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Pyridyl- and diphenylphosphinoethyl-functionalised *N*-heterocyclic carbene platinum methyl complexes

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ABSTRACT

The novel platinum (II) dimethyl complexes Pt(κ^2-L1)Me$_2$ and Pt(κ^2-L1)Me$_2$ (**1**), Pt(κ^2-L2a)Me$_2$ (**2a**) and Pt(κ^2-L2b)Me$_2$ (**2b**) bearing the functionalised *N*-heterocyclic carbenes (NHCs), **L1** = 1-(2-diphenylphosphinoethyl)-3-(2,6-di*iso*propyl-phenyl)-imidazol-2-ylidene, **L2a** = 1-(2-pyridyl)-3-(2,6-di*iso*propyl-phenyl)-imidazol-2-ylidene, **L2b** = 1-(2-(3-picolinyl))-3-(2, 6-di*iso*propyl-phenyl)-imidazol-2-ylidene, react with the acid [H(Et$_2$O)$_2^+$B(Ar^F)$_4^-$], Ar^F = 3, 5-(CF$_3$)$_2$C$_6$H$_3$, in the presence of various neutral donors (**Dn**) to give the salts [{Pt(κ^2-L)(Me)(Dn)}$^+${B(Ar^F)$_4$}$^-$], where **Dn** occupies specifically the site *trans* to the P and the C$_{NHC}$ donor atoms of the coordinated ligands **L1** and **L2a**, **L2b**, respectively. Spectroscopic data give evidence that the same selectivity prevails when other acids are employed. Activation of the Cl–CH$_2$Cl bond by **2b** led to [Pt(κ^2-L2b)(Me)Cl], while reaction of CH$_3$I with the dimethyl complexes led to isolable [Pt(κ^2-L)Me$_3$I] species.

Introduction

Platinum *N*-heterocyclic carbene (NHC) complexes of the type Pt(IMes)$_2$, IMes = 1,3-dimesitylimidazol-2-ylidene, were among the first reported transition metal complexes with NHC ligands after the introduction of stable imidazol-2-ylidenes [1]. Since then, the study of Pt complexes with monodentate NHCs continued, albeit at substantially slower pace than Pd complexes, mainly aiming at the development of novel catalysts for the hydrosilylation of alkenes and alkynes [2,3] and various types of C–H bond activation, including the C2–H of imidazoliums [4]. Recently, starting from [Pt(μ-Me$_2$S)Me$_2$]$_2$ and NHCs, NHC = IBu^t, IPr^i, IMes, diverse reactivity was observed, dependent on the steric properties of the NHCs, and led to either Pt(NHC)$_2$Me$_2$, coordinated NHC wingtip metallation *via* C–H activation, ethane reductive elimination, or abnormal NHC coordination [5]. The Pt(III) species [Pt(IPr)$_2$(I)$_2$]$^+$ obtained by the oxidation of [Pt(IPr)$_2$(Me)I] has been described [6]. Small monodentate NHCs with [Pt(IV)Me$_3$IL$_m$] or [Pt(IV)Me$_3$(Me$_2$CO)$_3$]BF$_4$, NHC = 1,3-dimethyl-imidazol-2-ylidene, 3-methyloxazol-2-ylidene, L = pyridine, *m* = 0, 2, led to diverse Pt(II) or Pt(IV) products, depending on the nature of the NHC used [7]. Chelating bidentate bis-NHC complexes of Pt(II)/(IV) have been studied in relation to Shilov-type C–H activation and alkane functionalisation and as possessing unique photophysical properties [8–11]. Furthermore, Pt complexes with bidentate ligands comprising NHCs functionalised with N-donors (pyridine, picoline, lutidine *etc.*) or cyclometallated, tridentate 'pincer' NHC ligands (aryl C$^-$-donor) have been studied for catalysis applications (hydroamination and hydrovinylation reactions) [12,13] and in relation to their interesting photophysical properties (luminescence, vapochromic behaviour *etc.*) [14,15], which can be combined with cytotoxicity for medicinal applications [16]. Oxidative addition and reductive elimination reactions involving Pt(II) and Pt(IV) methyl complexes stabilised by the linear κ^2- or κ^3-bis-1, 3-di(2-picolyl)imidazol-2-ylidene ligands have also been briefly studied [17].

