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Journal of Organometallic Chemistry 587 (1999) 195–199

Journal of Organometallic Chemistry

Trimethylplatinum hydroxy–fluorides

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Received 21 April 1999

Abstract

$[Me_3PtF]_4$ can be prepared from the action of AgF on $[Me_3PtI]_4$. In the presence of moisture it hydrolyses to give progressively $[(Me_3PtF)_3(Me_3PtOH)]$, $[(Me_3PtF)_2(Me_3PtOH)_2]$, $[(Me_3PtF)(Me_3PtOH)_3]$ and $[Me_3PtOH]_4$. Variable temperature NMR spectroscopy of these partially hydrolysed tetra-platinum fluorides shows that at higher temperatures the methyl groups within each Me_3Pt unit rapidly exchange sites by an intramolecular mechanism, but the cubic Pt_4X_4 cages retain their integrity. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organoplatinum; Fluorides; Hydroxides; Fluxionality

1. Introduction

Although trimethylplatinum halides, Me_3PtX ($X = Cl$, Br, I), were amongst the first organoplatinum compounds isolated [1], trimethylplatinum fluoride (**1**) was reported only recently [2]. Like the other halides, pseudohalides and the hydroxide, its structure was established as tetrameric, $[Me_3PtX]_4$, with triply bridging X groups resulting in a pseudo-octahedral coordination geometry about platinum. The halide bridges of all these compounds are readily broken by other ligands, making a convenient synthetic route to other trimethylplatinum derivatives.

$$[Me_3PtX]_4 + 8L \rightarrow 4[Me_3PtXL_2]$$

Similar compounds to these have also been made by oxidative additions of MeX to dimethylplatinum(II) complexes [3]. All of them are characterised by octahedral coordination about Pt, usually with a *facial* arrangement of the methyl groups.

Intramolecular scrambling of the three methyl groups was reported in $[Me_3Pt(acac)]_2$ [4] and $[Me_3Pt(bipy)OH_2]^-$ [5], both resulting from dissociative processes producing fluxional five-coordinate intermediates. An extensive study by Abel and co-workers on fluxionality in sulfide and selenide derivatives of trimethylplatinum species also detected rapid methyl group scrambling. Whilst this motion was often synchronous with other molecular librations and also frequently linked to dissociative loss of other ligands, independent non-dissociative processes could not be ruled out in some cases [6]. It was not until the isolation and examination of the mixed halide/thiomethyl complexes $[(Me_3PtSMe)_2(Me_3PtX)_2]$ ($X = Cl$, Br, or I) and $[(Me_3PtSMe)_3(Me_3PtCl)]$, however, that intramolecular exchange of the methyl groups within each Me_3Pt unit by a bond angle deformation route was proved [7]. Those authors commented that the likelihood of that mechanism operating within other tetra-platinum compounds of the $[Me_3PtX]_4$ type was high.

The report on the synthesis of the hydrolytically sensitive $[Me_3PtF]_4$ (**1**) from $[Me_3PtI]_4$ and XeF_2 indicated that the use of AgF as an alternative fluoridating agent was unsuitable [2]. (The action of KF on the dimethylplatinum(IV) compound $[PtMe_2Cl(C_6H_3Cl\text{-}CH{=}NCH_2C_6H_5)(SMe_2)]$ is also reported to be ineffective at replacing Cl by F, although that fluoro-analogue can be prepared by other means [8].) We had previously used AgF to replace the iodide groups of $[Me_3PtI]_4$, however, and during work to consolidate this we serendipitiously prepared the mixed hydroxy–fluorides $[(Me_3PtF)_3(Me_3PtOH)]$ (**2**), $[(Me_3PtF)_2(Me_3PtOH)_2]$ (**3**), and $[(Me_3PtF)(Me_3PtOH)_3]$ (**4**), as well as $[Me_3PtF]_4$ and $[Me_3PtOH]_4$ (**5**). NMR investigation of these new spe-

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PII: S0022-328X(99)00318-6

cies unequivocally shows that they, too, exhibit non-dissociative methyl scrambling.

