

Hydride platinum gold clusters: synthesis and characterization

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Abstract

$[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]^+$ and $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]^+$ were prepared from $[\text{Pt}(\text{AuPPh}_3)_8]^{2+}$ and $[\text{Pt}(\text{PPh}_3)(\text{AuPPh}_3)_6]^{2+}$, respectively, using an alkaline methanol solution as hydride forming reagent, while $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$ was prepared from $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ and SnCl_3^- . The clusters were characterized by ^{31}P , ^{195}Pt and ^1H NMR, analysis and by the reaction with acid. The cluster growth of PtAu_x clusters is discussed. The newly prepared compounds did not show any catalytic activity for the hydrogenation and isomerization of hexenes at ambient temperature and atmospheric pressure.

Introduction

Platinum–gold clusters of the type $\text{Pt}(\text{AuPPh}_3)_x$ ($x = 2\text{--}9$) resemble mononuclear platinum complexes in the way that they show electrophilic and nucleophilic addition reactions, substitution as well as oxidative addition reactions [1–3]. We have suggested that in the synthesis of these compounds starting from $\text{Pt}(\text{PPh}_3)_3$, AuPPh_3^+ and H_2 cluster growth proceeds by a sequence of oxidative additions of H_2 and electrophilic substitutions with AuPPh_3^+ [4], in which hydride containing clusters should be intermediates. However so far only $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ has been prepared and characterized [5]. Therefore we have studied the reactivity of platinum gold clusters towards hydride forming reagents [6] to see if new hydride platinum gold clusters could be identified. We report here the synthesis and characterization of three new cluster compounds $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]^+$, $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]^+$ and $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$. As mononuclear platinum hydride compounds are catalysts for isomerization and hydrogenation reactions, we have explored a possible catalytic activity of the newly prepared cluster compounds.

Experimental

Elemental analyses were carried out in the micro-analytical department of this university and by Dr

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A. Bernhard, Elbach über Engelskirchen, F.R.G. ICP analyses were carried out on a Plasma 200 ICP A-E spectrometer in DMSO solutions, with $\text{Pt}(\text{AuPPh}_3)_8(\text{NO}_3)_2$ as reference, giving Pt:Au:P ratios. ^{31}P NMR spectra were recorded on a Bruker WM 200 instrument at 81.02 MHz, using CH_2Cl_2 solutions and TMP in CD_2Cl_2 as reference; ^{195}Pt NMR at 43.02 MHz, using CD_2Cl_2 solutions and K_2PtCl_6 in D_2O as reference; and ^1H NMR at 200.13 MHz using CD_2Cl_2 solutions and TMS in CD_2Cl_2 as reference. All NMR spectra were measured at room temperature. IR spectra were recorded on a Perkin-Elmer 1720-X Fourier transform spectrometer.

Preparation

$[\text{Pt}(\text{AuPPh}_3)_8]^{2+}$, $[\text{Pt}(\text{PPh}_3)(\text{AuPPh}_3)_6]^{2+}$, $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ and NH_4SnCl_3 were prepared according to the literature [5, 7–9]. As hydride-forming reagents solutions of KOH in methanol and ethanol were used. The presence of formaldehyde or acetaldehyde was detected by a spot-test with fuchsine as described by Feigl [10]. Pure methanol and ethanol as well as KOH solutions in methanol and ethanol were measured as blanks. Methanol with formaldehyde and ethanol with acetaldehyde gave positive spot-test results.

$[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]\text{NO}_3$

$[\text{Pt}(\text{AuPPh}_3)_8](\text{NO}_3)_2$ (50 mg, 0.012 mmol) was dissolved in 30 ml methanol and 500 mg (8 mmol) KOH were added. After the KOH had dissolved

the solution was evaporated to dryness yielding a red solid. The red solid was dissolved in 20 ml CH_2Cl_2 , filtered and evaporated to dryness again. This last procedure was repeated twice. The red solid was dried *in vacuo*. Yield 40 mg (0.01 mmol, 80%).

