Journal of Organometallic Chemistry, 390 (1990) 399–407
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20800

Synthesis and decomposition of neutral palladium(IV) complexes containing *fac*-$PdMe_2R$ groups, including reductive elimination by η^1-propenylpalladium(IV) complexes to form η^3-propenylpalladium(II) species

Peter K. Byers, Allan J. Canty *, Peter R. Traill and Andrew A. Watson

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

(Received January 29th, 1990)

Abstract

Oxidative addition of ethyl iodide to $PdMe_2$(2,2′-bipyridyl) in $(CD_3)_2CO$ gives the unstable "$PdIMe_2Et$(bpy)", which undergoes reductive elimination to form PdIR(bpy) (R = Me, Et), ethane, and propane. Ethene and palladium metal are also formed, and are attributed to decomposition of PdIEt(bpy) via β-elimination. Similar results are obtained with n-propyl iodide, although a palladium(IV) intermediate was not detected, but CH_2=$CHCH_2X$ (X = Br, I) and PhCH=$CHCH_2Br$ give isolable complexes *fac*-$PdXMe_2(CH_2CH{=}CHR)(L_2)$ (R = H, Ph; L_2 = bpy, phen). The propenyl complexes decompose at ambient temperature to form ethane, a trace of $PdXMe(L_2)$, and mixtures of $[Pd(\eta^3\text{-}C_3H_5)(L_2)]X$ and $[Pd(\eta^3\text{-}C_3H_5)(L_2)]$-$[Pd(\eta^3\text{-}C_3H_5)X_2]$; for *fac*-$PdBrMe_2(CH_2CH{=}CH_2)$(bpy) the major palladium(II) product is $[Pd(\eta^3\text{-}C_3H_5)$(bpy)]Br.

Introduction

Hydrocarbylpalladium(IV) chemistry involving bidentate nitrogen donor ligands has developed recently [1], following the earlier reports of pentafluorophenylpalladium(IV) complexes [2], and has included the X-ray crystallographic characterisation of 2,2′-bipyridyl and 1,10-phenanthroline complexes containing the *fac*-PdC_3 group, $PdIMe_3$(bpy) [1,3] and $PdBrMe_2(CH_2$-*p*-$C_6H_4Br)$(phen) [4]. Tripodal nitrogen donor ligands (L_3) have given a wider range of cationic complexes, including allyl and higher alkyl complexes, $[PdMe_2R(L_3\text{-}N,N',N'')]X$ [5,6]. We report here an investigation of the reactivity of 2,2′-bipyridyl and 1,10-phenanthroline complexes, $PdMe_2(L_2)$, toward oxidative addition of ethyl, n-propyl, and allyl halides, resulting in ^1H NMR detection of the unstable neutral complex "$PdIMe_2Et$(bpy)" in $(CD_3)_2CO$ and isolation of the first neutral allyl complexes. A preliminary account of part of this work has appeared [5].

Results and discussion

Reaction of alkyl halides with $PdMe_2(L_2)$

Addition of excess ethyl iodide to $PdMe_2(bpy)$ in $(CD_3)_2CO$ gave ^1H NMR spectra showing the presence of PdIMe(bpy), PdIEt(bpy), ethane, propane, and ethene; resonances of an initially formed intermediate (designated 3_{IV}–6_{IV} in Fig. 1) decreased as the reaction proceeded. The assignment of spectra is straightforward when comparison is made with the reported spectrum of PdIMe(bpy) [7] and spectra for solutions of the hydrocarbons. The resonances assigned to dissolved gases disappear when the solution is purged with nitrogen gas. The low intensity bpy resonances of the intermediate occur downfield from $PdMe_2(bpy)$, and are very similar to resonances for $PdIMe_3(bipy)$ [3], leading to assignment of the intermediate as "$PdIMe_2Et(bipy)$".

$$PdMe_2(bpy) + EtI \rightarrow \text{"}PdIMe_2Et(bpy)\text{"} \rightarrow PdIMe(bpy) + MeEt + PdIEt(bpy) + MeMe \quad (1)$$

The singlet for ethene becomes apparent towards the end of the reaction, at the time of deposition of palladium metal, indicating that ethene probably arises by β-elimination from PdIEt(bpy) rather than directly from the palladium(IV) intermediate. NMR experiments at lower temperature do not improve the yield of the palladium(IV) intermediate, as the oxidative addition reaction is too slow and reductive elimination from the intermediate is facile.