2. Results and discussion

Anhydrous silver(I) fluoride has been employed to synthesise a number of platinum(II) or palladium(II) fluorides, sometimes with the assistance of sonication [9]. We find that reactions between $[Me_3PtI]_4$ and fresh samples of AgF proceed in the dark at room temperature (r.t.) over 24 h, though a 170% excess of AgF is necessary to achieve complete replacement of the iodide ions by fluoride. Acetonitrile or dichloromethane was used as solvent, since more strongly donating solvents such as THF or DMSO are known to react with $[Me_3PtF]_4$ by breaking the bridges and possibly displacing the fluoride also (the coupling between the methyl group protons and ^{19}F is lost) [2]. NMR spectroscopic examination of the reaction products in $CDCl_3$ after removal of the silver salts revealed the presence of a mixture of tetra-platinum compounds corresponding to $[Me_3PtF]_4$, $[(Me_3PtF)_3(Me_3PtOH)]$, $[(Me_3PtF)_2(Me_3PtOH)_2]$, $[(Me_3PtF)(Me_3PtOH)_3]$ and $[Me_3PtOH]_4$ (compounds **1** to **5**, Fig. 1: ^1H-NMR parameters are listed in Section 3.1 and ^{19}F-NMR parameters are in Table 1). $[Me_3PtF]_4$ is known to be very hydrolytically sensitive and slow access of moisture through the septum cap sealing the NMR tube or from out of the glass of the tube is clearly sufficient to produce the observed mixtures. On prolonged standing, the fluorides were progressively replaced by OH groups until only $[Me_3PtOH]_4$ remained.

$[(Me_3PtF)_3(Me_3PtOH)]$, $[(Me_3PtF)_2(Me_3PtOH)_2]$ and $[(Me_3PtF)(Me_3PtOH)_3]$ have not been identified previously. Donath et al. reported that $[Me_3PtOH]_4$ was the only platinum-containing hydrolysis product of $[Me_3PtF]_4$, though a number of the broad, unassigned bands in their ^1H-NMR spectum of $[Me_3PtF]_4$ in deuterochloroform correspond to our partially hydrolysed compounds. They also reported that mixtures of $[Me_3PtF]_4$ and $[Me_3PtOH]_4$ produced a material indistinguishable by X-ray diffractometry from the two starting materials [2].

The r.t. ^1H-NMR spectrum of the mixture of partially hydrolysed compounds shows sharp methyl signals (with ^{195}Pt satellites) assigned to $[Me_3PtF]_4$ (δ 0.92, J_{Pt-H} 78.4 Hz) and $[Me_3PtOH]_4$ (δ 0.89, J_{Pt-H} 78.2 Hz) [2]. Also in the methyl region were two broad unresolved signals at 1.07 and 1.24 ppm (with similarly-broadened satellites of about 81 and 83 Hz, respectively). On cooling to -60°C, these peaks resolved into eight of the ten methyl signals expected for the mixed hydroxy–fluoride compounds $[(Me_3PtF)_3(Me_3PtOH)]$, $[(Me_3PtF)_2(Me_3PtOH)_2]$ and $[(Me_3PtF)(Me_3PtOH)_3]$ (see Fig. 1). They were assigned unambiguously by assessing the relative abundances of the three compounds (along with $[Me_3PtF]_4$ and

