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Synthesis of *N*-heterocyclic carbene palladium(II) bis-phosphine complexes and their decomposition in the presence of aryl halides†‡

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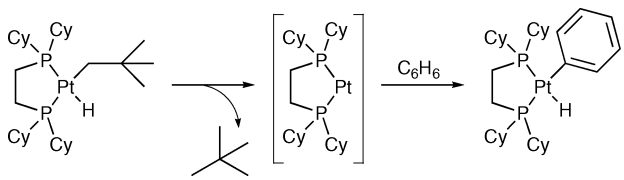
Methylpalladium(II) carbene complexes of the type [Pd(NHC)Me(P–P)]BF_4 (NHC = *N*-heterocyclic carbene, P–P = chelating phosphine) have been synthesised, the complex [Pd(tmiy)Me(dcype)]BF_4 (tmiy = 1,3,4,5-tetramethylimidazol-2-ylidene, dcype = 1,2-bis(dicyclohexylphosphino)ethane) being characterised crystallographically. Complexes bearing the tmiy ligands were shown to decompose in an analogous manner to complexes bearing monodentate phosphine ligands, with the rate of decomposition being nominally linked to the size of the chelate ring. The decomposition of these complexes in the presence of aryl halides—expected to yield Pd(Ar)X(P–P)—was studied and shown instead to yield PdX_2(P–P) and [Pd(tmiy)X(P–P)]BF_4. Additionally, Pd(Me)X(P–P) and Pd(Ar)X(P–P) were observed in some cases. Intermolecular cross-over reactions between the starting complex and Pd(Ar)X(P–P) were found to be the source of these unexpected products.

Introduction

The reductive elimination of 2-alkylimidazolium salts from alkyl-palladium carbene complexes is now recognised as a common decomposition mode for complexes of this type.[1–4] Previous studies[4,5] of this decomposition reaction in which phosphines are present as ancillary ligands (*i.e.* [Pd(carbene)Me$(PR_3)_2$]BF_4) have been, in all but one case,[4] limited to monodentate phosphines. These studies have shown that the decomposition yields the expected products, namely 2-methylimidazolium tetrafluoroborate salts and palladium(0) phosphine complexes (Pd$(PR_3)_2$).

Zero-valent, two-coordinate, bis-phosphine complexes of group 10 metals bearing monodentate phosphines are known to be less reactive than the analogous compounds bearing chelating bidentate ligands. Thus, Pt$(PCy_3)_2$ is inert to oxidative addition by non-activated C–H bonds,[6] but the chelated platinum fragment Pt(dcype) (dcype = 1,2-bis(dicyclohexylphosphino)ethane, formed *via* reductive elimination of neopentane from *cis*-[(dcype)hydridoneopentylplatinum(II)][7] reacts with the non-activated carbon–hydrogen bonds in benzene to yield *cis*-[(dcype)hydridophenylplatinum(II)].[8,9]

The high reactivity of these complexes is usually attributed to the fact that the chelate ring dictates a bent P–Pt–P configuration.



This bending has a dramatic effect on both the shape and energy of the frontier orbitals of the ML_2 complex. In the bent complex, the HOMO is an "in-L–M–L-plane" d-orbital that contains a single lone pair of electrons[10] (in fact these species are isolobal with methylene).[11] The orbital extends into space away from the L–M–L chelate ring, and is not shielded by the phosphine ligands.[10] In contrast, the HOMO of a linear ML_2 complex is sheltered between the two ligands.[10] This change in orbital shape was the original reason given for the higher reactivity.[6]

There have been several attempts made to synthesise Pd^0L_2 compounds containing chelating phosphines. The photolysis of (dcype)Pd(oxalate) gives high yields of the dinuclear palladium compound $Pd_2(\mu\text{-dcype})_2$.[12,13] In solution, this compound readily dissociates to form the reactive monomer Pd(dcype), and the subsequent reactivity of the system is dominated by this species, *e.g.* reaction with PhX (X = Br, I) to yield the monomeric Pd(Ph)X(dcype),[12] and with diphenyldiselenide to generate $Pd(SePh)_2$(dcype).[13] Similar reactivity has been reported for the compound $Pd_2(\mu\text{-dippe})_2$ (dippe = 1,2-bis(diisopropylphosphino)ethane).[14]

The reductive elimination of RCN (R = $CH_2Si(CH_3)_3$) from Pd(dppe)(R)(CN) in the presence of excess dppe yields the complex $Pd^0(dppe)_2$.[15] The authors of this study made no attempt to carry out oxidative addition reactions using the reactive Pd(dppe) fragment that is presumably generated during the course of the reaction.

The compound [Pd(dmiy)Me(dppp)]BF_4 (dmiy = 1,3-dimethylimidazol-2-ylidene; dppp = 1,3-bis(diphenylphosphino)propane) is stable at room temperature in solution for prolonged periods,[16] and is significantly more stable than analogous compounds

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‡ Electronic supplementary information (ESI) available: Detailed synthesis and characterisation of [Pd(tmiy)X(P–P)]BF_4, PdX_2(P–P) and Pd(Me)X(P–P) complexes; crystal structure of Pd(dppp)I_2. See DOI: 10.1039/b706053j

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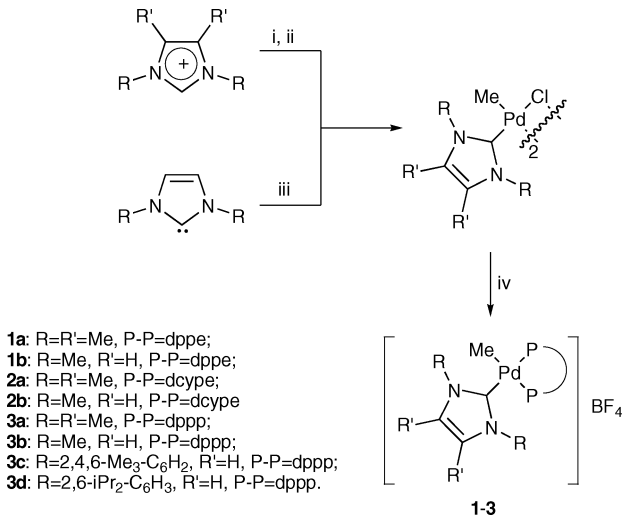
containing monodentate phosphines which commonly decompose within several hours at room temperature.[4] It would seem reasonable to assume that the reductive elimination of 2-methylimidazolium salts from compounds of the type [Pd(carbene)Me(P–P)]BF_4 (P–P = chelating phosphine) would yield the reactive fragment Pd(P–P) which could be trapped by further reaction with, for example, an aryl halide to yield a Pd(Ar)X(P–P) compound.

Herein the synthesis of a number of [Pd(carbene)Me(P–P)]BF_4 compounds and their subsequent decomposition in the presence of several trapping agents is described.

