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Synthesis of halogeno, pseudohalogeno, and carboxylatopalladium(IV) complexes by halogen exchange. Crystal structure of azido(2,2′-bipyridyl)-benzylpalladium(II), formed on reductive elimination of ethane from $Pd(N_3)Me_2(CH_2Ph)(bpy)$

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Abstract

The first examples of fluoro, pseudohalogeno, and carboxylatopalladium(IV) complexes have been obtained by the exchange of the bromo ligand in $PdBrMe_2(CH_2Ph)(bpy)$ (bpy = 2,2′-bipyridyl) on addition of a silver salt, or silver nitrate and the appropriate anion, in acetonitrile. The syntheses have permitted a study of the effect of groups X on the selectivity in reductive elimination of ethane and ethylbenzene from $PdXMe_2(CH_2Ph)(bpy)$. For X = Br, N_3, SCN, or O_2CPh, reductive elimination from the unstable palladium(IV) complexes in acetone gives ethane and $PdX(CH_2Ph)(bpy)$ only, but these products together with *ca.* 10% of ethylbenzene and PdXMe(bpy) are formed from the complexes $PdXMe_2(CH_2Ph)(bpy)$ (X = F, Cl, I, OCN, SeCN, O_2CCF_3). The binding mode of the ambidentate pseudohalides OCN^-, SCN^- and $SeCN^-$ has not been determined.

Introduction

Oxidative addition and reductive elimination reactions occupy pivotal roles in organometallic chemistry and some catalytic reactions [1]. The recent development of alkylpalladium chemistry involving the oxidation state + IV for palladium [2,3]

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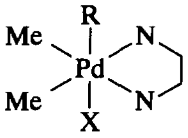
has provided new opportunities for the study of oxidative addition to d^8 complexes and decomposition of d^6 complexes (eq. 1).

$$\mathrm{PdMe_2(N{-}N) + RX} \xrightarrow[\text{addition}]{\text{oxidative}}$$



$$\xrightarrow[\text{elimination}]{\text{reductive}}$$

$$a[\mathrm{PdXR(N{-}N) + Me{-}Me}] + b[\mathrm{PdXMe(N{-}N) + R{-}Me}] \qquad (1)$$

N-N = 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen) [3,4]; N-N = tetramethylethylenediamine (tmeda) (R = CH_2Ph, η^1-C_3H_5 are *trans* to nitrogen for L_2 = tmeda) [5]

The reaction sequence of eq. 1 appears to be the only system reported in which both oxidative addition and reductive elimination occur under mild conditions; *e.g.* in related platinum chemistry oxidative addition reactivity is ideal for mechanistic studies, but organoplatinum(IV) nitrogen donor complexes undergo general decomposition at high temperatures [6].

We report here the synthesis of a range of dimethyl(benzyl)palladium(IV) complexes formed by exchange of the bromo ligand in $PdBrMe_2(CH_2Ph)(bpy)$. The first examples of fluoro, pseudohalogeno, and carboxylato complexes have been obtained. Isolation of these complexes has permitted studies of selectivity in reductive elimination, and the synthesis of a range of benzylpalladium(II) complexes by reductive elimination of ethane. A preliminary report of part of this work has appeared [7].

Results

Synthesis of palladium(IV) complexes

Successful exchange reactions (eq. 2) require that syntheses by conducted at low temperature, and in a coordinating solvent such as acetonitrile, possibly to stabilize an (expected) intermediate cation $[PdMe_2(CH_2Ph)(bpy)(NCMe)]^+$.

$$\mathrm{PdBrMe_2(CH_2Ph)(bpy)} \xrightarrow[\text{(ii) filtration}]{\substack{\text{(i) AgNO}_3\text{ (ii) X}^- \\ \text{or AgX (X = OCN, O}_2\text{CPh)}}} \mathrm{PdXMe_2(CH_2Ph)(bpy)} \qquad (2)$$

X = F, Cl, I, N_3, OCN, SCN, SeCN, O_2CPh, O_2CCF_3

In typical preparations, silver nitrate (or the silver salt) is added to a stirred suspension of $PdBrMe_2(CH_2Ph)(bpy)$ in acetonitrile, followed by addition of X^-, acetone, and filtration to remove AgBr. Hexane, which is required to precipitate the product, has low solubility in acetonitrile, and thus diethyl ether is added prior to hexane to allow dissolution of hexane. With this approach, and completion of syntheses within *ca.* 5 min., palladium(IV) complexes may be isolated (47–90% yield) that are not contaminated with palladium(II) reductive elimination products. The complexes are insufficiently stable for postage for microanalysis, but their ^1H NMR and infrared spectra, together with ^1H NMR studies of reductive elimination reactions (see below), establish that exchange of bromine has occurred as indicated in eq. 2.