Reaction of $PdMe_2(phen)$ with ethyl iodide is also slow at ambient temperature, giving products analogous to those from $PdMe_2(bpy)$, except that a palladium(IV) intermediate was not detected. Ethyl bromide was essentially unreactive towards $PdMe_2(L_2)$ at ambient temperature, and an increase in the reaction temperature resulted in general decomposition.

A palladium(IV) intermediate could also not be detected in the slow reaction of $PdMe_2(bpy)$ with n-propyl iodide, although the reductive elimination products (PdIMe(bpy), PdIPr(bpy), ethane, propane) were readily assigned. Propene and palladium metal formed late in the reaction. ^1H NMR studies of the reaction of $PdMe_2(phen)$ with Pr^nI were not interpretable because decomposition gave rise to poor spectra, and only ethane and PdIR(phen) were identified. The alkyl group(s) of PdIR(phen) could be not assigned owing to complexity of the spectra, e.g. a resonance for residual Pr^nI would obscure δ(PdMe) for PdIMe(phen) [7].

Slower oxidative addition of ethyl and n-propyl halides than of methyl iodide [1,3] is consistent with operation of the classic S_N2 mechanism for oxidative addition, which has been established for the reaction of methyl iodide with $MMe_2(L_2)$ (M = Pd, Pt) by kinetic studies [8,9] and supported by ^1H NMR detection of cation intermediates for both palladium [3,4] and platinum [10]. Ethyl iodide reacts 1000 times more slowly than methyl iodide with $PtMe_2(phen)$ [11], and a similar relationship is expected to apply for $PdMe_2(L_2)$.

Reaction of allyl halides with $PdMe_2(L_2)$

The allyl halides $CH_2{=}CHCH_2X$ (X = I, Br) and $PhCH{=}CHCH_2Br$ are more reactive than ethyl and n-propyl halides toward $PdMe_2(L_2)$, allowing the synthesis and isolation of the palladium(IV) complexes $PdXMe_2(CH_2CH{=}CHR)(L_2)$ at 0 °C.

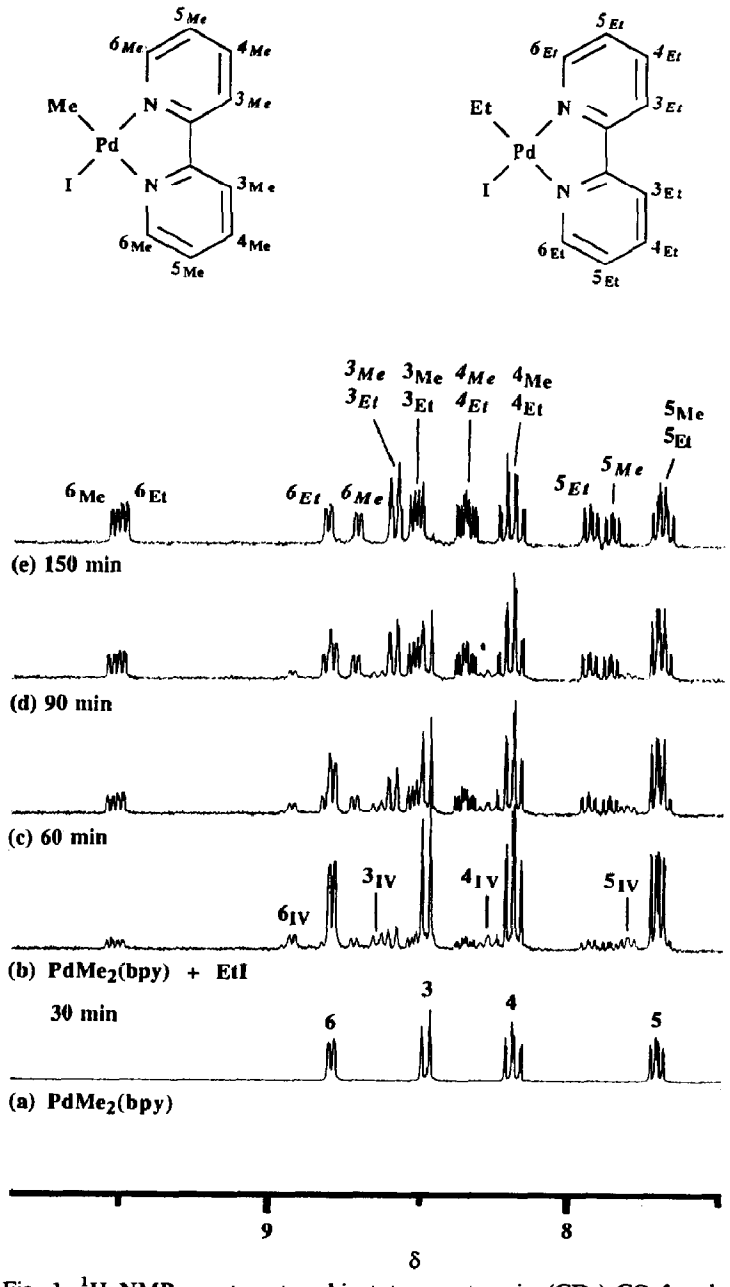
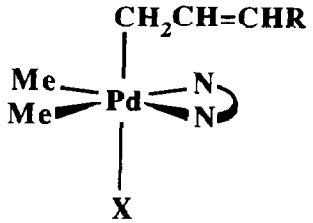


