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$SnBrMe_3$ and dichalcogenides $(ER)_2$ as oxidants: Synthesis of platinum(IV) complexes, and C···C and C···E coupling from pallada(IV)cyclopentane complexes and $PdMe_2(EPh)\{(pz)_3BH\}$ $\{E = O_2C, S, Se; [(pz)_3BH]^- = tris(pyrazol\text{-}1\text{-}yl)borate\}$[1]

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Abstract

Oxidation of the platinum(II) species $[PtMe_2\{(pz)_3BH\}]^-$ $\{[(pz)_3BH]^- = tris(pyrazol\text{-}1\text{-}yl)borate\}$ by $SnBrMe_3$ and the Group 16 oxidants $(ER)_2$ results in the formation of a series of stable platinum(IV) complexes $PtMe_2(SnMe_3)\{(pz)_3BH\}$ and $PtMe_2(ER)\{(pz)_3BH\}$ ($ER = O_2CPh$, SMe, SPh, SeMe, SePh). In contrast, the palladium(II) analogue does not react with $SnBrMe_3$ and reacts with $(O_2CPh)_2$ to form a 1:1 ratio of $PdMe_3\{(pz)_3BH\}$ and a $Pd^{II}Me$ species. The oxidants $(EPh)_2$ (E = S, Se) react with $[PdMe_2\{(pz)_3BH\}]^-$ to form unstable but NMR detectable species analogous to the platinum(IV) complexes followed by reductive elimination via C···C, C···S and C···Se bond formation processes. The pallada(II)cyclopentane species $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^-$ reacts with $(ER)_2$ to form unstable species $\overline{Pd(CH_2CH_2CH_2CH_2)}(ER)\{(pz)_3BH\}$ ($ER = O_2CPh$, SPh, SePh) followed by related decomposition reactions.

Keywords: Palladium; Platinum; Tin; Thiolate; Selenolate; Oxidation; Reductive elimination

1. Introduction

Tin(IV) reagents [1–3] and dichalcogenides $(ER)_2$ [4,5] have been used to oxidize platinum(II) complexes with the observation in some cases of Pt^{IV}–Sn and Pt^{IV}–E bonds, e.g. $PtMe_2(bpy)$ (bpy = 2,2′-bipyridine) reacts with $SnBrMe_3$ and $(SePh)_2$ to form $PtBrMe_2(SnMe_3)(bpy)$ ([3]a) and $PtMe_2(SePh)_2(bpy)$ [5]. We have recently explored the reactivity of $PdMe_2(bpy)$ toward a range of dichalcogenides leading to the isolation of the first stable dimethylpalladium(IV) complex, $PdMe_2(SePh)_2(bpy)$, and detection of C···C, C···O, C···S and C···Se coupling reactions at palladium(IV) centres [5]. These new decomposition pathways have prompted us to explore related chemistry where the ancillary ligand for palladium and platinum is tripodal tris(pyrazol-1-yl)borate $\{[(pz)_3BH]^-\}$ in view of the exceptional stability exhibited by complexes of this ligand [6,7]. We report here the synthesis of a new class of dialkylplatinum(IV) complex, $PtMe_2(ER)\{(pz)_3BH\}$ ($ER = O_2CPh$, SMe, SPh, SeMe, SePh, $SnMe_3$), and detection and decomposition studies for unstable dimethylpalladium(IV) and pallada(IV)cyclopentane complexes containing group 16 donor ligands.

2. Experimental section

The reagents $[PtMe_2(SEt_2)]_2$ [8], $PdMe_2(tmeda)$ (tmeda = *N*,*N*,*N*′,*N*′ tetramethylethylenediamine) [9,10], and $K[(pz)_3BH]$ [11] were prepared as described; other reagents were used as received and solutions of

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[1] Dedicated to Professor Michael Bruce on the occasion of his 60th birthday.

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$[PtMe_2\{(pz)_3BH\}]^-$ ([7]c), $[PdMe_2\{(pz)_3BH\}]^-$ and $[Pd(CH_2CH_2CH_2CH_2)\{(pz)_3BH\}]^-$ ([7]b) were generated as reported. Solvents were dried and distilled, and all procedures were carried out under nitrogen. Microanalyses were by the Central Science Laboratory, University of Tasmania, and NMR spectra were recorded with a Bruker AM 300 spectrometer with chemical shifts given in ppm relative to $SiMe_4$. The decomposition products of palladium(IV) complexes were analysed by sampling the gas–liquid phases using a microsyringe, and a HP 5890 gas chromatograph connected to a HP 5970B mass selective detector (70 eV ET with He carrier gas).

