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PREPARATION AND CHARACTERIZATION OF SOME CATIONIC FIVE-COORDINATE METHYLPLATINUM(II)TRIS(1-PYRAZOLYL)-METHANE COMPLEXES

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Summary

Methylplatinum(II) complexes of the type $[Pt(CH_3)(HCpz_3)L]^+PF_6^-$ (pz = 1-pyrazolyl; L = CO, $H_2C{=}CH_2$, $CH_3C{\equiv}CC_6H_5$, $CF_3C{\equiv}CCF_3$ or $CH_3O_2CC{\equiv}CCO_2CH_3$) have been prepared and characterised by means of elemental analysis, IR and ^1H NMR spectroscopy. Their structures have been deduced by comparing their NMR data with those of the analogous hydrotris(1-pyrazolyl)borate complexes. The stereochemical nonrigidity of these complexes is discussed on the basis of their variable temperature NMR spectra. The NMR studies indicate that the fluxionality of the tris(1-pyrazolyl)methane ligand decreases with increasing electron-withdrawing ability of L. The complexes are inert towards insertion of L into the Pt—CH_3 bond.

Introduction

Although the coordination chemistry of the uninegative poly(1-pyrazolyl)-borate ligands has been extensively studied [1—3], that of the isosteric and isoelectronic but neutral poly(1-pyrazolyl)alkanes has received scant attention [4—6]. In the former class, several neutral five-coordinate complexes of the type $Pt(CH_3)(HBpz_3)L$ (L = acetylene, allene, olefin or CO [7,8], $CNC(CH_3)_3$, CNC_6H_{11} or $P(OCH_3)_3$ [9]) have been reported. These olefin, allene and acetylene complexes have been shown [7] to be very stable and unreactive towards insertion reactions. Among the factors affecting the ease of insertion are (a) the ease of attainment of a mutual *cis*-geometry of the olefin or acetylene and the Pt—CH_3 bond, and (b) the electronic properties of the ligands about the platinum

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atom and of the olefinic or acetylenic substituents [10], and (c) the stereochemistry at the platinum centre. The fact that the above platinum complexes are unreactive towards insertion, even at elevated temperatures, may be attributed to the high electron density, which deactivates the Pt—C bond, imposed on Pt by the electron-rich poly(pyrazolyl)borate ligands, and/or to the inability to collapse to a four-coordinate intermediate from which insertion might be facile.

Since the coordinating behaviour of poly(1-pyrazolyl)borate and poly(1-pyrazolyl)alkane ligands is similar [5] it seemed useful to prepare the cationic analogs of $Pt(CH_3)(HBpz_3)L$, primarily to study the influence of the positive charge on the properties (e.g. insertion reactions, fluxional behaviour of the ligands etc.) of the complexes. With this in mind we have prepared complexes of the type $[Pt(CH_3)(HCpz_3)L]^+PF_6^-$ (L = CO, $H_2C{=}CH_2$, $CH_3C{\equiv}CC_6H_5$, $CF_3C{\equiv}CCF_3$). Their preparations, structures, ^1H NMR spectra and properties are discussed in this paper.

Results and discussion

(a) Preparation of the complexes

The cation, $[Pt(CH_3)(HCpz_3)]^+$, was prepared as the hexafluorophosphate salt by the method described in equation 1.

$$[Pt(CH_3)Cl(COD)] + AgPF_6 \xrightarrow{\text{acetone}} [Pt(CH_3)(COD)(acetone)]^+PF_6^- + AgCl$$

$$\downarrow \text{HCpz}_3$$

$$[Pt(CH_3)(HCpz_3)]^+PF_6^- \qquad (1)$$

COD = 1,5-cyclooctadiene

The IR spectrum of I shows the characteristic absorptions due to $HCpz_3$ [4,5] and the PF_6^- ion. The ^1H NMR spectrum shows the expected resonances [5] for the pyrazolyl rings in the region 6—8 ppm and for the platinum methyl group ($\delta(CH_3)$ 0.88 ppm, ^2J(Pt—H) 70.3 Hz, in acetone-d_6). The presence of traces of free COD was also apparent from the ^1H NMR spectrum; since it is well-known that in such syntheses [11] complete removal of COD is very difficult, the complex was used without further purification.