Fig. 1. ^{1}H NMR spectra at ambient temperature in $(CD_3)_2CO$ for the 2,2′-bipyridyl region of (a) $PdMe_2(bpy)$, (b) 30 min after addition of ethyl iodide showing resonances for "$PdIMe_2Et(bpy)$" and PdIR(bpy) (R = Me, Et), and (c)–(e), at later times, illustrating increased formation of PdIR(bpy) and loss of $PdIMe_2Et(bpy)$. At higher field: ethene, δ 5.38; ethane, 0.84; propane, 1.30q (^3J 7.4 Hz) and 0.88 (overlapping $Pd^{II}Et$ triplet); $Pd^{II}Et$, 2.11 (overlapping with acetone) and 0.91t (^3J 7.4 Hz); $Pd^{II}Me$, 0.83. Resonances of the $Pd^{IV}Me_2Et$ group not detected, perhaps owing to overlap with other resonances, in particular acetone, water, and ethyl iodide.

At 0 °C the complexes give simple ^{1}H NMR spectra consistent with *trans* oxidative addition (Table 1); e.g. the spectra show single PdMe (singlet) and $PdCH_2CH{=}CHR$ (doublet) resonances.



Decomposition of $PdXMe_2(CH_2CH{=}CH_2)(L_2)$ in acetone and the synthesis of η^3-allylpalladium(II) complexes

The cinnamyl complexes are stable at ambient temperature, but the propenyl complexes are unstable in both the solid state and in solution. In NMR experiments they form orange/brown solids within several minutes at ambient temperature. Spectra obtained initially show only $PdXMe_2(CH_2CH{=}CH_2)(L_2)$, but during precipitation they indicate the formation of ethane and a minor amount of $PdXMe(L_2)$, as the resonances of $PdXMe_2(CH_2CH{=}CH_2)(L_2)$ decrease in intensity.

Reaction of $CH_2{=}CHCH_2Br$ with $PdMe_2(bpy)$ in acetone on a preparative scale at ambient temperature, at lower concentrations than in the NMR experiments, gave a white solid; the filtrate gave a small amount of an orange solid. The white solid has a microanalysis consistent with "$PdBr(C_3H_5)(bpy)$", and it has a very low solubility in acetone, chloroform, and acetonitrile, but it is soluble in water and methanol, as noted for the white chloro complex $[Pd(\eta^3\text{-}C_3H_5)(bpy)]Cl$ [12]. A ^1H NMR spectrum in CD_3OD is consistent with the presence of $[Pd(\eta^3\text{-}C_3H_5)(bpy)]^+$ (Table 1), and thus the white solid is formulated as $[Pd(\eta^3\text{-}C_3H_5)(bpy)]Br$. A series of complexes of this type were prepared, by a procedure similar to that reported for $[Pd(\eta^3\text{-}C_3H_5)(bpy)]Cl$ [12] (eq. 2), for comparison of NMR spectra (Table 1) with those of products of decomposition of the palladium(IV) complexes.

$$\left[Pd(\eta^3\text{-}C_3H_5)X\right]_2 + 2L_2 \rightarrow 2\left[Pd(\eta^3\text{-}C_3H_5)(L_2)\right]X \qquad (2)$$

The orange solid has a very low solubility in CD_3OD but dissolves sufficiently in CD_3CN to show two $Pd(\eta^3\text{-}C_3H_5)$ resonances and a trace of PdBrMe(bpy). The allyl resonances are readily attributed to $[Pd(\eta^3\text{-}C_3H_5)(bpy)]^+$ and $[Pd(\eta^3\text{-}C_3H_5)Br_2]^-$ by comparison with a spectrum of $[Pd(\eta^3\text{-}C_3H_5)(bpy)][Pd(\eta^3\text{-}C_3H_5)Br_2]$, obtained as in eq. 3.