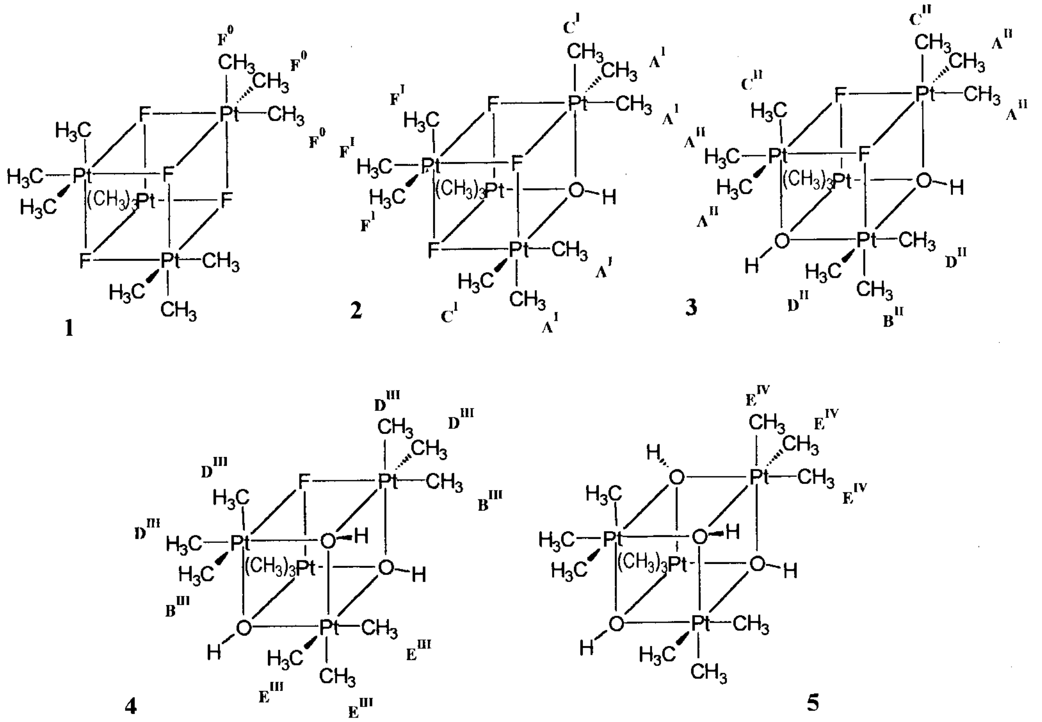

Fig. 1. Structures of $[Me_3PtF]_4$ (**1**), $[(Me_3PtF)_3(Me_3PtOH)]$ (**2**), $[(Me_3PtF)_2(Me_3PtOH)_2]$ (**3**), $[(Me_3PtF)(Me_3PtOH)_3]$ (**4**) and $[Me_3PtOH]_4$ (**5**). Distinguishable methyl groups are labelled A–F, with Roman numerals indicating the number of hydroxide groups in the compound.

Table 1
^{19}F-NMR parameters for compounds **1–4**

	δ (ppm)	$^1J_{F-PtF_2}$ (Hz)	$^1J_{F-PtF(OH)}$ (Hz)	$^1J_{F-Pt(OH)_2}$ (Hz)	$^2J_{F-F}$ (Hz)
$[(Me_3PtF)(Me_3PtOH)_3]$ **(4)**	−270.4	–	–	516	–
$[(Me_3PtF)_2(Me_3PtOH)_2]$ **(3)**	−260.8	–	608	529	64
$[(Me_3PtF)_3(Me_3PtOH)]$ **(2)**	−251.0	705	621	–	60
$[Me_3PtF]_4$ **(1)**	−241.0	708	–	–	45

$[Me_3PtOH]_4$) from the intensities of the hydroxide signals and the signals from their ^{19}F-NMR spectra (vide infra). The two missing signals proved to be coincident with the methyl resonances of $[Me_3PtF]_4$ and $[Me_3PtOH]_4$. It has already been established that the chemical shift values of the methyl groups in tetrameric trimethylplatinum complexes are predominantly affected by the *trans* ligands rather than the local environment at each Pt atom [7,10], and this interpretation allowed consistent assignments to be made in our case.

At +60°C those methyl resonances which are broad at r.t. sharpen to four new signals. Along with the two sharp signals from $[Me_3PtF]_4$ and $[Me_3PtOH]_4$, the new resonances can now be assigned to the four distinct platinum environments, Me_3PtF_3, $Me_3PtF_2(OH)$, $Me_3PtF(OH)_2$ and $Me_3Pt(OH)_3$ (parameters in Section 3).

These temperature variations are consistent with the three methyl groups of each platinum atom changing positions with respect to the Pt_4 cage without breaking any Pt–C bonds. This could be achieved by a turnstile-type rotation. A 60° rotation of the methyl groups will produce a transition state from which the individual methyl identities will be lost [7].

