

The Oxidative Addition of Iodomethane to $[\text{PdMe}_2(\text{bpy})]$ and the X-Ray Structure of the Organopalladium(IV) Product $\text{fac-}[\text{PdMe}_3(\text{bpy})\text{I}]$ (bpy = 2,2'-bipyridyl)

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Oxidative addition of iodomethane to dimethyl(2,2'-bipyridyl)palladium(II) in acetone has resulted in isolation of the first hydrocarbylpalladium(IV) complex, *fac*-trimethyl(2,2'-bipyridyl)iodopalladium(IV); the complex has been structurally characterized, and reductively eliminates ethane in solution to form methyl(2,2'-bipyridyl)iodopalladium(II).

While platinum forms numerous organoplatinum(IV) complexes,^{1a} with reports commencing in 1907,² organopalladium(IV) chemistry is represented only by the isolation of several mono- and bis-(pentafluorophenyl)-derivatives,^{1b,3} and by suggestions that spectroscopically undetected alkylpalladium(IV) species are formed as intermediates.^{1b,4-7} In developing the chemistry of mono- and di-methylpalladium(II) complexes with nitrogen donor ligands we have noted that dimethyl[2,2-bis(pyrazol-1-yl)propane]palladium(II) reacts

instantly and cleanly with iodomethane to form the palladium(II) complex, $[\text{PdMe}\{(\text{pz})_2\text{CMe}_2\}\text{I}]$.⁸ However, extension of this reaction chemistry to 2,2'-bipyridyl (bpy) has led to isolation of *fac*- $[\text{PdMe}_3(\text{bpy})\text{I}]$ and the first X-ray structural analysis in organopalladium(IV) chemistry.

Dimethyl(2,2'-bipyridyl)palladium(II) has been described,⁹ but may be more conveniently prepared in high yield[†] by the

[†] Yield >90%, does not require recrystallization.

method reported for analogous poly(pyrazol-1-yl)alkane complexes.⁸ A saturated solution of orange $[\text{PdMe}_2(\text{bpy})\text{I}]$ in acetone was treated with an excess of iodomethane at ambient temperature to give a colourless solution, and on evaporation to ca. 3/4 volume, colourless crystals of *fac*-trimethyl(2,2'-bipyridyl)iodopalladium(IV) were collected and dried under vacuum.†

The X-ray structural study§ of *fac*- $[\text{PdMe}_3(\text{bpy})\text{I}]$ reveals an octahedral geometry for palladium with a *fac*- PdMe_3 group (Figure 1), as found in related triorganoplatinum(IV) chemistry.^{1a,10–12} Some distortion from regular geometry results from the small 'bite' of 2,2'-bipyridyl, giving $\text{N}(\text{a}1)\text{--Pd--N}(\text{b}1)$ $75.6(2)^\circ$, $\text{C}(\text{a})\text{--Pd--N}(\text{b}1)$ $97.4(3)^\circ$, and $\text{C}(\text{b})\text{--Pd--N}(\text{a}1)$ $100.1(3)^\circ$, with the remaining angles $86.6(3)$ – $93.9(2)^\circ$. There are no reported structural studies of simple alkylpalladium(II) nitrogen donor complexes to allow a direct comparison of bond lengths in the two oxidation states. However, on comparison with the related platinum(IV) complex of bis-(3,5-dimethylpyrazol-1-yl)methane, *fac*- $[\text{PtMe}_3\{(\text{Me}_2\text{pz})_2\text{CH}_2\}\text{I}]$,¹² it is of interest that the complexes have similar M–C (within 3 σ) and M–I [2.834(1)(Pd), 2.843(1) Å (Pt)] bond distances.

