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Synthesis of organopalladium(IV) complexes by halogen exchange, and the structure of the azidopalladium(II) complex formed on reductive elimination of ethane from $Pd(N_3)Me_2(CH_2Ph)(bpy)$

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Abstract

A new route to organopalladium(IV) complexes is described, involving replacement of bromine in the 2,2′-bipyridyl complex $PdBrMe_2(CH_2Ph)(bpy)$, by other halogen or pseudohalogen groups. ^1H NMR studies of the decomposition of $PdXMe_2(CH_2Ph)(bpy)$ in warm $(CD_3)_2CO$ indicate that a selectivity in reductive elimination of alkanes occurs, to give ethane ($X = Br, N_3, NCS$), or a mixture of ethane and ethylbenzene in ca. 9/1 ratio ($X = F, Cl, I$). The reductive elimination product azido(2,2′-bipyridyl)benzylpalladium(II) has been characterized by X-ray crystallography.

The isolation of organopalladium(IV) complexes requires rapid oxidative addition of chlorine [1] or organohalides [2–8] to organopalladium(II) substrates under mild conditions in order to prevent reductive elimination from the palladium(IV) product prior to isolation. These requirements have hindered the development of organopalladium(IV) chemistry, and new synthetic routes that are less reliant upon oxidative addition are now being sought. The first reported hydrocarbylpalladium(IV) complex, $PdIMe_3$(2,2′-bipyridyl) [9], dissolves in acetonitrile to form an equilibrium with $[PdMe_3(bpy)(NCMe)]I$ while undergoing reductive elimination of ethane [2]. This behaviour indicates that halide exchange reactions may be possible in this solvent, and we report here that the more stable complex $PdBrMe_2(CH_2Ph)(bpy)$ [5,10] may be used as a reagent to obtain a range of complexes that are not accessible by oxidative addition. The complexes isolated include the first examples of fluoro and pseudohalogeno complexes, and they have permitted the first study of selectivity in reductive elimination of Me–Me and R–Me from *fac*-$Pd^{IV}XMe_2R$ complexes as X is varied.

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Table 1

Yield and characterization data for the new palladium(IV) complexes

Complex	Yield	^{1}H NMR [a]		
		δ(PdMe)	δ(PdCH$_2$)	δ(H6)
PdFMe$_2$(CH$_2$Ph)(bpy) [b]	89	1.87b	3.32b	8.57b
PdClMe$_2$(CH$_2$Ph)(bpy) [b,c]	88	2.04	3.08b	8.57b
PdIMe$_2$(CH$_2$Ph)(bpy)	67	2.05	3.27	8.61d
Pd(N$_3$)Me$_2$(CH$_2$Ph)(bpy) [d]	85	1.79	3.04	8.52d
Pd(NCS)Me$_2$(CH$_2$Ph)(bpy) [e,f]	52	1.78b	3.20b	8.52b

[a] In $CDCl_3$ at 0 °C, with integration as required for the formulae presented. The complex $PdBrMe_2(CH_2Ph)(bpy)$ is formed in 62% yield from $PdMe_2(bpy)$ and $PhCH_2Br$, and has δ(PdMe) 1.98, δ($PdCH_2$) 3.17, and δ(H6) 8.54 m [5].

[b] The phenyl resonances, but not H3,4,5 of bpy, are also broad. On cooling to −40 °C all resonances are sharp, with H6 resolved as a doublet.

[c] At −40 °C the $PdCH_2$ resonance has an additional low intensity (ca. 15%) resonance 0.12 ppm upfield, as found for several $PdBrMe_2(CH_2Ar)(bpy)$ complexes and attributed to rotation about the Pd–CH_2 bond [5].

[d] $\nu(N_3)$ 2008 cm^{-1} (KBr disk).

[e] ν(CN) 2089 cm^{-1}.

[f] Resonances sharp at −40 °C, with H6 resolved as a doublet.

Successful exchange reactions require temperatures of ca. 0 °C throughout, and minimum solvent volumes to ensure rapid isolation. In typical preparations, $AgNO_3$ (0.11 mmol in 0.5 mL MeCN) is added to a stirred suspension of $PdBrMe_2(CH_2Ph)(bpy)$ (0.11 mmol in 2 mL MeCN). After ca. 20 s one of the following salts (dissolved as indicated) is added: KF(MeCN, 1 mL), NH_4Cl (H_2O, 0.5 mL), NaI (MeCN, 2 mL), NaN_3 (H_2O, 0.5 mL and MeCN, 1 mL), NH_4NCS (MeCN, 1 mL). Acetone (5 mL) is added, the suspension stirred for ca 30 s, filtered quickly through filter aid, and the solution evaporated on a high vacuum rotary evaporator to ca. 3 mL (5 min). The products are precipitated with diethyl ether/hexane and collected. The complexes give ^{1}H NMR spectra (Table 1) similar to those reported for *fac*-$PdBrMe_2(CH_2Ar)(bpy)$ [Ar = C_6F_5, *p*-YC_6H_4(Y = H, Me, Br, NO_2)], all of which have the methyl groups *trans* to bpy [5,10]. The C–N stretching frequency for $Pd(NCS)Me_2(CH_2Ph)(bpy)$ occurs at 2089 cm^{-1}, consistent with the presence of Pd–N coordination although this infrared criterion for assignment of N or S coordination must be treated with caution [11].

