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Neopentyl- and trimethylsilylmethylpalladium chemistry: synthesis of reagents for organopalladium chemistry and the crystal structure of the neopentyl(phenyl)palladium(IV) complex [Pd(mq)(CH_2CMe_3)Ph(bpy)]Br (mq = 8-methylquinolinyl, bpy = 2,2′-bipyridine)

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Abstract

Synthetic routes to neopentyl and trimethylsilylmethyl complexes of Pd(II) are reported, Pd(CH_2EMe_3)Ph(tmeda) [E = C (**1**), Si (**3**); tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine] and Pd(CH_2EMe_3)Ph(bpy) [E = C (**2**), Si (**4**); bpy = 2,2′-bipyridine]. Complexes **1** and **3** are formed on the reaction of PdIPh(tmeda) with $LiCH_2EMe_3$, and they react with bpy to give **2** and **4**. Oxidative addition reactions of 8-(bromomethyl)quinoline (mqBr) with Pd(CH_2EMe_3)Ph(bpy) result in the formation of octahedral Pd(IV) complexes [Pd(mq)(CH_2EMe_3)Ph(bpy)]Br [E = C (**5**), Si (**6**)]. An X-ray structural analysis for **5**, the first example of a stable cationic arylpalladium(IV) complex, shows a *fac*-PdC_3N_3 configuration with the neopentyl group trans to the quinoline nitrogen donor atom.

Keywords: Organopalladium; Intramolecular coordination; Neopentyl; Trimethylsilylmethyl; Palladium(IV); 8-Methylquinolinyl

1. Introduction

Hydrocarbylpalladium(IV) complexes are a well-established feature of the organometallic chemistry of palladium and, prior to the first account of such complexes [1], there were several reports that are indicative of the formation of unstable Pd(IV) complexes that could not be detected spectroscopically. Among these reports is the observation that Pd(CH_2CMe_3)$_2$(bpy) (bpy = 2,2′-bipyridine) reacts with benzyl bromide to form PdBr(CH_2CMe_3)(bpy) and $PhCH_2$–CH_2CMe_3 [2]. The neopentyl and the closely related trimethylsilylmethyl groups have played an important role in the development of organometallic chemistry, including in recent reports of palladium chemistry [3–8]. In the absence to date of ambient temperature stable arylpalladium(IV) species, the potential roles of arylpalladium(IV) species in catalysis, and the interesting observation of Diversi et al., we have developed syntheses of Pd(CH_2EMe_3)Ph(bpy) (E = C, Si) and examined their reactivity toward 8-bromomethylquinoline (mqBr) in view of the enhanced stability for Pd(IV) complexes expected to be imparted by the presence of an intramolecular $[C–N]^-$ group [9,10]. The syntheses of potentially widely useful new alkyl(aryl)palladium(II) substrates Pd(CH_2EMe_3)Ph(L_2) [E = C, Si; L_2 = tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), bpy] are reported, together with an X-ray structural analysis for the octahedral Pd(IV) complex [Pd(mq)(CH_2CMe_3)Ph(bpy)]Br.

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2. Experimental

The reagents PdIPh(tmeda) [11] and 8-(bromomethyl)quinoline [12] were prepared as described. Neopentyllithium and trimethylsilylmethyllithium were prepared as described [13], except that hexane was used as a solvent and reflux undertaken for 2 days. Alkyllithium reagents were purified by means of sublimation [$LiCH_2CMe_3$ (110 °C, 0.01 mmHg), $LiCH_2SiMe_3$ (95 °C, 0.01 mmHg)] prior to use. All reactions and manipulations of air and moisture sensitive compounds were carried out under an argon atmosphere using glovebox and Schlenk techniques. Solvents were purified and dried in the usual manner [14]. Other reagents were purchased and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity Inova 400 WB spectrometer operating at 100.587 (^{13}C) or 399.703 (^{1}H) MHz. Chemical shifts are reported in ppm relative to $SiMe_4$. Microanalyses were performed by the Central Science Laboratory, University of Tasmania.

