

Supplementary Information

Studies Towards the Catalytic Anti-Markovnikov Functionalisation of Alkenes

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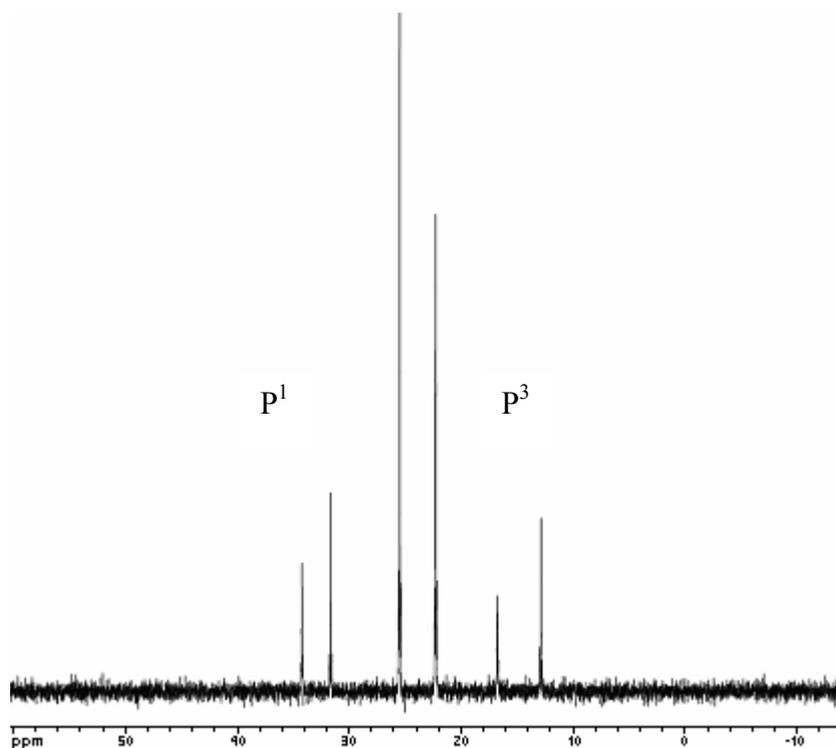
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Figure S1

The $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3) spectrum and hydride region of ^1H NMR spectrum of **4**. (see note below)

The $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) spectrum of **4** at 145.7MHz



The high field ^1H NMR (CDCl_3) spectrum of **4** at 360.1MHz

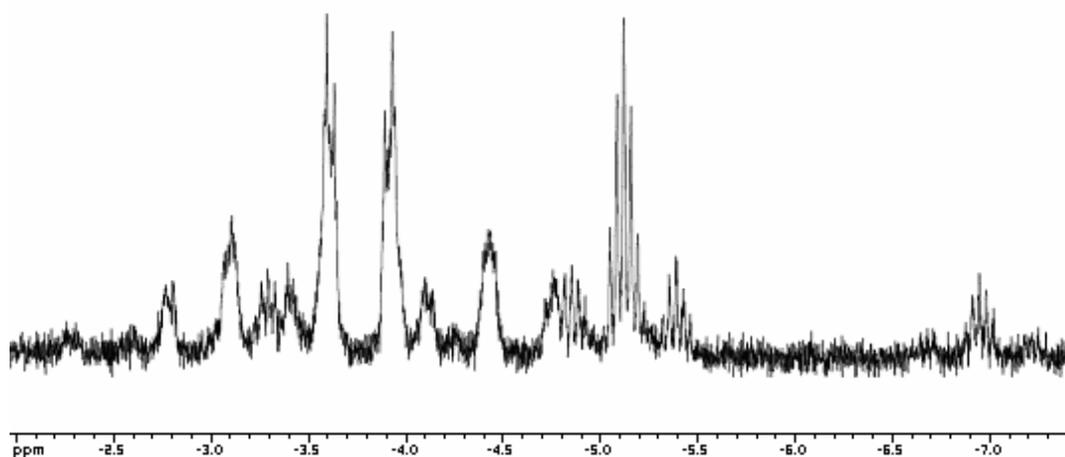


Figure S2

A typical $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3) spectrum of the clusters **6** and **10**, present as a mixture in the inorganic products derived from **5** according to eqn (S1)