IR: ν 1378 cm^{-1} , free NO_3^- . ICP:Pt: Au:P = 0.98:8.0:7.95. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 52.1$ ppm, $^2J(^{195}\text{Pt}-^{31}\text{P}) = 452$ Hz (Au-P). ^1H NMR: $\delta = 5.4$ ppm nonet, $^1J(^{195}\text{Pt}-^1\text{H}) = 705$ Hz, $^3J(^{31}\text{P}-^1\text{H}) = 14.3$ Hz (Pt-H). Phenyl protons 6.3–7.8 ppm. ^{195}Pt NMR: $\delta = -5673$ ppm (nonet), $^1J(^{195}\text{Pt}-^1\text{H}) = 721$ Hz; $^2J(^{195}\text{Pt}-^{31}\text{P}) = 453$ Hz. $^{195}\text{Pt}\{^1\text{H}\}$ NMR: $\delta = -5673$ ppm (nonet), $^2J(^{195}\text{Pt}-^{31}\text{P}) = 453$ Hz.

$[\text{Pt}(\text{H})(\text{AuPPh}_3)_8](\text{PF}_6)$

To a solution of 100 mg (0.025 mmol) $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]\text{NO}_3$ in 5 ml CH_2Cl_2 , 100 mg (0.3 mmol) Bu_4NPF_6 were added. After 15 min, 25 ml of methanol were added to this solution resulting in the formation of a red precipitate. The precipitate was filtered off, washed with 10 ml methanol and ether and dried *in vacuo*. Yield 80 mg (0.02 mmol).

IR: $\nu = 840$ cm^{-1} , free PF_6^- ; no NO_3^- bands. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 52.1$ ppm, $^2J(^{195}\text{Pt}-^{31}\text{P}) = 452$ Hz (Au-P).

$[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]\text{NO}_3$

The same procedure was used as for $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]\text{NO}_3$ but, instead of $[\text{Pt}(\text{AuPPh}_3)_8](\text{NO}_3)_2$, $[\text{Pt}(\text{PPh}_3)(\text{AuPPh}_3)_6](\text{NO}_3)_2$ was used. Yield 90% based on $\text{Pt}(\text{PPh}_3)(\text{AuPPh}_3)_6(\text{NO}_3)_2$.

IR; $\nu = 1372$ cm^{-1} , free NO_3^- . ICP:Pt: Au:P = 1.1:6.0:7.2. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 48.2$ ppm (doublet) $^2J(^{195}\text{Pt}-^{31}\text{P}) = 457$ Hz (Pt-P), 68.0 ppm (septet) $^3J(^{31}\text{P}-^{31}\text{P}) = 37$ Hz, $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2583$ Hz (Au-P). ^1H NMR: $\delta = 0.34$ ppm (doublet of septets), $^1J(^{195}\text{Pt}-^1\text{H}) = 687$ Hz, $^2J(^{31}\text{P}-^1\text{H}) = 9.3$ Hz, $^3J(^{31}\text{P}-^1\text{H}) = 18.3$ Hz (Pt-H). Phenyl protons 6.3–7.8 ppm. $^{195}\text{Pt}\{^1\text{H}\}$ NMR: $\delta = -5035$ ppm, $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2581$ Hz, $^2J(^{195}\text{Pt}-^{31}\text{P}) = 455$ Hz. ^{195}Pt NMR: $\delta = -0.5035$ ppm $^1J(^{195}\text{Pt}-^1\text{H}) = 690$ Hz, $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2581$ Hz, $^2J(^{195}\text{Pt}-^{31}\text{P}) = 454$ Hz.

$\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7^{2+}$

When a solution of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6](\text{NO}_3)$ in CH_2Cl_2 was treated with 1 equiv. $\text{AuPPh}_3\text{NO}_3$, $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7](\text{NO}_3)_2$ was formed in 90% yield. Crystallization takes place by slow diffusion of diethyl ether into the CH_2Cl_2 solution.