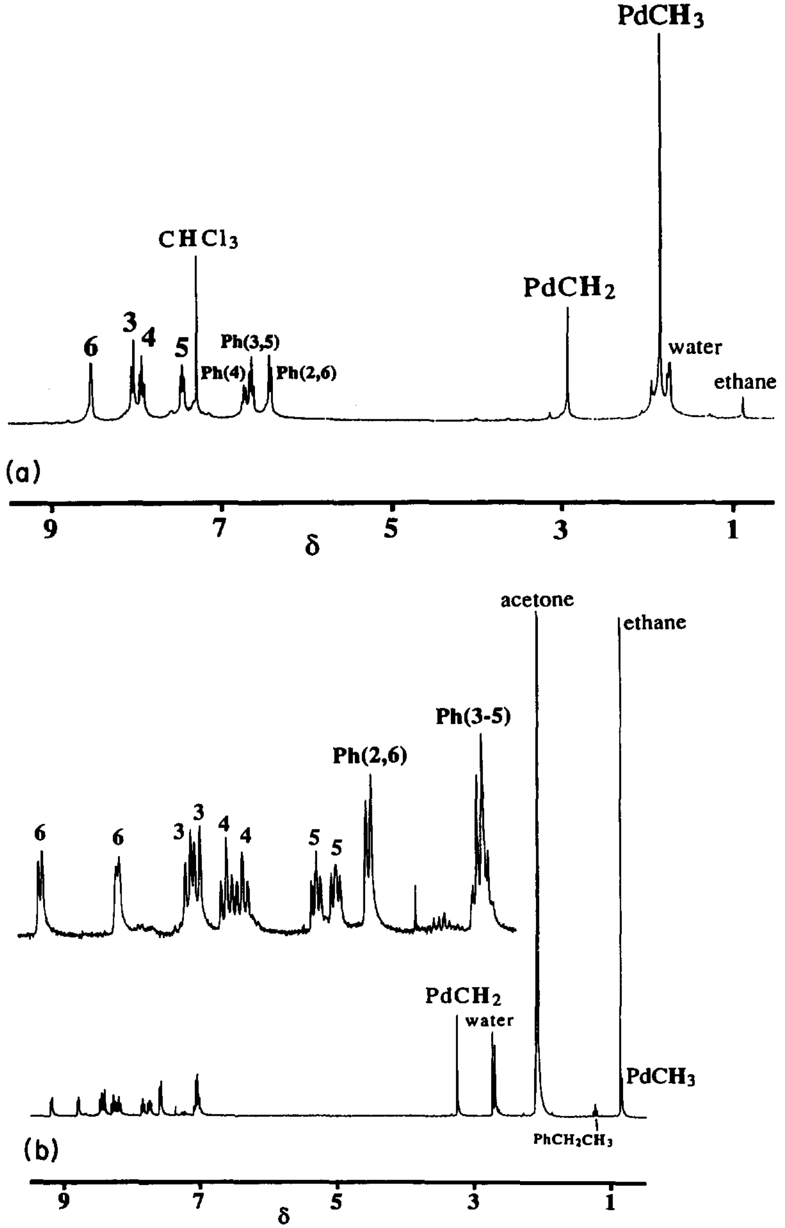


Fig. 1. ^{1}H NMR spectra: (a) $Pd(OCN)Me_2(CH_2Ph)(bpy)$ in $CDCl_3$ at 0°C, and (b) after warming a solution of $Pd(OCN)Me_2(CH_2Ph)(bpy)$ in $(CD_3)_2CO$ to *ca.* 30°C, showing resonances attributable to the reductive elimination products $Pd(OCN)(CH_2Ph)(bpy)$, ethane, and traces of $PdMe(OCN)(bpy)$ and ethylbenzene.