2.1. Synthesis of complexes

2.1.1. [Pd(CH_2CMe_3)Ph(tmeda)] (**1**)

A suspension of PdIPh(tmeda) (0.31 g, 0.73 mmol) in diethyl ether (10 ml) was cooled to −80 °C and transferred by cannula to a flask containing $LiCH_2CMe_3$ (66 mg, 0.85 mmol) which had been pre-cooled to −80 °C. The resulting suspension was stirred for 0.5 h while it was allowed to warm slowly to −40 °C. The mixture was stirred at −40 °C for 0.5 h, then warmed slowly to 0 °C. Water (2 ml) at 0 °C was added, yielding a black suspension which was stirred for a short period at 0 °C, then rapidly cooled to −40 °C. The clear yellow organic layer was separated by decantation, and the water layer was washed twice with diethyl ether (10 ml). The combined organic extracts were dried over sodium sulfate at 0 °C and filtered through cottonwool/Celite. All volatiles were removed in a vacuum leaving a yellow solid. Crystallisation from acetone at −40 °C gave white crystals (0.22 g, 82%). ^{1}H NMR (acetone-d_6, −20 °C): δ 7.42 (m, 2, Ph), 6.66–6.80 (m, 3, Ph), 2.49–2.66 (broad, overlapping, 10, NMe_2 and (CH_2)$_2$), 2.13 (s-broad, 6, NMe_2), 1.11 (s, 2, CH_2CMe$_3$), 0.72 (s, 9, CH$_2$CMe_3). ^{13}C{^{1}H} NMR (acetone-d_6, −20 °C): δ 164.3, 138.6, 125.4, 120.6, 59.8, 58.8, 48.0, 34.6. *Anal.* Calcd. for $C_{17}H_{32}N_2Pd$: C, 55.06; H, 8.70; N, 7.55. Found: C, 55.13; H 8.71; N, 7.56%.

2.1.2. [Pd(CH_2CMe_3)Ph(bpy)] (**2**)

A solution of Pd(CH_2CMe_3)Ph(tmeda) (**1**) (91 mg, 0.25 mmol) in acetone (1 ml) was cooled to −40 °C and mixed with a solution of 2,2′-bipyridine (53 mg, 0.37 mmol) in acetone (2 ml) at −80 °C. The resultant yellow solution was allowed to warm slowly to ambient temperature, then stored at −40 °C. Yellow–red crystals formed over several days (58 mg, 58%). ^{1}H NMR (acetone-d_6): δ 9.15 ('d', ^3J = 5.6 Hz, 1, H6-bpy), 8.52 ('d', ^3J = 8.0 Hz, 1, H3-bpy), 8.48 ('d', ^3J = 8.0 Hz, 1, H3′-bpy), 8.24 (dt, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1, H4′-bpy), 8.16 (d, ^3J = 5.6 Hz,1, H6′-bpy), 8.12 (dt, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1, H4-bpy), 7.80 (ddd, ^3J = 5.6 Hz, ^3J = 5.2 Hz, ^4J = 1.2 Hz, 1, H5′-bpy), 7.60 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 2, H2,6-Ph), 7.50 (ddd, ^3J = 7.6 Hz, ^3J = 5.2 Hz, ^4J = 1.2 Hz, 1, H5′-bpy), 6.95 (m, 2, H3,5-Ph), 6.82 (tt, ^3J = 7.2 Hz, ^4J = 1.6 Hz, H4-Ph), 1.72 (s, 2, CH_2CMe$_3$), 0.92 (s, 9, CH$_2$CMe_3). ^{13}C{^{1}H} NMR (acetone-d_6): δ 155.6, 149.7, 149.1, 139.3, 138.4, 123.5, 122.7, 122.3, 121.1, 117.0, 38.1, 35.1, 34.6. *Anal.* Calcd. for $C_{21}H_{24}N_2Pd$: C, 61.39; H, 5.89; N, 6.82. Found: C, 61.38; H,5.92; N, 6.88%.

