Organopalladium(IV) Chemistry: Oxidative Addition of Organohalides to Dimethylpalladium(II) Complexes to form Ethyl, σ-Benzyl, and σ-Allylpalladium(IV) Complexes

Peter K. Byers and Allan J. Canty*

Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia 7001

The first examples of ethyl, σ-benzyl, and σ-allylpalladium(IV) complexes are formed on oxidative addition of organohalides to $PdMe_2$\{(pyridin-2-yl)bis(*N*-methylimidazol-2-yl)methane\} [$PdMe_2$\{(py)$(mim)_2$CH\}]; the complexes [*fac*-$PdRMe_2$\{(py)$(mim)_2$CH-*N*,*N*′,*N*″\}]X (RX = EtI, $PhCH_2Br$, CH_2=$CHCH_2Br$) are stable at ambient temperature, with the cations present as two isomers, and benzyl bromide also forms the neutral complex *fac*-$Pd(CH_2Ph)Me_2$(bipy)Br on oxidative addition to $PdMe_2$(2,2′-bipyridyl), but EtI and CH_2=$CHCH_2Br$ form transient Pd^{IV} species, detectable by ^1H n.m.r. spectroscopy, prior to reductive elimination reactions.

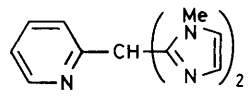
Although organoplatinum(IV) chemistry has developed steadily following the report of $[PtMe_3(\mu_3\text{-}I)]_4$ in 1907,[1] aryl- and alkyl-palladium(IV) compounds are limited to mono- and bis-pentafluorophenylpalladium(IV) complexes,[2] and recently reported trimethylpalladium(IV) complexes,[3—5] respectively. The $Pd^{IV}Me_3$ complexes, formed by oxidative addition of iodomethane to $Pd^{II}Me_2$ complexes, undergo reductive elimination in solution to form $Pd^{II}Me$ complexes and ethane, except for some cationic species involving tripodal nitrogen donor ligands, *e.g.* [*fac*-$PdMe_3$\{tris(pyridin-2-yl)methane\}]I.[4] In view of this we have attempted to expand organopalladium(IV) chemistry *via* synthesis of cationic complexes,

resulting in isolation of the first complexes containing ethyl, benzyl, and allyl groups, and thus demonstrating potential for development of an extensive organometallic chemistry of palladium(IV).

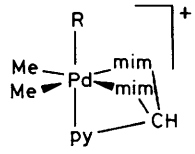
The stability of cations $[PdMe_3L]^+$ increases with increasing donor ability of the ligand,[4] and thus to maximize opportunities for isolation of $Pd^{IV}RMe_2$ complexes the new ligand (pyridin-2-yl)bis(*N*-methylimidazol-2-yl)methane $[(py)(mim)_2CH]$ was synthesized,† since the tripods studied to date contain pyridin-2-yl groups only $[(py)_3CH]$ or at least two weakly basic pyrazol-1-yl (pz) groups[4] with the order of donor ability of the groups mim > py > pz,[8] and the presence of two donor types is expected to facilitate interpretation of n.m.r. spectra of reaction products.

Experiments at ambient temperature, with reactions followed by ^1H n.m.r. spectroscopy, indicated immediate formation of $[fac\text{-}PdRMe_2\{(py)(mim)_2CH\}]^+$ on addition of excess of organohalide (RX = EtI, $PhCH_2Br$, $CH_2{=}CH\text{-}CH_2Br$) to $PdMe_2\{(py)(mim)_2CH\}$ in $(CD_3)_2CO$, without subsequent reductive elimination, and the complexes were then prepared in high yield from the substrate $[PdMe_2(pyridazine)]_n$[5] in acetone by direct addition of $[(py)(mim)_2CH]$ followed by RX and addition of hexane; a $Pd^{IV}Me_3$ complex was isolated (oxidative addition of MeI) for comparison of spectra.‡ The complexes are the most stable organopalladium(IV) complexes isolated to date, with no reductive elimination being detected on heating to *ca.* 60 °C in $(CD_3)_2CO$.

