

Preliminary communication

Trimethylpalladium(IV) complexes of flexible bidentate ligands. Conformational and fluxional effects in related $\text{Me}_3\text{Pd}^{\text{IV}}$ and $\text{Me}_3\text{Pt}^{\text{IV}}$ systems

Peter K. Byers, Allan J. Canty *, R. Thomas Honeyman and Andrew A. Watson

Chemistry Department, University of Tasmania, Hobart, Tasmania 7001 (Australia)

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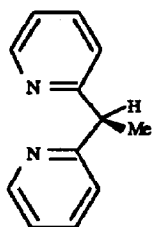
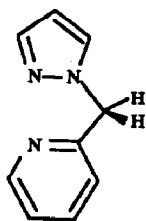
Abstract

A comparison of variable temperature ^1H NMR spectra for stable complexes $\text{fac-Me}_3\text{Pt}(\text{L}_2)\text{I}$ with low temperature spectra obtained after addition of iodomethane to $\text{Me}_2\text{Pd}(\text{L}_2)$ allows assignment of structure for unstable organopalladium(IV) complexes of the flexible bidentate ligands $(\text{py})_2\text{CHMe}$ and $(\text{py})(\text{pz})\text{CH}_2$ (py = pyridin-2-yl, pz = pyrazol-1-yl), together with the first comparison of conformational effects and fluxional processes for organo-palladium(IV) and -platinum(IV) systems. Oxidative addition of CD_3I at -50°C occurs with scrambling of CD_3 and Me positions in $\text{fac-Me}_2(\text{CD}_3)\text{Pd}(\text{L}_2)\text{I}$, but for the platinum analogues the CD_3 and iodo ligands remain *trans* until scrambling occurs on warming to ca. -10°C .

Since the initial report of the synthesis of the first hydrocarbylpalladium(IV) complex, $\text{fac-Me}_3\text{Pd}(\text{bipy})\text{I}$ [1,2*], subtle differences in the solution behaviour of organo-palladium(IV) and -platinum(IV) complexes have been noted; e.g. whereas $\text{Me}_3\text{Pt}(\text{bipy})\text{I}$ dissolves in acetonitrile without reaction, the palladium analogue forms a rapid equilibrium between $\text{Me}_3\text{Pd}(\text{bipy})\text{I}$ and $[\text{Me}_3\text{Pd}(\text{bipy})(\text{NCMe})]\text{I}$ in ca. 3/1 ratio [3]. Triorganopalladium(IV) complexes of bidentate ligands isolated to date have been restricted to 2,2'-bipyridyl and 1,10-phenanthroline complexes [1,4–6], and in extending these studies to more flexible bidentates we have found that unstable complexes are detectable by ^1H NMR spectroscopy at low temperatures. Comparison with spectra of stable $\text{Me}_3\text{Pt}^{\text{IV}}$ analogues confirm assignments for the $\text{Me}_3\text{Pd}^{\text{IV}}$ complexes, and we present here preliminary results for two of the ligands studied, $(\text{py})_2\text{CHMe}$ and $(\text{py})(\text{pz})\text{CH}_2$, as they exhibit interesting conforma-

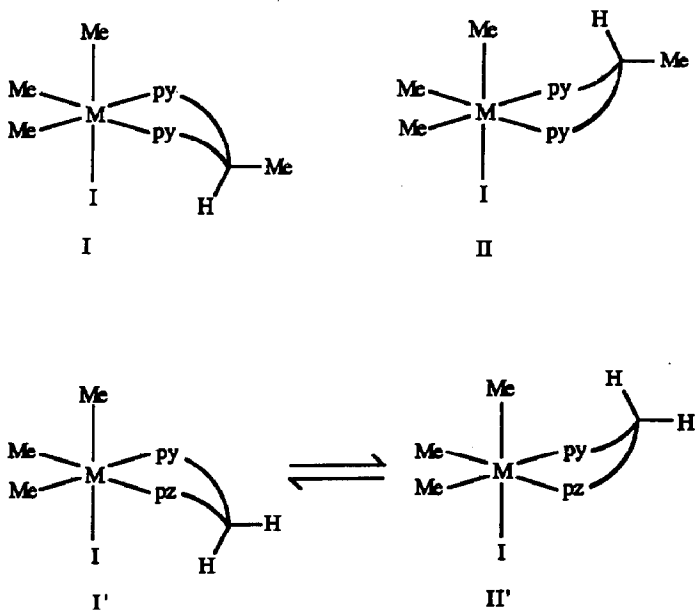
* Reference numbers with asterisks indicate notes in the list of references.