All of the complexes exhibit ^{1}H NMR spectra similar to those of $PdBrMe_2(CH_2Ph)(bpy)$, and of $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$ for which a structural analysis [4] has confirmed that the methyl groups are *trans* to the bidentate nitrogen donor ligand (eq. 1). Thus, single $Pd^{IV}Me$ and $Pd^{IV}CH_2Ph$ environments are indicated from the spectra in $CDCl_3$ or $(CD_3)_2CO$ [Fig. 1(a)], in contrast to the more complex spectra expected for the isomer with methyl groups *trans* to nitrogen and X, as observed for $PdBrMe_2(CH_2Ph)(tmeda)$ [5]. Spectra of four of the complexes also vary with temperature. At ambient temperature and at 0°C the resonances H6(bpy) and CH_2(X = F, Cl, SCN, O_2CCF_3), together with the three phenyl resonances (X = F, Cl, O_2CCF_3) and PdMe (X = F, O_2CCF_3) are broad, in contrast to the sharp and well resolved multiplets for the other protons. On cooling to −40°C, the broad resonances become well resolved, and for X = Cl an additional CH_2 resonance (intensity *ca.* 15% of major resonance) occurs 0.12 ppm upfield from the major CH_2 resonance. These effects may result from fluxional processes involving the benzyl group, possibly rotation about the Pd–C bond, since the protons that are expected to be most affected by this are those that show broadening.

The complexes give similar infrared spectra, and the complexity of the 2,2′-bipyridyl absorptions precludes full assignment of pseudohalogen and carboxylate bands.

Decomposition of palladium(IV) complexes

Decomposition of the complexes $PdXMe_2(CH_2Ph)(bpy)$ was monitored by ^1H NMR spectroscopy for $(CD_3)_2CO$ solutions warmed to *ca.* 30°C. Decomposition is complete in *ca.* 5–60 min, and the least stable complexes (X = F, Cl, OCN, SCN) decompose in *ca.* 5–10 min at 30°C. For all of the complexes, there were no indications of the formation of palladium metal, methane, or toluene. Ethane (0.84 ppm) was the only organic product detected, except for a small amount of ethylbenzene (1.21 t ppm) when X = F, Cl, I, OCN, SeCN, and O_2CCF_3 [eq. 3 and Fig. 1(b)].

$$PdXMe_2(CH_2Ph)(bpy) \xrightarrow[ca.\ 30°C]{(CD_3)_2CO}$$

$$a[PdX(CH_2Ph)(bpy) + Me\text{–}Me] + b[PdXMe(bpy) + PhCH_2\text{–}Me] \quad (3)$$

X = Br, N_3, SCN, O_2CPh: $a = 1$, $b = 0$
X = F, Cl, I, OCN, SeCN, O_2CCF_3: $a \sim 0.9$, $b \sim 0.1$

The palladium(II) products, PdXR(bpy), have very low solubilities and precipitate as mixtures, but ^1H NMR spectra obtained during reductive elimination permit detection of the predominant reductive elimination complexes $PdX(CH_2Ph)(bpy)$, exhibiting $PdCH_2$ resonances in the range 3.07–3.40 ppm. The 2,2′-bipyridyl and phenyl regions of the spectra are complex during reductive elimination, owing to the presence of both palladium(IV) and palladium(II) species. However, for the complexes PdXMe(bpy) (X = Cl, Br, I), the resonance for H6(bpy) adjacent to X occurs well downfield of other resonances [8], and for each reductive elimination reaction a resonance attributable to this environment occurs for the benzylpalladium(II) complexes at 8.79–9.38 ppm. Small amounts of PdXMe(bpy) are difficult to detect, although their presence is indicated by a singlet (PdMe) near that for ethane and, for some systems, an additional weak H6(bpy) resonance at low field. Low solubilities of the palladium(II) products, and the volatility of ethane, render assignment of stoichiometry for eq. 3 difficult, except for reactions in which $a = 1$, $b = 0$. When $b \neq 0$, the stoichiometry is estimated from the relative intensity of the ethylbenzene triplet at 1.21 ppm, giving a value of $b \sim 0.1$ for these reactions.

Two of the benzylpalladium(II) complexes ($X = N_3$, NCO) were sufficiently soluble in $(CD_3)_2CO$ that, on completion of the reductive elimination and prior to