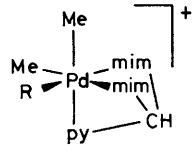
For the isolated cations $[fac\text{-}PdRMe_2\{(py)(mim)_2CH\}]^+$ in $CDCl_3$, two isomers, (**A**) and (**B**), are present in a similar ratio to that observed for the oxidative addition in $(CD_3)_2CO$ (as followed by n.m.r.): *ca.* 1 : 1 ratio for the benzyl complex, *ca.* 5 : 3 for the ethyl complex, and *ca.* 6 : 5 for the allyl complex.



$(py)(mim)_2CH$



(A)



(B)

Structures of (**A**) and (**B**) are readily assigned directly from spectra, in particular integration of ligand, Me, and R resonances, and the presence of inequivalent $PdCH_2$ protons for the ethyl, benzyl, and allyl complexes of isomer (**B**) owing to chirality at the palladium centre in (**B**), *e.g.* as shown in Figure 1 for the allyl complex.

In contrast to $PdMe_2\{(py)(mim)_2CH\}$, the bidentate ligand complex $PdMe_2$(2,2′-bipyridyl) on reaction with EtI and $CH_2{=}CHCH_2Br$ gave spectra showing the presence of only trace amounts (decreasing with time) of a Pd^{IV} intermediate with formation of reductive elimination products. The ethyl iodide intermediate formed ethane, propane, and PdR(bipy)I (R = Me, Et), and the allyl bromide intermediate formed ethane, PdMe(bipy)Br, and an insoluble solid of analytical composition $Pd(C_3H_5)(bipy)Br$.§ At −10 °C EtI did not react with $PdMe_2$(bipy), but $CH_2{=}CHCH_2Br$ gave a spectrum showing a high yield of $Pd(CH_2CH{=}CH_2)Me_2$(bipy)Br, *e.g.* δ 5.28 (m, CH, partly obscured by excess allyl bromide), 4.47 (dd, CH_{trans}, ^3J 16.88, ^2J 2.37 Hz), 4.37 (dd, CH_{cis}, ^3J 9.83, ^2J 2.38 Hz), 2.50 (dd, $PdCH_2$, ^3J 8.70, ^4J 0.98 Hz), 1.75 (s, $PdMe_2$) for the $Pd^{IV}(CH_2CH{=}CH_2)Me_2$ group, together with reductive elimination products, but the complex could not be isolated. However, benzyl bromide gave the isolable complex *fac*-$Pd(CH_2Ph)Me_2$(bipy)Br, the first organopalladium(IV) bromo-complex, which is more stable than the first reported neutral complex *fac*-$PdMe_3$(bipy)I,[3] undergoing reductive elimination over *ca.* 120 min at ambient temperature in $CDCl_3$ compared with *ca.* 30 min for the latter.

These results indicate that it is now possible to develop a wide-ranging organometallic chemistry of palladium(IV) to complement the well established chemistry of this oxidation state for platinum, and that tripodal nitrogen donor ligands, in particular $[(py)(mim)_2CH]$, may have an important role in developing high oxidation state organometallic chemistry. Aspects of the reactivity of organopalladium(II) and organopalladium(IV) compounds reported here are relevant to the

† Synthesised by reduction of $(mim)_2CO$ to $(mim)_2CH_2$ [as for $(py)_2CO$ to $(py)_2CH_2$],[6] followed by reaction with PhLi and 2-bromopyridine [as for $(py)_2CH_2$ to $(py)_3CH$],[7] m.p. 137—138 °C, δ (Me_4Si, in $CDCl_3$): 8.56 [1H, ddd, $H(6)_{py}$, ^3J 4.90, ^4J 1.83, ^5J 0.93 Hz], 7.69 [1H, ddd, $H(4)_{py}$, $^3J_{4,5}$ ~$^3J_{3,4}$ ~7.66, ^4J 1.84 Hz], *ca.* 7.26 [$H(3)_{py}$, (obscured by $CHCl_3$)], 7.20 [1H, ddd, $H(5)_{py}$, $^3J_{5,6}$ 4.88, $^3J_{4,5}$ 7.34, ^4J 1.11 Hz], 7.00 [2H, d] and 6.87 [2H, d, $H(4,5)_{mim}$, $^3J_{4,5}$ 1.23 Hz], 5.95 [1H, s, CH], 3.47 [3H, s, NCH_3].