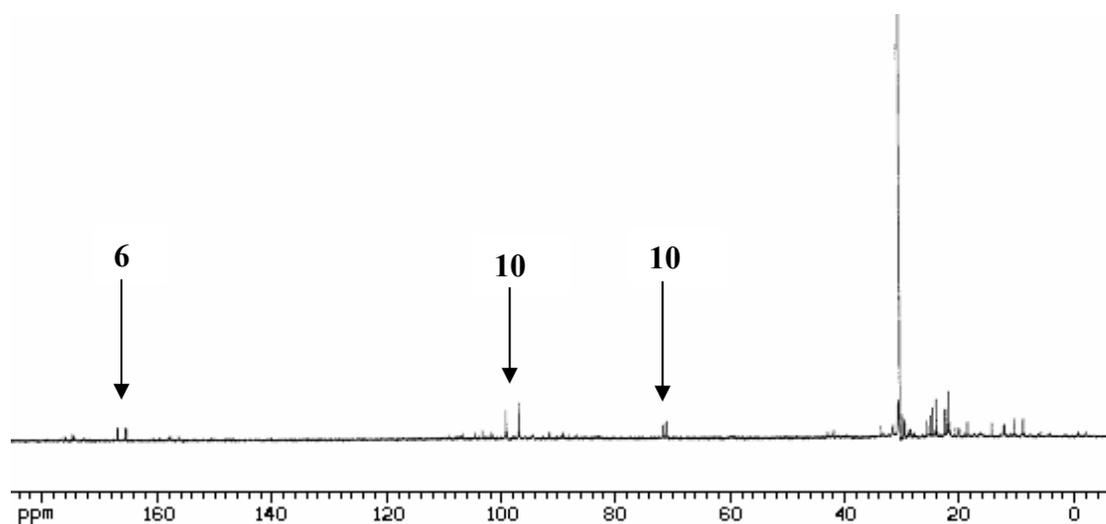
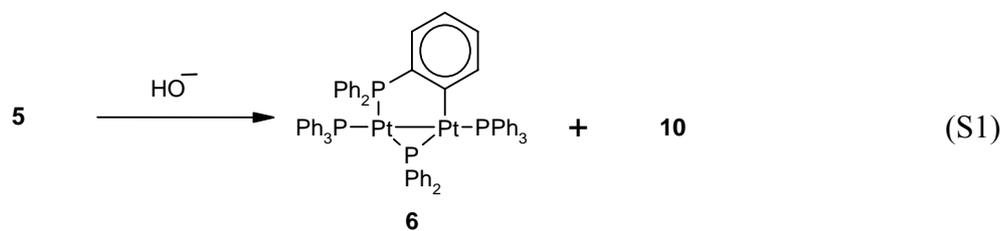


Figure S3

The $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3) spectrum of **6**, in the bridging phosphido region, derived from **5** by heating with 1-octene in 2-propanol under alkaline conditions. The spectrum shows excellent agreement with the spectrum published by Braunstein and co-workers.³

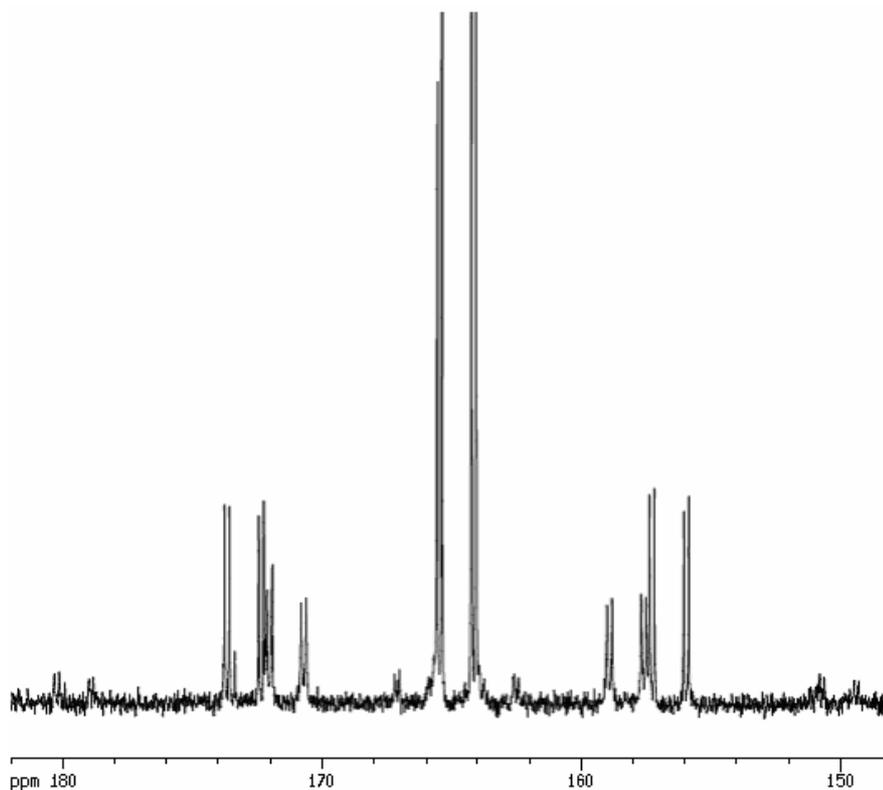


Figure S4

The $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3) spectrum of the mixture of products obtained by heating **5** with 1-octene in toluene with 2-propanol, but without added acid or base. The coupling constants observed for **7** within the mixture agree with those reported by Longoni and co-workers,⁴ and so provided a method of identification. The spectrum of **8** has been reported by Dixon and co-workers.⁵