2.1.3. [Pd(CH_2SiMe_3)Ph(tmeda)] (**3**)

A suspension of PdIPh(tmeda) (0.57 g, 1.3 mmol) in diethyl ether (10 ml) was cooled to −80 °C, and transferred by cannula to a flask containing $LiCH_2SiMe_3$ (0.25 g, 2.7 mmol), which had been pre-cooled to −80 °C. The resulting suspension was stirred for 0.5 h while it was allowed to warm slowly to −30 °C. The solution was then warmed quickly to 0 °C, and ice-cold water (5 ml) was added. The mixture was stirred for a few minutes, then rapidly cooled to −40 °C. The diethyl ether solution was separated by decantation, and the water layer was washed twice with diethyl ether (20 ml). The combined organic layers were dried over sodium sulfate, at 0 °C, and filtered through cottonwool/Celite. All volatiles were removed in a vacuum leaving a yellow solid, and crystallisation from acetone at −60 °C gave white crystals (0.35 g, 69%). ^{1}H NMR (acetone-d_6, −20 °C) δ 7.88 (d, ^3J = 6.79 Hz, 2, H2,6-Ph), 6.79 (t, ^3J = 7.59 Hz, 2, H3,5-Ph), 6.68 (t, ^3J = 7.20 Hz, 1, H4-Ph), 2.65 (s-broad, 4, (CH_2)$_2$), 2.49 (s, 6, NMe_2), 2.21 (s, broad, 6, NMe_2), −0.29 (s, 2, CH_2SiMe$_3$) −0.44 (s, 9, CH$_2$SiMe_3). ^{13}C{^{1}H} NMR (acetone-d_6, −20 °C) δ 161.6, 138.3, 125.6, 120.9, 59.7, 59.4, 48.2 (broad), 3.1, −1.59. *Anal.* Calcd. for $C_{16}H_{32}N_2SiPd$: C, 49.67; H, 8.34; N, 7.24. Found: C, 50.52; H, 8.46; N, 7.24%.

2.1.4. [Pd(CH_2SiMe_3)Ph(bpy)] (**4**)

A solution of [Pd(CH_2SiMe_3)Ph(tmeda)] (**3**) (0.28 g, 0.74 mmol) in acetone (2 ml) was cooled to −40 °C and mixed with a solution of 2,2′-bipyridine (0.23 g, 1.47 mmol) in acetone (2 ml) at −40 °C. The mixture was warmed slowly to −10 °C and the resultant yellow solution was concentrated to −0.5 ml and stored at −20 °C. Yellow crystals formed over several days (0.12 g, 38%). ^{1}H NMR (acetone-d_6) δ −8.86 (d, ^3J = 4.4 Hz, 1, H6-bpy), 8.52 (d, ^3J = 8.0 Hz, 1, H3-bpy), 8.47 (d, ^3J = 8.0 Hz, 1, H3-bpy), 8.24 (dt, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1,

H4-bpy), 8.15–8.11 (m, 2, H4-bpy and H6-bpy), 7.79 (ddd, $^3J = 7.5$ Hz, $^3J = 5.3$ Hz, $^4J = 1.2$ Hz, 1, H5-bpy), 7.49–7.52 (overlapping, 3, H2,6-Ph and H5-bpy), 6.96 (m, 2, H3,5-Ph), 6.83 (tt, $^3J = 7.2$ Hz, $^4J = 1.6$ Hz, 2, H4-Ph), 0.30 (s, 2, CH_2SiMe_3), 0.16 (s, 9, $CH_2Si\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 162.8, 155.6, 154.7, 149.7, 148.7, 139.0, 138.9, 138.4, 126.5, 126.2, 126.1, 122.7, 122.4, 121.5, 2.92, −8.14. *Anal.* Calcd. for $C_{20}H_{24}N_2SiPd$: C, 56.27; H, 5.67; N, 6.56. Found: C, 56.33; H, 5.76; N, 6.60%.