Results and discussion

The reaction of the chelating phosphines 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(dicyclohexylphosphino)ethane (dcype) or 1,3-bis(diphenylphosphino)propane (dppp) with dimeric mono-carbene palladium complexes in the presence of $AgBF_4$ furnishes the desired complexes in good yield (Scheme 1). In the case of **1a** and **2a** a highly coloured by-product is formed that may be removed by treatment with activated charcoal.



1a: R=R'=Me, P-P=dppe;
1b: R=Me, R'=H, P-P=dppe;
2a: R=R'=Me, P-P=dcype;
2b: R=Me, R'=H, P-P=dcype
3a: R=R'=Me, P-P=dppp;
3b: R=Me, R'=H, P-P=dppp;
3c: R=2,4,6-Me_3-C_6H_2, R'=H, P-P=dppp;
3d: R=2,6-iPr_2-C_6H_3, R'=H, P-P=dppp.

Scheme 1 i. 0.5 equiv. Ag_2O, DCM, r.t. 1 h. ii. Pd(Me)Cl(COD), 0 °C, 1 h. iii. Pd(Me)Cl(COD), THF, 0 °C, 20 min. iv. P–P, $AgBF_4$, 0 °C, 2 h.

Complexes **1–3** were characterised by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry and either microanalysis or high-resolution mass spectrometry. Compound **2a** was also characterised crystallographically. Selected NMR data are shown in Table 1. The $^{31}P\{^1H\}$ chemical shift of **3b** has been previously reported as δ 58.3 and 45.7 ppm.[16] A brief survey of the literature indicates that palladium(II) complexes of dppp typically resonate between 25 and −10 ppm in the $^{31}P\{^1H\}$ NMR spectrum.[17,18] This, coupled with the similar shifts for complexes **3a–d**, suggests that the previously reported chemical shift of **3b** is incorrectly reported.

The chemical shifts for complexes **1a–b** and **2a–b** are reasonably consistent within each group. This is not surprising, given the similarity of the tmiy and dmiy ligands. The chemical shifts within group **3** show dramatic changes upon moving from the simple methyl-substituted ligands (tmiy **3a**, dmiy **3b**) to the much larger aryl-substituted carbenes (IMes **3c**, IDipp, **3d**). In the $^{31}P\{^1H\}$ NMR spectrum, there is a large high-field shift of one phosphorus atom upon moving from **3a** (−0.67 ppm) to **3d** (−9.18 ppm),

Table 1 Selected NMR data for complexes **1–3**[a]

	Pd–CH_3	Pd–CH_3	NCN	Pd–*P*	
1a	0.35	−3.46	175.3	50.40	39.93
1b	0.35	−3.24	176.3	51.07	40.44
2a	0.10	−6.89	178.6	67.10	61.32
2b	0.06	−6.64	181.1	67.92	62.33
3a	0.14	0.66	175.3	11.96	−0.67
3b	0.12[b]	0.70[b]	179.5[b]	12.24	−0.45
3c	0.00	9.16	182.4	13.78	−6.12
3d	−0.04	8.62	186.0	15.08	−9.18

[a] Spectra recorded in $CDCl_3$ or CD_2Cl_2. [b] These shifts are taken from ref. 16.

coupled with a large down-field shift for the Pd–CH_3 signal in the $^{13}C\{^1H\}$ NMR spectrum (0.66 ppm (**3a**) *cf.* 8.62 ppm (**3d**)).

Crystals of **2a** suitable for X-ray structure determination were grown by solvent diffusion of diethyl ether into a DCM solution. This analysis (Fig. 1, Table 2) shows that the Pd centre in **2a** exhibits a distorted square planar core geometry, with the C_{tmiy}–Pd–C_{methyl} bond angle (84.90(8)°) being significantly smaller than the ideal 90°. Coupled with this is an increase in the P(1)–Pd–C_{tmiy} angle (98.02(5)°). The di-phosphine bite angle (86.17(2)°) is typical of palladium complexes bearing the dcype ligand. The distortions from ideal square planar metal coordination geometry presumably arise to minimise steric interaction between the cyclohexyl groups of the phosphine ligand and the methyl groups of the carbene ligand, in addition to accommodating the acute bite angle of the di-phosphorus ligand.

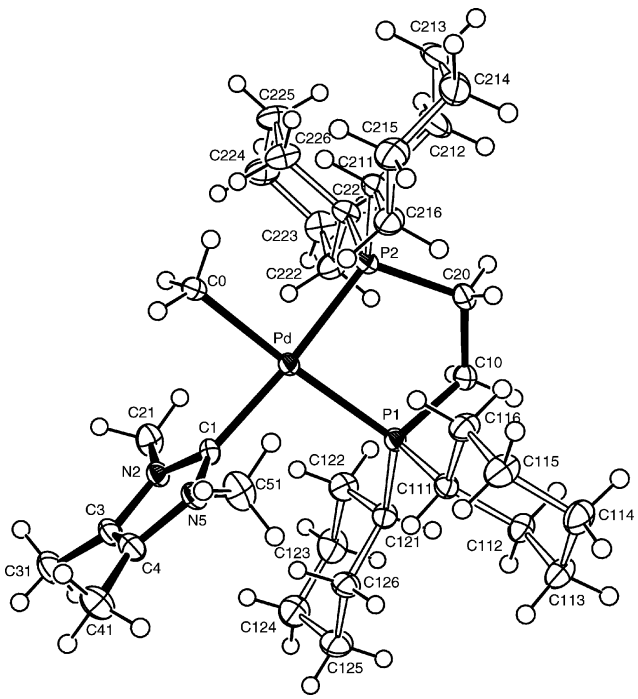


Fig. 1 Molecular projection of **2a** normal to the coordination plane showing the atom labelling scheme. Thermal ellipsoids are shown at the 50% probability level, while hydrogen atoms have arbitrary radii of 0.1 Å.

The Pd–C_{tmiy} bond distance (2.061(2) Å) is within the typical range reported for Pd(II) carbene complexes (1.96-2.09 Å),[1,16,19] albeit towards the higher end of the range. Pd–$C_{carbene}$ bond lengths

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Table 2 Selected bond lengths, angles and interplane angles for **2a**

Bond lengths/Å			
Pd–C(1)	2.061(2)	Pd–C(0)	2.147(2)
Pd–P(1)	2.3369(5)	Pd–P(2)	2.2864(5)
C(1)–N(2)	1.353(2)	C(1)–N(5)	1.343(3)
Bond angles/°			
C(1)–Pd–P(2)	175.12(5)	P(1)–Pd–C(0)	176.24(7)
C(1)–Pd–C(0)	84.90(8)	C(1)–Pd–P(1)	98.02(5)
P(1)–Pd–P(2)	86.17(2)	C(0)–Pd–P(2)	91.02(6)
Planes/Å			
I: P(1,2), C(0,1)	$\chi^2 = 2361$, δ Pd = 0.007(1) Å		
II: N(2,5), C(1,3,4)	$\chi^2 = 18$, δ Pd = 0.110(3) Å		
Interplane angles/°			
I/II	80.174(62)		

of this magnitude (*i.e.* > 2.05 Å) are most commonly found for chelating carbene complexes (*e.g.* Pd(^{tBu}CC^{eth})Me$_2$, which has Pd–C$_{carbene}$ bond distances of 2.070(3) and 2.089(3) Å[20] (^{tBu}CC^{eth} = 1,2-ethylene-3,3′-di-*tert*-butyldiimidazol-2,2′-diylidene)).