The complex I is soluble in acetone and acetonitrile but insoluble in dichloromethane, chloroform and many other common organic solvents. However, it readily dissolves in dichloromethane in the presence of carbon monoxide, ethylene or one of the various acetylenes used in this study to give stable 1 : 1 adducts which are easily isolated in good yield. The adducts are stable both in solution and in the solid state; they are readily soluble in dichloromethane, acetone or acetonitrile but are only sparingly soluble in chloroform, except the methylphenylacetylene complex which readily dissolves. Analytical, physical and relevant infrared data for the complexes are given in Table 1.

(b) Spectroscopic data for the complexes

(i) Infrared spectra. All of the complexes show the characteristic infrared absorption bands due to the $HCpz_3$ ligand and to the PF_6^- ion. The observed frequencies of the bands due to the acetylenic C≡C or CO stretching modes are given in Table 1. These values are entirely comparable to those of the cor-

TABLE 1

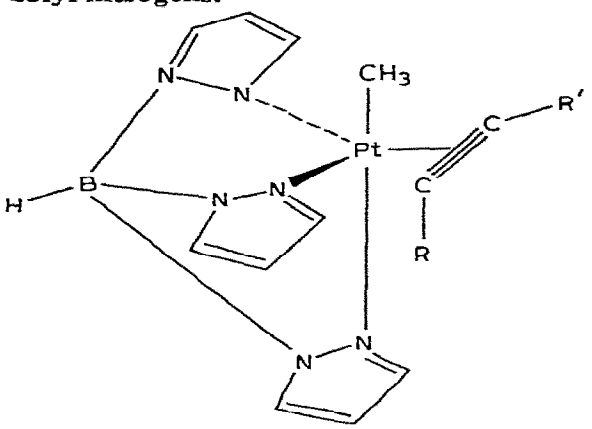
ANALYTICAL, PHYSICAL AND INFRARED DATA FOR THE CATIONIC COMPLEXES $[Pt(CH_3)(HCpz_3))L]^+PF_6^-$

L [a]	Colour	Yield (%)	M.p. (°C)	Analysis Found (calcd.) (%)			Infrared data (cm^{-1})
				C	H	N	
CO	white	58	150—165	24.09 (24.13)	2.19 (2.20)	14.09 (14.07)	ν(CO) 2100
$H_2C{=}CH_2$	white	51	>250 (dec.)	26.96 (26.13)	3.08 (2.87)	14.23 (14.07)	—
$CH_3C{\equiv}CC_6H_5$	yellow	83	150—152	35.25 (35.04)	3.42 (3.09)	12.00 (12.26)	ν(C≡C) 1852
$CF_3C{\equiv}CCF_3$	pale yellow	64	204—205	24.91 (24.63)	1.89 (1.80)	11.79 (11.49)	ν(C≡C) 1890
$CH_3O_2CC{\equiv}CCO_2CH_3$	yellow	83	175—177	28.00 (28.70)	2.85 (2.70)	11.29 (11.81)	ν(C≡C) 1820 ν(CO) 1685

[a] All the complexes were crystalline solids. They were crystallised from CH_2Cl_2/pentane, with the exception of $[Pt(CH_3)(HCpz_3)(CF_3C{\equiv}CCF_3)]^+PF_6^-$, which was crystallised from acetone.

responding hydrotris(1-pyrazolyl)borate complexes [7], thus indicating a similarity in both bonding and structure in the two classes of complexes.

(ii) ^1H NMR spectra. The stereochemistry of the complexes $[Pt(CH_3)(HCpz_3)L]^+PF_6^-$ is expected to be very similar to that of $Pt(CH_3)(HBpz_3)L$ (L = CO, olefin or acetylene). The trigonal bipyramidal structure of these neutral complexes has been established by NMR [7,8] and X-ray data [12], and has the ligand L in the trigonal plane defined by the platinum atom and two pyrazolyl nitrogens.