Acidimetric titration

Solutions of $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8](\text{NO}_3)$ and $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6](\text{NO}_3)$ in methanol were titrated with 0.025 M HCl, with potentiometric end point

detection. For both compounds a sharp end point could be detected after addition of 1 equiv. acid.

$[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7](\text{SnCl}_3)$

A suspension of 100 mg NH_4SnCl_3 (0.4 mmol) in 5 ml methanol at 55 °C was added to a solution of 100 mg $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7](\text{NO}_3)_2$ (0.025 mmol) in 5 ml methanol. A yellow precipitate was immediately formed. After stirring for 30 min the precipitate was filtered off, washed with 15 ml methanol, 15 ml ethanol and diethyl ether and dried *in vacuo*. The total procedure was carried out in a Schlenk apparatus under N_2 . Yield 80 mg, 80% on $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7](\text{NO}_3)_2$.

Anal. Calc. for $\text{Au}_7\text{C}_{126}\text{H}_{106}\text{Cl}_6\text{P}_7\text{PtSn}_2$ (molecular weight 3860.28): Sn, 6.15; Cl, 5.51. Found: Sn, 6.08; Cl, 5.37%. ICP:Pt: Au:P = 1.0:7.0:7.3. IR: $\nu = 305$, 275 cm^{-1} , coordinated SnCl_3 ; $\nu = 330$ cm^{-1} , free SnCl_3^- . $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 51.1$ ppm, $^2J(^{195}\text{Pt}-^{31}\text{P}) = 443$ Hz, $^3J(^{117}\text{Sn}-^{31}\text{P}) = 372$ Hz, $^3J(^{119}\text{Sn}-^{31}\text{P}) = 389$ Hz (Au-P). ^{195}Pt NMR: $\delta = -5634$ ppm (doublet of octets), $^1J(^{195}\text{Pt}-^1\text{H}) = 680$ Hz, $^2J(^{195}\text{Pt}-^{31}\text{P}) = 445$ Hz, Sn satellites with $^1J(^{195}\text{Pt}-^{117}\text{Sn}) = 8050$ Hz, $^1J(^{195}\text{Pt}-^{119}\text{Sn}) = 8200$ Hz. $^{195}\text{Pt}\{^1\text{H}\}$ NMR: $\delta = -5634$ ppm (octet), $^2J(^{195}\text{Pt}-^{31}\text{P}) = 445$ Hz. ^1H NMR: $\delta = 2.75$ ppm, $^1J(^{195}\text{Pt}-^1\text{H}) = 680$ Hz, $^3J(^{31}\text{P}-^1\text{H}) = 16.2$ Hz, $^2J(\text{Sn}-^1\text{H})$ not found, (Pt-H). Phenyl protons 6.6–7.5 ppm.

$[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]\text{PF}_6$

To a solution of 100 mg (0.03 mmol) $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7](\text{SnCl}_3)$ in 5 ml CH_2Cl_2 a suspension of 40 mg (0.2 mmol) KPF_6 in 5 ml methanol was added and stirred for 15 min. The solution was evaporated to dryness and the remaining yellow solid was redissolved in CH_2Cl_2 , filtered, and again evaporated to dryness. This procedure was repeated twice.

IR: $\nu = 305$, 275 cm^{-1} , coordinated SnCl_3^- ; 840 cm^{-1} free PF_6^- . $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 50.2$ ppm, $^2J(^{195}\text{Pt}-^{31}\text{P}) = 443$ Hz, $^3J(^{117}\text{Sn}-^{31}\text{P}) = 372$ Hz, $^3J(^{119}\text{Sn}-^{31}\text{P}) = 389$ Hz.

Catalytic studies

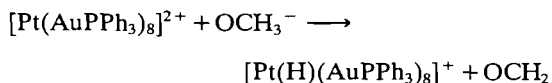
Methanol and CH_2Cl_2 solutions of the cluster compounds with 1-hexene, *cis* or *trans* 2-hexene were kept for several days at room temperature or 50 °C and atmospheric H_2 pressure. The reaction mixture was analysed daily for isomerization and hydrogenation products by GLC measurements, using a HP-1 apolar capillary column at 40 °C.