2.1.5. [Pd(mq)(CH$_2$CMe$_3$)Ph(bpy)]Br (5)

A solution of Pd(CH_2CMe_3)Ph(bpy) (**2**) (15 mg, 0.04 mmol) in acetone (1 ml) was mixed with a solution of 8-(bromomethyl)quinoline (8.7 mg, 0.04 mmol) and stirred for 5 min. Diethyl ether was added dropwise until the solution became cloudy, then refrigerated. After 12 h crystals had formed, the solution was decanted and the crystals washed with pentane (3 × 5 ml) and dried in a vacuum (14 mg, 61%). ^1H NMR ($CDCl_3$) δ 9.56 (d, $^3J = 8.0$ Hz, 1, H3-bpy), 9.52 (d, $^3J = 8.0$ Hz, 1, H3-bpy), 8.58 (d, $^3J = 4.4$ Hz, 1, H6-bpy), 8.51 (t, $^3J = 7.8$ Hz, 1, H4-bpy), 8.37 (d, $^3J = 5.2$ Hz, 1, H6-bpy), 8.20 (t, $^3J = 7.8$ Hz, 1, H4-bpy), 8.11 (d, $^3J = 8.4$ Hz, 1, H5-mq), 7.93 (d, $^3J = 4.4$ Hz, 1, H7-mq), 7.77–7.71 (m, 2, H2-mq and H5-bpy), 7.59 (d, $^3J = 8.0$ Hz, 1, H4-mq), 7.49 (t, $^3J = 7.6$ Hz, 1, H3-mq), 7.38 (dd, $^3J = 4.8$ Hz, $^3J = 8.4$ Hz, 1, H6-mq), 7.30 (t, $^3J = 6.4$ Hz, 1, H5-bpy), 7.22 (d, $^3J = 8.0$ Hz, 2, H2,6-Ph), 7.06-7.00 (m, 3, H3,4,5-Ph), 4.52 (d, $^2J = 13.8$ Hz, 1, CH_2-mq), 4.01 (d, $^2J = 13.8$ Hz, 1, CH_2-mq), 2.79 (d, $^3J = 9.8$ Hz, 1, CH_2CMe_3), 2.70 (d, $^2J = 9.8$ Hz, 1, CH_2CMe_3), 0.60 (s, 9, $CH_2C\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 154.6, 154.0.150.4, 149.5, 146.9, 146.8, 146.1, 144.1, 142.0, 141.5, 138.9, 133.3, 129.9, 129.0, 128.1, 127.7, 127.3, 127.0, 126.1, 125.9, 123.1, 121.8, 59.4, 43.9, 36.8, 31.0. *Anal.* Calcd. for $C_{30}H_{32}BrN_3Pd$: C, 58.03; H, 5.70; N, 6.77. Found: C, 58.15; H, 5.32; N, 6.55%.

2.1.6. [Pd(mq)(CH$_2$SiMe$_3$)Ph(bpy)]Br (6)