tional and fluxional behavior not possible for the planar ligands. The rigid 1,10-phenanthroline ligand has been included for comparison.

(py)₂CHMe(py)(pz)CH₂

The complexes $\text{Me}_2\text{M}(\text{L}_2)$ were obtained on reaction of $[\text{Me}_2\text{Pd}(\text{pyridazine})]_n$ [4] with the ligands in acetone (phen) or benzene followed by filtration, partial evaporation, and addition of hexane, or reaction of $[\text{Me}_2\text{Pt}(\text{SEt}_2)]_2$ with the ligands in refluxing acetone for 15 min, followed by addition of hexane and rotary evaporation to lower volume. The complexes give satisfactory ^1H NMR spectra and microanalyses (C, H, N). The Pd^{II} and Pt^{II} complexes show similar fluxional behaviour, involving boat-to-boat ring inversion of the chelate ring, with the single CH_2 resonance for $\text{Me}_2\text{M}\{(\text{py})(\text{pz})\text{CH}_2\}$ at ambient temperature resolved into two doublets (axial, equatorial) at -50°C , e.g. 5.71d and 5.64d with J 14.4 Hz for $\text{M} = \text{Pd}$, and the CHMe resonances for $\text{Me}_2\text{M}\{(\text{py})_2\text{CHMe}\}$ are resolved near ambient temperature.

The $\text{Me}_2\text{Pd}^{\text{II}}$ complexes react readily with MeI at ca. -30°C in acetone to give spectra consistent with formation of *fac*- $\text{Me}_3\text{Pd}(\text{L}_2)\text{I}$, but the complexes reductively eliminate ethane with formation of $\text{MePd}(\text{L}_2)\text{I}$ at temperatures $>$ ca. -30°C ,



except for $\text{Me}_3\text{Pd}(\text{phen})\text{I}$ which may be prepared and isolated at ca. 0°C and satisfactorily stored at ca. -20°C although it slowly undergoes reductive elimination in solution.

Spectra obtained on oxidative addition of MeI to $\text{Me}_2\text{Pd}\{(\text{py})_2\text{CHMe}\}$ indicate the presence of two $\text{Me}_3\text{Pd}^{\text{IV}}$ complexes in ca. 1/1 ratio; the spectra are unchanged over the range -30 to -60°C , and the isolated $\text{Me}_3\text{Pt}^{\text{IV}}$ complexes (also obtained by oxidative addition) give similar spectra. The spectra are most readily interpreted as resulting from isomers I and II, both involving the bridgehead methyl group in an 'equatorial' position since molecular models indicate that an axial orientation would give close interaction with either a methyl or iodo group bound to the metal atom. The bridgehead hydrogen gives well separated resonances, e.g. at 6.82q and 4.82q ppm for the palladium complex, reflecting the marked difference in environment in the isomers. The downfield resonance (6.82 ppm) is assigned to the environment adjacent to iodine (isomer I), since the upfield resonance (4.82 ppm) is similar to that for the free ligand (4.46 ppm) and protons adjacent to halogens are expected to be deshielded.