‡ The Pd^{IV} complexes (formed in 58—76% yield) and $PdMe_2\{(py)(mim)_2CH\}$ {prepared from $[PdMe_2(pyridazine)]_n$[5] and the ligand in acetone, with addition of hexane, 76% yield} have satisfactory microanalyses (C, H, N) and ^1H n.m.r. spectra (300 MHz), and $Pd(CH_2Ph)Me_2$(bipy)Br has molecular weight 527 (osmometric in chloroform at 25 °C, calc. 510). ^1H N.m.r. spectra for the $Pd^{II}Me_2$ and $Pd^{IV}RMe_2$ groups in the isolated complexes are given, with relative intensities appropriate for the isomer ratios, and ligand resonances as expected, including two environments in the Pd^{IV} cations that form isomers.

$PdMe_2\{(py)(mim)_2CH\}$: δ [Me_4Si, in $(CD_3)_2CO$] 0.03 [6H, s, PdMe].

$[PdMe_3\{(py)(mim)_2CH\}]I$: δ[$Me_4Si$, in $CDCl_3$] 1.55 [3H, s, Me], 1.33 [6H, s, Me].

$[PdEtMe_2\{(py)(mim)_2CH\}]I$: 2.56 [2H, q, $CH_2(A)$, ^3J 7.53 Hz], 2.32 [1H, m, $CHH(B)$] and 2.28 [1H, m, $CHH(B)$, ^2J ~^3J 7.57 Hz], 1.55 [3H, s, PdMe(B)], 1.30 [6H, s, PdMe(A)], 1.29 [3H, s, PdMe(B)], 1.09 [3H, t, $CH_3(A)$], 1.02 [3H, t, $CH_3(B)$].

$[Pd(CH_2Ph)Me_2\{(py)(mim)_2CH\}]Br$: *ca.* 7.2—6.8 [5H, m, Ph(A,B)], 3.67 [2H, s, $CH_2(A)$], 3.57 [1H, d, $CHH(B)$] and 3.29 [1H, d, $CHH(B)$, ^2J 8.36 Hz], 1.66 [3H, s, PdMe(B)], 1.46 [6H, s, PdMe(A)], 1.44 [3H, s, PdMe(B)].

$[Pd(CH_2CH{=}CH_2)Me_2\{(py)(mim)_2CH\}]Br$: 5.84 [1H, m, CH=(A,B)], 5.07 [1H, m, CHH *cis* to CH=(A,B)], 5.25 [1H, m, CHH *trans* to CH=(A,B)], 3.16 [2H, d, $PdCH_2(A)$, ^3J 8.16 Hz], 2.93 [2H, m, $PdCH_2(B)$], 1.62 [3H, s, PdMe(B)], 1.40 [6H, s, PdMe(A)], 1.38 [3H, s, PdMe(B)].

$Pd(CH_2Ph)Me_2$(bipy)Br: 6.73 [1H, t, H(4)], 6.60 [2H, t, H(3,5)], 6.40 [2H, d, H(2,6)], 3.17 [2H, s, $PdCH_2$], 1.98 [6H, s, PdMe].

§ The complexes PdMe(bipy)X (X = Br,[5] I[3,9]) have been synthesized independently from $Pd^{II}Me$ substrates, and their spectra reported. The complex $Pd(C_3H_5)$(bipy)Br is too insoluble for n.m.r. characterization, and probably has the structure $[(\eta^3\text{-}C_3H_5)Pd(bipy)]^+Br^-$, in view of the proposal that the insoluble chloro analogue has this structure,[10] and spectroscopic and structural studies of related complexes, *e.g.* the η^3-2-methylpropenyl complex $[(\eta^3\text{-}C_4H_7)Pd(pyridine)_2]^+BF_4^-$,[11] and the tetramethylethylenediamine complex $[(\eta^3\text{-}C_3H_5)Pd(tmeda)]^+[(\eta^3\text{-}C_3H_5)PdCl_2]^-$.[12] The other expected reductive elimination product from the allyl bromide reaction, but-1-ene, was not detected, owing to the complexity of the n.m.r. spectrum in the high field region and the expected low yield of but-1-ene [*ca.* 20% of reductive elimination product, estimated from ethane : PdMe(bipy)Br relative integration].