2.1. Synthesis of platinum(IV) complexes $PtMe_2(ER)\{(pz)_3BH\}$ [ER = O_2CPh, SMe, SPh, SeMe, SePh, $SnMe_3$]

2.1.1. $PtMe_2\{O_2CPh\}\{(pz)_3BH\}$ (1)

A solution of $[PtMe_2(SEt_2)_2]_2$ (0.040 g, 0.063 mmol) and $K[(pz)_3BH]$ (0.032 g, 0.130 mmol) in tetrahydrofuran (2 ml) was stirred for ca. 1 h, and on cooling to 0°C dibenzoyl peroxide (0.031 g, 0.130 mmol) was added. A white solid formed immediately, and after stirring for 1 h at ambient temperature the solvent was evaporated in a vacuum. The residue was extracted with diethyl ether and filtered to remove a white solid, and the filtrate evaporated to give a pale yellow solid. The solid was washed with pentane (2 × 3 ml) and recrystallized from tetrahydrofuran/pentane to give the product as a white solid (0.044 g, 62%). ^{1}H-NMR ($CDCl_3$): δ 8.10 (d, $^3J = 2.0$ Hz, 1, H3 or 5 trans to O_2CPh), 8.00 (d, $^3J = 2.0$ Hz, 1, H3 or 5 trans to O_2CPh), 7.71 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.68 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.3–7.6 (m, 5, Ph), 6.31 (t, $^3J = 2.0$ Hz, 2, H4), 6.22 (t, $^3J = 2.0$ Hz, 1, H4 trans to O_2CPh), 1.96 (s, $^2J_{PH} = 68.0$ Hz, 3, PtMe), 1.82 (s, $^2J_{PtH} = 68.0$ Hz, 3, PtMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 170.8 (CO_2), 140.7, 139.2, 137.0, 135.6, 135.4, 132.2, 106.7, 106.2, −1.38 ($^1J_{PtC} = 591$ Hz, PtMe), −2.80 (PtMe). $\nu_{as}(CO_2)$ (KBr disk) = 1640s cm^{-1}, $\nu_{as}(CO_2)$ (in dichloromethane) = 1760m, 1700m, 1660m cm^{-1}. Anal. Calcd. for $C_{18}H_{21}BN_6PtO_2$: C, 38.65; H, 3.78; N, 15.03. Found: C, 38.60; H, 4.43; N, 15.10%.

2.1.2. $PtMe_2(SMe)\{(pz)_3BH\}$ (2)

A solution of $[PtMe_2(SEt_2)]_2$ (0.040 g, 0.060 mmol) and $K[(pz)_3BH]$ (0.032 g, 0.130 mmol) in tetrahydrofuran (4 ml) was stirred for ca. 1 h, and on cooling to 0°C dimethyldisulfide (0.012 g, 0.132 mmol) was added. The colorless solution immediately became yellow and a white solid precipitated. After stirring at ambient temperature for 2 h the solvent was evaporated. The yellow oil thus obtained was dissolved in diethyl ether (5 ml), centrifuged to remove the white solid, the solid treated again similarly with diethyl ether (5 ml), and the combined diethyl ether solutions evaporated in a vacuum. The residue was washed with pentane to give the product as a yellow solid (0.050 g, 83%). ^{1}H-NMR ($CDCl_3$): δ 7.86 (d, $^3J = 2.0$ Hz, $J_{PtH} = 4.4$ Hz, 2, H3 or 5), 7.69 (d, $^3J = 2.0$ Hz, 1, H3 or 5 trans to SMe), 7.68 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.53 (d, $^3J = 2.0$ Hz, $J_{PtH} = 10.0$ Hz, 1, H3 or 5 trans to SMe), 6.29 (t, $^3J = 2.0$ Hz, $^4J_{PtH} = 8.0$ Hz, 1, H4 trans to SMe), 6.28 (m, $^3J = 2.0$ Hz, 2, H4), 1.53 (s, $^3J_{PtH} = 48.0$ Hz, 3, SMe), 1.38 (s, $^2J_{PtH} = 68.0$ Hz, 6, PtMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 141.5, 138.7 ($J_{PtC} = 16$ Hz), 137.0 ($J_{PtH} = 33$ Hz), 135.4, 106.6 ($J_{PtC} = 20$ Hz), 106.3 ($J_{PtC} = 13$ Hz,), 11.6 ($^2J_{PtC} = 18$ Hz, SMe), −5.54 ($^1J_{PtC} = 557$ Hz, PtMe). Anal. Calcd. for $C_{12}H_{19}BN_6PtS$ C, 29.70; H, 3.95; N, 17.32; S, 6.60. Found: C, 29.50; H, 3.87; N, 17.12; S, 6.51%.