A solution of Pd(CH_2SiMe_3)Ph(bpy) (**4**) (25 mg, 0.058 mmol) and 8-(bromomethyl)quinoline (13 mg, 0.058 mmol) was stirred in acetone (2 ml) at 0 °C for 15 min. The solvent was reduced to −0.5 ml in a vacuum and pentane was added to the solution until cloudiness developed. The solution was stored at −20 °C, giving a colourless microcrystalline product after 3 days (26 mg, 69%); despite the crystalline nature of this complex and its complete dissolution to give high quality NMR spectra, microanalyses from several preparations differ slightly from expected values (see below). ^1H NMR ($CDCl_3$) δ 9.43 (d, $^3J = 7.6$ Hz, 1, H3-bpy), 9.32 (d, $^3J = 8.0$ Hz, 1, H3-bpy), 8.63 (d, $^3J = 4.0$ Hz, 1, H6-bpy), 8.49 (dt, $^3J = 7.9$ Hz, $^4J = 2.0$ Hz, 1, H4-bpy), 8.28 (d, $^3J = 4.0$ Hz, 1, H6-bpy), 8.20–8.17 (m, 2, H5-mq and H4-bpy), 7.83 (dd, $^3J = 4.8$ Hz, $^4J = 1.2$ Hz, 1, H7-mq), 7.81 (d, $^3J = 7.2$ Hz, 1, H2-mq), 7.74 (m, 1, H5-bpy), 7.66 (d, $^3J = 7.6$ Hz, 1, H4-mq), 7.54 (m, 1, H3-mq), 7.43-7.37 (m, 2, H6-mq and H5-bpy), 7.18 (m, 2, Ph), 7.05 (m, 3, Ph), 4.46 (d, $^2J = 14.0$ Hz, 1, CH_2-mq), 4.20 (d, $^2J = 14.0$ Hz, 1, CH_2-mq), 1.60 (d, $^3J = 12.8$ Hz, 1, CH_2SiMe_3), 1.58 (d, $^2J = 12.8$ Hz, 1, CH_2SiMe_3), −0.46 (s, 9, $CH_2Si\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 154.1, 153.7, 149.1, 146.9, 146.4, 143.8, 142.2, 141.7, 139.3, 134.4, 134.1, 130.5, 129.3, 129.1, 128.9, 128.4, 127.8, 127.4, 127.0, 126.3, 125.9, 123.3, 43.1, 1.14, 0.92. *Anal.* Calcd. for $C_{29}H_{32}BrN_3SiPd$: C, 55.52; H, 4.97; N, 6.48. Found: C, 54.27; H, 6.26; N, 5.25%.

2.2. X-ray structure determination for 5

Crystals were obtained from a concentrated solution of the complex in acetone at 0 °C. A full sphere of CCD area-detector diffractometer data as measured ($2\theta_{max} = 58°$, ω scan mode, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; $T \sim 150$ K) yielding 13 468 total reflections, these being merged to 6769 unique after 'empirical'/multiscan absorption correction, 5420 with $F > 4\sigma(F)$ being considered 'observed' and used in the full-matrix least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimates. Conventional residuals R, R_w were 0.055, 0.044, reflection weights being $(\sigma^2(F) + 0.0004F^2)^{-1}$. Neutral atom complex scattering factors were employed and computation used the XTAL 3.7 program system [15].

Crystal data: $C_{31}H_{32}BrN_3Pd$, $M = 632.9$, Triclinic, space group $P\bar{1}$, $a = 8.748(2)$, $b = 10.063(2)$, $c = 17.398(4)$ Å, $\alpha = 99.214(4)$, $\beta = 99.762(4)$, $\gamma = 109.821(3)°$, $V = 1380$ Å^3, D_{calc} $(Z = 2) = 1.52_3$ g cm^{-3}; $F(000) = 640$, specimen $0.09 \times 0.05 \times 0.04$ mm, $\mu_{Mo} = 21.4$ cm^{-1}, 'T'$_{min,max} = 0.57, 0.84$.

Selected structural data are given in Table 1 and a view of the complex is shown in Fig. 1.

3. Results and discussion

3.1. Synthesis of complexes

The new arylpalladium(II) complexes Pd(CH_2CMe_3)-Ph(tmeda) and Pd(CH_2SiMe_3)Ph(tmeda) have been obtained (Eq. (1)) and converted to bpy derivatives (Eq. (2)). Yields of **1** and **3** were maximised by addition of suspensions of PdIPh(tmeda) to excess solid Li-CH_2EMe_3 at low temperature, rather than addition of $LiCH_2EMe_3$ to solutions or suspensions of PdIPh(t-meda).