$$\left[Pd(\eta^3\text{-}C_3H_5)X\right]_2 + L_2 \rightarrow \left[Pd(\eta^3\text{-}C_3H_5)(L_2)\right]\left[Pd(\eta^3\text{-}C_3H_5)X_2\right] \qquad (3)$$

The anion resonances appear upfield from that for the cation, as observed for the tetramethylethylenediamine complex $[Pd(\eta^3\text{-butenyl})(tmeda)][Pd(\eta^3\text{-butenyl})Cl_2]$ [13], and similar η^3-propenyl complexes of 2,2-bis(pyrazol-1-yl)propane and tris(pyrazol-1-yl)methane [6]. Although $[Pd(\eta^3\text{-}C_3H_5)(bpy)]Br$ is insoluble in CD_3CN, the tetrafluoroborate salt, obtained readily by addition of $AgBF_4$ to $[Pd(\eta^3\text{-}C_3H_5)(bpy)]Br$, is soluble, and this allows confirmation of assignment of resonances for the cation and anion in the double salts. Variable temperature ^1H NMR spectra (0–60 °C) of the double salts in CD_3CN indicate presence of intramolecular exchange of *syn*- and *anti*-protons, with broadening of resonances at higher temperatures observed (Table 1, footnotes *c–e*). The central allyl resonances remain separate, and thus exchange of allyl groups between cation and anion, as reported for the tmeda [13], $(pz)_2CMe_2$ and $(pz)_3CH$ complexes [6], may not occur for these complexes.

Table 1

Selected ^{1}H NMR data for η^1-allylpalladium(IV) and η^3-allylpalladium(II) complexes

Palladium(IV) complexes in $CDCl_3$ at 0 °C	δ(PdMe)	δ($PdCH_2CH$=CHR)		
		CH	CH_2 [a]	CHR [a]
$PdIMe_2(CH_2CH=CH_2)$(bpy)	1.95	5.18m	2.66d (8.7 Hz)	4.48m
$PdBrMe_2(CH_2CH=CH_2)$(bpy)	1.87	5.22m	2.57d (8.4 Hz)	4.50d (16.8 Hz, *trans* to CH)
				4.42d (9.3 Hz, *cis* to CH)
$PdBrMe_2(CH_2CH=CH_2)$(phen)	2.01	5.08m	2.65d (8.8 Hz)	4.33d (15.9 Hz, *trans* to CH)
				4.20d (11.1 Hz, *cis* to CH)
$PdIMe_2(CH_2CH=CH_2)$(phen)	2.08	5.01m	2.73d (8.6 Hz)	4.30d (16.2 Hz, *trans* to CH)
				4.21d (10.1 Hz, *cis* to CH)
$PdBrMe_2(CH_2CH=CHPh)$(bpy)	1.92		2.79d (7.6 Hz)	5.65m (CH and CHPh)
$PdBrMe_2(CH_2CH=CHPh)$(phen)	2.06	5.53m	2.86d (8.7 Hz)	5.35d (15.6 Hz, *trans* to CH)

Palladium(II) complexes	δ($Pd[CH_3(CH_{syn}H_{anti})_2]$)		
	CH	CH_{syn} [a]	CH_{anti} [a]
$[Pd(\eta^3\text{-}C_3H_5)(L_2)]X$ in CD_3OD			
$[Pd(\eta^3\text{-}C_3H_5)$(bpy)]X, X = Br, I [g]	6.10m	4.38d (7.0 Hz)	3.61d (12.5 Hz)
$[Pd(\eta^3\text{-}C_3H_5)$(phen)]X, X = Br at 20 °C	6.17m	4.55d (7.0 Hz)	3.67d (12.6 Hz)
X = I at 0 °C [b]	6.16b	4.54b	3.67d, b
$[Pd(\eta^3\text{-}C_3H_5)(bpy)]BF_4$ and $[Pd(\eta^3\text{-}C_3H_5)(L_2)][Pd(\eta^3\text{-}C_3h_5)X_2]$ in CD_3CN			
$[Pd(\eta^3\text{-}C_3H_5)$(bpy)]$^+$ at 0 °C [i]	6.07m [c]	4.35d (7.1 Hz) [c]	3.60d (12.7 Hz) [c]
$[Pd(\eta^3\text{-}C_3H_5)$(phen)]$^+$ [j], X = Br at 0 °C	6.13m	4.55d (6.9 Hz) [d]	3.70d (12.4 Hz) [d]
X = I at 20 °C [f]	6.07m	[f]	~ 3.7–3.8vb
$[Pd(\eta^3\text{-}C_3H_5)Br_2]^-$ at 0 °C	5.47b	4.02b [e]	2.96d, b [e]
$[Pd(\eta^3\text{-}C_3H_5)I_2]^-$ at 20 °C	5.29b	4.25d, b [e]	2.97d, b [c]