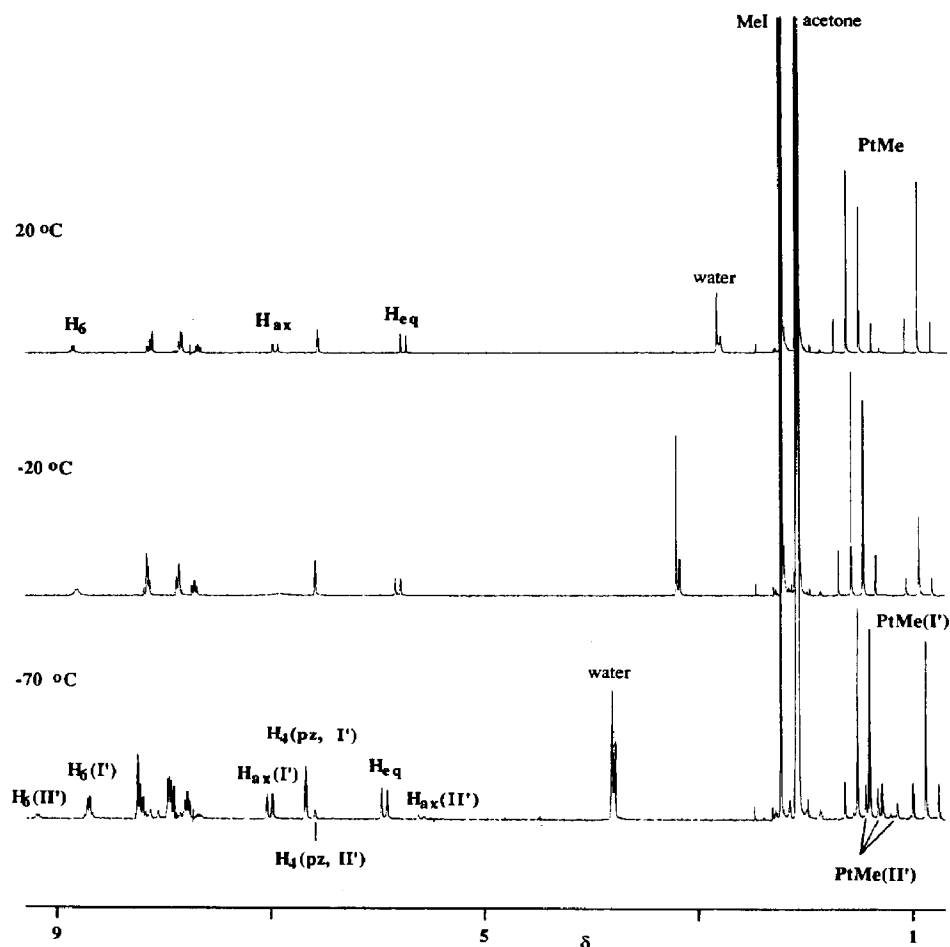


Fig. 1. Variable temperature ^1H NMR spectra for $\text{Me}_2\text{Pt}\{(\text{py})(\text{pz})\text{CH}_2\}\text{I}$.