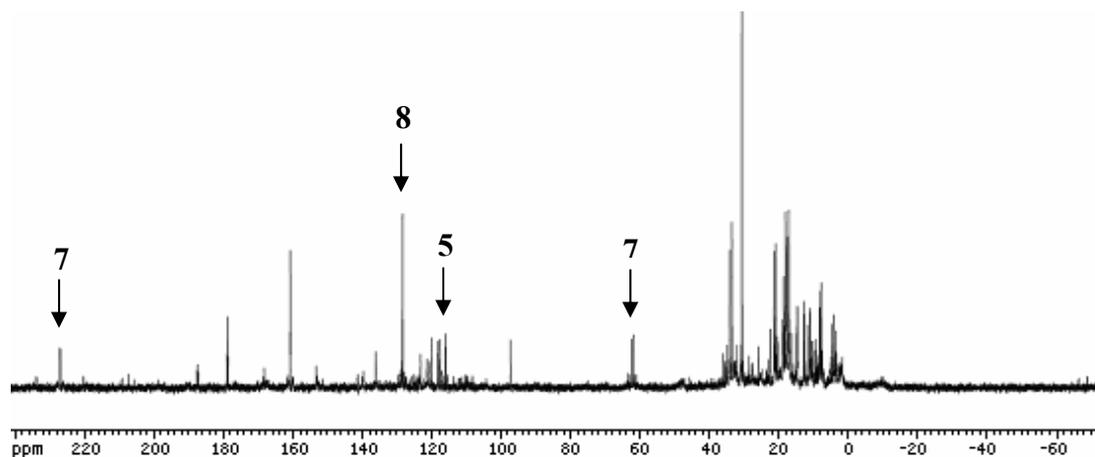


Figure S5

Expansion of the $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3) spectrum of **7** in the bridging phosphido region ~ 225 ppm and at ~ 60 ppm. Longoni and co-workers,⁴ also show these expansions.

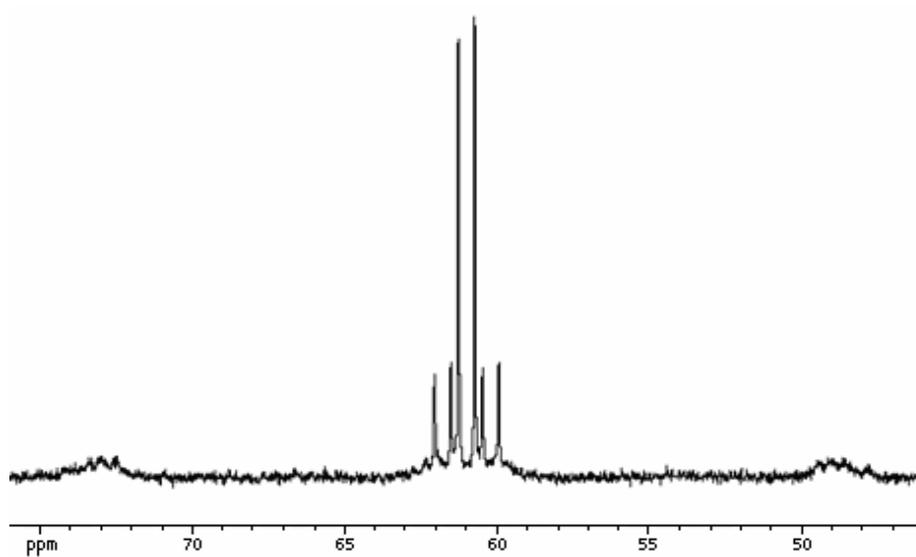
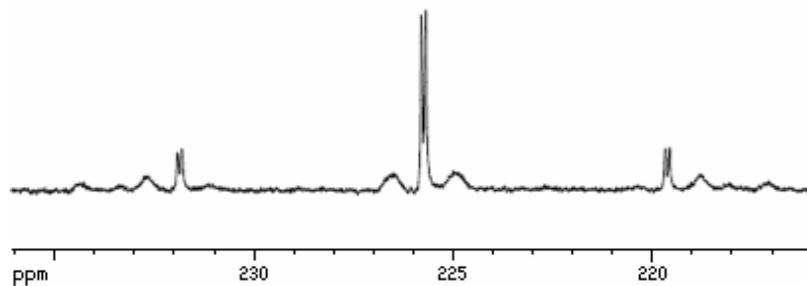