[a] ^3J(HH) in parentheses. [b] CH_2 resonances are broad at 20 °C, precipitation occurring at 0 °C. [c] Broadened at 20 °C for X = Br, I, in particular for X = I. [d] Broadened at 20 °C. [e] Further broadened at 60 °C. [f] Insufficiently soluble at 0 °C, CH_{syn} very broad and beneath CH_{syn} of anion. [g] bpy: 8.93(m, H(6)), 8.55 (d, H(3)), 8.29 ('td', H(4)), 7.73 (m, H(5)). [h] phen: 9.18 (d, H(2,9)), 8.78 (d, H(4,7)), 8.10 (s, H(5,6)), 7.99 (dd, H(3,8)). [i] bpy: 8.91 (m, H(6)), 8.46 (dd, H(3)), 8.30 ('td', H(4)), 7.74 (m, H(5)). [j] phen: 9.25 (dd, H(2,9)), 8.85 (dd, H(4,7)), 8.23 (s, H(5,6)), 8.06 (m, (3,8)).

For the ambient temperature reaction of $PdMe_2(phen)$ with $CH_2{=}CHCH_2X$ (X = Br, I), and of $PdMe_2(bpy)$ with $CH_2{=}CHCH_2I$, orange-brown precipitates formed that contained several products which could not be separated. The precipitates partially dissolve in CD_3CN to show the presence of $PdXMe(L_2)$, $[Pd(\eta^3\text{-}C_3H_5)(L_2)]^+$ and $[Pd(\eta^3\text{-}C_3H_5)X_2]^-$; relative intensities of ^1H resonances do not reveal the proportions of these components owing to low solubility. The products formed from $PdMe_2(phen)$ gave microanalyses consistent with $[Pd(\eta^3\text{-}C_3H_5)(phen)]X$. The product obtained from reaction of $PdMe_2(bpy)$ with $CH_2{=}CHCH_2I$ gave a microanalysis intermediate between those for $[Pd(\eta^3\text{-}C_3H_5)(bpy)]I$ and PdIMe(bpy), although calculated values for these complexes differ by only 3.6% in carbon. Calculated carbon and nitrogen microanalysis values for the double salts differ substantially from those for $PdXMe(L_2)$ and $[Pd(\eta^3\text{-}C_3H_5)(L_2)]X$, e.g. PdIMe(bpy) (C, 32.7; N, 6.9%), $[Pd(\eta^3\text{-}C_3H_5)(bpy)]I$ (C, 36.3; N, 6.5%), and $[Pd(\eta^3\text{-}C_3H_5)(bpy)][Pd(\eta^3\text{-}C_3H_5)I_2]$ (C, 27.3; N, 4.0%). Thus, from the microanalysis and NMR results the orange solids appear to be predominantly $[Pd(\eta^3\text{-}C_3H_5)(L_2)]X$. Attempts to separate the components were unsuccessful; e.g. $PdXMe(L_2)$ could not be satisfactorily removed by washing with chloroform without substantial removal of the η^3-allylpalladium(II) complexes.

However, for the reaction of $PdMe_2(bpy)$ with $CH_2{=}CHCH_2Br$ at ambient temperature, a pure sample of $[Pd(\eta^3\text{-}C_3H_5)(bpy)]Br$ was isolated in 79% yield, and thus, at least for this system, the reaction proceeds predominantly as in eq. 4.

$$PdMe_2(bpy) + C_3H_5X \rightarrow PdXMe_2(\eta^1\text{-}C_3H_5)(bpy) \rightarrow [Pd(\eta^3\text{-}C_3H_5)(bpy)]X + MeMe \quad (4)$$

Formation of $PdXMe(L_2)$ and $[Pd(\eta^3\text{-}C_3H_5)(L_2)][Pd(\eta^3\text{-}C_3h_5)X_2]$ as minor products of reductive elimination is expected to result in formation of butene and free L_2, respectively, but these products could not be detected in NMR spectra.