2.1.3. $PtMe_2(SPh)\{(pz)_3BH\}$ (3)

A solution of $[PtMe_2(SEt_2)]_2$ (0.040 g, 0.060 mmol) and $K[(pz)_3BH]$ (0.032 g, 0.130 mmol) in tetrahydrofuran (4 ml) was stirred for ca. 1 h and diphenyldisulfide (0.028 g, 0.130 mmol) was added. After stirring for 2 h the solvent was evaporated to give a yellow oily residue which was extracted with diethyl ether (2 × 5 ml) and filtered to remove a small amount of solid. The diethyl ether solution was washed with water and dried over $MgSO_4$. After filtration the solvent was removed in a vacuum to give a yellow–orange oil which was redissolved in a minimum amount of acetone. Petroleum ether (b.p. 40–60°C) was added until cloudiness developed and the mixture stored at −20°C for 5 h. A small amount of yellow solid was removed by filtration and the filtrate evaporated slowly under a stream of nitrogen until a yellow solid precipitated. The solid was collected and dried in a vacuum (0.048 g, 83%). ^{1}H-NMR ($CDCl_3$): δ 7.72 (d, $^3J = 2.0$ Hz, 1, H3 or 5 trans to SPh), 7.68 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.53 (d, $^3J = 2.0$ Hz, 1, H3 or 5 trans to SPh), 7.50 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 6.9–7.35 (m, 5, Ph), 6.29 (t, $^3J = 2.0$ Hz, $^4J_{PtH} = 8.3$ Hz, 1, H4 trans to SPh), 6.17 (t, $^3J = 2.0$ Hz, 2, H4), 1.39 (s, $^2J_{PtH} = 68.0$ Hz, 6, PtMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 138.9 ($J_{PtC} = 15$ Hz), 137.5, 136.0, 135.4, 129.5, 128.2 ($J_{PtC} = 7$ Hz), 128.0, 126.0 ($J_{PtC} = 9$ Hz), 106 7 ($J_{PtC} = 20$ Hz), 106.1 ($J_{PtC} = 12$ Hz) −3.75 ($^1J_{PtC} = 592$ Hz, PtMe) Anal. Calcd. for $C_{17}H_{21}BN_6PtS$: C, 37.30; H, 3.87; N, 15.35; S, 5.86. Found: C, 37.37; H, 3.92; N, 15.43; S, 6.01%.

2.1.4. $PtMe_2(SeMe)\{(pz)_3BH\}$ (4)

A solution of $[PtMe_2(SEt_2)]_2$ (0.040 g, 0.060 mmol) and $K[(pz)_3BH]$ (0.032 g, 0.130 mmol) in tetrahydrofuran (5 ml) was stirred for 1 h, and on cooling to 0°C dimethyldiselenide (0.024 g, 0.130 mmol) was added. The solution changed immediately from

pale yellow to orange. After stirring at ambient temperature for 3 h the product was isolated and purified as for complex **3**, and obtained as a yellow solid (0.08 g, 53%). ^{1}H-NMR ($CDCl_3$): δ 7.90 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.71 (d, $^3J = 2.0$ Hz, 1, H3 or 5 trans to SeMe), 7.68 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.53 (d, $^3J = 2.0$ Hz, $J_{PtH} = 11.0$ Hz, 1, H3 or 5 trans to SeMe), 6.30 (t, $^2J = 2.0$ Hz, 1, H4 trans to SeMe), 6.27 (t, $^3J = 2.0$ Hz, 2, H4), 1.39 (s, $^3J_{SeH} = 5.0$ Hz, $^2J_{PtH} = 69.0$ Hz, 6, PtMe), 1.32 (s, $^2J_{SeH} = 11.0$ Hz, $^3J_{PtH} = 42.0$ Hz, 3, SeMe). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 139.3 ($J_{PtC} = 16$ Hz), 136.6, 135.9, 135.5, 106.7 ($J_{PtC} = 21$ Hz), 106.3 ($J_{PtC} = 14$ Hz), 1.52 (SeMe), −8.35 ($^1J_{PtC} = 585$ Hz, PtMe). Anal. Calcd. for $C_{12}H_{19}BN_6PtSe$: C, 27.08; H, 3.60; N, 15.79. Found: C, 27.04; H, 3.58; N, 15.58%.