The pyrazolyl ring protons absorb in the region 6—8 ppm; the 4-H resonance appears at about 6.5 ppm as a triplet due to spin—spin interactions with 3-H and 5-H. The 3-H and 5-H resonances appear at 7—8 ppm as doublets due to coupling with 4-H. Complete assignments of all the pyrazolyl ring protons for the hydrotris(1-pyrazolyl)borate complexes have been made using homonuclear double-resonance techniques [7]. On this basis also, we have assigned all the pyrazolyl ring proton resonances for the complexes in this study. The observed chemical shifts and coupling constants for the platinum methyl, pyrazolyl ring protons and olefins or acetylenes are given in Table 2. It was not possible to measure the $J(^{195}Pt, ^1H)$ coupling constants for the pyrazolyl ring protons because the ^{195}Pt satellites were unresolved at the operating frequency (60 MHz) of the spectrometer. The values in Table 2 are very similar, as expected, to those of the corresponding neutral complexes, except of course for the H–C≡ resonance which appears as a singlet in the region 9—10 ppm.

NMR studies [7] of hydrotris(1-pyrazolyl)boratemethylplatinum(II) complexes with acetylenes have shown that for those containing symmetrically substituted acetylenes, such as $CF_3C{\equiv}CCF_3$, two distinct 4-H resonances are observed in a 2 : 1 intensity ratio indicating that (a) the pyrazolylborate ligand is stereochemically rigid on the NMR time scale and (b) two pyrazolyl rings are magnetically equivalent and different from the third ring. This gives rise to a total of six resonances in the 6—8 ppm region. In contrast, the room temperature NMR spectra of some of the present complexes indicated that the tris(1-pyrazolyl)methane ligand was fluxional. Accordingly, variable temperature NMR studies were undertaken.

Carbonyl complex, $[Pt(CH_3)(HCpz_3)(CO)]^+PF_6^-$

The ^1H NMR spectrum shows only one 4-H resonance at 33 and 0°C but two resonances in the ratio 2 : 1 at —20°C and lower temperatures (see Table 2).

TABLE 2

^{1}H NMR DATA [a] FOR THE COMPLEXES $[Pt(CH_3)(HCpz)_3)L]^+PF_6^-$

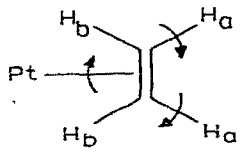
L (solvent)	Temp. (°C)	Platinum methyl		Pyrazole ring [b]	3-H		4-H		5-H		δ(HC—)	Other resonances
		δ(Pt—CH_3)	^2J(Pt—H)		δ	J(H—H_4)	δ	J(H—$H_{3,5}$)	δ	J(H—H_4)		
CO	33	1.17	71.5		8.23(br)		6.82	2.0	8.38(br)		9.4	—
(acetone-d_6)	−20	1.17	71.5	eq	8.32	2.4	6.83	2.4	8.21	2.0	9.53	—
				ax	8.70	2.4	7.05	2.0	8.90	2.7		
$H_2C{=}CH_2$	33	0.68	66.2		7.89(br)		6.52	2.7	8.44	2.7	9.27	δ(CH_2) 2.58 ^3J(Pt—H) 82.0
(chloroform-d)	0	0.67	66.2		7.90	2.2	6.50	2.9	8.40	2.7	9.18	δ(CH_2) 2.55 J(H—H) 3.2
$CH_3C{\equiv}CC_6H_5$	33	0.81	66.2		7.98(br)		6.54(br)		8.41	2.7	9.21	δ(CH_3) 2.37 ^3J(Pt—H) 57.9
(chloroform-d)	−20	0.80	69.8	eq	8.44	2.2	6.64	2.4	8.13	2.0	9.13	δ(CH_3) 2.40
				ax	8.00	2.2	6.35	2.2	8.35	2.4		^3J(Pt—H) 58.3
$CF_3C{\equiv}CCF_3$ (acetone-d_6)	25	1.38	67.1	eq	8.76	2.4	6.88	2.2	8.51	2.2	9.9	—
				ax	7.93	2.2	6.73	2.2	8.67	2.7		
$CH_3OCC{\equiv}CCO_2CH_3$ (acetone-d_6)	33	1.18	68.9	eq	8.67	2.7	6.82	2.2	8.38	2.2	9.76	δ(OCH_3) 3.86
				ax	7.72	2.4	6.64	2.4	8.57	2.7		

