

Organoplatinum(II) Complexes with Hydrogen-Bonding Functionality and Their Potential Use as Molecular Receptors for Adenine



A Thesis Submitted for the
Degree of Master of Science

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Errata

Table of Contents (pages viii and ix): The titles of complexes should commence with “*trans*” not “*Trans*”.

Page 10, paragraph 1: Should read “Complexation plays...” not “Complexations play...”.

Page 11, paragraph 1: Should read “...binding to the host...” not “...host binding...”.

Page 20: The iodo ligand is used in this reaction as (**36**) is more reactive than the corresponding chloro complex (**35**) in the presence of silver ions.

Page 23, Table 1: “na” and “n/a” refer to the term “not applicable”.

Page 29, paragraph 2, line 2: Picolinic acid complexes (**50**) - (**53**) contained more chemically-inequivalent protons than the other isomers owing to their low symmetry, thus leading to more complicated ¹H NMR spectra.

Page 29, paragraph 2, line -2: Should start “Complexes (**52**) and (**53**) were the only two complexes...”.

Page 34: Entry for (**54**) H³ should read “Obscured by PMePh₂” and not “Obscure d by PMePh₂”. Entry for (**55**) H⁵ should read “As for H⁴” not “e”.

Page 39: Preparation of the platinum(II)-iodo complex (**59**) is shown in Scheme 2.6.

Page 41, Table 9 and Page 52, Table 11: The IR spectra were recorded as Nujol mulls.

Page 60, paragraph 2: Should read “¹⁴N” not “N¹⁴”.

Page 72, paragraph 1, line -3: should be “possess” not “posses”.

Page 73: 2D NMR spectra were recorded at 600 MHz and not 300 MHz.

Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university and, to the best of my knowledge, contains no material previously published or written by another person, except where due reference is made.

I consent for the thesis being made available for photocopying and loan if accepted for the award of this degree.

Michael G. Crisp

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Abstract

The preparation and characterisation of a novel series of organoplatinum(II) complexes with hydrogen-bonding functionality are described. The mononuclear platinum(II) complexes of the type *trans*-[Pt(σ -aryl)L(PPh₃)₂]OTf (L = nicotinic acid, picolinic acid, isonicotinic acid) and the dinuclear complexes of the type *trans*-[Pt(σ -aryl)(PPh₃)(μ -Y)Pt(σ -aryl)(PPh₃)₂](OTf)₂ (Y = 4,4'-bipyridyl, 4,7-phenanthroline, 4,4'-dipyrazolylmethane, 1,1'-phenyl-4,4'-dipyrazolylmethane) were investigated. The complexes were primarily characterised by multinuclear (³¹P, ¹H) 1-D and 2-D NMR spectroscopy, IR spectroscopy and, in some cases, X-ray crystallography. These platinum(II) complexes, both mono-nuclear and di-nuclear, have the potential to act as hosts for nucleobase guests such as adenine, and this was investigated also. The mono-platinum complexes were found to interact with the guest 9-sec-pentyladenine in a variety of ways in CDCl₃ solution including, 1:1, 2:1 and in some cases 3:1 association ratios at both the Watson-Crick and the Hoogsteen site. The dinuclear platinum(II) molecular "tweezers" were found to bind simultaneously to two 9-sec-pentyladenine molecules in CDCl₃ solution.

Abbreviations

General:

°	degrees
°C	degrees Celsius
ΔG	change in free energy
1-D	one dimensional
2-D	two dimensional
Å	Angstrom
cm	centimetre
DNA	deoxyribonucleic acid
DPZM	4,4'-dipyrazolymethane
g	gram
h	hour
K	Kelvin
MS	mass spectrometry
mL	millilitre
OTf, triflate	CF ₃ SO ₃ ⁻ , trifluoromethanesulfonate
Ph	phenyl
THF	tetrahydrofuran

Nuclear magnetic resonance spectroscopy:

δ	nuclear magnetic resonance chemical shift in ppm
¹ H NMR	proton nuclear magnetic resonance
³¹ P{ ¹ H} NMR	proton decoupled ³¹ P nuclear magnetic resonance
d	doublet
dd	doublet of doublets
Hz	Hertz
<i>I</i>	nuclear spin quantum number
m	multiplet

MHz	megahertz
${}^nJ_{ij}$	n bond coupling constant between nuclei i and j
NMR	nuclear magnetic resonance
ppm	parts per million
s	singlet
t	triplet

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