Results

$[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]^+$

The NO_3^- and PF_6^- salts of this cluster ion can be prepared in high yield by the reaction of

$[\text{Pt}(\text{AuPPh}_3)_8]^{2+}$ with an alcoholic solution of KOH.



The compounds are stable in air but react with dilute acids, consuming 1 equiv. H^+ to produce the parent compound in nearly 100% yield and H_2 . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows one signal at 52.0 ppm with Pt satellites with a coupling constant of 452 Hz. This is in the range of $^2J(^{195}\text{Pt}-^{31}\text{P})$ couplings [3, 4] and is thus interpreted as such. The ^1H NMR spectrum shows a nonet at 5.4 ppm, with a coupling of 14.3 Hz, which is interpreted as a $^3J(^{31}\text{P}-^1\text{H})$. There are Pt satellites with a coupling of 705 Hz which is in the range of $^1J(^{195}\text{Pt}-^1\text{H})^5$.

The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum contains a nonet at -5671 ppm ($^2J(^{195}\text{Pt}-^{31}\text{P}) = 452$ Hz), without H decoupling the spectrum changes into a doublet of nonets, indicating the presence of one H atom (see Fig. 1). These NMR data indicate a cluster with a composition of $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]$, with Pt in the centre, bonded to one H atom and eight AuPPh_3 groups. The composition $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]\text{NO}_3$ is indicated

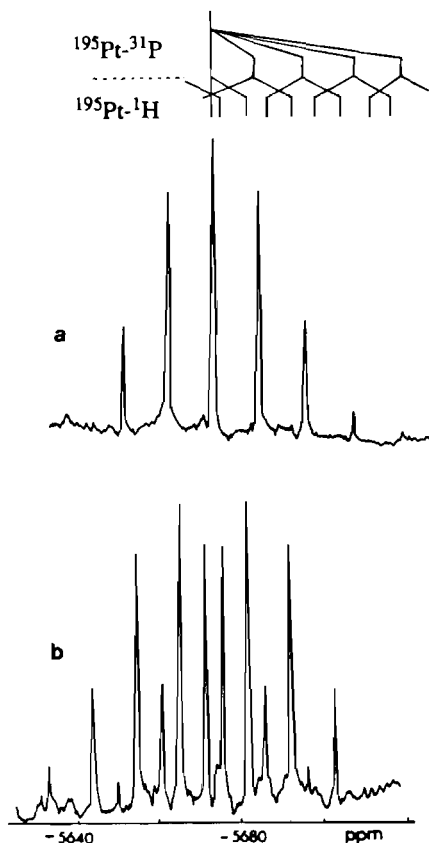
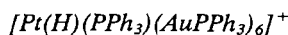
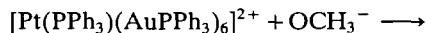


Fig. 1. $^{195}\text{Pt}\{^1\text{H}\}$ NMR (a) and ^{195}Pt NMR (b) of $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]^+$.

by elemental analysis, IR spectra, the reaction with one equiv. of H^+ and the diamagnetism.

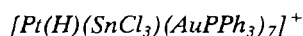


The nitrate salt of this cluster ion can be prepared in high yield by the reaction of $[\text{Pt}(\text{PPh}_3)(\text{AuPPh}_3)_6](\text{NO}_3)_2$, with an alcoholic solution of KOH.

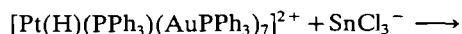


The compound is stable in air but reacts with dilute acid consuming 1 equiv. of H^+ to produce the parent compound in high yield and H_2 . With 1 equiv. of AuPPh_3^+ the well-known $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ is formed in high yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a septet at 68.0 ppm and a doublet at 48.2 ppm both with coupling constants of 36.7 Hz, which is interpreted as a $^3J(^{31}\text{P}-^1\text{H})$. Both the septet and the doublet have Pt satellites with coupling constants $^1J(^{195}\text{Pt}-^{31}\text{P})$ of 2583 Hz and $^2J(^{195}\text{Pt}-^{31}\text{P})$ of 457 Hz, respectively. These data are close to those of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ [6], and indicate that there is one PPh_3 group and six AuPPh_3 groups bonded to Pt.