[a] Chemical shifts are in ppm. downfield of TMS, and coupling constants are in Hz. [b] eq = equatorial and ax = axial; br = broad.

This implies that the $HCpz_3$ ligand is fluxional at 33°C, but with decreasing temperature has become stereochemically rigid at −20°C. Similar behaviour has been observed for the $HBpz_3$ ligand in the hydrotris(1-pyrazolyl)boratecarbonylmethylplatinum(II) complex [8,9].

Ethylene complex, $[Pt(CH_3)(HCpz_3)(H_2C{=}CH_2)]^+PF_6^-$

In this case the ^1H NMR spectrum shows the $HCpz_3$ ligand to be fluxional down to −30°C. Unfortunately, at −40°C the solubility is too low for further study. The ethylene resonance appears as a singlet at room temperature but is split into a doublet as the temperature is lowered. Rotation of the ethylene about the Pt—ethylene bond may account for this.



At room temperature all the ethylene protons are equivalent due to the rotatory process, but at lower temperatures, as rotation of the ethylene becomes frozen, H_a and H_b are non-equivalent.

Methylphenylacetylene complex $[Pt(CH_3)(HCpz_3)(CH_3C{\equiv}CC_6H_5)]^+PF_6^-$

The ^1H NMR spectra show that at 33°C the $HCpz_3$ ligand is fluxional but becomes stereochemically rigid at lower temperatures. Thus, at 0°C and lower temperatures two 4-H resonances in 2 : 1 intensity ratio are observed, indicating that the two equatorial pyrazolyl rings are equivalent. This implies that the acetylene is rotating freely about the Pt—acetylene bond or is perpendicular to the trigonal plane defined by the platinum and two equatorial nitrogen atoms. This behaviour is in contrast to that of the $[Pt(CH_3)(HBpz_3)(CH_3C{\equiv}CC_6H_5)]$ complex where the two equatorial pyrazolyl rings were observed to be inequivalent [7]. This requires the acetylene to be constrained within the equatorial plane.

Hexafluorobut-2-yne complex, $[Pt(CH_3)(HCpz_3)(C_4F_6)]^+PF_6^-$

Two distinct 4-H resonances in the ratio 2 : 1 are observed at 25°C, indicating that the HCpz ligand is stereochemically rigid. The lower temperature spectra show the same nonfluxional behaviour.

Dimethylacetylene dicarboxylate complex $[Pt(CH_3)(HCpz_3)(CH_3O_2CC{\equiv}CCO_2CH_3)]^+PF_6^-$

As for the hexafluorobut-2-yne complex, the spectrum for the dimethylacetylene analog at 33°C shows two 4-H resonances in a 2 : 1 ratio, implying that $HCpz_3$ is non-fluxional with two pyrazolyl rings being equivalent and different from the third.

Qualitatively, it appears from the ^1H NMR spectra for the complexes $[Pt(CH_3)(HCpz_3)L]^+PF_6^-$ that the barrier to stereochemical non-rigidity decreases in the order $L = MeO_2CC{\equiv}CCO_2Me \sim CF_3C{\equiv}CCF_3 > CH_3C{\equiv}CC_6H_5 > CO > CH_2{=}CH_2$. For the acetylenic ligands, therefore, the barrier increases as the electron-withdrawing ability of L increases.