Table 1
Selected bond distances (Å) and angles (°) for [Pd(mq)(CH_2CMe_3)Ph(bpy)]Br (**5**)

Bond distances			
Pd–C(01)	2.031(5)	Pd–N(1)	2.193(5)
Pd–C(1)	2.085(6)	Pd–N(11)	2.181(5)
Pd–C(81)	2.030(5)	Pd–N(11′)	2.206(5)
Bond angles			
C(01)–Pd–C(1)	85.5(2)	Pd–C(01)–C(06)	113.7(4)
C(01)–Pd–C(81)	89.0(2)	Pd–C(1)–C(11)	122.4(4)
C(1)–Pd–C(81)	89.5(2)	Pd–C(81)–C(8)	109.0(3)
C(01)–Pd–N(1)	92.1(2)	Pd–N(1)–C(2)	130.7(4)
C(01)–Pd–N(11)	98.4(2)	Pd–N(1)–C(8a)	110.1(3)
C(01)–Pd–N(11′)	168.6(2)	Pd–N(11)–C(12)	115.3(4)
C(1)–Pd–N(1)	171.9(2)	Pd–N(11)–C(16)	125.6(4)
C(1)–Pd–N(11)	91.4(2)	Pd–N(11′)–C(12′)	113.2(3)
C(1)–Pd–N(11′)	104.4(2)	Pd–N(11′)–C(16′)	125.6(4)
N(1)–Pd–N(11)	96.6(2)	C(1)–C(11)–C(111)	112.4(5)
N(1)–Pd–N(11′)	78.8(2)	C(1)–C(11)–C(112)	104.6(5)
N(11)–Pd–N(11′)	76.1(2)	C(1)–C(11)–C(113)	113.2(4)
N(11)–Pd–C(81)	172.6(2)	C(111)–C(11)–C(112)	107.8(4)
N(11′)–Pd–C(81)	96.5(2)	C(111)–C(11)–C(113)	110.1(5)
N(1)–Pd–C(81)	82.7(2)	C(112)–C(11)–C(113)	108.4(5)
Pd–C(01)–C(02)	127.6(3)		

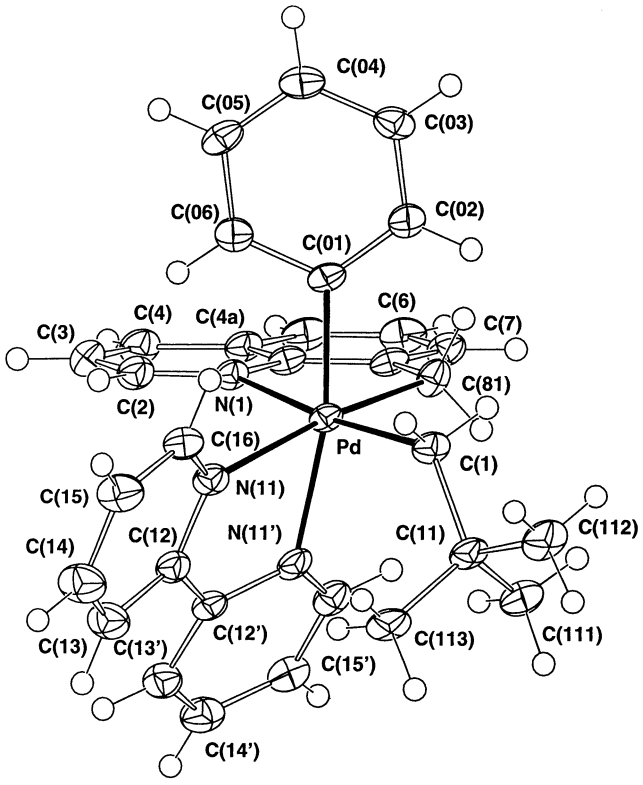

Fig. 1. Projection of the cation in [Pd(mq)(CH_2CMe_3)Ph(bpy)]Br (**5**). Thermal ellipsoids (50%) are shown for non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

$$PdIPh(tmeda) + LiCH_2EMe_2 \rightarrow Pd(CH_2EMe_3)Ph(tmeda) + LiI \quad (1)$$