2.1.5. $PtMe_2(SePh)\{(pz)_3BH\}$ (5)

A solution of $[PtMe_2(SEt_2)]_2$ (0.045 g, 0.070 mmol) and K[$(pz)_3$BH] (0.036 g, 0.140 mmol) in acetone (4 ml) was stirred for ca. 1 h and diphenyldiselenide (0.045 g, 0.140 mmol) was added to immediately form an orange solution. After stirring for 3 h the solvent was evaporated in a vacuum and the brown residue obtained was washed twice with pentane and then extracted with diethyl ether. The diethyl ether solution was evaporated to give an orange oil which was dissolved in acetone (1 ml) and added to water (10 ml) to precipitate a yellow solid. The solid was isolated by centrifugation, washed with petroleum ether, and dried in a vacuum (0.038 g, 45%). ^{1}H-NMR ($CDCl_3$): δ 7.70 (d, $^3J = 2.0$ Hz, 1, H3 or 5 trans to SePh), 7.68 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.66 (d, $^3J = 2.0$ Hz, 1, H3 or 5 trans to SePh), 7.63 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 6.9–7.60 (m, 5, Ph), 6.29 (t, $^3J = 2.0$ Hz, 1, H4 trans to SePh), 6.16 (t, $^3J = 2.0$ Hz, 2, H4), 1.37 (s, 6, $^2J_{PtH} = 68.0$ Hz, $^3J_{SeH} = 4.0$ Hz, 6, PtMe). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 139.5 ($J_{PtC} = 17$ Hz), 137.1, 136.9, 135.4, 132.0, 129.6, 128.2, 126.4, 106.6, 106.2, −6.60 ($^1J_{PtC} = 581$ Hz, PtMe). Anal. Calcd. for $C_{17}H_{21}BN_6PtSe$: C, 34.36; H, 3.56; N, 14.14. Found: C, 34.57; H, 3.56; N, 14.01%.

2.1.6. $PtMe_2(SnMe_3)\{(pz)_3BH\}$ (6)

A solution of $[PtMe_2(SEt_2)]_2$ (0.040 g, 0.060 mmol) and K[$(pz)_3$BH] (0.032 g, 0.130 mmol) in acetone (2 ml) was stirred for ca. 1 h and bromotrimethyltin (0.031 g, 0.130 mmol) was added at 0°C to immediately form a white solid. After stirring for 1 h at ambient temperature the solvent was evaporated in a vacuum and the oily residue obtained was extracted with diethyl ether (2 × 5 ml) and filtered to remove KBr. The diethyl ether solution was evaporated and the residue crystallized from acetone/petroleum ether (b.p. 40–60°C) and dried in a vacuum to give a white crystalline solid (0.070 g, 92%). ^{1}H-NMR ($CDCl_3$): δ 7.72 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.67 (d, $^3J = 2.0$ Hz, $^3J_{PtH} = 8.4$ Hz, 1, H3 trans to $SnMe_3$), 7.58 (m, 1, H 5 trans to $SnMe_3$), 7.55 (d, $^3J = 2.0$ Hz, $^3J_{PtH} = 8.0$ Hz, 2, H3), 6.24 (t, $^3J = 2.0$ Hz, 1, H4 trans to $SnMe_3$), 6.22 (t, $^3J = 2.0$ Hz, 2, H4), 0.95 (s, $^2J_{PtH} = 62.0$ Hz, 6, PtMe), 0.08 (s, $^3J_{PtH} = 48.0$ Hz, $^2J_{SnH} = 8.4$ Hz, 9, SnMe). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 140.3 ($J_{PtC} = 30$ Hz), 166.2 ($J_{PtC} = 10$ Hz), 134.9, 105.9 ($J_{PtC} = 19$ Hz), 105.6 ($J_{PtC} = 12$ Hz) −10.0 ($^1J_{SnC} = 60$ Hz, SnMe), −17.3 ($^1J_{PtC} = 612$ Hz, $^1J_{PtSn} = 50$ Hz, PtMe). Anal. Calcd. for $C_{14}H_{25}BN_6PtSn$: C, 27.93; H, 4.18; N, 13.96. Found: C, 28.04; H, 4.27; N, 13.67%.

