^{1}H NMR (CD$_3$OD, 500 MHz): δ 0.43 (3H, s, Pd(CH_3)), 1.41 (9H, s, C(CH_3)$_3$), 1.82 (9H, s, C(CH_3)$_3$), 6.74 (2H, s, CH_2), 7.55 (1H, m, Pd(N$_2$C$_{10}H_8$)), 7.61 (1H, m, Pd(N$_2$C$_{10}H_8$)), 7.86 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.87 (1H, m, Pd(N$_2$C$_{10}H_8$)), 7.97 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 8.25 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.37 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.59 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.63 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.77 (1H, m, Pd(N$_2$C$_{10}H_8$)). ^{13}C{^{1}H} NMR (CD$_3$OD, 125.7 MHz): δ −3.8 (Pd*C*H$_3$), 29.5 (C(*C*H$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 61.2 (*C*(CH$_3$)$_3$), 62.1 (*C*(CH$_3$)$_3$), 64.1 (*C*H$_2$), 122.4 (N*C*H), 123.4 (N*C*H), 124.6 (Pd(N$_2$*C*$_{10}$H$_8$)), 124.8 (Pd(N$_2$*C*$_{10}$H$_8$)), 128.5 (Pd(N$_2$*C*$_{10}$H$_8$)), 128.8 (Pd(N$_2$*C*$_{10}$H$_8$)), 135.9 (NC(D)N), 141.7 (Pd(N$_2$*C*$_{10}$H$_8$)), 142.0 (Pd(N$_2$*C*$_{10}$H$_8$)), 149.4 (Pd(N$_2$*C*$_{10}$H$_8$)), 151.3 (Pd(N$_2$*C*$_{10}$H$_8$)), 155.6 (Pd(N$_2$*C*$_{10}$H$_8$)), 157.6 (Pd(N$_2$*C*$_{10}$H$_8$)), 173.3 (N*C*N). MS (electrospray; *m*/*z* (%)): 540 (25) [M$^+$], 484 (25) [M$^+$ − ^{t}Bu], 270 (25) [M^{2+}], 242 (25) [(M − ^{t}Bu)$^{2+}$].

[Pd(^{tBu}C(D)-η-C^{eth})Me(η^2-bipy)]$^+$ (6). To a mixture of Pd(^{tBu}CC^{eth})Me$_2$ (**2**) (0.060 g, 0.15 mmol) and 2,2′-bipyridyl (0.023 g, 0.15 mmol) in air was added *d*^{4}-methanol (1 mL) to give a colourless solution with concomitant evolution of a gas. ^{1}H NMR (CD$_3$OD, 500 MHz): δ 0.28 (3H, s, Pd(CH_3)), 1.63 (9H, s, C(CH_3)$_3$), 1.82 (9H, s, C(CH_3)$_3$), 4.75 (1H, m, CH_2), 4.77 (1H, m, CH_2), 4.80 (1H, m, CH_2), 5.39 (1H, m, CH_2), 7.55 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.62 (1H, m, Pd(N$_2$C$_{10}H_8$)), 7.77 (1H, m, Pd(N$_2$C$_{10}H_8$)), 7.79 (1H, d, $^3J_{HH}$ = 2 Hz, CH), 7.83 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.25 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.34 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.57 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.60 (1H, m, Pd(N$_2$C$_{10}H_8$)), 8.71 (1H, m, Pd(N$_2$C$_{10}H_8$)). ^{13}C{^{1}H} NMR (CD$_3$OD, 125.7 MHz): δ −4.3 (Pd*C*H$_3$), 29.7 (C(*C*H$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 50.0 (*C*H$_2$), 53.2 (*C*H$_2$), 60.5 (*C*(CH$_3$)$_3$), 61.7 (*C*(CH$_3$)$_3$), 121.7 (N*C*H), 123.5 (N*C*H), 124.4 (Pd(N$_2$*C*$_{10}$H$_8$)), 124.7 (Pd(N$_2$*C*$_{10}$H$_8$)), 128.3 (Pd(N$_2$*C*$_{10}$H$_8$)), 128.8 (Pd(N$_2$*C*$_{10}$H$_8$)), 135.8 (NC(D)N), 141.5 (Pd(N$_2$*C*$_{10}$H$_8$)), 141.8 (Pd(N$_2$*C*$_{10}$H$_8$)), 149.2 (Pd(N$_2$*C*$_{10}$H$_8$)), 151.3 (Pd(N$_2$*C*$_{10}$H$_8$)), 155.7 (Pd(N$_2$*C*$_{10}$H$_8$)), 157.7 (Pd(N$_2$*C*$_{10}$H$_8$)), 171.5 (N*C*N). MS (electrospray; *m*/*z* (%)): 553 (25) [M$^+$], 498 (10) [M$^+$ − ^{t}Bu], 277 (40) [M^{2+}], 249 (25) [(M − ^{t}Bu)$^{2+}$].

Decomposition studies

Yellow diphenylmethane solutions (0.25 mL) of [Pd(^{tBu}CC^{meth})Me$_2$] (0.025 g, 0.06 mmol) or [Pd(^{tBu}CC^{eth})Me$_2$] (0.025 g, 0.06 mmol) were heated at 80 °C for 2 h in an evacuated tube sealed with a Teflon stopcock. The pressure was then recorded and identification of the volatiles evolved was achieved by GCMS.

X-Ray crystallography

Crystals were isolated under dinitrogen, covered with a polyfluoroether and mounted on a glass fibre. Data were collected on an Enraf–Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). The images were processed with the DENZO and SCALEPACK programs.[45] All solution, refinement and graphical calculations were performed using the CRYSTALS[46] and CAMERON[47] software packages. Crystal structures were solved by direct methods using the SIR 92 program[48] and were refined by full-matrix least squares on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters.

Crystal structure determination of compound 2. $C_{18}H_{32}N_4Pd(C_4H_{10}O_1)$, M = 485.00, monoclinic, a = 10.141(1), b = 10.001(1), c = 24.746(1) Å, β = 94.24(2)°, U = 2502.9 Å^3, T = 180(2) K, space group $P2_1/n$, Z = 4, μ = 0.75 cm^{-1}, 12317 reflections measured, number of reflections used in refinement $I > 3\sigma(I)$ 3583, (R_{int} = 0.033), final $R1/wR2$ 0.033/0.039, max/min residual density 1.14/−1.59 e Å^{-3}.

CCDC reference number 173901.

See http://www.rsc.org/suppdata/dt/b1/b110261n/ for crystallographic data in CIF or other electronic format.

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