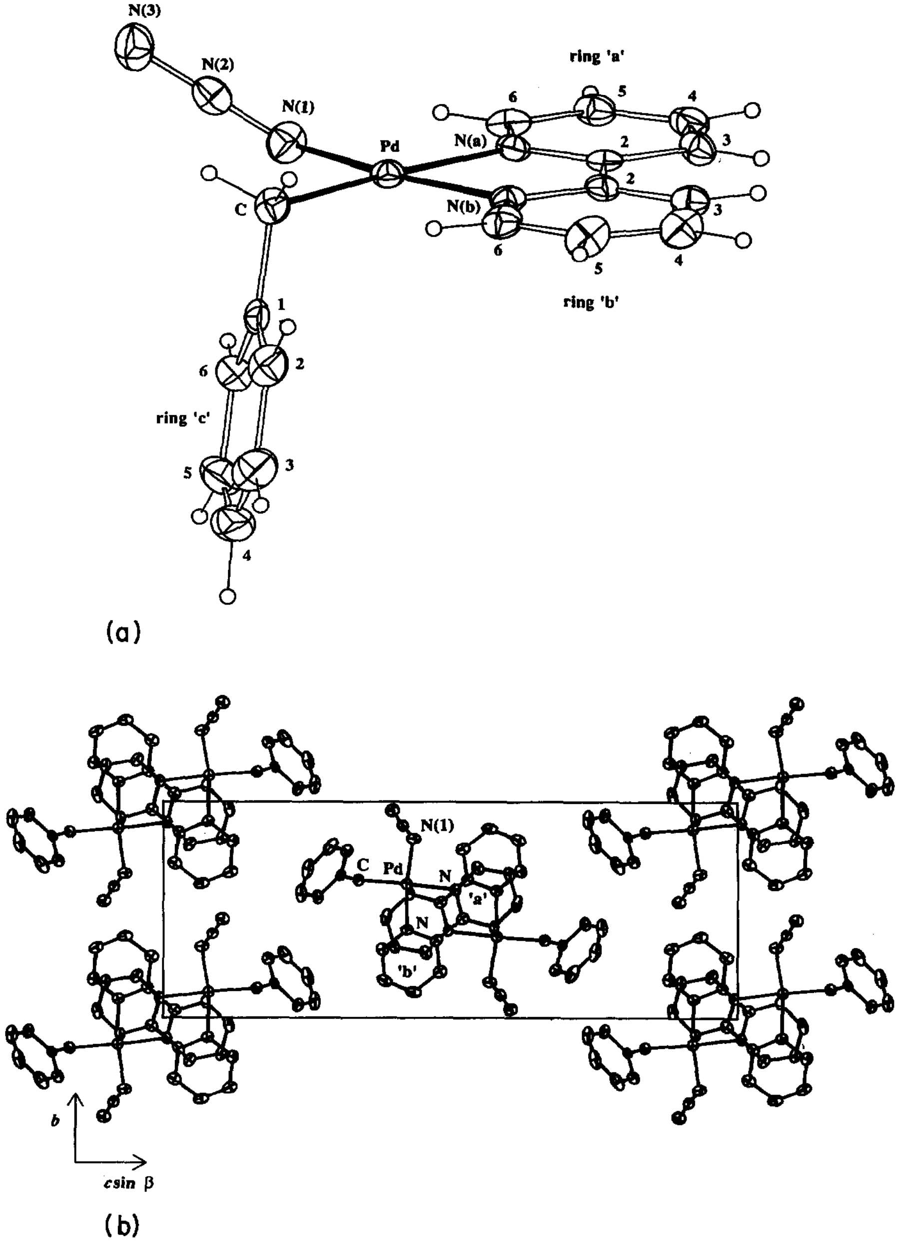


Fig. 2. (a) Molecular projection for $Pd(N_3)(CH_2Ph)(bpy)$ showing the atom numbering scheme. Thermal ellipsoids (20%) are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated positions) have been given an arbitrary radius of 0.1 Å. (b) The unit cell contents of $Pd(N_3)(CH_2Ph)(bpy)$ projected down a, illustrating the packing of molecules and showing views of the complex normal to the coordination plane.

Table 1
Non-hydrogen atom coordinates and equivalent isotropic thermal parameters (Å^2) for Pd(N$_3$)(CH$_2$Ph)(bpy)

Atom	x	y	z	U_{eq} (Å^2)
Pd	0.65271(8)	0.37710(8)	0.57863(3)	0.0424(2)
N(a)	0.7163(8)	0.4045(8)	0.4936(3)	0.043(2)
C(a2)	0.774(1)	0.537(1)	0.4806(3)	0.046(3)
C(a3)	0.826(1)	0.577(1)	0.4260(3)	0.051(3)
C(a4)	0.814(1)	0.468(1)	0.3860(4)	0.067(4)
C(a5)	0.756(1)	0.332(1)	0.3999(4)	0.056(4)
C(a6)	0.708(1)	0.304(1)	0.4543(4)	0.055(3)
N(b)	0.7286(8)	0.5896(7)	0.5775(3)	0.044(2)
C(b2)	0.779(1)	0.642(1)	0.5268(3)	0.048(3)
C(b3)	0.831(1)	0.785(1)	0.5200(4)	0.059(4)
C(b4)	0.833(1)	0.877(1)	0.5662(5)	0.068(4)
C(b5)	0.779(1)	0.825(1)	0.6159(5)	0.070(4)
C(b6)	0.727(1)	0.682(1)	0.6204(4)	0.055(3)
C	0.605(1)	0.360(1)	0.6620(3)	0.051(3)
C(c1)	0.783(1)	0.3395(9)	0.6928(3)	0.043(3)
C(c2)	0.841(1)	0.439(1)	0.7331(4)	0.066(4)
C(c3)	1.012(2)	0.421(2)	0.7619(4)	0.090(6)
C(c4)	1.124(2)	0.309(2)	0.7501(5)	0.093(6)
C(c5)	1.070(2)	0.208(1)	0.7105(5)	0.090(5)
C(c6)	0.901(1)	0.226(1)	0.6818(4)	0.060(4)
N(1)	0.583(1)	0.1685(8)	0.5666(3)	0.065(3)
N(2)	0.457(1)	0.1085(9)	0.5853(3)	0.058(3)
N(3)	0.328(1)	0.041(1)	0.6027(3)	0.079(4)