Figure S 6

The $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3) spectrum of the mixture of products obtained by heating **5** with 1-octene in toluene with 2-propanol, with added HBF_4 . Although this is a complex mixture, the peaks assigned to **11** can be used to suggest a structure (see below)

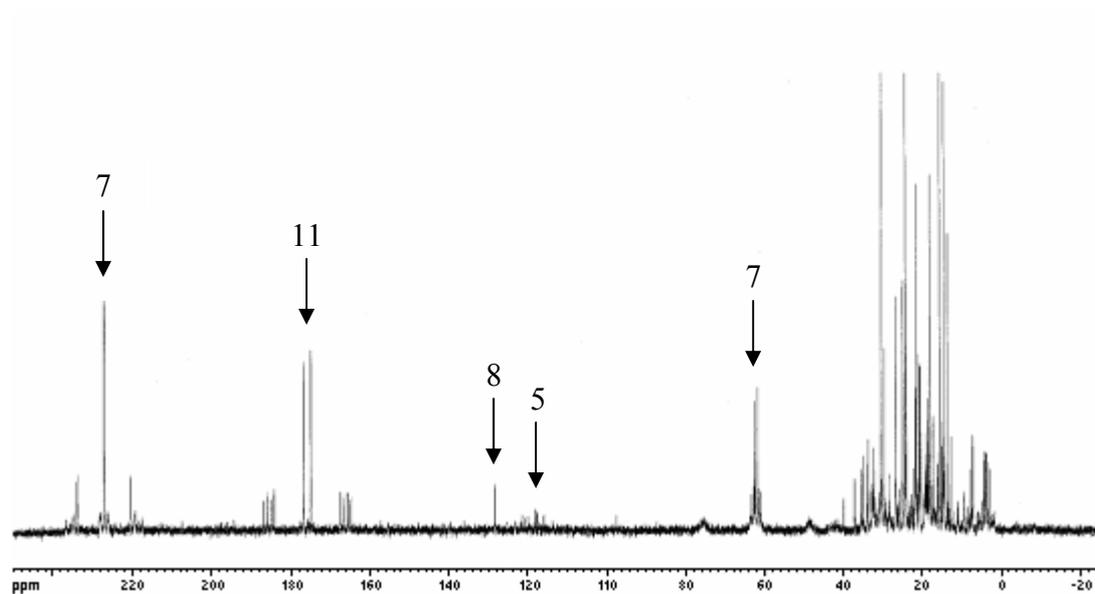


Figure S7

The $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3) spectrum of **11** in the bridging phosphido region. The structure was assigned on the basis of the similarity of the spectrum in the bridging phosphido region to that of $[\text{Pt}_2(\mu\text{-H})(\mu\text{-PPh}_2)\text{Br}(\text{PPh}_3)_3]\text{PF}_6$ as reported by Braunstein and co-workers⁶