2.2. ^{1}H-NMR studies of the reactions of palladium(II) complexes with oxidizing agents

2.2.1. $[PdMe_2\{(pz)_3BH\}]^-/(O_2CPh)_2$

A solution of $[PdMe_2\{(pz)_3BH\}]^-$ was prepared by stirring $PdMe_2$(tmeda) (0.01 g, 0.040 mmol) and K[$(pz)_3$BH] (0.01 g, 0.040 mmol) in acetone-d_6 (0.5 ml) for 1 h. The solution was cooled to −70°C and a pre-cooled solution of dibenzoyl peroxide (0.01 g, 0.04 mmol) in acetone-d_6 was added. NMR spectra were obtained at −70°C, and the temperature raised in 10°C intervals until −50°C, when reaction commenced to form a white solid (KO_2CPh) and to give a solution exhibiting resonances for $PdMe_3\{(pz)_3BH\}$. When all of the dimethylpalladium(II) reagent was consumed the yellow suspension was filtered, and triphenylphosphine added to the filtrate to give a pale yellow solution containing equimolar quantities of $PdMe_3\{(pz)_3BH\}$ and $PdMe\{(pz)_3BH\}(PPh_3)$.

2.2.2. $[PdMe_2\{(pz)_3BH\}]^-/(SPh)_2$

Following a similar procedure, reaction commenced on warming to about −10°C with decomposition of an intermediate occurring at the same temperature to form ethane, S(Ph)Me, SPh_2 and a red solid. A resonance at 1.80 ppm is assigned to the $Pd^{IV}Me$ group of unstable $PdMe_2(SPh)\{(pz)_3BH\}$.

2.2.3. $[PdMe_2\{(pz)_3BH\}]^-/(SePh)_2$

Following a similar procedure, reaction commenced on warming to about 0°C with decomposition of an intermediate occurring at the same temperature to form ethane, Se(Ph)Me, $SePh_2$ and a red solid. A resonance at 1.84 ppm is assigned to the $Pd^{IV}Me$ group ofunstable$PdMe_2(SePh)\{(pz)_3BH\}$.

2.2.4. $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^-/(O_2CPh)_2$

A solution of $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^-$ was prepared by stirring $[\overline{Pd(CH_2CH_2CH_2CH_2)}$(tmeda) (0.010 g, 0.035 mmol) and K[$(pz)_3$BH] (0.009 g, 0.035 mmol) in acetone-d_6 (0.5 ml) for 2 h. The solution was cooled to −40°C and a

pre-cooled solution of $(O_2CPh)_2$ (0.009 g, 0.035 mmol) in acetone-d_6 was added. NMR spectra were obtained at −40°C, and the temperature raised in 10°C intervals until 20°C, at which temperature reaction commenced. A red-orange solid precipitated and GC-MS analysis of the red-orange solution revealed the presence of butenes, cyclobutane, $C_4H_7O_2CPh$, $C_4H_9O_2CPh$ and $PhCO_2H$.