precipitation, the spectra could be fully assigned as due solely to PdX(CH$_2$Ph)(bpy) and ethane [Fig. 1(b)]. The azidopalladium(II) complex formed as crystals suitable for X-ray diffraction studies.

Structure of Pd(N$_3$)(CH$_2$Ph)(bpy)

A crystallographic study of Pd(N$_3$)(CH$_2$Ph)(bpy) was undertaken since structural parameters for benzylpalladium(II) or azidopalladium(II) complexes have not been reported, and structural data would allow a comparison of the palladium environment with that in related palladium(II) and palladium(IV) complexes. A projection of the structure is shown in Fig. 2, and structural parameters are given in Tables 1 and 2. *

The 'PdCN$_3$' group deviates only trivially from planarity (χ^2 29.3). The pyridine rings form angles of 1.9(3)° (ring a) and 2.0(3)° (ring b) with the PdCN$_3$ mean plane, and 1.1(3)° with each other, the bipyridyl skeleton again being only trivially non-planar (χ^2 15.1). The benzyl phenyl group lies at 79.7(3)° to the PdCN$_3$ plane, while τ(Pd–C–C(c1)–C(2,6)) are −120.1(7)° and 57.9(9)° respectively.

The Pd–CH$_2$ bond length, 2.036(8) Å, is similar to that reported for Pd–C in a range of alkylpalladium(II) [9–15] and palladium(IV) complexes [14,16] of nitrogen

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* Thermal parameters, calculated hydrogen atom positions and least squares planes data will be deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ (UK). Any request should be accompanied by a full literature citation for this article. A list of structure factors is available from the authors.

Table 2

Bond distances (Å) and angles (deg) for $Pd(N_3)(CH_2Ph)(bpy)$

Coordination geometry and azido group			
Pd–C	2.036(8)	Pd–N(1)	2.003(8)
Pd–N(a)	2.104(6)	N(1)–N(2)	1.15(1)
Pd–N(b)	2.030(7)	N(2)–N(3)	1.18(1)
C–Pd–N(b)	97.7(3)	Pd–C–C(c1)	110.5(5)
C–Pd–N(1)	91.4(3)	Pd–N(a)–C(a2)	114.1(5)
N(a)–Pd–N(b)	79.2(3)	Pd–N(a)–C(a6)	126.7(6)
N(a)–Pd–N(1)	91.8(3)	Pd–N(b)–C(b2)	115.1(6)
C–Pd–N(a)	176.2(3)	Pd–N(b)–C(b6)	126.9(6)
N(b)–Pd–N(1)	170.9(3)	Pd–N(1)–N(2)	126.8(7)
		N(1)–N(2)–N(3)	177(1)
Benzyl and 2,2′-bipyridyl groups			
C–C(c1)	1.48(1)	C(a3)–C(a4)	1.39(1)
C(c1)–C(c2)	1.39(1)	C(a4)–C(a5)	1.37(2)
C(c1)–C(c6)	1.37(1)	C(a5)–C(a6)	1.37(1)
C(c2)–C(c3)	1.41(2)	N(b)–C(b2)	1.36(1)
C(c3)–C(c4)	1.33(2)	N(b)–C(b6)	1.33(1)
C(c4)–C(c5)	1.38(2)	C(b2)–C(b3)	1.38(1)
C(c5)–C(c6)	1.38(1)	C(b3)–C(b4)	1.40(1)
N(a)–C(a2)	1.33(1)	C(b4)–C(b5)	1.34(2)
N(a)–C(a6)	1.32(1)	C(b5)–C(b6)	1.38(1)
C(a2)–C(a3)	1.41(1)	C(a2)–C(b2)	1.47(1)
N(a)–C(a2)–C(a3)	122.8(8)	N(b)–C(b2)–C(b3)	121.0(8)
N(a)–C(a2)–C(b2)	115.5(7)	N(b)–C(b2)–C(a2)	116.1(8)
C(a3)–C(a2)–C(b2)	121.7(8)	C(b3)–C(b2)–C(a2)	122.8(8)
C(a2)–C(a3)–C(a4)	116.1(9)	C(b2)–C(b3)–C(b4)	119.4(9)
C(a3)–C(a4)–C(a5)	120.7(8)	C(b3)–C(b4)–C(b5)	119(1)
C(a4)–C(a5)–C(a6)	118.6(9)	C(b4)–C(b5)–C(b6)	119(1)
N(a)–C(a6)–C(a5)	122.6(9)	N(b)–C(b6)–C(b5)	123.2(9)
C(a2)–N(a)–C(a6)	119.2(7)	C(b2)–N(b)–C(b6)	118.0(7)
C–C(c1)–C(c2)	120.6(8)	C(c2)–C(c3)–C(c4)	120(1)
C–C(c1)–C(c6)	121.9(7)	C(c3)–C(c4)–C(c5)	120(1)
C(c2)–C(c1)–C(c6)	117.5(8)	C(c4)–C(c5)–C(c6)	120(1)
C(c1)–C(c2)–C(c3)	121(1)	C(c1)–C(c6)–C(c5)	121.3(9)