The ^{1}H-NMR spectra of the OH groups show patterns characteristic of coupling to 0, 1, 2 and 3 adjacent ^{195}Pt atoms (^{195}Pt, $I = 1/2$, 33.8%. $^2J_{H-O-Pt}$ are about 11 Hz; the outer lines of the pseudo-septets produced are not always discernible). No long-range coupling to distant platinum atoms was apparent, and the patterns were practically temperature invariant, indicating that the cubic Pt_4 cages are essentially rigid over the temperature range covered. The r.t. spectra reveal a pseudo-septet at −0.55 ppm from $[Me_3PtOH]_4$ (**5**) [11,12]. More complex patterns at −0.35, −0.15 and 0.05 ppm could be assigned to $[(Me_3PtF)(Me_3PtOH)_3]$ (**4**), $[(Me_3PtF)_2(Me_3PtOH)_2]$ (**3**) and $[(Me_3PtF)_3(Me_3PtOH)]$ (**2**), respectively, due to additional $^3J_{H-O-Pt-F}$ couplings of about 4 Hz.

In the ^{19}F-NMR spectra of the mixtures, signals at −241.0, −251.0. −260.8 and −270.4 ppm could be assigned to $[Me_3PtF]_4$, $[(Me_3PtF)_3(Me_3PtOH)]$, $[(Me_3PtF)_2(Me_3PtOH)_2]$ and $[(Me_3PtF)(Me_3PtOH)_3]$, respectively, by comparing their intensities to those of the CH_3 or OH signals in the corresponding ^{1}H spectra. The patterns were again largely temperature invariant and can be interpreted, like the OH region of the ^{1}H-NMR spectra, in terms of the triply bridging F atoms coupling to 0, 1, 2 or 3 ^{195}Pt atoms in the various isotopomers present. Thus these spectra also confirm the rigidity of the Pt_4 cages.

For $[(Me_3PtF)(Me_3PtOH)_3]$, the single value of $^1J_{F-Pt}$ (516 Hz) accounts for the simple pseudo-septet pattern observed in the ^{19}F-NMR spectrum. The others are more complicated, however, as different $^1J_{F-Pt}$ values are observed depending on whether the F atom couples to $^{195}PtF_2$, $^{195}PtF(OH)$ or $^{195}Pt(OH)_2$, and the effects of $^2J_{F-F}$ in some isotopomers are apparent. Fig. 2 shows the spectrum of a typical mixture of $[(Me_3PtF)_3(Me_3PtOH)]$, $[(Me_3PtF)_2(Me_3PtOH)_2]$ and $[(Me_3PtF)(Me_3PtOH)_3]$, along with the simulated spectrum calculated using the parameters in Table 1.

The ^{13}C-NMR spectra of these cubic compounds are complicated by the very large number of isotopomers present in each of the compounds. (Appleton and Hall [12] discuss these for the simplest of our compounds, $[Me_3PtOH]_4$.) The r.t. ^{13}C-NMR spectrum of a mixture containing only $[(Me_3PtF)(Me_3PtOH)_3]$ and $[Me_3PtOH]_4$ revealed sharp resonances for the $Me_3Pt(OH)_3$ environments of the two compounds (δ −11.11 and −11.35, respectively), and broad resonances centred on δ −10 and −13 due to the methyl groups *trans* to OH and F, respectively, of the $Me_3PtF(OH)_2$ environments of $[(Me_3PtF)(Me_3PtOH)_3]$. The broadness of these signals is presumably indicative once again of the fluxional motion of the methyl groups. Increasing the temperature to 60°C caused further broadening and did not reach the high-temperature limiting spectra. At −50°C, however, these signals sharpened to δ −10.05 ($^1J_{Pt-C}$ 745 Hz) and δ −11.77 ($^2J_{F-C}$ 368 Hz; coupling to ^{195}Pt could not distinguished from the background noise). The values of *trans* couplings are well known to exceed those of *cis* couplings in octahedral complexes but the very small *cis* $^2J_{F-C}$ of ≈1 Hz is striking in view of the large *trans* value. In the compound *cis*-$[OsF_2(CO)_4]$ *trans* $^2J_{C-F}$ is 65 Hz whereas *cis* $^2J_{C-F}$ is <2 Hz [13].