2.2.5. $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^-/(SPh)_2$

A solution of $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3\text{-}BH\}]^-$ was prepared by stirring $[\overline{Pd(CH_2CH_2CH_2CH_2)}(tmeda)$ (0.008 g, 0.039 mmol) and $K[(pz)_3BH]$ (0.010 g, 0.039 mmol) in acetone-d_6 (0.3 ml) for 2 h. The solution was cooled to −40°C and a pre-cooled solution of dimethyldisulfide (0.0085 g, 0.039 mmol) in acetone-d_6 was added. NMR spectra were obtained at −40°C, and the temperature raised in 10°C intervals until −20°C, at which temperature reaction commenced. The complex $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}$ was detected (see below), but an orange–red solid also precipitated (exceptionally insoluble in common solvents) with concurrent disappearance of resonances of the palladium(IV) complex and appearance of resonances attributable to alkene protons (5.1 ppm). Other resonances were broad and assignments were not attempted. GC-MC analysis indicated the formation of butenes, cyclobutane, $S(Ph)C_4H_9$, $S(Ph)C_4H_7$ and SPh_2. ^{1}H-NMR (acetone-d_6) resonances attributable to $Pd(C_4H_8)(SPh)\{(pz)_3BH\}$: δ 8.18 (d, $^3J = 3$ Hz, 1, H3 or 5 trans to SPh), 8.01 (d, $^3J = 3$ Hz, 2, H3 or 5), 7.92 (d, $^3J = 3$ Hz, 1, H3 or 5 trans to SPh), 7.88 (d, $^3J = 3$ Hz, 2, H3 or 5), (7.43, 7.15, 7.12, 7.0) (m, Ph), 6.49 (t, $^3J = 3$ Hz, 1, H4 trans to SPh), 6.23 (t, $^3J = 3$ Hz, 2, H4), (4.04, 3.75) (m, 8, CH_2).

2.2.6. $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^-/(SePh)_2$

Following a similar procedure a palladium(IV) species was detected at −20°C, but at higher temperatures a brown-red solid precipitated (insoluble) and alkene resonances occurred at 4.8–5.2 ppm. GC-MS analysis indicated the formation of butenes, cyclobutane, $Se(Ph)C_4H_9$, $Se(Ph)C_4H_7$ and $SePh_2$. ^{1}H-NMR (acetone-d_6) resonances attributable to pallada(IV)cyclic protons of $\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}$ (3.55 and 4.07 ppm).

2.2.7. $[PdMe_2\{(pz)_3BH\}]^-/BrSnMe_3$ and $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^-/BrSnMe_3$

Following similar procedures reaction could not be detected after 24 h at ambient temperature.

3. Results and discussion

A convenient route to organopalladium(IV) and platinum(IV) complexes containing the tris(pyrazol-1-yl)borate ligand employs the reaction of oxidizing agents with diorganometal(II) species, e.g. iodomethane with $[MMe_2\{(pz)_3BH\}]^-$ (M = Pt, Pd) to give $MMe_3\{(pz)_3BH\}$ ([7]a,c). Solutions of the anionic reagents may be generated at ambient temperature on addition of $K[(pz)_3BH]$ to $[PtMe_2(SEt_2)]_2$ or $PdMe_2(tmeda)$. The solutions may be cooled to low temperatures for NMR studies of reactivity, ideal for probing the formation of potentially unstable complexes.

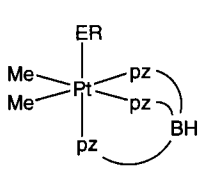
Platinum(IV) complexes are more stable than palladium(IV) complexes, and a series of benzoate, thiolate, selenolate and trimethylstannyl complexes could be isolated in 45–92% yield (Scheme 1).

^{1}H-NMR spectra of the complexes may be readily assigned and are in accord with the formulations presented in Scheme 1, e.g. occurrence of two pyrazole ring environments in 2:1 ratio, and coupling to the ^{195}Pt nucleus for the thiomethyl group of **2** ($^3J_{PtH}$ = 48 Hz), the selenomethyl group of **4** ($^3J_{PtH} = 42$ Hz) and the trimethylstannyl group of **6** ($^3J_{PtH} = 48$ Hz). Spectra show one PtMe environment for all complexes except **1**, which exhibits two ^{1}H-NMR resonances in 1:1 ratio with identical $^2J_{PtH}$ (68.0 Hz). The reason for this is not clear, but may result from presence of conformational isomers formed by rotation about the Pt–O bond, since the infrared spectrum of **1** in dichloromethane shows splitting of $\nu_{as}(CO_2)$ into three absorptions.

For $[PdMe_2\{(pz)_3BH\}]^-$, ^{1}H-NMR studies of reactions with $(O_2CPh)_2$ at −50°C in acetone-d_6 show that $PdMe_3\{(pz)_3BH\}$ is rapidly formed, together with insoluble KO_2CPh. After filtration, addition of PPh_3 results in NMR spectra showing the presence of $PdMe_3\{(pz)_3BH\}$ and $PdMe\{(pz)_3BH\}(PPh_3)$ in 1:1 ratio (Eq. 1).