As was previously found for the hydrotris(1-pyrazolyl)borate complexes, $[Pt(CH_3)(HBpz_3)L]$, there was no evidence for insertion of the olefin or acetylene into the platinum—methyl bond in these complexes, even after refluxing the hexafluorobut-2-yne and dimethylacetylene dicarboxylate (in the presence of excess dimethylacetylene dicarboxylate) complexes in acetone for 2 1/2 days. Since the same bahaviour is observed for the complexes of both the anionic $HBpz_3^-$ and the neutral $HCpz_3$ ligands, the low reactivity towards insertion cannot be attributed to electronic effects. The inability to undergo insertion can therefore be attributed uniquely to the fact that these five-coordinate complexes, because of the chelate effect of the ligands, cannot collapse to an appropriate four-coordinate intermediate.

Experimental

The following chemicals were obtained commercially and were used without further purification: silver hexafluorophosphate, tris(1-pyrazolyl)methane), carbon monoxide, ethylene, methylphenylacetylene, hexafluorobut-2-yne, dimethylacetylene dicarboxylate. Acetone was distilled from 4A molecular sieve under nitrogen prior to use in the preparation of $[Pt(CH_3)(HCpz_3)]^+PF_6^-$. $[Pt(CH_3)Cl(\pi\text{-}1,5\text{-}C_8H_{12})]$ was prepared by the established procedure [13].

Microanalyses were performed by MidWest Microlab Ltd., Indianapolis or Guelph Chemical Lab. Ltd., Guelph. Infrared spectra were recorded using Nujol mulls on a Perkin-Elmer model 180 spectrophotometer. The ^1H NMR spectra were run in chloroform-*d* or acetone-d_6 solutions with tetramethylsilane as reference at 60 MHz on a Brüker WP-60 spectrometer operating in the F.T. mode.

Preparation of $[Pt(CH_3)(HCpz_3)]^+PF_6^-$

To a magnetically stirred solution of $[Pt(CH_3)Cl(COD)]$ (4.48 g, 12.7 mmol) in 50 ml of freshly distilled acetone was added $AgPF_6$ (3.20 g, 12.7 mmol) under nitrogen. After 15 min the AgCl produced in the reaction was removed by centrifugation and filtration to give a clear solution. A solution of tris(1-pyrazolyl)methane (2.72 g, 12.7 mmol) in about 20 ml of acetone was added to the filtrate with stirring. After 1 h the solvent was removed on a rotary evaporator to give a brown-yellow oil. The oil was dried under vacuum to give a creamy white solid, which was washed with CH_2Cl_2 and dried. Yield 5.61 g, m.p. 170—175°C (dec.).

Preparation of the complexes

All the complexes were prepared at room temperature by essentially the same procedure as described for the dimethylacetylene dicarboxylate complex.

Preparation of $[Pt(CH_3)(HCpz_3)(CH_3O_2CC{\equiv}CCO_2CH_3)]^+PF_6^-$

To a suspension of $[Pt(CH_3)(HCpz_3)]^+PF_6^-$ (202.8 mg, 0.35 mmol) in 15 ml CH_2Cl_2 was added 0.044 ml dimethylacetylene dicarboxylate from a syringe. The mixture was magnetically stirred for 20 min to give a clear, light yellow solution. This was passed through a 1 in Florisil column, eluting with dichloromethane. The solvent was reduced to about 3 ml on a rotary evap-

orator. Pentane was slowly added to give yellow crystals. The flask was cooled in ice for 3 h before decanting the solvent. The crystals were dried under vacuum and recrystallised from CH_2Cl_2/pentane.

To prepare the CO, C_2H_4 and $CF_3C{\equiv}CCF_3$ complexes the appropriate gas was bubbled through a suspension of $[Pt(CH_3)(HCpz_3)]PF_6$ in CH_2Cl_2 until a clear solution was obtained. The reaction with $CF_3C{\equiv}CCF_3$ was very slow; the mixture saturated with the gas was stirred for 2 days and the solution was filtered to remove any unreacted starting material. The filtrate was worked up as described above.

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