The ^{1}H-NMR spectra of the mixed hydroxy–iodo tetramers [(Me$_3$PtI)(Me$_3$PtOH)$_3$], [(Me$_3$PtI)$_2$(Me$_3$PtOH)$_2$] and [(Me$_3$PtI)$_3$(Me$_3$PtOH)], obtained from the sodium hydroxide partial hydrolysis of [Me$_3$PtI]$_4$, have been briefly described in the past [11]. At r.t., methyl peaks for the four environments Me$_3$PtI$_3$, Me$_3$PtI$_2$(OH), Me$_3$PtI(OH)$_2$ and Me$_3$Pt(OH)$_3$ were reported. This is unexpected in view of our observations and would suggest either that the methyl environments are already averaged at this temperature or that the chemical shifts and coupling constants of the methyl groups *trans* to I or OH are very similar. The authors also reported that those mixed hydroxy–iodo compounds steadily dismuted to [Me$_3$PtI]$_4$ and [Me$_3$Pt(OH)]$_4$, a process that did not appear to apply to our mixed hydroxy–fluoro compounds. Clearly this and related systems with other halogens would repay further investigation.

3. Experimental

NMR spectra were recorded on either a Bruker WP 200 SY or an AM 360 NMR spectrometer. ^{19}F chemical shifts are reported relative to replacement CFCl$_3$, those of ^{1}H and ^{13}C relative to replacement TMS. Simulations of the ^{19}F spectra were carried out using the Bruker program PANIC, version 850501.1, employing the parameters of Table 1 with a Lorentzian line shape and line width of 23 Hz. The spectra in Fig. 2 are the weighted sum of the several isotopomer components, with $^3J_{\mathrm{Pt-F}}$ and $^2J_{\mathrm{Pt-Pt}}$ set at zero (the large experimental line width effectively rendered the spectra insensitive to small changes in these parameters).

IR spectra were recorded on a Jasco FT/IR-410 spectrometer. Acetonitrile was dried by distillation from phosphorus pentoxide, dichloromethane from cal-