The plane of the carbene ligand is twisted by 80.17(6)° relative to the plane defined by P(1), P(2), C(1), C(0). This is typical behaviour for carbene ligands, which adopt a twisted orientation to minimise steric interactions with other ligands in the metal coordination sphere.[21,22]

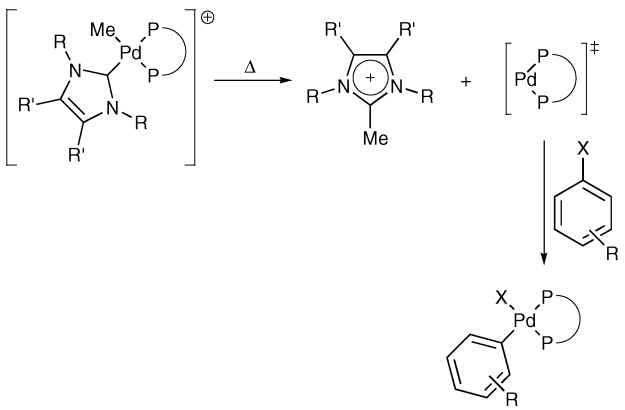
The 0.05 Å difference between the Pd–P(1) (2.3369(5) Å) and Pd–P(2) (2.2864(5) Å) bond lengths demonstrates that the methyl ligand exerts a stronger *trans* influence than the tmiy ligand. This observation is consistent with the findings of previous studies.[23] Both Pd–P bond lengths are comparable to those found in other palladium(II) complexes of dcype, *e.g.* Pd(dcype)Cl$_2$ (2.233(1) Å, 2.232(1) Å),[8] Pd(dcype)(SiHMe$_2$)$_2$ (2.3518(7) Å, 2.3614(8) Å),[24] and Pd(dcype)Cl(C(O)CMe$_3$) (2.366(1) Å, 2.254(1) Å).[25]

The Cambridge Crystallographic Database[26] suggests that **2a** is the first methylpalladium complex bearing the dcype ligand to be crystallographically characterised. As such, direct comparison of Pd–CH$_3$ bond lengths with analogous complexes is not possible, although palladium–methyl complexes bearing the dppe and dmpe ligands are known. Based on comparisons with methylpalladium complexes bearing other chelating phosphines,[27] it may be seen that the Pd–CH$_3$ bond length in **2a** (2.147(2) Å) is quite long (*cf.* Pd(dmpe)Me$_2$ (2.087(4) Å),[28] Pd(dmpe)Me(OPh) (2.101(9) Å)[29] and [Pd(dmpe)Me(NH$_3$)]PF$_6$ (2.081(4) Å).[30]) This is presumably due to increased electron density on the metal centre, arising from donation by the carbene ligand, leading to a decrease in σ-donation from the methyl group. This characteristic has been observed previously.[23]

Decomposition of complexes

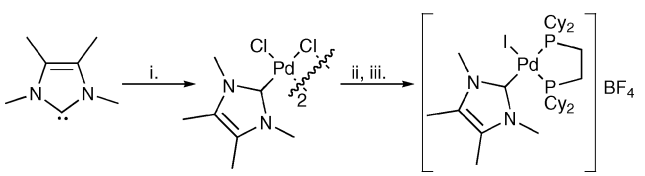
The previous investigation of the decomposition of methylpalladium carbene complexes bearing bidentate phosphines has shown that these complexes do not decompose at room temperature, even after 24 h.[4] The decomposition of **1b** and **3b** was studied by ^{1}H NMR spectroscopy in acetonitrile-d$_3$ at 65 °C; it was found that both complexes decompose to yield 1,2,3-trimethylimidazolium tetrafluoroborate and palladium black. The decomposition of **3b** is considerably faster than for **1b**, with all resonances attributable to **3b** being essentially absent after 6 h; in contrast large quantities of **1b** remain in the reaction mixture after this time. An increase in the rate of reductive elimination reactions is known to occur upon widening of the bite-angle of the P–P chelate.[15,31,32] Thus, on moving from the smaller bite angle of dppe to dppp a qualitatively dramatic rise in the rate of decomposition is observed.

It was initially envisaged that, in the presence of excess aryl halide, complexes **1–3** would decompose *via* reductive elimination to give products as shown in Scheme 2.



Scheme 2 Possible mode of decomposition for methylpalladium carbene complexes of chelating phosphines in the presence of aryl halides. P–P = dppe, dcype, dppp.

The decomposition of **2a** in the presence of 4-iodotoluene or 4-iodoanisole was studied in THF-d$_8$. Complex **2a** is soluble in this solvent only at elevated temperatures. In addition, electrospray ionisation mass spectroscopy (ESI-MS) and GC-MS analyses of the crude reaction mixture was undertaken. By ^{31}P{^{1}H} NMR spectroscopy, both the decomposition reactions were found to yield two phosphorus-containing products, with one identified as the known, but unexpected, complex PdI$_2$(dcype).[12] ESI-MS showed the presence of the [Pd(tmiy)I(dcype)]$^+$ ion (correct isotope pattern) in the reaction mixture, thus an independent synthesis of [Pd(tmiy)I(dcype)]BF$_4$ was undertaken (Scheme 3). The ^{31}P{^{1}H} NMR spectrum of this complex was identical with that observed for the second decomposition product.



Scheme 3 Synthesis of [Pd(tmiy)I(dcype)]BF$_4$. i. Pd(PhCN)$_2$Cl$_2$. ii. AgBF$_4$, dcype. iii. NaI, acetone.

In addition to the cationic palladium complex, 1,2,3,4,5-pentamethylimidazolium and 1,3,4,5-tetramethyl-2-phenylimidazolium were observed by ESI-MS, whilst GC-MS revealed

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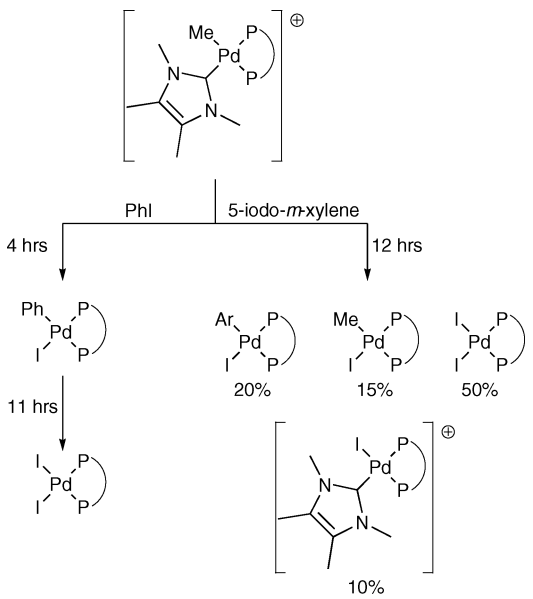
the presence of biaryls (*e.g.* 4,4′-bitolyl in the case of 4-iodotoluene), and confirmed the presence of species arising from methyl–aryl coupling.