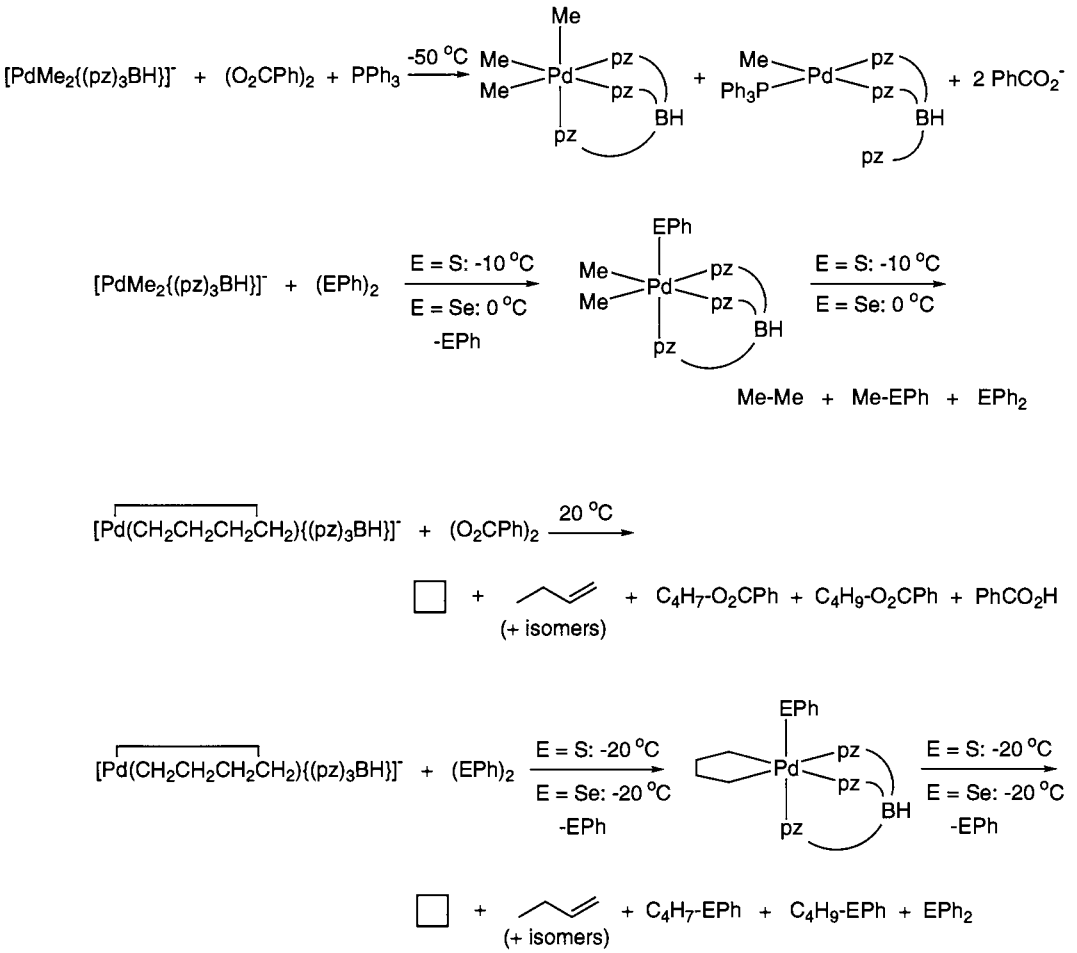
$[PtMe_2\{(pz)_3BH\}]^- + (ER)_2 \rightarrow PtMe_2(ER)\{(pz)_3BH\} + ER^-$

1: ER = O_2CPh
2: ER = SMe
3: ER = SPh
4: ER = SeMe
5: ER = SePh



$[PtMe_2\{(pz)_3BH\}]^- + SnBrMe_3 \rightarrow PtMe_2(SnMe_3)\{(pz)_3BH\}$ (**6**) $+ Br^-$

Scheme 1.