The reductive elimination behaviour observed for $PdBrMe_2(\eta^1\text{-}C_3H_5)(bpy)$ differs from that reported for the cationic tris(pyrazol-1-yl)methane complexes $[PdMe_2(\eta^1\text{-}C_3H_5)\{(pz)_3CH\}]X$ (X = Br, I) [6]. These complexes do not give simple η^3-propenyl complexes $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3CH\}]X$ but they give instead a complex ion pair from $[PdMe_2(\eta^1\text{-}C_3H_5)\}(pz)_3CH\}]Br$ (eq. 5) and $[PdI(\eta^3\text{-}C_3H_5)]_2$ from $[PdMe_2(\eta^1\text{-}C_3H_5)\{(pz)_3CH\}]I$ (eq. 6).

$$PdMe_2\{(pz)_3CH\} + C_3H_5Br \rightarrow [PdMe_2(\eta^1\text{-}C_3H_5)\{(pz)_3CH\}]Br \rightarrow \tfrac{1}{2}[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3CH\}][PdBr_2(\eta^3\text{-}C_3H_5)] + \tfrac{1}{2}(pz)_3CH + MeMe \quad (5)$$

$$PdMe_2\{(pz)_3CH\} + C_3H_5I \rightarrow [PdMe_2(\eta^1\text{-}C_3H_5)\{(pz)_3CH\}]I \rightarrow \tfrac{1}{2}[PdI(\eta^3\text{-}C_3H_5)]_2 + (pz)_3CH + MeMe \quad (6)$$

A similar overall reaction to that shown in eq. 5 occurs when propen-2-yl bromide interacts with the 2,2-bis(pyrazol-1-yl)propane complex, $PdMe_2\{(pz)_2CMe_2\}$ but a palladium(IV) intermediate could not be detected.

Experimental

The reagents $PdMe_2(bpy)$ and $PdMe_2(phen)$ [7], and $[Pd(\eta^3\text{-}C_3H_5)X]_2$ (X = I [14], Br [15]) were prepared as reported, cinnamyl bromide (Aldrich) was sublimed,

and the solvents, alkyl and allyl halides were dried and distilled. Microanalyses were performed by the Canadian Microanalytical Service, Vancouver. ^{1}H NMR spectra were recorded with a Bruker AM 300 spectrometer; chemical shifts are given in ppm relative to Me_4Si. NMR studies of the reactions of $Pd^{II}Me_2$ complexes with organic halides were carried out as described elsewhere [3]. ^{1}H NMR spectra for the $Pd^{IV}Me_2(CH_2CH{=}CHR)$ groups and the allylpalladium(II) complexes are given in Table 1, and the data below include 2,2′-bipyridyl, 1,10-phenanthroline, and phenyl group resonances for the palladium(IV) complexes.

Synthesis of palladium(IV) complexes fac-$PdXMe_2R(L_2)$

The complexes were formed on addition of the organic halide (ca. 4 mmol) to solutions of $PdMe_2(L_2)$ (ca. 3 mmol) in acetone (20 ml) at −20 °C and hexane added to assist the precipitation of $PdIMe_2(CH_2CH{=}CH_2)$(phen). The complexes were obtained in moderate yield (37–73%) as pale yellow microcrystals, except in the case of $PdBrMe_2(CH_2CH{=}CH_2)$(bipy) which was colourless, and were dried under high vacuum. All of the complexes gave satisfactory ^{1}H NMR spectra in $CDCl_3$ at 0 °C, and although $PdIMe_2(CH_2CH{=}CH_2)$(phen) gave a satisfactory microanalyses (C, H, N), the propenyl complexes are unstable at ambient temperature. The complexes $PdXMe_2(CH_2CH{=}CH_2)(L_2)$ (X = Br, L_2 = phen; X = I, Br, L_2 = bpy) gave microanalyses between those expected for the complexes and reductive elimination products.

$PdBrMe_2(CH_2CH{=}CH_2)$(bpy). δ: 8.80 (2H, d, H(6), ^3J 5.1 Hz), 8.21 (2H, d, H(3), ^3J 8.0 Hz), 7.98 (2H, 't', H(4)), 7.59 (2H, 't', H(5)).

$PdIMe_2(CH_2CH{=}CH_2)$(bpy). δ: 8.83 (2H, d, H(6), ^3J 4.9 Hz), 8.21 (2H, d, H(3), ^3J 8.1 Hz), 8.03 (2H, 't', H(4)), 7.61 (2H, 't', H(5)).

$PdBrMe_2(CH_2CH{=}CH_2)$(phen). δ: 9.14 (2H, m, H(2,9)), 8.51 (2H, d, H(4,7)), 8.00 (2H, s, H(5,6)), 7.90 (2H, m, H(3,8)).