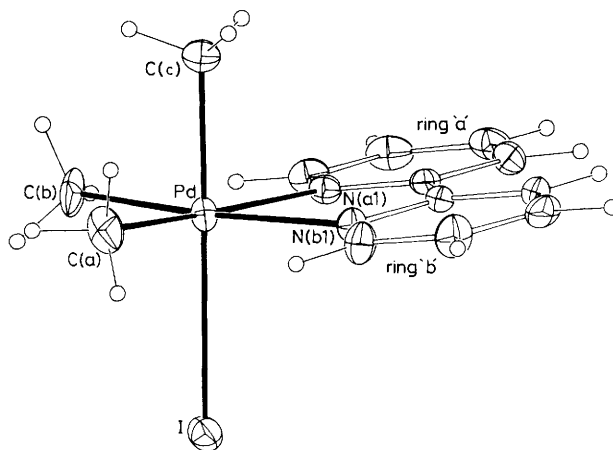


Figure 1. A molecular projection for *fac*- $[\text{PdMe}_3(\text{bpy})\text{I}]$ showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions from difference map locations) have been given an arbitrary radius of 0.1 Å. Selected bond distances and angles: Pd–C(a,b,c) 2.046(7), 2.034(7), 2.040(6) Å, Pd–N(a1,b1) 2.188(5), 2.173(5) Å, Pd–I 2.834(1) Å, C(a)–Pd–C(b,c) $86.6(3)$, $87.0(3)^\circ$, C(b)–Pd–C(c) $86.8(3)^\circ$, C(a)–Pd–N(a1,b1) $172.3(3)$, $97.4(3)^\circ$, C(b)–Pd–N(a1,b1) $100.1(3)$, $174.2(3)^\circ$, C(c)–Pd–N(a1,b1) $89.5(2)$, $89.3(3)^\circ$, I–Pd–C(a,b,c) $93.9(2)$, $91.7(2)$, $178.1(2)^\circ$, I–Pd–N(a1,b1) $89.8(1)$, $92.1(1)^\circ$, N(a1)–Pd–N(b1) $75.6(2)^\circ$. The bpy system is substantially planar ($\chi^2 = 70$) with deviations of Pd, C(a), and C(b) being 0.218, 0.496, and 0.556 Å, respectively.

† Dimethyl(2,2'-bipyridyl)platinum(II) reacts similarly.¹⁰ The new complexes *fac*- $[\text{PdMe}_3(\text{bpy})\text{I}]$ (ca. 60% yield) and $[\text{PdMe}(\text{bpy})\text{I}]$ (ca. 90%) have satisfactory microanalyses (C, H, N, I) and ¹H n.m.r. spectra $[(\text{CD}_3)_2\text{CO}$, 300 MHz] that differ from each other and $[\text{PdMe}_2(\text{bpy})\text{I}]$.

fac- $[\text{PdMe}_3(\text{bpy})\text{I}]$: δ (Me₄Si) 8.95 [2H, ddd, H(6), ³J(5,6) 5.27, ⁴J(4,6) 1.66, ³J(3,6) 0.78 Hz], 8.65 [2H, m, H(3), ³J(3,4) 8.12, ⁴J(3,5) ca. 1 Hz], 8.25 [2H, ddd, H(4), ³J(3,4) 8.12, ³J(4,5) 7.60, ³J(4,6) 1.66 Hz], 7.80 [2H, ddd, H(5), ³J(4,5) 7.60, ³J(5,6) 5.27, ⁴J(3,5) 1.17 Hz], 1.85 [6H, s, CH₃ (equatorial)], 1.14 [3H, s, CH₃ (axial)].

$[\text{PdMe}(\text{bpy})\text{I}]$: 9.53 [1H, ddd, H(6)_{trans-I}, ³J(5,6) 5.31, ⁴J(4,6) 1.73, ⁵J(3,6) 0.84 Hz], 8.70 [1H, m, H(6)_{trans-Me}, ³J(5,6) 5.56 Hz], 8.58 [1H, m, H(3)_{trans-Me}, ³J(3,4) 8.08, ⁴J(3,5) 1.40, ⁵J(3,6) 0.82 Hz], 8.51 [1H, m, H(3)_{trans-I}, ³J(3,4) 8.12, ⁴J(3,5) ca. 1 Hz], 8.34 [1H, ddd, H(4)_{trans-Me}, ³J(3,4) 8.08, ³J(4,5) 7.56, ⁴J(4,6) 1.60 Hz], 8.20 [1H, ddd, H(4)_{trans-I}, ³J(3,4) 8.12, ³J(4,5) 7.58, ⁴J(4,6) 1.73 Hz], 7.85 [1H, ddd, H(5)_{trans-Me}, ³J(4,5) 7.56, ³J(5,6) 5.56, ⁴J(3,5) 1.40 Hz], 7.70 [1H, ddd, H(5)_{trans-I}, ³J(4,5) 7.58, ³J(5,6) 5.31, ⁴J(3,5) 1.20 Hz], 0.83 [3H, s, CH₃].