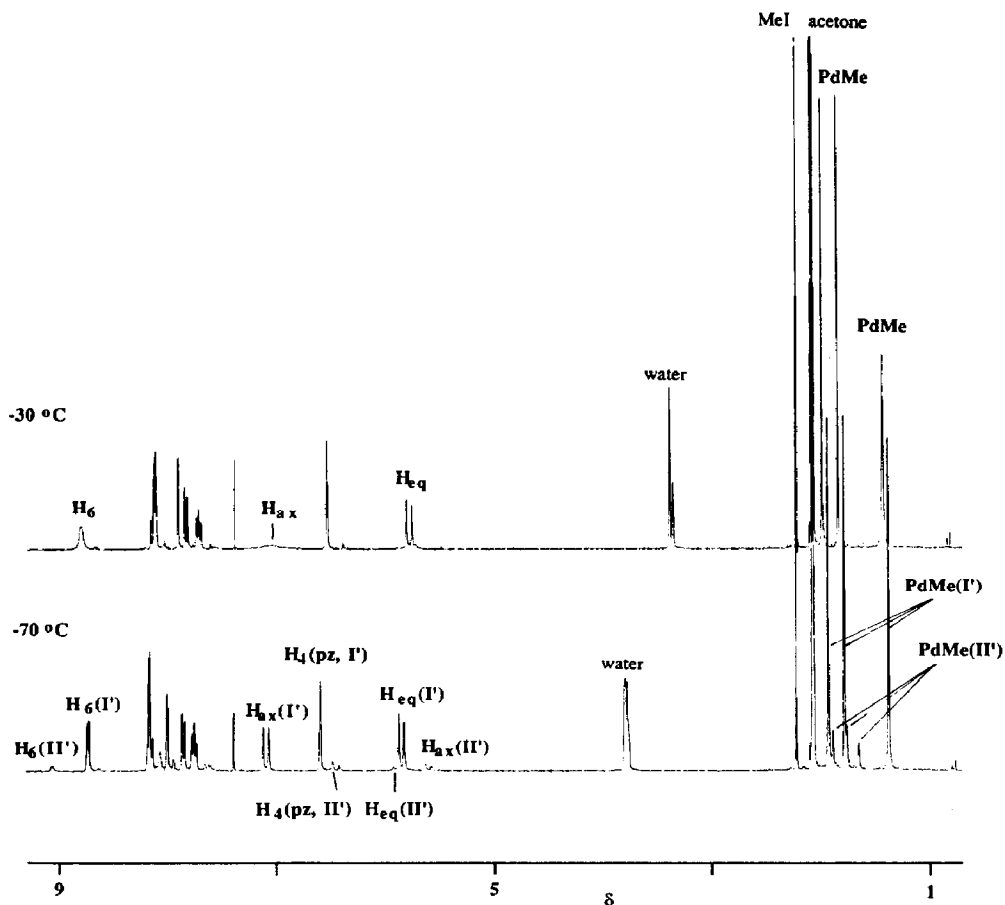


Fig. 2. Variable temperature ^1H NMR spectra for $\text{Me}_3\text{Pd}\{(\text{py})(\text{pz})\text{CH}_2\}\text{I}$.

The complexes $\text{Me}_3\text{M}\{(\text{py})(\text{pz})\text{CH}_2\}\text{I}$ give spectra at -70°C consistent with two conformers I' and II' , related to the conformations adopted by the isomers I and II for $\text{Me}_3\text{M}\{(\text{py})_2\text{CHMe}\}\text{I}$. Thus, for both palladium and platinum, doublets at 7.09 (Pd) and 7.01 (Pt) correspond to conformer I' as they occur ca. 1–1.5 ppm downfield from the other methylene resonances (Figures 1 and 2). Conformers I' and II' are present in the ratio 7/1 (Pd) and 5/1 (Pt), and on warming rapid exchange results in broadening and coalescence (ca. -30°C) with the more stable platinum complex giving sharp resonances at ca. 20°C .

Oxidative addition of iodomethane to $\text{Me}_2\text{M}(\text{bipy})$ is known to occur by the $\text{S}_{\text{N}}2$ -mechanism [3], with *trans* oxidative addition established for $\text{Me}_2\text{Pt}(\text{bipy})$ [7]. This appears to be the case also for the flexible bidentate ligands, since oxidative addition of CD_3I to $\text{Me}_2\text{Pt}(\text{L}_2)$ at -50°C gives ^1H NMR spectra corresponding to $\text{Me}_2(\text{CD}_3)\text{Pt}(\text{L}_2)\text{I}$ with CD_3 *trans* to iodine, with scrambling of methyl and CD_3 groups occurring above ca. -10°C . In contrast, for the palladium system, scrambling is complete at -50°C by the time of collection of the first spectrum (ca. 2 min), indicating that scrambling is more facile for palladium(IV). It is possible that an ionic intermediate formed during $\text{S}_{\text{N}}2$ oxidative addition may facilitate scrambling for the palladium complexes.

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References and notes

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