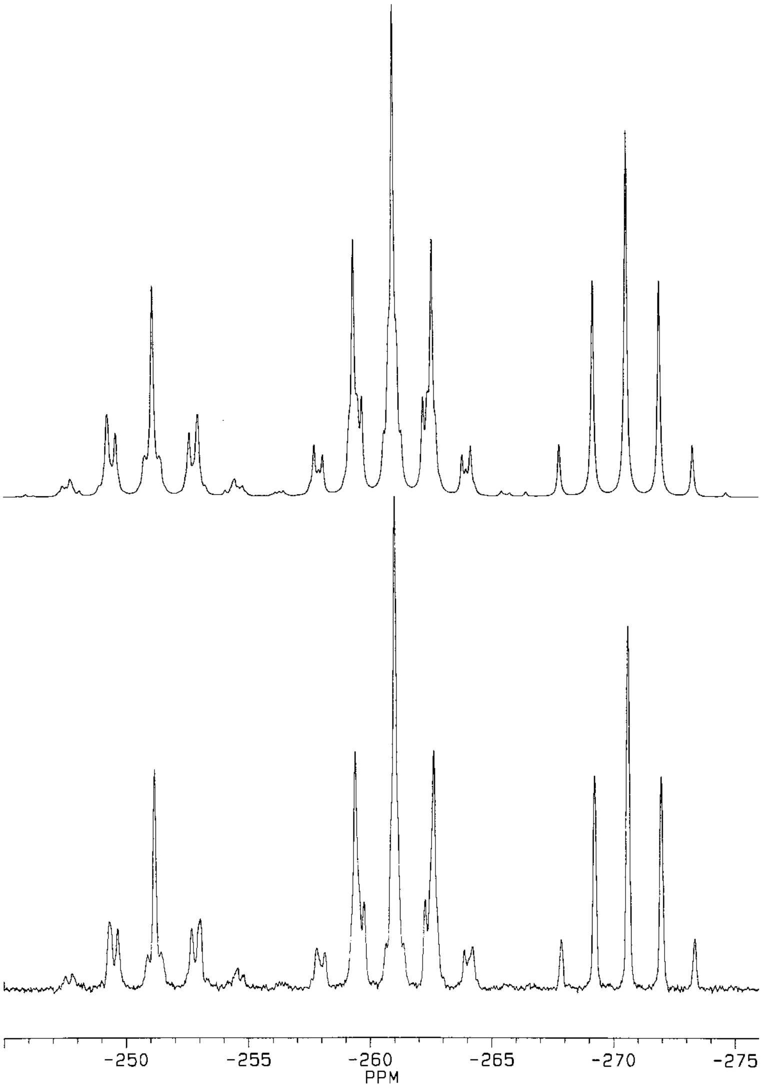

Fig. 2. Typical 188.3 MHz ^{19}F-NMR spectrum (CDCl$_3$ solution at 25°C) of [(Me$_3$PtF)$_3$(Me$_3$PtOH)] (**2**), [(Me$_3$PtF)$_2$(Me$_3$PtOH)$_2$] (**3**) and [(Me$_3$PtF)(Me$_3$PtOH)$_3$] (**4**) (left to right). The lower trace is the experimental spectrum. The upper trace was simulated using the Bruker program PANIC with the parameters in Table 1 and a 23 Hz line width.

cium hydride, diethyl ether and THF from sodium and benzophenone. Toluene was dried over sodium. Deuterodichloromethane and deuterochloroform were dried over molecular sieves type 13X. Trimethylplatinum iodide was synthesised from MeMgI and either K_2PtCl_6 or $(NH_4)_2PtCl_6$ by the method of Baldwin and Kaska [14]. Silver(I) fluoride was purchased from Fluorochem and manipulated under dry nitrogen in a glove box.

3.1. Reactions between $[Me_3PtI]_4$ and AgF

In a typical experiment, silver(I) fluoride (0.288 g, 2.27 mmol) and trimethylplatinum iodide (0.306 g, 0.208 mmol) were weighed in a glove box into a two-limbed Schlenk flask with a frit between the limbs. Dichloromethane (10 ml) was added and the solution was stirred for 24 h under nitrogen, the vessel being wrapped in aluminium foil to protect the silver compounds from light. The orange suspension turned green during the reaction. The precipitate of AgI and the excess AgF were too finely divided to be separated either by decantation or by filtration, so the solvent was removed under vacuum. The dried powder was extracted into dried dichloromethane. The insoluble residue was allowed to settle and the colourless solution was transferred by syringe into a dried, nitrogen-filled Schlenk flask. The solvent was removed under vacuum leaving a colourless powder. For the NMR spectroscopic analyses, a few milligrams of the dried product were placed in an NMR tube in the glove box, sealed with a septum and the appropriate solvent syringed in. NMR spectroscopic analysis revealed a mixture of products, **1**–**5**. The final hydrolysis product, $[Me_3PtOH]_4$, was recrystallised from dichloromethane and petroleum, and identified by its IR spectrum [11].

^{1}H-NMR parameters of products in $CDCl_3$; assignments are those shown in Fig. 1.

(a) − 60°, 200 MHz. $[Me_3PtF]_4$ (**1**) δ 0.86 (s + d, $^2J_{H-Pt} = 78.4$ Hz, H–F^0); $[(Me_3PtF)_3(Me_3PtOH)]$ (**2**) δ 0.34 (m, OH), 0.86 (s + d, $^2J_{H-Pt} = 78.4$ Hz, H–F^I), 1.15 (s + d, $^2J_{H-Pt} = 86$ Hz, H–C^I), 1.25 (s + d, $^2J_{H-Pt} = 83.5$ Hz, H–A^I); $[(Me_3PtF)_2(Me_3PtOH)_2]$ (**3**) δ 0.11 (m, OH), 0.95 (s + d, $^2J_{H-Pt} = 76.0$ Hz, H–D^{II}), 1.11 (s + d, $^2J_{H-Pt} = 86$ Hz, H–B^{II}), 1.17 (s + d, $^2J_{H-Pt} = 85.1$ Hz, H–C^{II}), 1.26 (s + d, $^2J_{H-Pt} = 83.3$ Hz, H–A^{II}); $[(Me_3PtF)(Me_3PtOH)_3]$ (**4**) δ − 0.14 (d of pseudo-septets, $^2J_{H-Pt} = 10.1$ Hz, $^3J_{H-F} = 4.1$ Hz, OH), 0.82 (s + d, $^2J_{H-Pt} = 77.6$ Hz, H–E^{III}), 0.98 (s + d, $^2J_{H-Pt} = 76.9$ Hz, H–D^{III}), 1.14 (s + d, $^2J_{H-Pt} = 85.9$ Hz, H–B^{III}); $[Me_3PtOH]_4$ (**5**) δ − 0.39 (pseudo-septet, $^2J_{H-Pt} = 10.9$ Hz, OH), 0.82 (s + d, $^2J_{H-Pt} = 77.6$ Hz, H–E^{IV}).