$[\text{PdMe}_2(\text{bpy})\text{I}]$: 8.87 [2H, ddd, H(6), ³J(5,6) 5.26, ⁴J(4,6) 1.64, ⁵J(3,6) 0.78 Hz], 8.46 [2H, m, H(3), ³J(3,4) 8.10, ⁴J(3,5) ca. 1 Hz], 8.27 [2H, ddd, H(4), ³J(3,4) 8.11, ³J(4,5) 7.56, ⁴J(4,6) 1.70 Hz], 7.69 [2H, ddd, H(5), ³J(4,5) 7.56, ³J(5,6) 5.25, ⁴J(3,5) 1.23 Hz], 0.24 [6H, s, CH₃].

§ *Crystal data*: C₁₃H₁₇IN₂Pd, $M = 434.6$, monoclinic, space group $P2_1/c$ (C_{2h}^2 , No. 14), $Z = 4$, $a = 7.917(4)$, $b = 9.528(4)$, $c = 20.207(8)$ Å, $\beta = 104.28(4)^\circ$, $U = 1477(1)$ Å³, $D_c = 1.95$ g cm⁻³, $F(000) = 832$. The structure was determined using diffractometer data (Mo-K α radiation, $\lambda = 0.71069$ Å) at 295 K, and refined to $R = 0.032$ for 1822 'observed' reflections. Crystal size 0.10 × 0.25 × 0.08 mm.

A unique data set was measured at 295 K within the limit $2\theta_{\text{max}} = 50^\circ$ using a Syntex P₂ four-circle diffractometer in conventional $2\theta/\theta$ scan mode; 2619 independent reflections were measured, 1822 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z)_H$ were constrained at estimates idealized from difference map locations, while $U_{\text{iso}}(H)$ were estimated. Residuals (F) at convergence were $R = 0.032$, $R' = 0.027$ [statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{\text{diff}} + 0.00005\sigma^4(I)_{\text{diff}}$]. Neutral complex scattering factors were used;¹⁴ computation used the XTAL program system¹⁵ implemented by S. R. Hall on a Perkin-Elmer computer.

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, 1986.

In $(\text{CD}_3)_2\text{CO}$ at 10°C, the ¹H n.m.r. spectrum of the complex initially shows *fac*- $[\text{PdMe}_3(\text{bpy})\text{I}]$ only, but disappearance of resonances of the complex occurs over several hours with concurrent appearance of resonances arising from ethane and methyl(2,2'-bipyridyl)iodopalladium(II); at 25°C this reductive elimination reaction requires 30–40 min for completion. The new complex $[\text{PdMe}(\text{bpy})\text{I}]$ may be synthesized independently, forming as yellow crystals on addition of bpy to an acetone solution of *trans*- $[\{\text{PdMe}(\text{SMe}_2)(\mu\text{-I})_2\}]$.¹³ Both oxidative addition and reductive elimination may be monitored by n.m.r. spectroscopy, e.g. on addition of iodomethane in $(\text{CD}_3)_2\text{CO}$ to $[\text{PdMe}_2(\text{bpy})\text{I}]$ in $(\text{CD}_3)_2\text{CO}$ to give a 1:1 mol ratio of reactants, spectra show *immediate* complete conversion into *fac*- $[\text{PdMe}_3(\text{bpy})\text{I}]$ followed by subsequent slow formation of ethane and $[\text{PdMe}(\text{bpy})\text{I}]$.

Solid *fac*- $[\text{PdMe}_3(\text{bpy})\text{I}]$ also reductively eliminates ethane, with violent conversion into a yellow solid at 100–110°C and subsequent melting at 212–214°C (decomp.), the melting point of $[\text{PdMe}(\text{bpy})\text{I}]$. However, the complex is stable when stored at –20°C, and becomes pale yellow over several days at ambient temperature.

The results reported here support earlier suggestions that transient alkylpalladium(IV) species occur as intermediates,^{4–7} in particular in coupling reactions catalysed by palladium substrates.⁶ The oxidative addition–reductive elimination reactivity, and the stability of neutral *fac*- $[\text{PdMe}_3(\text{bpy})\text{I}]$ at temperatures near ambient, suggest that development of a rich organometallic chemistry of palladium(IV) may be possible.

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