On warming to ca. 30 °C in $(CD_3)_2CO$ the new complexes undergo clean reductive elimination reactions (eq. 1), with all products detectable by ^{1}H NMR spectroscopy on comparison with reported spectra of ethane [2], ethylbenzene [5], $PdBr(CH_2Ph)(L_2)$ (L_2 = tris(pyrazol-1-yl)methane [3], tetramethylethylenediamine [8]), and PdXMe(bpy) (X = Cl, Br, I) [12]. The complex PdFMe(bpy) has been synthesized from $[PdIMe(SMe_2)]_2$ in the same manner as reported for the bromo and chloro complexes. Selectivity in reductive elimination is dependent upon X, complementing earlier reports of the dependence of selectivity upon both Ar and L_2 in the bromo complexes $PdBrMe_2(CH_2Ar)(L_2)$ (L_2 = bpy, phen [5,10], tmeda [8]).

$$PdXMe_2(CH_2Ph)(bpy) \xrightarrow[(CD_3)_2CO]{\Delta} a\left[PdX(CH_2Ph)(bpy) + Me\text{–}Me\right]$$

$$+\, b\left[PdXMe(bpy) + PhCH_2\text{–}Me\right] \qquad (1)$$

$X = Br[5,10], N_3, NCS\colon a = 1,\ b = 0.\ X = F, Cl, I\colon a = 0.9,\ b = 0.1$

The azido complex $Pd(N_3)(CH_2Ph)(bpy)$ formed as orange needles in an NMR tube during reductive elimination and, since structural studies of organopalladium(II)

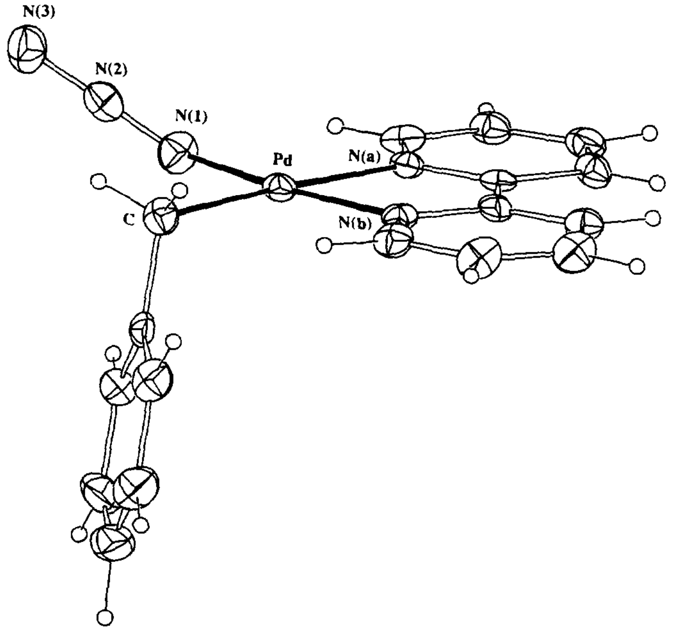

Fig. 1. A molecular projection for $Pd(N_3)(CH_2Ph)(bpy)$ showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions) have been given an arbitrary radius of 0.1 Å. Selected bond distances and angles: Pd–C 2.036(8) Å, Pd–N(1, a, b) 2.003(8), 2.104(6), 2.030(7) Å, C–Pd–N(1, a, b) 91.4(3), 176.2(3), 97.7(3)°, N(1)–Pd–N(a, b) 91.8(3)°, 170.9(3)°, N(a)–Pd–N(b) 79.2(3)°, Pd–C–C(1) 110.5(5)°, Pd–N(1)–N(2) 126.8(7)°, N(1)–N(2)–N(3) 177(1)°.

complexes containing azido or benzyl groups do not appear to have been reported, the crystals were examined by X-ray crystallography *. Crystals of $C_{17}H_{15}N_5Pd$ are monoclinic, $M = 395.7$, space group $P2_1/n$, with a 7.113(2), b 9.208(7), c 23.958(7) Å, β 90.44(2)°, $Z = 4$. 1837 "observed" ($I > 3\sigma(I)$) and absorption corrected diffractometer reflections to $2\theta_{max}$ 50° (Mo-K_α radiation) collected at ~ 295 K were refined by full-matrix least squares to $R = 0.048$. The square-planar complex is shown in Fig. 1. The Pd^{II}–CH_2 bond length in $Pd(N_3)(CH_2Ph)(bpy)$, 2.036(8) Å, is within 2σ of reported Pd^{II}–Me (2.01(1)–2.041(12) Å) [7,13,14] and Pd^{IV}–Me bond lengths (2.034(7)–2.060(9) Å) [2,5,10] in related nitrogen-donor complexes, but the Pd^{IV}–CH_2 bond length in $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$, 2.091(6) Å, is ca. 0.06 Å longer [5,10], suggesting that the Pd–benzyl bond may be weaker in the higher oxidation state.

Kinetic studies of reductive elimination of ethane from $PdIMe_3(bpy)$ indicate that the major pathway involves preliminary dissociation of the iodo group [15]. Differential scanning calorimetry studies of reductive elimination from $PdBrMe_2(CH_2Ph)(L_2)$(L_2 = bpy, phen) indicate that elimination of ethane is ca. 60 kJ mol^{-1} more exothermic than elimination of ethylbenzene, and that the selectivity

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* Tables of atom coordinates and bond lengths and angles are available from the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW (UK). Tables of thermal parameters and structure factors are available from the authors.

for ethane evolution (eq. 1) may be controlled by thermochemical factors [16] in addition to the possible formation of transient η^3-benzyl coordination during reductive elimination [8]. One factor contributing to the enthalpy difference is the stronger C–C bond for ethane compared to PhH_2C-CH_3, and the comparison of $Pd^{II}-CH_2$ and $Pd^{IV}-CH_2$ distances indicate that another factor may be a stronger $Pd-CH_2$ bond in the lower oxidation state.

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