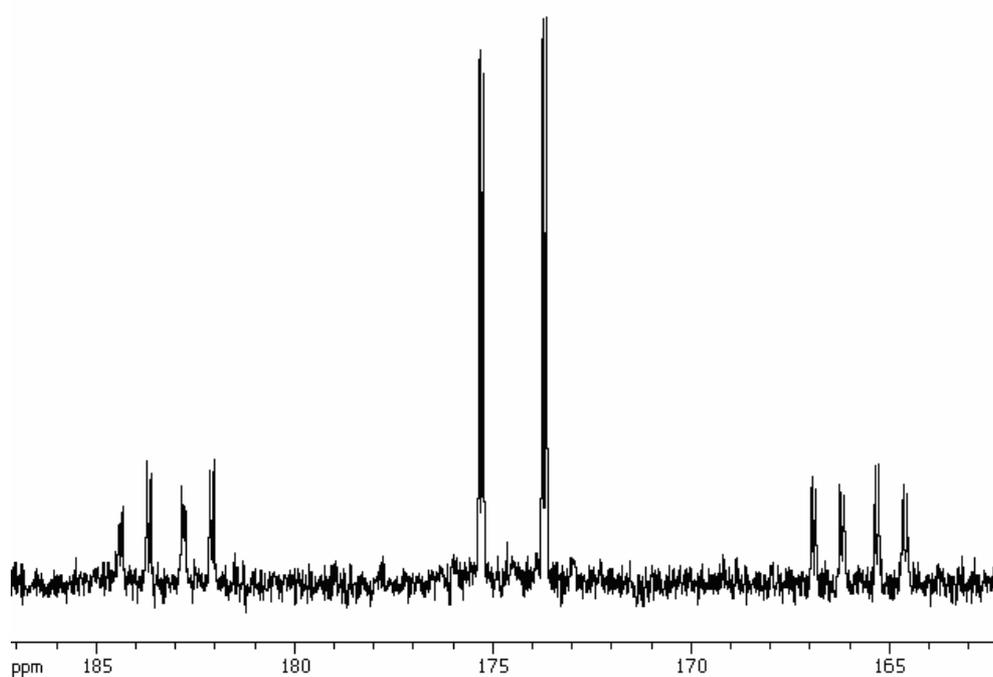
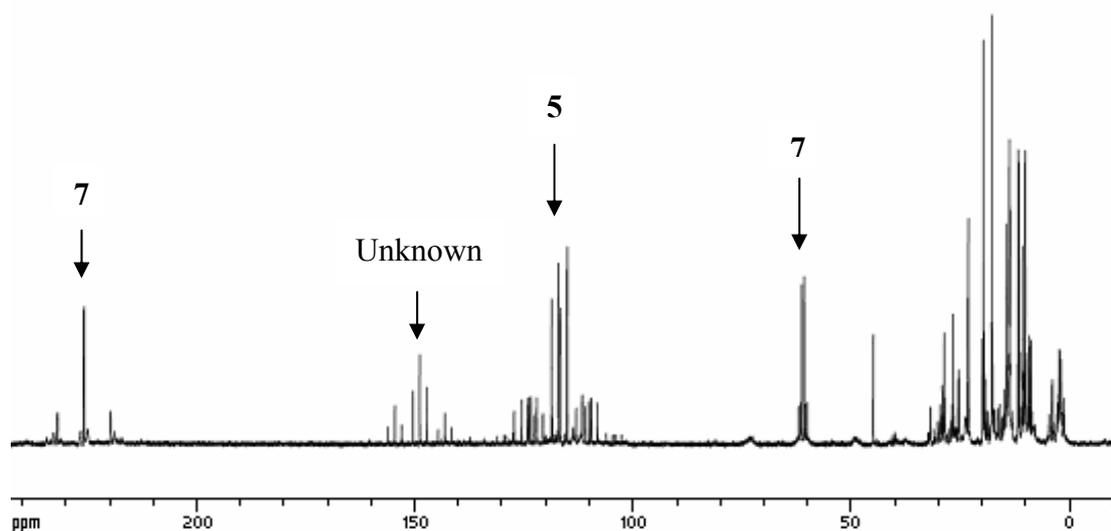


Figure S8

The $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3) spectrum of the mixture of products obtained by heating **5** in methanol but without 1-octene, and without the addition of acid or alkali.

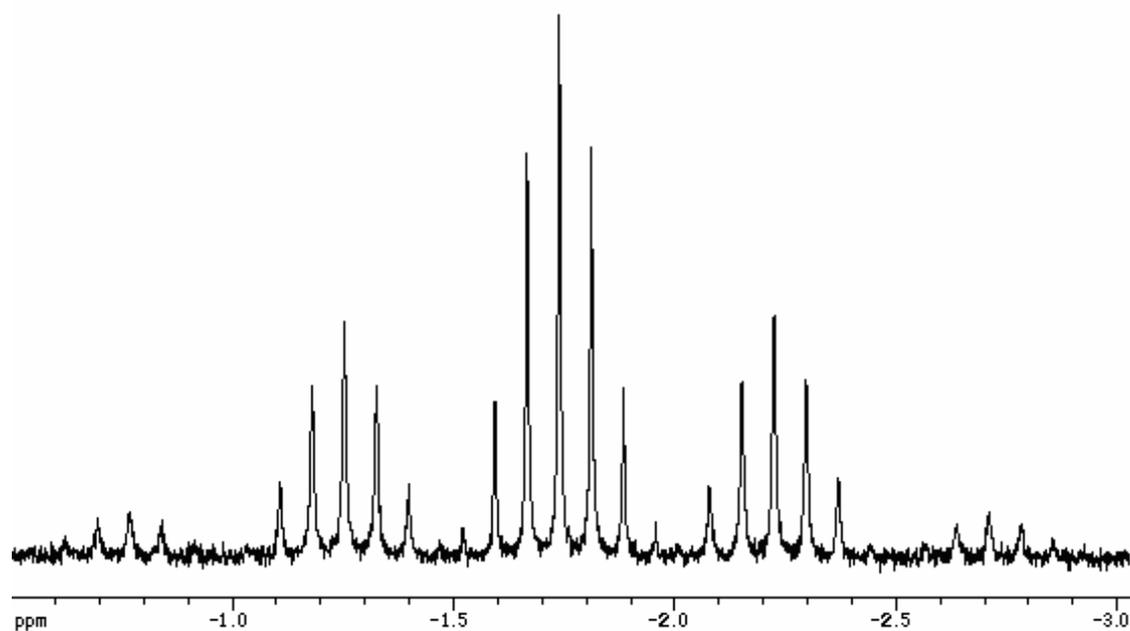


$^{31}\text{P}\{^1\text{H}\}$ NMR data corresponding to the multiplet marked unknown:

δ 149 [$^1\text{J}(\text{Pt-P})$ 1854.4 Hz; $^2\text{J}(\text{P-P})$ 255.1 Hz]

Figure S9

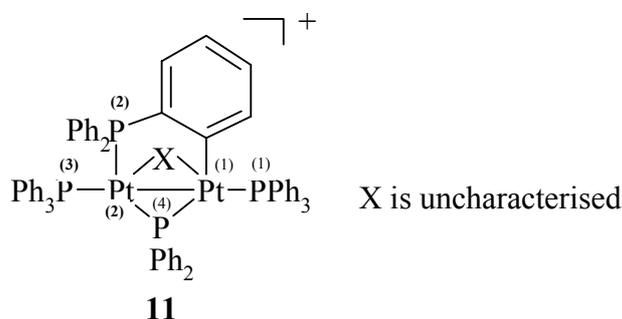
The high field proton ^1H NMR spectrum of **12** in CD_2Cl_2



Notes concerning the NMR spectra

Figure S1 The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** shown in Figure S1 has been reported previously by Venanzi and co-workers¹ and Paonessa and Trogler², but in each case at ~ 36 MHz. The superficial appearance of the published spectrum² is therefore quite different to that given here, which was recorded at 145.7 MHz. The numbering of the phosphorus atoms is that used by Venanzi. Our chemical shifts in CDCl_3 corresponded closely to those given previously, which were measured in acetone- d_6 .

Figure S7 The structure assigned to **11** from the recorded $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) data is:



The details of the spectrum are: δ P(1) 12.81; δ P(2) 24.45 dd; δ P(3) 19.81 ddd; δ P(4) 174.5 dd in phosphido region.

$^1\text{J}[\text{P}(1)\text{-Pt}(1)] = 2978.6$ Hz; $^1\text{J}[\text{P}(2)\text{-Pt}(2)] = 3080$ Hz; $^1\text{J}[\text{P}(3)\text{-Pt}(2)] = 3543$ Hz; $^1\text{J}[\text{P}(4)\text{-Pt}(1)] = 2729$ Hz; $^1\text{J}[\text{P}(4)\text{-Pt}(2)] = 3000$ Hz; $^2\text{J}[\text{P}(2)\text{-P}(3)] = 8.7$ Hz; $^2\text{J}[\text{P}(2)\text{-P}(4)] = 257$ Hz; $^2\text{J}[\text{P}(3)\text{-P}(4)] = 15$ Hz; $^2\text{J}[\text{P}(2)\text{-Pt}(1)] = 4.6$ Hz; $^2\text{J}[\text{P}(3)\text{-Pt}(1)] = 456$ Hz; $^3\text{J}[\text{P}(1)\text{-P}(3)] = 139.6$ Hz.

11 was also detected in a solution of **5** (20.0 mg, 0.0131 mmol) in methanol (35.0 cm^3) which had been irradiated with *uv* light (366 nm) from a medium pressure mercury lamp for $2\frac{3}{4}$ hours, by which time the solution had developed a deep clear-yellow colouration. The methanol was removed under reduced pressure, to yield a yellow powder which was analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3). The powder was found to be a mixture of **5** and **11**. The integrated ratio of these products was approximately 3:1.

Figure S10 Mass Spectrum of 1-methoxy-1-vinyloxyhexane, showing peak at $m/z=115$ not present in 4-methoxyoctane.