1,2,3,4,5-Pentamethylimidazolium is the expected product of the initial reductive elimination from **1a**. However the presence of toluene and 1,3,4,5-tetramethyl-2-phenylimidazolium as by-products is surprising, and suggests one of two possibilities: firstly, that rather than by the generation of a Pd(0) species and subsequent oxidative addition of the aryl halide, the reaction is proceeding *via* a Pd(IV) intermediate resulting from oxidative addition of the aryl halide to the initial Pd(II) species followed by reductive elimination to regenerate Pd(II) species, or, secondly, that there are intermolecular exchange reactions occurring (*vide infra*).

The formation of unexpected by-products in the reactions of **3a** with aryl halides prompted further investigation into the generality of the reaction. The reaction of **3a** with phenyl iodide or 5-iodo-*m*-xylene in acetone-d_6 was studied (Scheme 4). In the former case, while the reaction gave Pd(Ph)I(dppp)[18,31,33] after 4 h at 60 °C, the major phosphorus-containing product after 11 h was Pd(dppp)I_2, as shown by the presence of a singlet at δ 1.76 in the $^{31}P\{^1H\}$ NMR spectrum. This final complex was previously unreported in the literature, and an independent synthesis was undertaken (see ESI‡ for further details, including crystal structure).



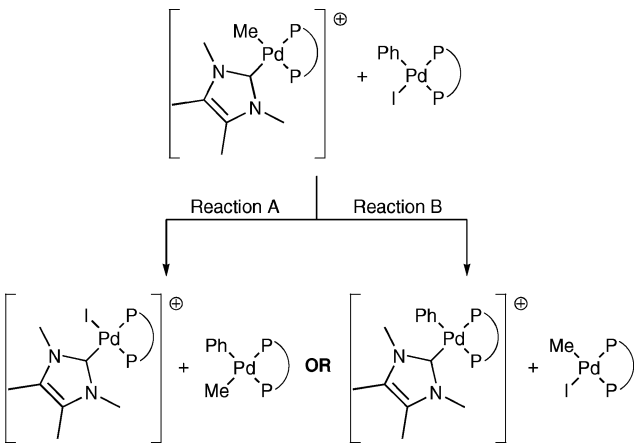
Scheme 4 Product distribution for the reaction of **3a** with aryl iodides (P–P = dppp).

In order to ascertain if this unexpected reactivity was restricted to aryl iodides, the reaction of **3a** with 4-bromoacetophenone was studied at 65 °C in acetonitrile-d_3. The reaction was relatively clean with (4-acetylphenyl)PdBr(dppp) being formed as the major product, together with minor amounts of other phosphorus-containing products later identified as Pd(dppp)Br_2 ($^{31}P\{^1H\}$ NMR: δ 9.85 ppm),[34] Pd(Me)Br(dppp) (δ 26.2, −5.2 ppm) and [Pd(tmiy)Br(dppp)]BF_4 (δ 10.67, −4.08 ppm) were also observed by $^{31}P\{^1H\}$ NMR spectroscopy. The two latter complexes were previously unreported in the literature, and independent syntheses were undertaken to confirm their identities. The formation of (4-acetylphenyl)PdBr(dppp) in good yields confirmed that our initial premise of this study, relating to the formation of the reactive fragment [Pd(P–P)], was sound.

In contrast, the reaction of **3a** with 4-bromotoluene yielded none of the expected (4-methylphenyl)PdBr(dppp); instead, the major product was identified as [Pd(tmiy)Br(dppp)]BF_4, while Pd(dppp)Br_2 and several unidentified species were observed in minor quantities.

To determine whether the products [Pd(tmiy)X(P–P)]BF_4 and Pd(Me)X(P–P) arise from an intermolecular rearrangement or possibly from an intermediate Pd(IV) species, the reaction between compound **1a** and Pd(Ph)I(dppe) was studied in the presence of MAH (maleic anhydride).[35] The reaction between a 1 : 1 mixture of **1a** and Pd(Ph)I(dppe) was performed in acetone-d_6 and followed by $^{31}P\{^1H\}$ NMR spectroscopy. As the latter complex is only moderately soluble in acetone-d_6 at room temperature, the mixture was gently warmed to 45 °C for 5 min before any spectra were recorded. Surprisingly, the first $^{31}P\{^1H\}$ NMR spectrum run after this time showed complete consumption of Pd(Ph)I(dppe), coupled with the formation of [Pd(tmiy)I(dppe)]$^+$ and Pd(Me)I(dppe). No formation of MAH complexes was observed.

This result demonstrates that Pd(II) carbene complexes may undergo intermolecular rearrangements of the type shown below in Scheme 5. Two different reaction pathways are shown. Reaction A shows the cross-over reaction which generates the ionic [Pd(tmiy)I(P–P)]$^+$ complex, together with Pd(Ph)Me(P–P), by exchange of the methyl and iodide ligands. Complexes of the latter type (where P–P = dppp) have been shown to reductively eliminate toluene.[31] Reaction B generates Pd(Me)I(P–P) and [Pd(tmiy)Ph(P–P)]$^+$ by exchange of the methyl and phenyl ligands. The reductive elimination of arylimidazolium salts from palladium carbene complexes is a known reaction,[1,3,22] while theoretical calculations suggest this type of decomposition is a more facile reaction than the elimination of alkyl imidazolium salts from the analogous complexes.[32] In this case, the expected product of reductive elimination would be the 2-phenyl-1,3,4,5-tetramethylimidazolium ion.



Scheme 5 Intermolecular rearrangements during the reaction of **1a** with Pd(Ph)I(P–P) (P–P = dppe).