In the ^1H NMR spectrum there is a multiplet signal at 0.34 ppm with Pt satellites ($^1J(^{195}\text{Pt}-^1\text{H}) = 687$ Hz). The multiplet can be interpreted as $^2J(^1\text{H}-^{31}\text{P}) = 9.3$ Hz and $^3J(^1\text{H}-^{31}\text{P}) = 18.3$ Hz. These data are close to those of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$. The $^{195}\text{Pt}\{^1\text{H}\}$ spectrum shows a doublet of septets at -5035 ppm, with $^1J(^{195}\text{Pt}-^{31}\text{P}) = 2582$ Hz and $^2J(^{195}\text{Pt}-^{31}\text{P}) = 454$ Hz which doubles without ^1H decoupling showing $^1J(^{195}\text{Pt}-^1\text{H}) = 689$ Hz (see Fig. 2). These data indicate the presence of only one H atom attached to platinum. The cluster cation can thus be formulated as $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]$ with Pt in the centre, coordinated by H, PPh_3 and six (AuPPh_3) groups. The reactions with H^+ and $(\text{AuPPh}_3)^+$ as well as elemental analysis, IR spectra and diamagnetism indicate the composition $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]\text{NO}_3$ for the newly prepared cluster compound.



The SnCl_3 salt of this cluster ion can be synthesized by the reaction of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ with NH_4SnCl_3 , the corresponding PF_6 salt is obtained in a metathesis reaction of the SnCl_3 salt with KPF_6 .



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a signal at 51.1 ppm with Pt satellites with $^2J(^{195}\text{Pt}-^{31}\text{P}) = 443$ Hz and ^{119}Sn , ^{117}Sn satellites with $^3J(^{119}\text{Sn}-^{31}\text{P}) = 389$ Hz and

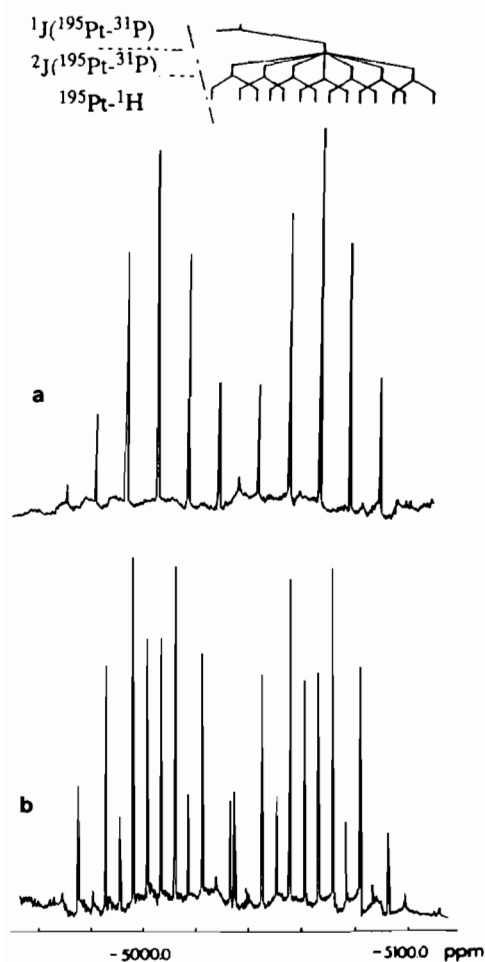


Fig. 2. $^{195}\text{Pt}\{^1\text{H}\}$ NMR (a) and ^{195}Pt NMR (b) of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]^+$.