donor ligands, 2.01(1)–2.060(9) Å, except for the significantly longer $Pd-CH_2$ bond length found for the palladium(IV) complex $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$ [2.091(6) Å] [4]. The Pd–N(bpy) distances, 2.030(7) and 2.104(6) Å, are very disparate and appear to reflect the high *trans* effect of the alkyl group since the longer Pd–N bond is *trans* to the benzyl group. Similar effects occur in closely related square planar complexes [11,12,14], *e.g.* $[PdMe(bpy)(4\text{-methylpyridine})]BF_4$ has a '$PdCN_3$' group with Pd–N 2.049(4) and 2.131(4) Å [11].

The coordination plane lies approximately normal to *a* (Table 1 and Fig. 2) with inversion related, interleaved planes stacking along that direction. The closest contacts for the asymmetric unit along positive and negative *a* directions are, respectively, Pd ··· C(a2,3′): 3.430(8), 3.429(8); C(a5) ··· C(b6′): 3.47(1); C(a6) ··· N(b′): 3.34(1) Å; C(a2) ··· C(a2″): 3.41(1); C(a4) ··· N(b″): 3.41(1); C(a6) ··· C(b3″): 3.43(1) Å.

Discussion

Exchange of the bromo group in $PdBrMe_2(CH_2Ph)(bpy)$ provides a route for expansion of organopalladium(IV) chemistry to include aniono groups (X) that cannot be incorporated by oxidative addition reactions of RX with dimethylpalladium(II) complexes.

Thermochemical studies of elimination from $PdIMe_3(L'_2)$ and $PdBrMe_2(CH_2Ph)(L'_2)(L'_2 = bpy, phen)$ show that ethane elimination is *ca.* 60 kJ mol^{-1} more exothermic than ethylbenzene elimination, perhaps mainly as a result of the stronger Me–Me bond energy (368 kJ mol^{-1}) than the $PhCH_2$–Me bond energy (301 kJ mol^{-1}) [17]. Kinetic studies of reductive elimination from $PdIMe_3(bpy)$ indicate the occurrence of two reaction pathways, with *ca.* 97.7% of the reaction occurring *via* preliminary dissociation of iodide [6]. The minor pathway involves direct reductive elimination from the octahedral complex, although the kinetic parameters suggest that a polar transition state occurs, possibly involving weakening of the Pd–I bond or formation of a tight ion pair $[PdMe_3(bpy)]^+I^-$ [6].

The thermodynamic factors discussed above are expected to apply in the present study, but the relative importance of the two possible reaction pathways is not established. The relatively small differences in selectivity as X is varied do not appear to correlate with the type of group X, and thus a simple explanation for the small differences is not apparent.

Experimental

The reagent $PdBrMe_2(CH_2Ph)(bpy)$ was prepared as described previously [4]. Solvents were dried and distilled. Microanalyses were by the Canadian Microanalytical Service, Vancouver, and infrared spectra of the complexes were obtained with KBr discs. ^1H NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si.