The overall reaction is related to that reported for the reaction of $[PdMe_2\{(pz)_3BH\}]^-$ with halogens (Cl_2, Br_2, I_2) as oxidants ([7]b). For halogens, and presumably $(O_2CPh)_2$, reactions of this type occur via oxidation to give undetected '$PdXMe_2\{(pz)_3BH\}$' (X = C1, Br, I, O_2CPh) followed by attack at a $Pd^{IV}Me$ group by the strong nucleophile $[PdMe_2\{(pz)_3BH\}]^-$ leading to Me^+ transfer and formation of $PdMe_3\{(pz)_3BH\}$ and a $Pd^{II}Me$ species. The analogous reactions of $[\overline{Pd(CH_2CH_2CH_2CH_2}\{(pz)_3BH\}]^-$ with halogens to give stable complexes $[\overline{Pd(CH_2CH_2CH_2CH_2}) (X)\{(pz)_3BH\}$ (X = C1, Br, I) ([7]b), and with $(O_2CPh)_2$ (Eq. 3), proceed differently, presumably because an alkyl transfer process is not possible for a pallada(IV)cyclic intermediate.

For $(SPh)_2$ and $(SePh)_2$ as oxidants reacting with $[PdMe_2\{(pz)_3BH\}]^-$, NMR studies in acetone-d_6 show that reactions at low temperature are slower than for $(O_2CPh)_2$ and give unstable intermediates that do not lead to $Pd^{IV}Me_3$ and $Pd^{II}Me$ products, instead decomposing by C···C and C···E coupling to give Me–Me, Me–EPh and EPh_2 (Eq. 2). The intermediates are assigned as analogues of platinum(IV) complexes, $PdMe_2(EPh)\{(pz)_3BH\}$ (E = S, Se), e.g. exhibiting two pyrazole ring environments in 2:1 ratio and downfield shifts of $Pd^{IV}Me$ resonances compared with $[PdMe_2\{(pz)_3BH\}]^-$, occurring at positions (ca. 1.8 ppm) similar to those observed for platinum complexes (ca. 1.4 ppm) in acetone-d_6. Approximate yields of non-volatile products Me–EPh and EPh_2 were determined by a combination of NMR and GC-MS methods to be Me–SPh (ca. 52%), SPh_2 (ca. 64%), Me–SePh (ca. 40%) and $SePh_2$ (6%).

The pallada(IV)cyclic reagent $[\overline{Pd(CH_2CH_2CH_2CH_2}\{(pz)_3BH\}]^-$ exhibits different reactivity (Eqs. 3 and 4) than the dimethylpalladium(II) substrate, although the product distributions are consistent with formation of $[\overline{Pd(CH_2CH_2CH_2CH_2}(ER)\{(pz)_3BH\}$ (E = O_2CPh, S, Se) intermediates, and for S and Se these unstable species were detected by ^{1}H-NMR spectroscopy. As for unstable dimethylpalladium(IV) complexes, the pallada(IV)cyclic complexes decompose by a combination of C···C (to form cyclobutane), C···O, C···S and C···Se coupling, but in addition the palladacyclic ring fragments to give butenes. Intramolecular carbon···heteroatom coupling involving the pallada(IV)cycle presumably leads to intermediate Pd^{II} $CH_2CH_2CH_2CH_2EPh$ (E = O_2C, S, Se) species which decompose to give alkenes (C_4H_7–EPh) and alkanes

Formation of $(SPh)_2$ and $(SePh)_2$ as products of decomposition (Eqs. 2 and 4) is not expected to occur directly from the palladium(IV) complexes, and may result from complex reactions between organic and inorganic products, e.g. E(Ph)Me addition to a 'Pd^{II}(EPh)' species to give 'Pd^{IV}(Ph)(EPh)' followed by reductive elimination of EPh_2.

No reaction was observed between $SnBrMe_3$ and palladium(II) reagents, presumably reflecting the lower oxidizing ability of the tin(IV) reagent which is sufficient to oxidize platinum(II) but not palladium(II).

The results reported here show that the new type of Pt^{IV}–Sn complex and the new class of chalcogenide complex $PtMe_2(ER)\{(pz)_3BH\}$ ($E = O_2C$, S, Se) are stable, and that these complexes provide suitable models for establishing that far less stable palladium(IV) chalcogenide analogues are formed in similar synthetic procedures. The reactivity observed for the palladium(IV) complexes illustrate, for new systems, central features of emerging organopalladium(IV) chemistry [12], in particular the facile nature of methyl group exchange (Eq. 1) [13], and decomposition under mild conditions in solution via C···C, C···O, C···S and C···Se coupling (Eqs. 2–4) [5].

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