Synthesis of the First Organopalladium(IV) Cations, including the First *X*-Ray Study of Isostructural Organopalladium(IV) and Platinum(IV) Complexes, [*fac*-MMe$_3${tris(pyrazol-1-yl)methane-*N,N′,N″*}]I

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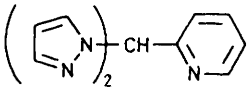
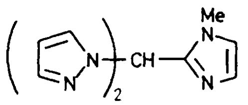
Stable organopalladium(IV) complexes [*fac*-PdMe$_3$(L)]I (L = tridentate nitrogen donor ligand) are formed on oxidative addition of iodomethane to PdMe$_2$(L); the tris(pyrazol-1-yl)methane complex is isostructural with the platinum(IV) analogue.

Organoplatinum(IV) chemistry has been extensively developed since the initial report of [PtMe$_3$(μ_3-I)]$_4$ and related compounds in 1907,[1,2] and although palladium has a well established role in organic synthesis and catalysis,[3] the organometallic chemistry of palladium(IV) is limited. The main reports are suggestions that organopalladium(IV) species are formed as intermediates in some reactions and catalytic processes,[2,4—9] and the isolation of several neutral pentafluorophenyl complexes[10] and a single hydrocarbyl complex, *fac*-[PdMe$_3$(2,2′-bipyridyl)I].[11] This complex, obtained by oxidative addition of iodomethane to the palladium(II) complex PdMe$_2$(bpy) (bpy = 2,2′-bipyridine), reductively eliminates ethane in solution to form PdMe(bpy)I, and is the only