$PdIMe_2(CH_2CH{=}CH_2)$(phen). δ: 9.16 (2H, d, H(2,9), ^3J 4.0 Hz), 8.52 (2H, d, H(4,7), ^3J 8.2 Hz), 8.01 (2H, s, H(5,6)), 7.92 (2H, dd, H(3,8), ^3J 8.1, ^4J 4.9 Hz). (Anal. Found: C, 42.2; H, 3.9; N, 5.8, $C_{17}H_{19}N_2IPd$ calcd.: C, 42.1; H, 3.9; N, 5.8%).

$PdBrMe_2(CH_2CH{=}CHPh)$(bpy). δ: 8.83 (2H, d, H(6), ^3J 4.7 Hz), 8.06 (2H, d, H(3), ^3J 8.0 Hz), 7.92 (2H, 't', H(4)), 7.54 (2H, 't', H(5)), 7.10 (3H, m, Ph(3–5)), 6.65 (2H, d, Ph(2,6), ^3J 6.4 Hz). (Anal. Found: C, 51.7; H, 4.9; N, 5.7. $C_{21}H_{24}N_2BrPd$ calcd.: C, 51.4; H, 4.9; N, 5.7%).

$PdBrMe_2(CH_2CH{=}CHPh)$(phen). δ: 9.15 (2H, d, H(2,9), ^3J 4.8 Hz), 8.38 (2H, d, H(4,7), ^3J 7.9 Hz), 7.85 (s, H(5,6)), 7.82 (m, H(3,8)), 7.02 (1H, m, Ph(4)), 6.94 (2H, m, Ph(3,5)), 6.31 (2H, d, Ph(2,6), ^3J 7.8 Hz). (Anal. Found: C, 53.6; H, 4.5; N, 5.3. $C_{23}H_{23}N_2BrPd$ calcd.: C, 53.8; H, 4.5; N, 5.4%).

Synthesis of [Pd(η^3-C_3H_5)(bpy)]Br from $PdMe_2$(bpy)

Propen-2-yl bromide (0.1 ml) was added to a solution of $PdMe_2$(bpy) (0.1 g) in acetone (50 ml) and the solution stirred for 45 min at ambient temperature. A white solid was filtered off from the yellow solution, washed with hexane, and air- and vacuum-dried (0.1 g, 79%). (Anal. Found: C, 40.3; H, 3.4; N, 7.2. $C_{13}H_{11}BrN_2Pd$ calcd.: C, 40.7; H, 3.4; N, 7.3%).

Synthesis of [Pd(η^3-C_3H_5)(bpy)]BF_4

Silver tetrafluoroborate (0.026 g, 0.13 mmol) was added to a stirred solution of [Pd(η^3-C_3H_5)(bpy)]Br (0.05 g, 0.13 mmol) in methanol (20 ml). A white precipitate

separated, and the suspension was stirred for 15 min before filtration. Rotary evaporation of the filtrate to ca. 3 ml was followed by addition of diethyl ether (3 ml) to give a pale yellow precipitate, which was filtered off (0.11 g). The filtrate was evaporated to dryness, and was extracted with acetonitrile (5 × 4 ml). Rotary evaporation of the extract and addition of diethyl ether gave a pale yellow precipitate (0.041 g). The yellow solids were combined and dissolved in warm acetonitrile and the solution was centrifuged to remove AgBr, diethyl ether added, to give the product as a buff solid. (Anal. Found: C, 39.8; H, 3.3; N, 7.2. $C_{13}H_{13}BF_4N_2Pd$ calcd.: C, 40.0; H, 3.4; N, 7.2%).

Synthesis of [Pd(η^3-C_3H_5)(L_2)]X from [Pd(η^3-C_3H_5)X]$_2$

[Pd(η^3-C_3H_5)(bpy)]I. [Pd(η^3-C_3H_5)I]$_2$ (0.05 g, 0.091 mmol) in acetone (15 ml) was added during 5 min to a stirred solution of 2,2′-bipyridyl (0.032 g, 0.205 mmol) in acetone (5 ml), and a white precipitate separated out. Hexane (5 ml) was added, and the buff precipitate filtered off and washed with hexane, then air- and vacuum-dried (0.061 g, 78%). (Anal. Found: C, 36.3; H, 3.0; N, 6.4. $C_{13}H_{13}IN_2Pd$ calcd.: C, 36.3; H, 3.0; N, 6.5%).

The other complexes are obtained similarly; addition of [Pd(η^3-C_3H_5)X]$_2$ to the ligand is required to ensure absence of the double salt from the product.

[Pd(η^3-C_3H_5)(phen)]Br. White solid, 80% yield. (Anal. Found: C, 43.6; H, 3.6; N, 6.8. $C_{13}H_{13}BrN_2Pd$ calcd.: C, 44.2; H, 3.2; N, 6.9%).