$^3J(^{117}\text{Sn}-^{31}\text{P}) = 373$ Hz. In the ^1H NMR spectrum there is an octet at 2.75 ppm with $^3J(^{31}\text{P}-^1\text{H}) = 16.2$ Hz; there are Pt satellites with $^1J(^{195}\text{Pt}-^1\text{H}) = 680$ Hz. The ^{195}Pt NMR spectrum shows an octet at -5634 ppm with $^2J(^{195}\text{Pt}-^{31}\text{P}) = 445$ Hz and Sn satellites with $^1J(^{117}\text{Sn}-^{195}\text{Pt}) = 8050$ Hz and $^1J(^{119}\text{Sn}-^{195}\text{Pt}) = 8200$ Hz. Without ^1H decoupling this spectrum doubles showing $^1J(^{195}\text{Pt}-^1\text{H}) = 680$ Hz (see Fig. 3). All these data indicate the cluster cation to be $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$ with one H atom, one SnCl_3 group and seven (AuPPh_3) groups attached to the central Pt atom. The composition of the SnCl_3^- and PF_6^- salts was confirmed by elemental analysis and IR spectra.

Catalytic study

The catalytic behaviour of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]^+$, $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ and $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$ with respect to the hydrogenation and isomerization of 1-hexene and *cis* and *trans* 2-hexene was investigated. Methanol and CH_2Cl_2

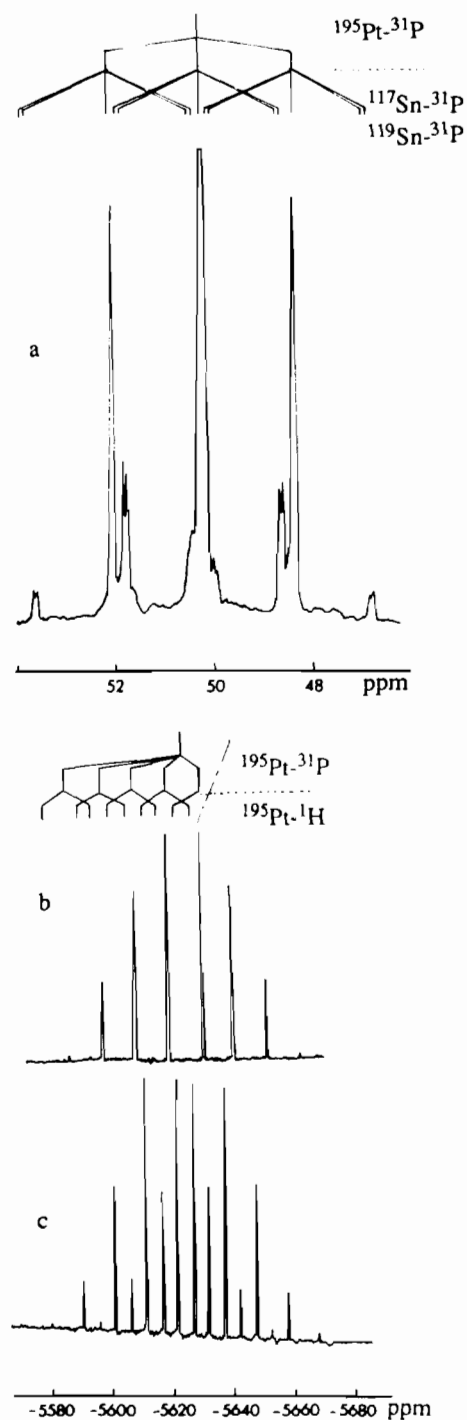


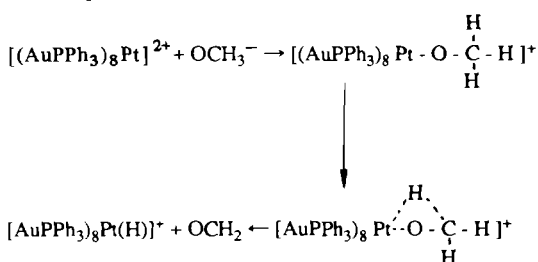
Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR (a), $^{195}\text{Pt}\{^1\text{H}\}$ NMR (b) and ^{195}Pt NMR (c) of $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$.

solutions of these clusters and the olefines were kept for several days at room temperature and 50°C at atmospheric H_2 pressure. However, no indications of isomerization or hydrogenation could be detected in the analysis of the reaction product. In an attempt to abstract PPh_3 from the cluster and to create a

free coordination site for the olefine $\text{AuPPh}_3\text{NO}_3$ was added to the reaction mixture but no catalytic effect was achieved.