(pz)$_2$(py)CH



(pz)$_2$(mim)CH

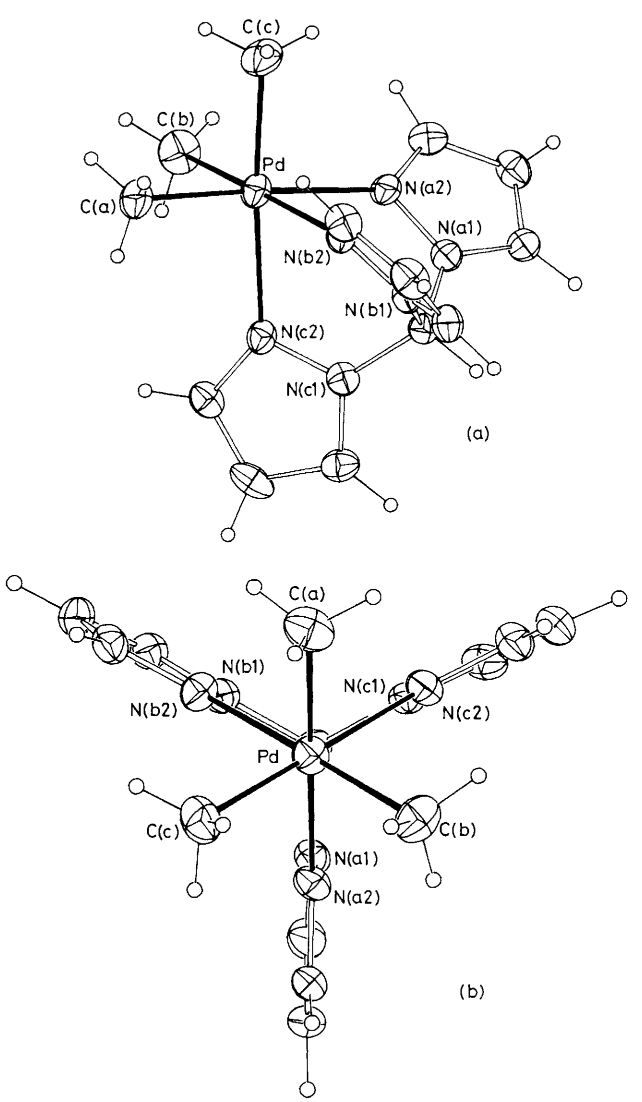


Figure 1. Two projections of the cation $[PdMe_3\{(pz)_3CH\}]^+$ showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions) have been given an arbitrary radius of 0.1 Å. Projection (b) is a view directly along the (non-crystallographic) three-fold axis. Selected bond distances (Å) and angles (°) for the isostructural palladium and platinum complexes, with values for platinum given in brackets []: M–C(a) 2.036(11) [2.031(8)], M–C(b) 2.060(9) [2.056(7)], M–C(c) 2.049(10) [2.056(7)], M–N(a2) 2.191(8) [2.156(6)], M–N(b2) 2.207(7) [2.156(5)], M–N(c2) 2.225(7) [2.189(5)] Å, C(a)–M–C(b) 86.6(4) [87.9(3)], C(a)–M–C(c) 88.0(4) [89.2(3)], C(b)–M–C(c) 87.4(4) [88.4(3)], N(a2)–M–N(b2) 83.2(3) [84.1(2)], N(a2)–M–N(c2) 81.7(3) [82.9(2)], N(b2)–M–N(c2) 82.4(2) [83.7(2)], C(a)–M–N(a2) 176.8(3) [177.3(2)], C(a)–M–N(b2) 95.1(3) [94.4(2)], C(a)–M–N(c2) 95.4(3) [94.6(2)], C(b)–M–N(a2) 95.0(3) [93.5(3)], C(b)–M–N(b2) 177.8(3) [176.9(3)], C(b)–M–N(c2) 96.1(3) [94.0(2)], C(c)–M–N(a2) 94.8(3) [93.2(3)], C(c)–M–N(b2) 94.1(3) [93.8(2)], C(c)–M–N(c2) 175.3(3) [175.6(3)]°.

organopalladium(IV) complex characterised by *X*-ray crystallography.[11] We report here the synthesis of organopalladium(IV) cations which are stable at ambient temperature, and a crystallographic study of isostructural palladium(IV) and platinum(IV) organometallic compounds.

The tris(pyrazol-1-yl)methane complex $PdMe_2\{(pz)_3CH\}$ reacts readily with iodomethane in acetone at ambient temperature to give immediately crystals of $[PdMe_3\{(pz)_3CH\}]I$.† A series of complexes involving tripodal nitrogen donor ligands‡ containing pyrazol-1-yl (pz), pyridin-2-yl (py), and *N*-methylimidazol-2-yl (mim) groups were also readily obtained, $[PdMe_3(L)]I$ [L = $(pz)_2(py)CH$, $(pz)_2(mim)CH$, and $(py)_3CH$]. The palladium(II) precursors, $PdMe_2(L)$, were synthesized in a manner similar to that reported earlier for $PdMe_2\{(pz)_3CH\}$.[14]

Crystals of $[MMe_3\{(pz)_3CH\}]I$ (M = Pd, Pt§) are isomorphous,¶ and the isostructural cations have octahedral '*fac*-

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† The complexes $[PdMe_3(L)]I$ [L = $(pz)_2(py)CH$, $(pz)_2(mim)CH$, $(py)_3CH$], and $[MMe_3\{(pz)_3CH\}]I$ (M = Pd, Pt) have satisfactory microanalyses (C, H, N) and ^1H n.m.r. spectra ($CDCl_3$, 300 MHz). N.m.r. spectra for $[PdMe_3(L)]I$ are different from their $PdMe_2(L)$ and $PdMe(L)I$ analogues.

$[PtMe_3\{(pz)_3CH\}]I$: δ (Me_4Si) 12.24 [1H, s, CH], 9.08 [3H, dd, 5-H, ^3J(4,5) 2.7, ^4J(3,5) 0.6 Hz], 7.73 [3H, d, 3-H, ^3J(3,4) 2.1 Hz], 6.54 [3H, dd, 4-H, ^3J(4,5) 2.7, ^3J(3,4) 2.1 Hz], 1.14 [9H, pseudo t, Me, $^2J(^1H-^{195}Pt)$ 72 Hz].

$[PdMe_3\{(pz)_3CH\}]I$: 12.02 [1H, s, CH], 8.99 [3H, dd, 5-H, ^3J(4,5) 2.7, ^4J(3,5) 0.6 Hz], 7.70 [3H, d, 3-H, ^3J(3,4) *ca.* 1.8 Hz], 6.47 [3H, dd, 4-H, ^3J(4,5) 2.7, ^3J(3,4) *ca.* 2 Hz], 1.58 [9H, s, Me].