In a similar reaction, the intermolecular rearrangement between **2a** and Pd(Ph)I(dppe) was studied. This reaction was found to give two major phosphorus-containing products: [Pd(tmiy)I(dcype)]BF_4

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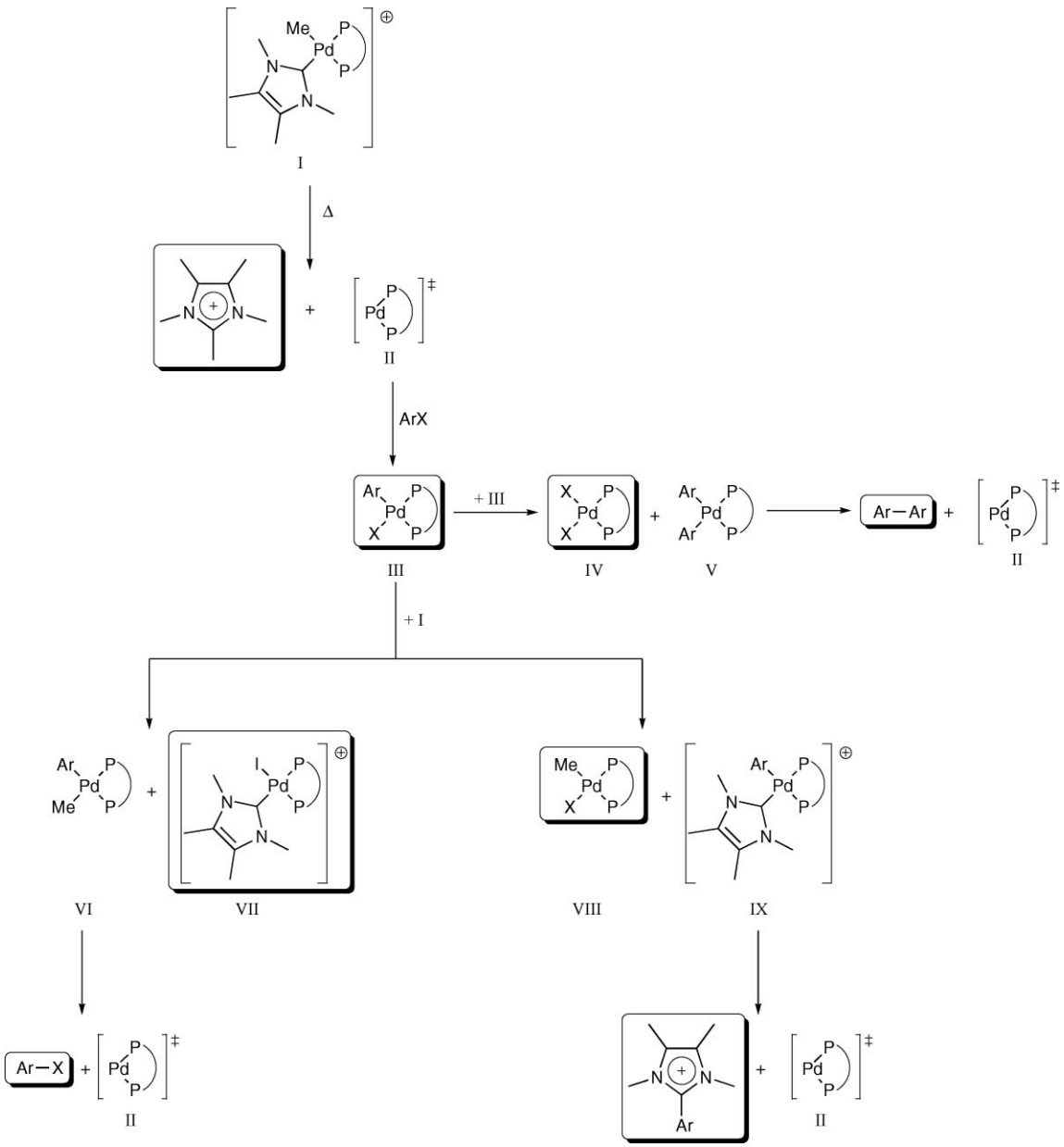
and Pd(Me)I(dppe), suggesting that the carbene remains tightly bound to the metal centre and does not participate in the cross-over reaction. Given this, a proposal for the mechanism of the reaction of [Pd(carbene)Me(P–P)]$^+$-type complexes with aryl halides may now be made (Scheme 6).

The starting complex **I** decomposes on warming to yield the reactive palladium(0) fragment **II**. This then undergoes oxidative addition with the aryl halide to yield the Pd(Ar)X(P–P) complex **III**. An intermolecular exchange between two molecules of **III** would then generate complexes **IV** and **V**, with complex **V** undergoing reductive elimination to yield a biaryl species, and reforming **II**.

Compound **III** also undergoes exchange reactions with **I**, as was shown previously. These reactions generate complexes **VI–IX**, two of which (**VII** and **VIII**) are commonly observed during or upon completion of the reactions. Complex **VI** would be expected to reductively eliminate ArMe compounds, while **IX** would eliminate 2-arylimidazolium salts. These two compounds are also commonly noted upon completion of the reactions.

It may be expected then, that the presence of 2-arylimidazolium salts would always be coupled with the presence of **VIII**, but this is not the case. It is possible that **VIII** undergoes another intermolecular exchange reaction with **III** to generate PdX_2(P–P) and Pd(Ar)Me(P–P). Once again, the latter would undergo reductive elimination of ArMe, whilst the former compound is one of the observed reaction products. Similar reactions have been reported previously.[36] Clearly, this cross-over reaction is not favourable in all cases, particularly when aryl bromides are used.



Scheme 6 Proposed mechanism for the reaction of [Pd(NHC)Me(P–P)]BF_4 with aryl halides. Counter-ions have been omitted for clarity. Shaded compounds are those that were observed experimentally.

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Conclusion

Methylpalladium(II) complexes bearing *N*-heterocyclic carbenes and chelating phosphines have been synthesised in moderate to excellent yields. Initial studies regarding the stability of these complexes showed that they decomposed at elevated temperatures to yield the expected 2-methylimidazolium salts, free phosphine and Pd(0). The rate of decomposition could be nominally linked to the size of the phosphine chelate ring.

The chelate complexes could be used to generate reactive Pd(0) fragments by reductive elimination of 2-methylimidazolium salts. In the presence of aryl halides, these reactive fragments undergo oxidative addition to yield Pd(II) complexes of the type Pd(Ar)X(P–P), however at the elevated temperatures required for decomposition, these complexes undergo further intermolecular cross-over reactions.

These cross-over reactions may occur between two molecules of the arylpalladium species, generating PdX_2(P–P) and $PdAr_2$(P–P), with the latter undergoing reductive elimination to yield biaryl compounds. Cross-over reactions may also occur between the arylhalopalladium(II) complexes and the methylpalladium(II) carbene complexes, which yield a number of products, including those arising from methyl–aryl coupling. It was shown that the carbene ligand does not move between metal centres, rather that the methyl group is transferred, while both the halide and the aryl group may be transferred from Pd(Ar)X(P–P). The degrees to which these cross-over reactions occurred appeared highly dependent on the nature of the aryl halide, with aryl bromides only occasionally yielding the desired arylhalogenatopalladium(II) complexes.

This study demonstrates that the desired coordinatively unsaturated Pd^0(P–P) species is generated. However, for this approach to be generally useful, cross-over reactions would need to be controlled or preferably prevented altogether.