Synthesis of palladium(IV) complexes

$PdFMe_2(CH_2Ph)(bpy)$. Silver nitrate (0.11 mmol) in acetonitrile (0.5 mL) at 0°C was added to a stirred suspension of $PdBrMe_2(CH_2Ph)(bpy)$ (0.11 mmol) in acetonitrile (2 mL) at 0°C. After *ca.* 30 sec. potassium fluoride (0.11 mmol) in acetonitrile (1 mL) at 0°C was added, followed by acetone (5 mL) and the suspension was stirred for *ca.* 30 sec. then filtered quickly through filter aid. The filtrate was evaporated to *ca.* 3 mL on a high vacuum rotary evaporator (*ca.* 5 min). The product was precipitated as a pale yellow solid by addition of diethyl ether (*ca.* 4 mL) and hexane (*ca.* 6 mL); yield 90%. ^1H NMR ($CDCl_3$, O°C): δ 8.57 (2H, b, H(6)), 7.99 (2H, d, H(3)), 7.90 (2H, "t", H(4)), 7.44 (2H, "t", H(5)), *ca.* 6.81 and *ca.* 6.68 and *ca.* 6.53 (5H, b, Ph), 3.32 (2H, b, CH_2), 1.87 (6H, b, PdMe); at −40°C the broad H(6), Ph, CH_2, and PdMe resonances occur as sharp resonances at *ca.* 8.59 (2H, d, H(6)), 6.61 (1H, t, Ph(4)), 6.68 (2H, "t", Ph(3,5)), 6.50 (2H, d, Ph(2,6)), 3.29 (2H, s, CH_2), 1.89 (6H, s, PdMe).

The following complexes were prepared similarly. For each complex the conditions for addition of the anion are indicated.

$PdClMe_2(CH_2Ph)(bpy)$. Addition of NH_4Cl in water (0.5 mL), pale yellow powder, yield 88%. ^1H NMR ($CDCl_3$, 0°C): δ 8.57 (2H, b, H(6)), 8.01 (2H, d, H(3)), 7.91 (2H, "t", H(4)), 7.44 (2H, "t", H(5)), *ca.* 6.61 and *ca.* 6.68 and *ca.* 6.53 (5H, b, Ph), 3.31 (2H, b, CH_2), 2.04 (6H, s, PdMe); at −40°C the broad H(6), Ph,

and CH_2 resonances occur as sharp resonances at 8.61 (2H, d, H(6)), 6.62 (1H, t, Ph(4)), 6.68 (2H, "t", Ph(3,5)), 6.51 (2H, d, Ph(2,6)), and 3.29 (2H, s, CH_2), with an additional low intensity (*ca.* 15%) resonance for CH_2 at 3.17 ppm.

$PdIMe_2(CH_2Ph)(bpy)$. Addition of NaI in acetonitrile (2 mL), pale yellow powder, yield 47%. ^1H NMR ($CDCl_3$, 0°C): δ 8.61 (2H, d, H(6)), 8.01 (2H, d, H(3)), 7.70 (2H, "t", H(4)), 7.42 (2H, "t", H(5)), 6.77 (1H, t, Ph(4)), 6.63 (2H, "t", Ph(3,5)), 6.40 (2H, d, Ph(2,6)), 3.27 (2H, s, CH_2), 2.05 (6H, s, PdMe).

$Pd(N_3)Me_2(CH_2Ph)(bpy)$. Addition of NaN_3 in water (0.5 mL) and acetonitrile (1 mL), pale yellow powder, yield 85%. ^1H NMR ($CDCl_3$, 0°C): δ 8.52 (2H, d, H(6)), 8.05 (2H, d, H(3)), 7.95 (2H, "t", H(4)), 7.47 (2H, "t", H(5)), *ca.* 6.60 (3H, m, Ph(3, 4, 5)), 6.43 (2H, d, Ph(2,6)), 3.04 (2H, s, CH_2), 1.79 (6H, s, PdMe). IR: $\nu(N_3)$ 2008 cm^{-1}.

$Pd(SCN)Me_2(CH_2Ph)(bpy)$. Addition of NH_4SCN in acetonitrile (1 mL), pale yellow powder, yield 67%. ^1H NMR ($CDCl_3$, 0°C): δ 8.52 (2H, d, H(6)), 8.07 (2H, d, H(3)), 7.96 (2H, "t", H(4)), 7.48 (2H, "t", H(5)), 6.74 (1H, t, Ph(4)), 6.64 (2H, "t", Ph(3,5)), 6.41 (2H, d, Ph(2,6)), 3.20 (2H, b, CH_2), 1.78 (6H, s, PdMe). IR: ν(NCS) 2089 cm^{-1}.