[Pd(η^3-C_3H_5)(phen)]I. White solid, 95% yield. (Anal. Found: C, 40.2; H, 3.3; N, 6.0. $C_{15}H_{13}IN_2Pd$ calcd.: C, 39.6; H, 2.9; N, 6.2%).

Synthesis of [Pd(η^3-C_3H_5)(L_2)][Pd(η^3-C_3H_5)X_2]

[Pd(η^3-C_3H_5)(bpy)][Pd(η^3-C_3H_5)Br_2]. A solution of 2,2′-bipyridyl (0.034 g, 0.22 mmol) in acetone (15 ml) was added to a stirred solution of [Pd(η^3-C_3H_5)Br]$_2$ (0.10 g, 0.22 mmol) in acetone (15 ml) to give a yellow precipitate. After 5 min stirring, hexane (5 ml) was added, and the product filtered off, washed with hexane, and air- and vacuum-dried (0.12 g, 89%). (Anal. Found: C, 32.2; H, 3.0; N, 4.6. $C_{16}H_{18}Br_2N_2Pd_2$ calcd.: C, 31.5; H, 3.0; N, 4.6%).

The other complexes were obtained similarly; addition of the ligand to [Pd(η^3-C_3H_5)X]$_2$ is required to ensure absence of [Pd(η^3-C_3H_5)(L_2)]X from the product.

[Pd(η^3-C_3H_5)(bpy)][Pd(η^3-C_3H_5)I_2]. Buff solid, 96% yield. (Anal. Found: C, 27.3; H, 2.5; N, 3.9. $C_{16}H_{18}I_2N_2Pd_2$ calcd.: C, 27.3; H, 2.6; N, 4.0%).

[Pd(η^3-C_3H_5)(phen)][Pd(η^3-C_3H_5)Br_2]. Yellow solid, 72% yield. (Anal. Found: C, 34.7; H, 2.8; N, 4.5. $C_{18}H_{18}Br_2N_2Pd_2$ calcd.: C, 34.1; H, 2.9; N, 4.4%).

[Pd(η^3-C_3H_5)(phen)][Pd(η^3-C_3H_5)I_2]. Buff solid, 96% yield. (Anal. Found: C, 30.2; H, 2.4; N, 3.9. $C_{18}H_{18}I_2N_2Pd_2$ calcd.: C, 29.7; H, 2.5; N, 3.8%).

Acknowledgements

We thank the Australian Research Council and The University of Tasmania for financial support, the Commonwealth Government for a Postgraduate Research Award (to P.K.B.), and Johnson Matthey Ltd. for a generous loan of palladium chloride.

References and notes

1 P.K. Byers, A.J. Canty, B.W. Skelton, and A.H. White, J. Chem. Soc., Chem. Commun., (1986) 1722.
2 R. Uson, J. Fornies, and R. Navarro, J. Organomet. Chem., 96 (1975) 307; Synth. React. Inorg. Met.-Org. Chem., 7 (1977) 235.
3 P.K. Byers, A.J. Canty, B.W. Skelton, and A.H. White, Organometallics, 9 (1990) 826.
4 A.J. Canty, A.A. Watson, B.W. Skelton, and A.H. White, J. Organomet. Chem., 367 (1989) C25.
5 P.K. Byers and A.J. Canty, J. Chem. Soc., Chem. Commun., (1987) 639.
6 D.G. Brown, P.K. Byers, and A.J. Canty, Organometallics, 9 (1990) in press.
7 P.K. Byers and A.J. Canty, Organometallics, 9 (1990) 210.
8 P.K. Byers, A.J. Canty, M. Crespo, R.J. Puddephatt, and J.D. Scott, Organometallics, 7 (1988) 1363.
9 K.-T. Aye, A.J. Canty, M. Crespo, R.J. Puddephatt, J.D. Scott, and A.A. Watson, Organometallics, 8 (1989) 1518.
10 M. Crespo and R.J. Puddephatt, Organometallics, 6 (1987) 2548.
11 P.K. Monaghan and R.J. Puddephatt, J. Chem. Soc., Dalton Trans., (1988) 595.
12 G. Paiaro and M. Musco, Tetrahedron Lett., (1965) 1583.
13 L.S. Hegedus, B. Akermark, D.J. Olsen, O.P. Anderson, and K. Zetterberg, J. Am. Chem. Soc., 104 (1982) 697.
14 J. Powell and B.L. Shaw, J. Chem. Soc. A, (1967) 1839.
15 M. Sakakibara, Y. Takahashi, S. Sakai, and Y. Ishii, Chem. Commun., (1969) 36.