Discussion

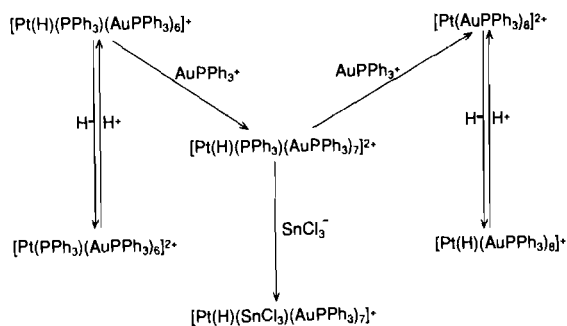
The formation of $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]^+$ and $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]^+$ from $[\text{Pt}(\text{AuPPh}_3)_8]^{2+}$ and $[\text{Pt}(\text{PPh}_3)(\text{AuPPh}_3)_6]^{2+}$, respectively, with methanolate is analogous with the hydride formation in mononuclear Pt compounds [11–13]. CH_3O^- could add to Pt completing the 18 electron configuration, but the compound is unstable as it could not be detected. The hydride is formed probably via a β -H transfer. Formaldehyde was detected as the reaction product.



Unfortunately no suitable crystals for X-ray structure determination could be obtained but the NMR data give a reliable picture of the structure. For $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]^+$ and $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]^+$, both 18 electron systems, spherical structures are expected [14–16], in contrast to the toroidal 16 electron systems of $[\text{Pt}(\text{AuPPh}_3)_8]^{2+}$ and $[\text{Pt}(\text{PPh}_3)(\text{AuPPh}_3)_6]^{2+}$. The fast and clean conversion $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]^+ + \text{AuPPh}_3^+ \rightarrow [\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ gives further evidence for the structural relationship between both clusters; the X-ray structure of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ is known [5]. In a further reaction with AuPPh_3^+ and a base the Pt bonded PPh_3 is substituted and $\text{Au}(\text{PPh}_3)_2^+$ is formed, a second AuPPh_3^+ is bonded to Pt at least forming $[\text{Pt}(\text{H})(\text{AuPPh}_3)_8]^{2+}$.

Up to now, in the reaction of $\text{Pt}(\text{PPh}_3)_3$ and $\text{AuPPh}_3\text{NO}_3$ with H_2 as reducing agent, $[\text{Pt}(\text{AuPPh}_3)_8]^{2+}$ is the ultimate product with a Au:Pt ratio of 8. The proposed growth mechanism [4] is a succession of oxidative additions of H_2 at the Pt center and electrophilic substitutions of AuPPh_3^+ .

Further growth beyond $[\text{Pt}(\text{AuPPh}_3)_8]^{2+}$ is probably blocked by the steric hindrance of eight voluminous triphenyl-phosphine groups, that almost completely fill the peripheral space, and clusters with more than eight phosphines have never been detected [17]. The interconversion of the different known hydride clusters is shown in Scheme 1. The structure of $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$ will not only be related



Scheme 1.

to $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ but also to $[\text{Au}(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$ [18]. However the positions of the (AuPPh_3) groups in $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$ and $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ may differ like they do in the $[\text{Au}(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$ and $[\text{Au}(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$ clusters.

Hydrogenation and isomerization of 1-hexene and 2-hexene in the presence of $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_7]^{2+}$, $[\text{Pt}(\text{H})(\text{SnCl}_3)(\text{AuPPh}_3)_7]^+$ or $[\text{Pt}(\text{H})(\text{PPh}_3)(\text{AuPPh}_3)_6]^+$ is not detected.

Steric hindrance, the nucleophilic behavior of the 18 electron system and/or the lack of dissociation of PPh_3 or SnCl_3 of the Pt atom obviously prevent a reaction with olefines.

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