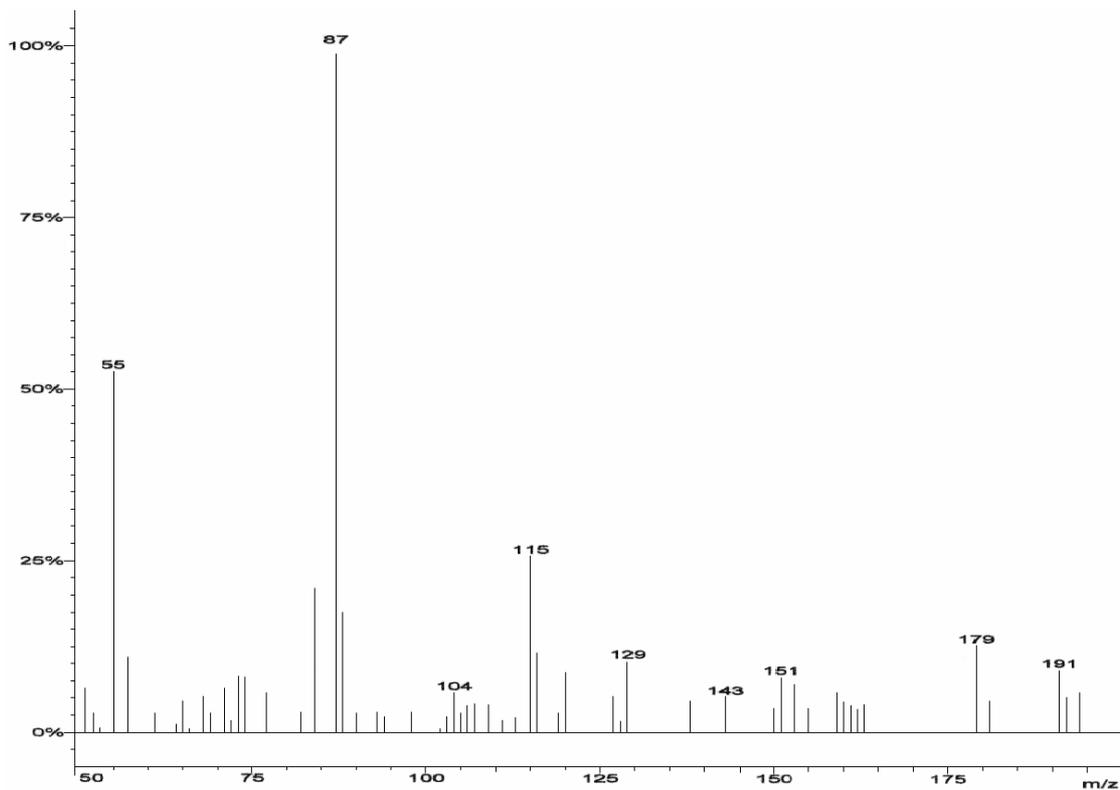
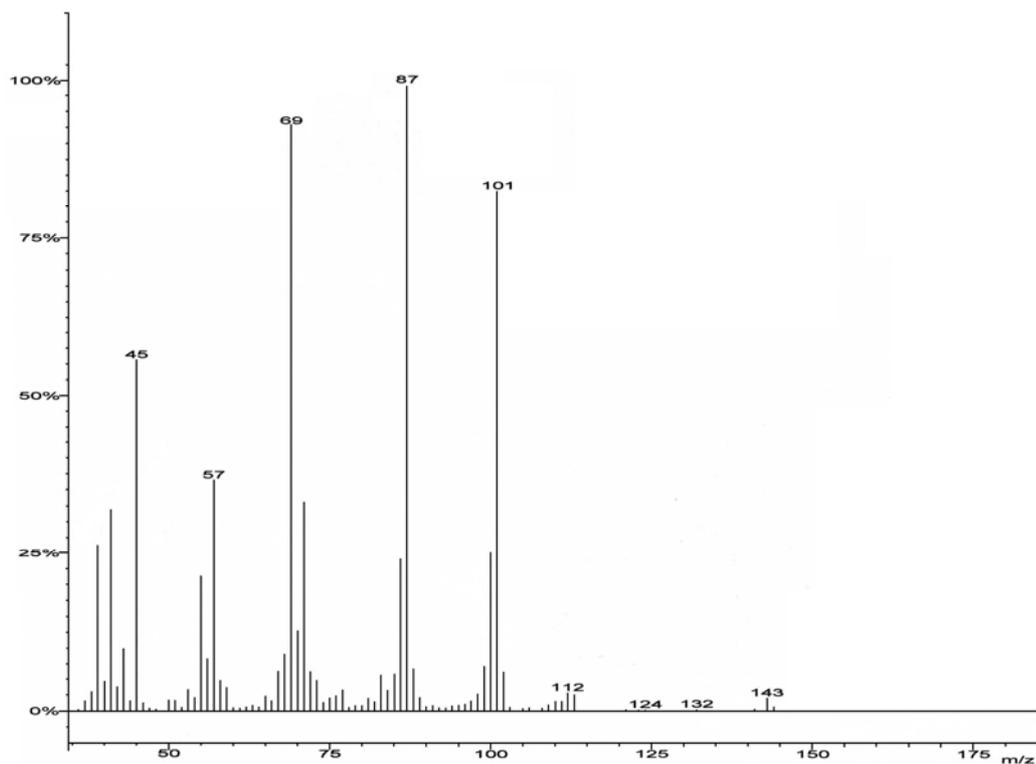


Figure S11 Mass Spectrum of 4-methoxyoctane showing peak at $m/z=101$ not present in 1-methoxy-1-vinyloxyhexane.



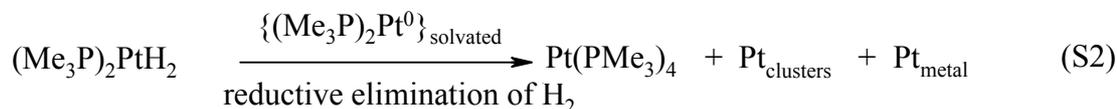
Comments on the fate of **12 during the catalytic reactions, and some background information relating the newly discovered catalytic activity of **12** to Jensen and Trogler's earlier work.**

We were not able to characterise any of the inorganic products derived from **12** in the catalytic tests. However, on the basis of our $^{31}\text{P}\{^1\text{H}\}$ NMR studies, we deduced that some of these products may have contained a catalytic cluster, with one or more Pt-PPh₂-Pt bonds, which may have been responsible for the formation of *trans*-2-octenal. The role of **12** in the formation of *trans*-2-octenal is unknown.