We have described palladium dimethyl complexes with the chelating bidentate 2-diphenylphosphinoethyl-, 2-pyridyl- and 2-(3-picolyl)-functionalized NHCs (**L1** and **L2a**, **L2b**, respectively, see Scheme 1) and their protonolysis by [H(Et$_2$O)$_2$]$^+$[B(Ar^F)$_4$]$^-$ followed by association of a neutral donor (*e.g.* pyridine, MeCN *etc.*) at the created vacant site. The regiospecificity of the substitution, although in line with the relative *trans* influence of the pyridine and NHC donors of **L2a** and **L2b**, was unexpected for the P and NHC donors of the **L1**. Rationalisation of the observations by DFT methods invoked a subtle balance of electronic and steric factors and secondary

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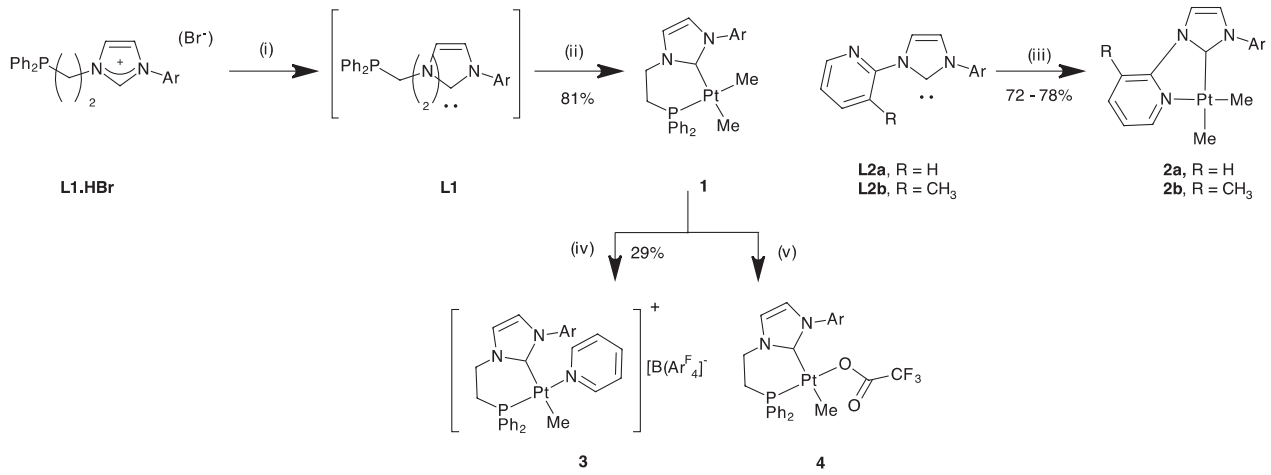


Scheme 1. The synthesis of Pt(II) dimethyl complexes, Ar = 2,6-$^{i}Pr_2C_6H_3$ (DiPP): (i) 1 equiv. $KN(SiMe_3)_2$, THF; (ii) $[Pt(\mu\text{-}Me_2S)Me_2]_2$, THF; (iii) $[Pt(\mu\text{-}Me_2S)Me_2]_2$, THF; (iv) 1 equiv. $[H(Et_2O)_2]^+[B(Ar^F)_4]^-$ in CH_2Cl_2 (−78 °C, −40 °C) followed by 1 equiv. pyridine (−40 °C); (v) 1 equiv. CF_3COOH in CD_2Cl_2, room temperature.

(agostic) interactions [18,19]. Protonolysis with CF_3COOH followed the same selectivity albeit association of CF_3COO^- with the Pd complex at the created vacant site was observed.