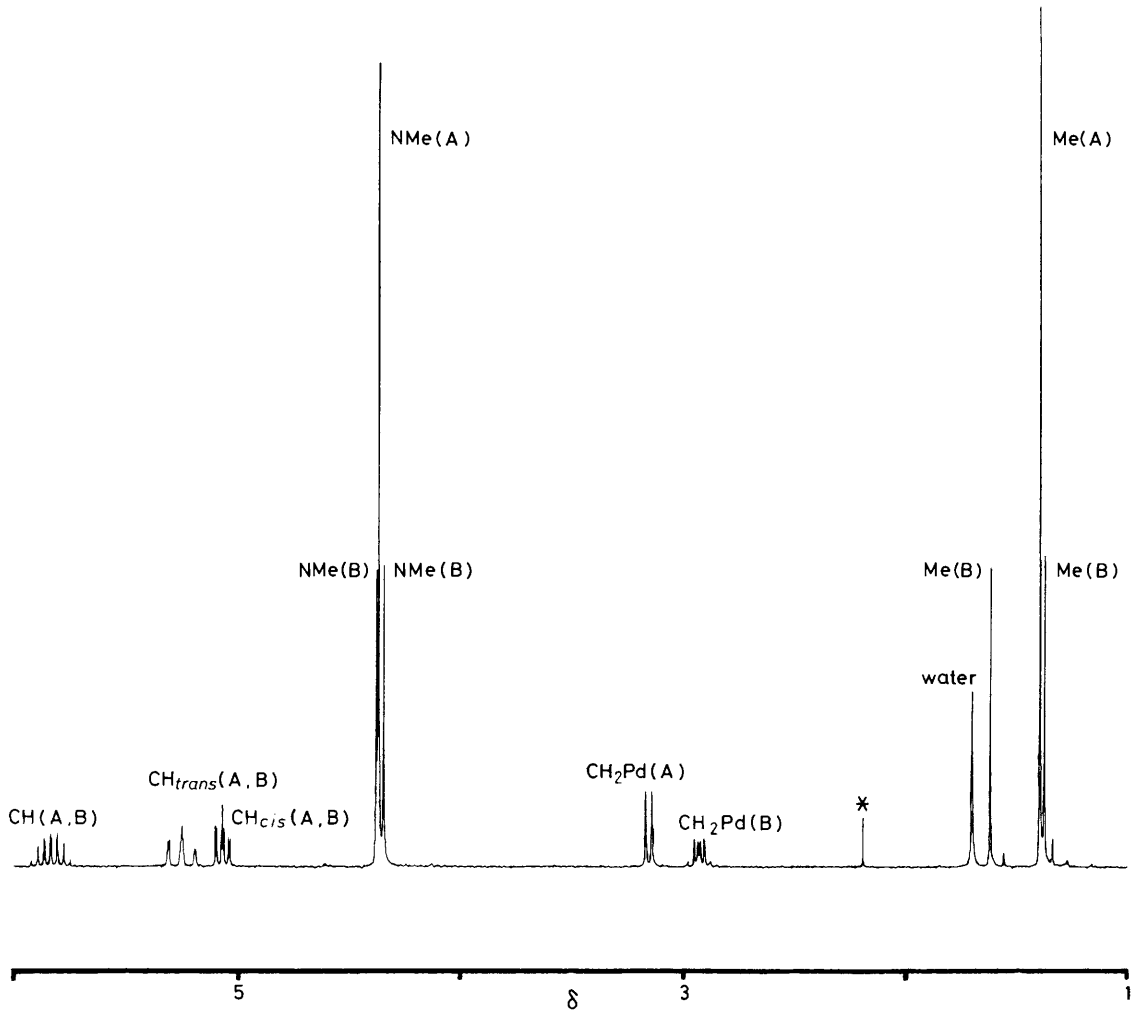


Figure 1. ^{1}H n.m.r. spectrum of [*fac*-Pd($CH_2CH{=}CH_2$)Me_2{(py)(mim)$_2$CH}]Br in $CDCl_3$, in the region showing the Pd^{IV}-($CH_2CH{=}CH_{cis}CH_{trans}$)$Me_2$ groups and methyl groups of the *N*-methylimidazol-2-yl rings, with assignment as isomer (**A**) or (**B**) indicated; H_{cis} and H_{trans} refer to the orientation with respect to the =CH proton; * is an impurity in the solvent.

possible role of Pd^{IV} in organic synthesis and catalysis,[13,14] in particular the feasibility of neutral intermediates 'PdR'R_2-L_2X' in some coupling reaction systems to form R'R and R_2.[14]

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