An attempt was made to compare the reactivity of **1**[BF₄] and **12**[BF₄] towards 1-octene, and if possible, to characterise any compounds arising from the interaction of these catalytic precursors and 1-octene. In the absence of 1-octene both complexes are stable in CD₂Cl₂ for many months at room temperature in the dark, but on the addition of 1-octene a reaction occurs in both cases. In the case of **12**[BF₄] the peak at ~59 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum decreases over a period of a month and new peaks with coupling to ^{195}Pt appear at δ 44.2, 43.58, and 43.0 ppm. These peaks may be due to organometallic compounds of platinum. We were unable to isolate and characterise this species, which on further standing led to dppePtCl₂. The ^1H NMR spectrum showed that there was very little isomerisation of the 1-octene to internal isomers. In contrast **1**[BF₄] caused the double bond isomerisation of the 1-octene within a few hours, but there was little change in the $^{31}\text{P}\{^1\text{H}\}$ spectrum of the complex until after a month. These experiments were carried out with both treated and untreated 1-octene, and also in CDCl₃ in place of CD₂Cl₂, but with the same results. These NMR observations demonstrate that the reactivity of **12**[BF₄] and **1**[BF₄] towards 1-octene differ fundamentally. However, further work is necessary to establish the reactivity of the trinuclear complex **12**[BF₄] towards 1-octene and any intermediates that might participate in a catalytic cycle leading to the formation of 1-methoxyoctane. Both **1**[BF₄] and **12**[BF₄] catalysed the double bond isomerisation of 1-octene in the catalytic experiments.

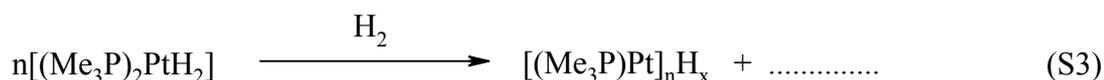
It is possible that Jensen and Trogler's original catalytic system contained a trinuclear complex. In later studies, Trogler⁷ suggested that the 3-coordinate species (Me₃P)PtH₂ was a viable intermediate in the decomposition of (Me₃P)₂PtH₂, given in

eqn (S2). He discovered that solutions of $(\text{Me}_3\text{P})_2\text{PtH}_2$ decomposed to $\text{Pt}(\text{PMe}_3)_4$, “unidentified cluster complexes” and platinum metal, according to eqn (S2). The highly reactive 14-electron species $[(\text{Me}_3\text{P})_2\text{Pt}^0]_{\text{solv}}$ in THF, was considered to be a transient intermediate in this reaction.

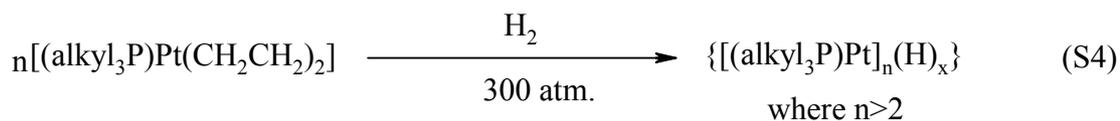


Therefore, as part of his workup procedure, Trogler⁸ purged the residual hydrogen gas from his freshly prepared solutions of *trans*- $[(\text{Me}_3\text{P})_2\text{PtHCl}]$ with nitrogen, to decompose any impurities of $(\text{Me}_3\text{P})_2\text{PtH}_2$.

We postulate that an alternative to eqn (S2) is the formation of clusters as given in eqn (S3),



so that Trogler may have unwittingly had a cluster complex in his catalytic system. The feasibility of eqn (2) is implied by the already known syntheses of the four platinum clusters $\{\text{Pt}_5\text{H}_8[\text{P}(\text{Bu}^t)_2\text{Ph}]_5\}$,⁹ $\{\text{Pt}_4\text{H}_2[\text{P}(\text{Bu}^t)_3]_4\}$, $\{\text{Pt}_4\text{H}_8[\text{PPt}^i_2\text{Ph}]_4\}$ and $\{\text{Pt}_3(\mu\text{-H})_3\text{H}_3[\text{P}(\text{Bu}^t)_3]_3\}$ ¹⁰ which were successfully carried out according to eqn (S4) albeit at high pressure with hydrogen gas at 300 atm., although at room temperature.



References for Supplementary Information

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