1 : E = C (82%) **3** : E = Si (69%)

$$Pd(CH_2EMe_3)Ph(tmeda) + bpy \rightarrow Pd(CH_2EMe_3)Ph(bpy) + tmeda \quad (2)$$

2 : E = C (58%) **4** : E = Si (38%)

Reactions of **2** and **4** with 8-bromomethylquinoline as a potential oxidant were productive in terms of detecting Pd(IV) chemistry in NMR reactions in acetone-d_6, with isolation of complexes also subsequently achieved (Eq. (3)). Acetone-d_6 was chosen as a solvent in view of the instability of the diorganopalladium(II) reagents in chlorinated solvents, as commonly observed for such complexes. For Pd(CH_2CMe_3)Ph(bpy), crystals of [Pd(mq)(CH_2CMe_3)Ph(bpy)]Br (**5**) suitable for an X-ray structural analysis were obtained (Fig. 1). ^{1}H NMR spectra show very low intensity resonances indicating the presence of a minor isomer (−5%) for **5** and **6**, presumably resulting from interchange of CH_2EMe_3 and phenyl group positions to retain the *fac*-PdC_3 configuration.

$$Pd(CH_2EMe_3)Ph(bpy)\ (\mathbf{2},\mathbf{4}) + mqBr \rightarrow [Pd(mq)(CH_2EMe_3)Ph(bpy)]Br \quad (3)$$

5 : E = C, **6** : E = Si

3.2. X-ray structural study of [Pd(mq)(CH_2CMe_3)Ph(bpy)]Br (5)

The cation has a distorted octahedral *fac*-PdC_3 configuration with the neopentyl group *trans* to the quinoline nitrogen donor atom (Fig. 1, Table 1), and angles at palladium in the range 85.5(2)–98.4(2)°. The 8-methylquinolinyl-*N*,*C* group forms an essentially planar chelate ring in which the palladium and benzylic carbon atoms deviate by 0.328(5) and 0.509(9) Å from the mq mean planes; the pyridine rings form a dihedral angle of 19.0(2)°, and the Pd atom lies 0.012(8), 0.280(8), 0.662(8) and 0.328(5) Å from the mean planes of the Ph, py, py′, and mq groups respectively.

The phenyl ring is skewed away from the C(1)PdC(81) plane, such that the PdC(01)C(06) angle is ~14° smaller than PdC(01)C(02). This would appear to result from close contacts between the *ortho*-hydrogen atom H(02) and the hydrogen atoms of the methylene groups of mq and CH_2CMe_3, H(02)···H(81a) 2.2_3 and H(02)···H(1b),C(1) 2.1_5, 2.7_5 Å, respectively, where the latter contact may be related to a preferred staggered configuration for CH_2–CMe_3 in concert with orientation of the CMe_3 group to minimise methyl···py′ interactions.

Ambient temperature stable arylpalladium(IV) complexes are formed on the interaction of 8-(bromo-

methyl)quinoline with neopentyl and trimethylsilylmethyl complexes of Pd(II), and are more stable than complexes decomposing at or below ambient temperature in solution [16–20], e.g. $PdCl_3(C_6F_5)$(bpy) [16], $PdIMe_2Ph$(bpy) [18] and $Pd(C_6H_4CH_2N(Me)CH_2CH_2NMe_2-C,N,N')Cl_3$ [20]. The stability of the new complexes most likely arises from several factors, in particular the presence of bidentate bpy and mq groups disfavoring formation of five-coordinate species expected as precursors to decomposition [21], and presence of bidentate mq and bulky CH_2EMe_3 (E = C, Si) groups hindering the formation of appropriate transition states for C···C bond forming reductive elimination reactions. The new Pd(II)(CH_2EMe_3)Ph reagents are expected to be valuable in the further development of organopalladium chemistry.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 174767. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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