$[PdMe_3\{(pz)_2(py)CH\}]I$: 10.73 [1H, s, CH], 9.01 [2H, d, 5-H (pz), ^3J(4,5) 2.7 Hz], 8.87 [1H, d, 6-H (py), ^3J(5,6) 7.8 Hz], 8.56 [1H, d, 3-H (py), ^3J(3,4) 5.4 Hz], 8.06 [1H, ddd, 5-H (py), ^3J(5,6) 7.8, ^4J(4,5) 7.8, ^5J(3,5) 1.8 Hz], *ca.* 7.6 [3H, m, 3-H (pz) and 4-H (py)], 6.43 [2H, dd, 4-H (pz), ^3J(4,5) 2.6, ^3J(3,4) *ca.* 1.9 Hz], 1.59 [3H, s, Me *trans*-py], 1.53 [6H, s, Me *trans*-pz].

$[PdMe_3\{(pz)_2(mim)CH\}]I$: 10.60 [1H, s, CH], 9.24 [2H, dd, 5-H (pz), ^3J(4,5) 2.7, ^4J(3,5) 0.6 Hz], 7.62 [2H, d, 3-H (pz), ^3J(3,4) 1.8 Hz], 7.15 [1H, d, 5-H (mim), ^3J(4,5) 1.5 Hz], 7.00 [1H, d, 4-H (mim), ^3J(4,5) 1.5 Hz], 6.39 [2H, dd, 4-H (pz), ^3J(4,5) 2.7, ^3J(3,4) 1.7 Hz], 4.36 [3H, s, NMe], 1.56 [6H, s, Me *trans*-pz], 1.38 [3H, s, Me *trans*-mim].

$[PdMe_3\{(py)_3CH\}]I$: 8.93 [3H, d, 6-H, ^3J(5,6) 7.7 Hz], 8.47 [3H, dd, 3-H, ^3J(3,4) 5.6, ^4J(3,5) 1.7 Hz], 8.27 [1H, s, CH], 7.96 [3H, ddd, 5-H, ^3J(5,6) 7.7, ^4J(4,5) 7.7, ^5J(3,5) 1.7 Hz], 7.45 [3H, ddd, 4-H, ^3J(4,5) 7.7, ^3J(3,4) 5.6, ^4J(4,6) 1.3 Hz], 1.50 [9H, s, Me].

‡ The new ligands (pyridin-2-yl)bis(pyrazol-1-yl)methane $[(pz)_2(py)CH]$[12] and (*N*-methylimidazol-2-yl)bis(pyrazol-1-yl)methane $[(pz)_2(mim)CH]$ were obtained on condensation of bis(pyrazol-1-yl) ketone with pyridine-2-carbaldehyde and *N*-methylimidazole-2-carbaldehyde, respectively, with the former synthesis employing cobalt(II) chloride catalysis following the reported procedure for synthesis of related bis(pyrazol-1-yl)alkanes.[13]

§ The platinum(IV) complex, $[PtMe_3\{(pz)_3CH\}]I$, was obtained directly from $[PtMe_3(\mu_3\text{-}I)]_4$ and $(pz)_3CH$ in acetone. In contrast to the reactivity observed for $PdMe\{(pz)_3CH\}$, $PtMe_2\{(pz)_3CH\}$ reacts with MeI in acetone to form a Pt(IV) complex containing cyclometallated $(pz)_3CH$, $[PtMe_2\{(pz)_2(C_3H_2N_2)CH\text{-}N,N,C^5\}I]$.[12] The complex has spectra similar to that reported for its pyridine derivative $[PtMe_2\{(pz)_2(C_3H_2N_2)CH\text{-}N,N,C^5\}(py)]I$, formed on oxidative addition of MeI to $[PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C^5\}(py)]$,[15] and the new complex is assumed to be formed similarly *via* cyclometallation of $PtMe_2[(pz)_3CH]$.