Experimental

Unless otherwise stated, all reactions were carried out under an atmosphere of dry dinitrogen or argon using standard Schlenk techniques. Solvents were purified and dried by the usual methods.[37] [Pd(NHC)Me(μ-Cl)]$_2$ complexes were prepared as described previously.[5] ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR were run on Varian Gemini 200, Varian Mercury Plus 300 and Varian Unity Inova 400 instruments at ambient temperature and referenced to residual solvent signals for ^{1}H and ^{13}C{^{1}H}. ^{31}P{^{1}H} NMR spectra were referenced to external H_3PO_4. Elemental analyses (Carlo Erba EA1108 or ThermoFinnigan Flash 1112 Series EA) and Liquid Secondary Ion Mass Spectrometry (LSI-MS, Kratos Concept ISQ) were performed by the Central Science Laboratory, University of Tasmania.

[Pd(tmiy)Me(dppe)]BF_4 (1a)

[Pd(tmiy)Me(μ-Cl)]$_2$ (0.0698 g, 0.124 mmol) and dppe (0.0995 g, 0.249 mmol) were taken up in DCM (2.5 mL). This mixture was cooled to 0 °C before being transferred into a cold solution of $AgBF_4$ (0.050 g, 0.257 mmol) in DCM (2.5 mL). The reaction mixture was stirred for 50 min before being filtered through Celite®. The sepia-coloured filtrate was treated with activated charcoal, which was removed by filtration with a filter cannula. The clear, colourless filtrate was concentrated *in vacuo* to approx. 2 mL, layered with Et_2O and placed at −20° for 2 d. The mother-liquor was decanted and the off-white crystalline product was dried *in vacuo*. ^{1}H NMR indicated the presence of ~0.5 Et_2O per product molecule. Yield: 0.13 g (76%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.7–7.2 (m, 20H, ArH), 3.25 (s, 6H, N–CH_3), 2.4 (m, 4H, PCH_2), 2.05 (s, 6H, C–CH_3), 0.355 (t, 3H, Pd–CH_3, J = 6.6 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 50.40 (d, J = 22.6 Hz), 39.93 (d, J = 22.6 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 175.29 (dd, J_{CP} = 137.3 Hz, J_{CP} = 15.7 Hz) 133.4 (d, J = 11.4 Hz), 132.6 (d, J = 12.0 Hz), 131.9 (d, J = 2.9 Hz), 131.6 (d, J = 1.7 Hz), 131.4 (s), 129.8 (s), 129.6 (d, J = 10.8 Hz), 129.4 (d, J = 9.7 Hz), 129.2 (s), 126.7 (d, J = 3.4 Hz), 35.03 (s, N–CH_3), 27.59 (dd, J_{CP} = 29.2 Hz, J_{CP} = 20.0 Hz, PCH_2), 25.82 (dd, J_{CP} = 26.4 Hz, J_{CP} = 14.3 Hz, PCH_2), 9.01 (s, C–CH_3), −3.46 (d, J = 92.5 Hz, Pd–CH_3). MS (LSI-MS) m/z (relative intensity): 643 (10; M^+), 139 (100; ylidene + CH_3). HR-MS for $C_{34}H_{39}N_2{}^{104}PdP_2$: calc, 641.16288; obsd, 641.16252.

[Pd(dmiy)Me(dppe)]BF_4 (1b)

To a −20 °C suspension of [Pd(dmiy)Me(μ-Cl)]$_2$ (0.1241 g, 0.245 mmol) in DCM (2 mL) was added a solution of dppe (0.2003 g, 0.5035 mmol) in DCM (3 mL). This mixture was stirred at −20 °C for 30 min, before being transferred into a solution of $AgBF_4$ (0.110 g, 0.565 mmol) in DCM (3 mL). The resultant mixture was stirred for 3 h before being filtered through Celite®. The filtrate was concentrated to dryness *in vacuo* and the residue recrystallised from DCM–Et_2O (1 mL : 15 mL) to give a pink–brown oil. The mother-liquor was removed and the oil triturated with DCM–THF (1 mL : 5 mL) to give a pale pink powder. This was washed with THF–Et_2O and Et_2O and dried *in vacuo* to yield a very pale pink powder. Yield: 0.26 g (76%). Anal. Calc. for $C_{32}H_{35}N_2PdP_2BF_4$: C, 54.69; H, 5.02; N, 3.99. Found: C, 54.66; H, 5.10; N, 4.05. MS (LSI-MS) m/z (relative intensity): 615 (100; M^+), 291 (28). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.7–7.2 (m, 20H, ArH), 7.03 (s, 2H, *H*C=C*H*), 3.40 (s, 6H, N–CH_3), 2.7–2.2 (m, 4H, PCH_2CH_2P), 0.35 (t, 3H, J = 6.5 Hz, Pd–CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 176.34 (dd, J = 135.2, 16.1 Hz) 133.8 (d, J = 11.4 Hz), 133.2 (d, J = 13.6 Hz), 131.7 (s), 131.2 (s), 130.9 (s), 129.9 (s), 129.6 (d, J = 12.4 Hz), 129.1 (d, J = 9.1 Hz), 128.5 (s), 125.9 (s), 122.4 (s), 36.12 (s, N–CH_3), 27.37 (dd, J_{CP} = 28.3 Hz, J_{CP} = 18.4 Hz, PCH_2), 26.74 (dd, J_{CP} = 25.1 Hz, J_{CP} = 13.7 Hz, PCH_2), −3.24 (d, J = 91.6 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 51.1 (d, J = 23.6 Hz), 40.4 (d, J = 23.6 Hz).

[Pd(tmiy)Me(dcype)]BF_4 (2a)

This was prepared as described for **1a**, from [Pd(tmiy)Me(μ-Cl)]$_2$ (0.0969 g, 0.172 mmol), dcype (0.1459 g, 0.345 mmol) and $AgBF_4$ (0.069 g, 0.354 mmol) in DCM (3 mL). Yield: 0.23 g (88%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 3.61 (s, 6H, N–CH_3), 2.2–2.0 (m, 4H, PCH_2CH_2P), 2.18 (s, 6H, C–CH_3), 2.0–1.6 (br m, 22H, CyH), 1.4–1.1 (m, 20H, CyH), 0.8–0.6 (br, 2H, CyH), 0.10 (t, 3H, Pd–CH_3, J = 5.7 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 67.1 (d, J = 16.5 Hz), 61.3 (d, J = 16.5 Hz). MS (ESI) m/z (intensity): 687.1 (15%), 667.0 (100%) $[M]^+$. X-Ray quality crystals were grown by solvent diffusion of Et_2O into a DCM solution of the product.