$Pd(SeCN)Me_2(CH_2Ph)(bpy)$. Addition of KSeCN in acetonitrile (1 mL), pale yellow powder, yield 78%. ^1H NMR ($CDCl_3$, 0°C): δ 8.54 (2H, d, H(6)), 8.07 (2H, d, H(3)), 7.95 (2H, "t", H(4)), 7.48 (2H, "t", H(5)), 6.74 (1H, t, Ph(4)), 6.63 (2H, "t", Ph(3,5)), 6.38 (2H, d, Ph(2,6)), 3.20 (2H, b, CH_2), 1.77 (6H, s, PdMe). IR: ν(NCSe) 2097 cm^{-1}.

$Pd(O_2CCF_3)Me_2(CH_2Ph)(bpy)$. Addition of $NH_4O_2CCF_3$ in water (0.5 mL) and acetonitrile (1 mL), pale yellow powder, yield 90%. ^1H NMR ($CDCl_3$, 0°C): δ 8.60 (2H, d, H(6)), 8.00 (2H, d, H(3)), 7.92 (2H, "t", H(4)), 7.45 (2H, "t", H(5)), *ca.* 6.80 and *ca.* 6.69 and *ca.* 6.53 (5H, b, Ph), 3.21 (2H, b, CH_2), 1.66 (6H, b, PdMe); at −20°C the broad H(6), Ph, CH_2, and PdMe resonances are sharpened but precipitation prevents collection of high quality spectra. IR: $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ could not be readily assigned.

$Pd(OCN)Me_2(CH_2Ph)(bpy)$. A suspension of AgOCN (11 mmol) in acetonitrile (*ca.* 5 mL) at 0°C was added to a stirred solution of $PdBrMe_2(CH_2Ph)(bpy)$ (11 mmol) in acetonitrile (*ca.* 7 mL) at 0°C. After *ca.* 60 sec. the suspension was filtered through filter aid, and the filtrate evaporated to *ca.* 2 mL on a high vacuum rotary evaporator (*ca.* 5 min.). The product was collected as an off-white powder on addition of diethyl ether (*ca.* 4 mL) and hexane (*ca.* 6 mL); yield 70%. ^1H NMR ($CDCl_3$, 0°C): δ 8.51 (2H, d, H(6)), 8.03 (2H, d, H(3)), 7.92 (2H, "t", H(4)), 7.44 (2H, "t", H(5)), 6.72 (1H, t, Ph(4)), 6.63 (2H, "t", Ph(3,5)), 6.41 (2H, d, Ph(2,6)), 2.92 (2H, b, CH_2), 1.83 (6H, s, PdMe). IR: ν(OCN) 2180 cm^{-1}.

$Pd(O_2CPh)Me_2(CH_2Ph)(bpy)$. This was prepared similarly and obtained as a pale yellow powder in 77% yield. ^1H NMR ($CDCl_3$, 0°C): δ 8.69 (2H, d, H(6)), 7.84 (4H, m, H (3,4)), 7.64 (2H, d, $PhCO_2$(2,6)), 7.19 (3H, mb, $PhCO_2$(3, 4, 5)), 6.72 (1H, m, Ph(4)), 6.62 (2H, "t", Ph(3,5)), 6.44 (2H, d, Ph(2,6)), 3.01 (2H, s, CH_2), 1.97 (6H, s, PdMe). IR: $\nu_{as}(CO_2)$ 1551 cm^{-1}.

Crystallography

A unique data set measured to $2\theta_{max} = 50°$ was measured with an Enraf–Nonius CAD-4 diffractometer operating in conventional 2θ–θ scan mode. A total of 2764 independent reflections was obtained at *ca.* 295 K, 1837 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after

Gaussian absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Residuals R and R_w on $|F|$ at convergence were 0.048 and 0.050; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were employed. Neutral-atom complex scattering factors were used [18]; computation used the XTAL 3.0 program system implemented by Hall [19].

Crystal data

$Pd(N_3)(CH_2Ph)(bpy)$, $C_{17}H_{15}N_5Pd$, M 395.7, monoclinic, space group $P2_1/n$, a 7.113(2), b 9.208(7), c 23.958(7) Å, $\beta = 90.44(2)°$, U 1569 Å^3, D_c $(Z = 4)$ 1.68 g cm^{-3}, $F(000)$ 792. Specimen size: 0.20 by 0.31 by 0.04 mm. Monochromatic Mo-K_α radiation, λ 0.7107$_3$ Å, μ 10.7 cm^{-1}, $A^*_{min,max}$ 1.05, 1.25.

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