¶ *Crystal data:* Crystals of the palladium complex obtained from its preparation were suitable for *X*-ray studies, and crystals of the platinum complex were obtained from an acetone solution exposed to diethyl ether vapour in a sealed chamber at *ca.* −20 °C. The complexes $[MMe_3\{(pz)_3CH\}]I$ (M = Pd, Pt) are monoclinic, space group *C*2/*c*, with $Z = 8$. Palladium [platinum] complex cells, determined on the same instrument on the same day are $a = 21.254(8)$ [21.253(8)], $b = 9.213(5)$ [9.099(4)], $c = 19.144(8)$ [19.284(8)] Å, $\beta = 105.65(3)$ [105.63(3)]°, $D_c = 1.81[2.15]$ g cm^{-3}, $F(000) = 1904[2160]$. The structures were determined using diffractometer data (Mo-K_α radiation, $\lambda = 0.7106_9$ Å) at 295 K, and refined to *R* 0.040 (Pd), 0.031 (Pt) for 2030 (Pd), 3284 (Pt) 'observed' $I > 3\sigma I$ absorption corrected reflections μ(Mo-K_α) = 25[91] cm^{-1} (full-matrix least squares; anisotropic thermal parameters for the non-hydrogen atoms). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

MC_3N_3' geometry (Figure 1), with analogous angles at Pd and Pt within *ca.* 2°. The complexes have C–M–C angles 86.6(4)—88.0(4) (Pd) and 87.9(3)—89.2(3)° (Pt), with smaller N–M–N angles owing to the 'bite' of tridentate $(pz)_3CH$, 81.7(3)—83.2(3) (Pd) and 82.9(2)—84.1(2)° (Pt). The M–C distances are identical in the complexes, 2.04_8 (Pd) and 2.04_8 Å (Pt), but there is an appreciable difference in M–N distances, with that for the palladium complex being appreciably longer than that for platinum, 2.20_8 and 2.16_7 Å respectively; *cf.* the difference reported for metal–phosphorus bond lengths in the isostructural M(II) complexes *cis*-$MMe_2(PPh_2Me)_2$ (M = Pd, Pt), where the more precise M–P bond length determinations give Pd–P *ca.* 0.039(1) Å longer than Pt–P.[16] In these complexes, Pd–C distances were appreciably shorter than Pt–C distances by 0.030(4) Å.[16]

The palladium(IV) complexes exhibit ^1H n.m.r. spectra in $CDCl_3$ which are consistent with the presence of cations [*fac*-$PdMe_3$(L-*N*,*N'*,*N''*)]$^+$ with tridentate L, as in the solid state for the $(pz)_3CH$ complex, rather than neutral [$PdMe_3$(L-*N*,*N'*)I] with bidentate L; *e.g.* spectra of [$PdMe_3$(L)]I [L = $(pz)_3CH$, $(py)_3CH$] exhibit a single methyl and donor ring environment, and the spectrum of [$PdMe_3\{(pz)_2(py)CH\}$]I exhibits two methyl environments, in a 2 : 1 ratio, and single pyrazole and pyridine environments, in a 2 : 1 ratio. The platinum(IV) complex, [$PtMe_3\{(pz)_3CH\}$]I, has a spectrum similar to that reported for the hexafluorophosphate salt,[17] and similar to that for [$PdMe_3\{(pz)_3CH\}$]I with the addition of $^2J(^1H-^{195}Pt)$ satellites. The ligand methine protons for the complexes [$PdMe_3$(L)]I [L = $(pz)_3CH$, $(pz)_2(py)CH$, and $(pz)_2(mim)CH$] exchange with the deuterium of $CDCl_3$, over several hours, and the exchange may be reversed on addition of $CHCl_3$ to the solid obtained on removal of $CDCl_3$–$CHCl_3$.

The 2,2'-bipyridyl complex, *fac*-[$PdMe_3$(bpy)I] requires storage at < *ca.* −20 °C,[11] and reductively eliminates ethane to form PdMe(bpy)I in $CDCl_3$, with complete reaction after *ca.* 30—40 min at ambient temperature. In contrast, for [$PdMe_3$(L)]I in $CDCl_3$, only the $(pz)_3CH$ complex gave trace amounts of ethane and $PdMe\{(pz)_3CH\}I$[‖] after *ca.* 2—4 h, indicating that development of a wide range of stable organometallic compounds of palladium(IV) may be possible.

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[‖] Prepared as reported,[14] or more conveniently on reaction of *trans*-[$\{PdMe(SMe_2)(\mu\text{-}I)\}_2$][18] with $(pz)_3CH$ in acetone.