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[Pd(dmiy)Me(dcype)]BF_4 (2b)

This was prepared as described for **1b**, from [Pd(dmiy)Me(μ-Cl)]$_2$ (0.0772 g, 0.153 mmol), dcype (0.1291 g, 0.305 mmol) and $AgBF_4$ (0.062 g, 0.318 mmol) to give an off-white powder. Yield: 0.15 g (68%). Anal. Calc. for $C_{32}H_{59}N_2PdP_2BF_4$: C, 52.87; H, 8.18; N, 3.85. Found: C, 52.52; H, 8.33; N, 4.00. MS (ESI) *m/z* (intensity): 663.2 (15%), 643.0 (30%), 639.0 (100%) [M$^+$], 624.2 (20%), 563.1 (13%), 527.1 (23%), 458.9 (25%), 377.0 (12%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.24 (s, 2H, HC=CH), 3.76 (s, 6H, N–CH_3), 2.2–1.6 (br m, 28H, PCH_2CH_2P + CyH), 1.5–1.1 (br m, 18H, CyH), 0.9–0.6 (br, 2H CyH), 0.057 (t, 3H, J = 5.8 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 67.9 (d, J = 16.0 Hz), 62.3 (d, J = 16.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 181.10 (dd, J = 132.0, 13.7 Hz, N*C*N), 123.86 (d, J = 3.4 Hz, H*C*=*C*H), 37.89, 34.77, 34.58, 34.47, 34.37, 29.77 (d, J = 2.9 Hz), 29.13, 28.05, 27.4–26.7 (m), 26.18, 24.18–23.61 (m, P*C*H_2*C*H_2P), 20.18–19.73 (m, PCH_2CH_2P), −6.64 (dd, J = 89.7, 4.0 Hz, Pd–*C*H_3).

[Pd(tmiy)Me(dppp)]BF_4 (3a)

[Pd(tmiy)Me(μ-Cl)]$_2$ (0.0379 g, 0.0674 mmol) and dppp (0.0565 g, 0.137 mmol) were taken up in DCM (2 mL). This mixture was cooled to 0 °C before being transferred into a cold solution of $AgBF_4$ (0.027 g, 0.138 mmol) in DCM (3 mL). The reaction mixture was stirred for 90 min before being filtered through Celite®. Ether (40 mL) was added to the filtrate and the volatiles concentrated *in vacuo* to approx. 10 mL. The mother-liquor was decanted off the resultant white precipitate. This was washed with Et_2O and dried *in vacuo* to yield a white powder. Yield: 0.08 g (80%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.6 (m, 10H, ArH), 7.3 (m, 3H, ArH), 7.1 (m, 7H, ArH), 3.27 (s, 6H, N–CH_3), 2.29 (m, 4H, PCH_2), 1.90 (s + m, 8H, C–CH_3 + $PCH_2CH_2CH_2P$), 0.14 (t, 3H, J = 6.9 Hz, Pd–CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.4 MHz): δ 175.33 (dd, J = 135.1 Hz, J = 16.6 Hz, N*C*N), 134.25 (s), 133.76 (s), 133.42 (d, J = 10.6 Hz), 132.98 (d, J = 11.5 Hz), 131.49 (s), 130.95 (s), 130.81 (s), 130.22 (s), 129.62 (d, J = 9.7 Hz), 128.96 (d, J = 9.2 Hz), 126.57 (d, J = 3.5 Hz), 35.26 (s, N–*C*H_3), 27.8 (m, P*C*H_2), 18.76 (d, J = 3.4 Hz, $PCH_2CH_2CH_2P$) 9.13 (s, C–*C*H_3), 0.66 (d, J = 91.0 Hz, Pd–*C*H_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz): δ 11.95 (d, J = 48.0 Hz), −0.67 (d, J = 48.0 Hz). Anal. Calc. for $C_{35}H_{41}N_2PdP_2BF_4$: C, 56.43; H, 5.55; N, 3.76. Found: C, 56.26; H, 5.50; N, 3.66. MS (LSI-MS) *m/z* (relative intensity): 657 (4; M$^+$), 139 (100; ylidene + CH_3). HR-MS for $C_{35}H_{41}N_2{}^{104}PdP_2$: calc, 655.17853; obsd, 655.17740.

[Pd(dmiy)Me(dppp)]BF_4 (3b)

To a solution of [Pd(dmiy)Me(μ-Cl)]$_2$ (0.0573 g, 0.113 mmol) in DCM (5 mL) was added a solution of dppp (0.0933 g, 0.226 mmol) in DCM (2 mL). This mixture was stirred for 5 min, before being transferred into a solution of $AgBF_4$ (0.048 g, 0.247 mmol) in DCM (2 mL). The resultant mixture was stirred for 2.5 h before being filtered through Celite®. The solvent was concentrated *in vacuo* to approx. 2 mL and 10 mL of Et_2O was added to precipitate the product. The supernatant was decanted, and the product recrystallised from DCM–Et_2O (4 mL : 10 mL), washed with Et_2O (2 × 5 mL) and dried *in vacuo* to yield a white powder. Yield: 0.13 g (83%). The ^{1}H NMR was identical to the reported spectrum.[16] ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.3 MHz): δ 12.24 (d, J = 49 Hz), −0.45 (d, J = 49 Hz).

[Pd(IMes)Me(dppp)]BF_4 (3c)

To a 0 °C solution of [Pd(IMes)Me(μ-Cl)]$_2$ (0.1096 g, 0.119 mmol) in DCM (8 mL) was added dppp (0.0984 g, 0.239 mmol) in DCM (3 mL). The phosphine was rinsed over with DCM (2 mL), and the reaction mixture stirred at 0 °C for 20 min. After this time the clear solution was transferred into a cold suspension of $AgBF_4$ (0.046 g, 0.236 mmol) in DCM (3 mL). After stirring for 2.5 h, the mixture was filtered through Celite® and the volatiles concentrated *in vacuo* to approx. 4 mL. Ether (12 mL) was added, and the mixture stored at −20 °C overnight to complete precipitation of the product. The mother liquor was decanted and the product dried *in vacuo* to yield a white powder. Yield: 0.17 g (75%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.4–6.8 (m, 26H, ArH + MesH + HC=CH), 2.40 (s, 6H, Mes–CH_3), 2.32 (m, 2H, PCH_2), 2.21 (s, 6H, Mes–CH_3), 2.03 (m, 2H, PCH_2), 1.75 (br m, 2H, $PCH_2CH_2CH_2P$), 1.74 (s, 6H, Mes–CH_3), 0.00 (t, 3H, Pd–CH_3, J = 6.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 13.8 (J = 51.1 Hz), −6.1 (J = 51.1 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 182.42 (dd, J_{CP} = 132.8 Hz, J_{CP} = 13.7 Hz, N*C*N), 139.9 (s), 136.2 (s), 135.9 (s), 135.5 (s), 135.0 (s), 133.9 (s), 133.5 (d, J = 10.3 Hz), 133.3 (d, J = 8.6 Hz), 131.1 (d, J = 18.8 Hz), 130.4 (s), 130.2 (s), 129.6 (d, J = 2.9 Hz), 129.1 (t, J = 10.3 Hz), 125.2 (d, J = 3.4 Hz), 28.26 (d, J = 22.9 Hz), 25.28 (dd, J = 26.4 Hz, J = 9.2 Hz), 21.40 (d, J = 1.2 Hz), 19.80 (s), 19.66 (s), 19.48 (s), 17.48 (s), 9.16 (d, J = 85.3 Hz, Pd–CH_3). Anal. Calc. for $C_{49}H_{53}N_2P_2PdBF_4$: C, 63.62; H, 5.77; N, 3.03. Found: C, 63.51; H, 5.55; N, 2.92. MS (LSI-MS) *m/z* (relative intensity): 837.4 (12, M$^+$), 717.4 (16), 319.2 (100, ylidene+CH_3).