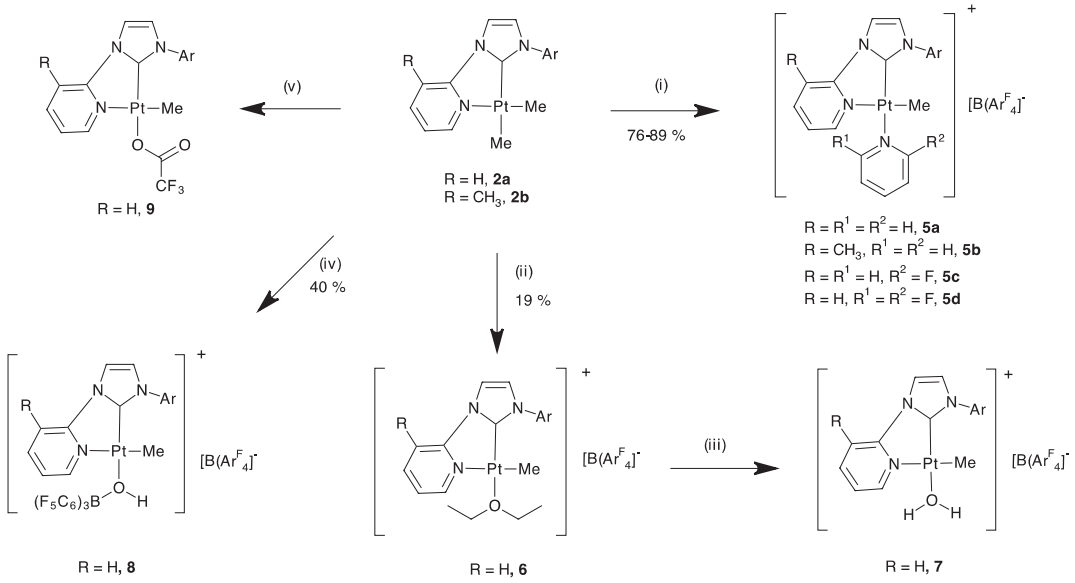
As an extension of these studies, herein we describe (i) novel Pt(II) dimethyl complexes coordinated by the ligands κ^2-**L1** and κ^2-**L2a** or κ^2-**L2b** ligand coordination, and (ii) a range of novel cationic derivatives obtained either by their protonolysis with $[H(Et_2O)_2]^+[B(Ar^F)_4]^-$ in the presence of neutral donors (**Dn**), or by acids with coordinating anions. We also report the reactions of Pt(II) dimethyl complexes with MeI leading to stable Pt(IV) species. The synthetic transformations are summarised in Schemes 1–3.

Results and discussion

Neutral Pt dimethyl complexes

The synthesis of the neutral Pt dimethyl complexes involved the substitution of the labile ligand Me_2S in $[Pt(\mu\text{-}Me_2S)(CH_3)_2]_2$ either by the *in situ* generated NHC (for **L1**) or the isolated free NHC (for **L2a** and **L2b**) (Scheme 1). The new complexes were isolated in high yields as colourless or yellow, air stable powders. Solutions of **1** and **2a**, **2b** in CH_2Cl_2 have limited stability even under inert atmosphere (*i.e.* after 2–3 h the formation of a mixture of species becomes evident by ^{1}H NMR, see also below). However, characterisation of the complexes was carried out by analytical, spectroscopic (taking care to minimise the duration of the experiment) and diffraction methods.

The ^{1}H NMR spectra of the complexes concur with non-symmetric solution structures. Thus the inequivalent Pt–CH_3 signals appeared as a pair of doublets or as a pair of singlets for **1** or **2a**, **2b**, respectively, accompanied by Pt satellites. The Pt–CH_3 signals in **1** are shifted upfield relative to the corresponding signals in **2a** and **2b**. The shielding may be ascribed to the better σ-donor ability of phosphine donor in **1**; interestingly, the value of the $^2J_{Pt-H}$ of the Pt–CH_3 signals is larger in **2a**, **2b** than the in **1**. The stronger electron donating character of the **L1** may also be responsible for the



Scheme 2. The synthesis of Pt methyl complexes containing the ligands **L2a** and **L2b**: (i) 1 equiv. $[H(Et_2O)_2]^+[B(Ar^F)_4]^-$ in CH_2Cl_2 (−78 °C, −40 °C) followed by 1 equiv. pyridine derivative (−40 °C) (76–89%); (ii) 1 equiv. $[H(Et_2O)_2]^+[B(Ar^F)_4]^-$ and 1 equiv. CF_3CH_2OH in CH_2Cl_2 (−78 °C, room temperature) followed by crystallisation from ether (19%); (iii) H_2O in chlorobenzene-d^5; (iv) $B(C_6F_5)_3$, H_2O, ether, (−78 °C to room temperature, 40%); (v) 1 equiv. CF_3COOH, CD_2Cl_2, room temperature.