(b) + 25°, 360 MHz. $[Me_3PtF]_4$ (**1**) δ 0.92 (s + d, $^2J_{H-Pt} = 78.4$ Hz, H–F^0); $[(Me_3PtF)_3(Me_3PtOH)]$ (**2**) δ 0.05 (m, OH), 0.92 (s + d, $^2J_{H-Pt} = 78.4$ Hz, H–F^I), 1.24 (br, s + d, $^2J_{H-Pt} = 83.4$ Hz, H–(A–C)^I); $[(Me_3PtF)_2(Me_3PtOH)_2]$ (**3**) δ − 0.15 (t of pseudo-septets, $^2J_{H-Pt} = 10.9$ Hz, $^3J_{H-F} = 4.1$ Hz, OH), 1.07 (br, s + d, $^2J_{H-Pt} = 81.0$ Hz, H–(B–D)^{II}), 1.24 (br, s + d, $^2J_{H-Pt} = 83.4$ Hz, H–(A–C)^{II}); $[(Me_3PtF)(Me_3PtOH)_3]$ (**4**) δ − 0.35 (d of pseudo-septets, $^2J_{H-Pt} = 11.1$ Hz, $^3J_{H-F} = 4.1$ Hz, OH), 0.89 (s + d, $^2J_{H-Pt} = 78.2$ Hz, H–E^{III}), 1.07 (br, s + d, $^2J_{H-Pt} = 81.0$ Hz, H–(B–D)^{III}): $[Me_3PtOH]_4$ (**5**) δ − 0.55 (pseudo-septet, $^2J_{H-Pt} = 11.0$ Hz, OH), 0.89 (s + d, $^2J_{H-Pt} = 78.2$ Hz, H–E^{IV}).

(c) + 60°, 200 MHz. $[Me_3PtF]_4$ (**1**) δ 0.94 (s + d, $^2J_{H-Pt} = 78.2$ Hz, H–F^0); $[(Me_3PtF)_3(Me_3PtOH)]$ (**2**) δ − 0.05 (m,z OH), 0.94 (s + d, $^2J_{H-Pt} = 78.2$ Hz, H–F^I), 1.27 (s + d, $^2J_{H-Pt} = 82$ Hz, H–(A–C)^I); $[(Me_3PtF)_2(Me_3PtOH)_2]$ (**3**) δ − 0.24 (t of pseudo-septets, $^2J_{H-Pt} = 10.1$ Hz, $^3J_{H-F} = 4.3$ Hz,z OH), 1.09 (s + d, $^2J_{H-Pt} = 79.8$ Hz, H–(B–D)^{II}), 1.26 (s + d, $^2J_{H-Pt} = 82.0$ Hz, H–(A–C)^{II}); $[(Me_3PtF)(Me_3PtOH)_3]$ (**4**) δ − 0.42 (d of pseudo–septets, $^2J_{H-Pt} = 10.5$ Hz, $^3J_{H-F} = 4.4$ Hz, OH), 0.92 (s + d, $^2J_{H-Pt} = 78.2$ Hz, H–E^{III}), 1.10 (s + d, $^2J_{H-Pt} = 79.9$ Hz, H–(B,D)^{III}): $[Me_3PtOH]_4$ (**5**) δ − 0.61 (pseudo-septet, $^2J_{H-Pt} = 10.9$ Hz, OH), 0.92 (s + d, $^2J_{H-Pt} = 78.2$ Hz, H–E^{IV}).

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