[Pd(IDipp)Me(dppp)]BF_4 (3d)

To a 0 °C solution of [Pd(IDipp)Me(μ-Cl)]$_2$ (0.0962 g, 0.0882 mmol) in DCM (8 mL) was added dppp (0.0732 g, 0.177 mmol) in DCM (2 mL). The phosphine was rinsed over with DCM (2 mL), and the reaction mixture stirred at 0 °C for 25 min. After this time the clear solution was transferred into a cold suspension of $AgBF_4$ (0.035 g, 0.180 mmol) in DCM (3 mL). After stirring for 2.5 h, the mixture was filtered through Celite® and the volatiles concentrated *in vacuo* to approx. 1 mL. Ether (10 mL) was added, and the mixture stored at −20 °C overnight to complete precipitation of the product. The mother liquor was decanted and the product dried *in vacuo* to yield a white powder. Yield: 0.13 g (72%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.6–7.0 (m, 26H, ArH + DippH + HC=CH), 3.21 (quintet, 2H, J = 7.7 Hz), 2.65 (quintet, 2H, J = 7.7 Hz), 2.40 (q, 2H, J = 6.6 Hz), 2.01 (m, 2H, PCH_2), 1.80 (br m, 2H, $PCH_2CH_2CH_2P$), 1.14 (d, 6H, J = 6.7 Hz, $(CH_3)_2CH$), 1.06 (d, 6H, J = 6.7 Hz, $(CH_3)_2CH$), 0.95 (d, 6H, J = 6.7 Hz, $(CH_3)_2CH$), 0.41 (d, 6H, J = 6.6 Hz, $(CH_3)_2CH$), −0.04 (dd, 3H, J = 7.8 Hz, J = 6.5 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 15.1 (J = 47.7 Hz), −9.2 (J = 47.7 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 186.0 (dd, J = 132.8 Hz, J = 13.2 Hz), 147.5 (s), 145.6 (s), 136.1 (s), 133.7 (s), 133.6 (s), 133.4 (s), 132.3 (s), 131.9 (s), 131.5 (d, J = 9.1 Hz), 131.3 (s), 129.9 (s), 129.5 (d, J = 9.2 Hz), 129.3 (s), 129.1 (d, J = 10.3 Hz), 127.0 (s), 125.4 (s), 124.9 (s), 29.4 (s), 26.77 (d, J = 8.6 Hz), 24.41 (dd,

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J = 26.4 Hz, J = 10.0 Hz), 22.58 (s), 21.84 (s), 18.67 (s), 8.62 (d, J = 83.0 Hz, Pd–CH_3). Anal. Calc. for $C_{55}H_{65}N_2P_2PdBF_4$: C, 65.45; H, 6.49; N, 2.76. Found: C, 65.66; H, 6.36; N, 2.83. MS (LSI-MS) m/z (relative intensity): 921.7 (20, M^+), 721.6 (16), 403.4 (100, ylidene + CH_3).

Reaction of 3a with 4-bromoacetophenone

A CD_3CN solution of **3a** (0.0402 g, 0.0561 mmol) and 4-bromoacetophenone (0.0552 g, 0.277 mmol) was made up in an NMR tube fitted with a Young's tap. This solution was heated to 65 °C overnight. After this time, the reaction mixture was chromatographed on silica gel using $CHCl_3$–CH_3CN (20 : 1) as eluent. The fractions containing a product with R_f = 0.15 were combined and concentrated *in vacuo*. The residue was taken up in CD_3CN, which caused large diamond-shaped crystals of (4-acetylphenyl)PdBr(dppp) to form. These were collected and dried *in vacuo*. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.85–7.78 (m, 4H), 7.50–7.48 (m, 6H), 7.36–7.29 (m, 6H), 7.20–7.04 (m, 8H), 2.64–2.55 (m, 2H, PCH_2), 2.47–2.40 (m, 2H, PCH_2), 2.35 (s, 3H, $C(O)CH_3$), 1.95–1.76 (br m, 2H, $PCH_2CH_2CH_2P$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 15.92 (d, J = 51 Hz), −8.01 (d, J = 51 Hz). Anal. Calc. for $C_{37}H_{33}P_2PdBrO$: C, 59.90; H, 4.48. Found: C, 59.71, H, 4.69. MS (LSI-MS) m/z (relative intensity): 719.1 (5, M + H^+), 637.2 (25, M^+ − Br), 599.0 (33, M^+ − PhC(O)CH_3), 518.1 (68, M^+ − Br-PhC(O)CH_3), 391.3 (100). HR-MS for $C_{35}H_{34}OBr^{104}PdP_2$ (M + H): calc, 715.03085; obsd, 715.01510.

Structure determination

Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans, $2\theta_{max}$ = 75°; monochromatic Mo-Kα radiation, λ = 0.71073 Å; T *ca.* 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction, N_o with $F > 4\sigma(F)$ being employed in the full matrix least squares refinements on $|F|$; anisotropic displacement parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ estimates. Conventional residuals R, R_w on $|F|$ are cited at convergence (reflection weights: $(\sigma^2(F) + 0.00n_wF)^2)^{-1}$. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[38] Pertinent results are presented in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Crystal/refinement data 2a·Et$_2$O. $C_{38}H_{73}BF_4OP_2Pd$, M = 829.3. Monoclinic, space group $P2_1/c$ (C^5_{2h}, No 14), a = 11.7468(7), b = 12.3711(8), c = 28.598(2) Å, β = 94.917(1)°, V = 4141 Å^3. D_c (Z = 4) = 1.33$_0$ g cm^{-3}. μ(Mo) = 0.57 mm^{-1}; specimen: 0.21 × 0.20 × 0.16 mm, $T_{min/max}$ = 0.89. N_t = 82 879, N = 21 630 (R_{int} = 0.045), N_o = 15400; R = 0.045, R_w = 0.065 (n_w = 2); S = 1.06. $|\Delta\rho_{max}|$ = 1.1 e Å^{-3}.

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