Determination of Signs of Coupling Constants for (Ethene)bis-(triphenylphosphane)platinum(0)

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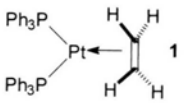
The signs of coupling constants [$^1J(^{195}Pt,^{13}C)$ (> 0), $^2J(^{195}Pt,^1H)$ (< 0), $\Sigma^2J(^{31}P,^{13}C)_{trans}$ + $^2J(^{31}P,^{13}C)_{cis}$ (> 0) and $\Sigma^3J(^{31}P,^1H)_{trans}$ + $^3J(^{31}P,^1H)_{cis}$ (< 0)] in (ethene)bis(triphenylphosphane)platinum(0) (**1**) were determined by selective heteronuclear double and triple resonance experiments of the type $^1H\{^{31}P\}$, $^{13}C\{^1H,^{31}P\}$ and two-dimensional heteronuclear shift correlations (HETCOR) of the type $^{13}C/^1H$, $^{195}Pt/^1H$, and $^{31}P/^1H$, either by observing the heteronucleus or ^1H in the more sensitive inverse mode.

Alkene complexes of platinum(0) have received considerable attention with respect to their structure [1], molecular dynamics [2] and extensive use in synthesis [3]. Especially, (ethene)bis(triphenylphosphane)platinum(0) (**1**) has found widespread applications. However, NMR data of **1** are scattered in the literature [4], and the data set is not complete, in particular as far as signs of various important coupling constants involving the ethene ligand are concerned [e.g. [$^1J(^{195}Pt,^{13}C)$, $^2J(^{195}Pt,^1H)$, $\Sigma^2J(^{31}P,^{13}C)_{trans}$ + $^2J(^{31}P,^{13}C)_{cis}$ and $\Sigma^3J(^{31}P,^1H)_{trans}$ + $^3J(^{31}P,^1H)_{cis}$]. In the following it is shown that this information can be gained by selective heteronuclear double or triple resonance experiments and / or two-dimensional (2D) heteronuclear shift correlations (HETCOR).



Experimental

The complex **1** was prepared as described in the literature [5], and handled in an Ar atmosphere. Solutions in CD_2Cl_2 (*ca.* 0.05 g in 0.5 ml; at 25 ± 1 °C) were used for NMR measurements (Bruker ARX 250 and DRX 500). Conditions for HETCOR experiments were optimized in one-dimensional polarisation transfer experiments. A triple resonance probehead served for heteronuclear $^{13}C\{^1H,^{31}P\}$ triple resonance experiments. – Chemical shifts are given with respect to Me_4Si [δ^1H ($CHDCl_2$) = 5.33; $\delta^{13}C$ (CD_2Cl_2) = 53.8], external H_3PO_4 (85%, aq.) for $\delta^{31}P$ = 0, Ξ (^{195}Pt) = 21.4 MHz for $\delta^{195}Pt$ = 0.

The NMR data of **1** are listed in Table I. There is reasonably good agreement with data from the literature. The coupling sign determinations are based on the analysis of the energy level diagram typical of a three spin system with two active spins A and M, and a passive spin X. Either heteronuclear A{M} or M{A} double resonance experiments [6] or, often more conveniently, 2D A / M or M / A HETCOR experiments [7] can then be used to compare the relative signs of the coupling constants J(A, X) and J(M, X).

Table I. NMR data [a] for (ethene)bis(triphenylphosphane)platinum(0) (**1**).

δ^1H [$^2J(^{195}Pt,^1H)$] ($J(^{31}P,^1H)$)[b]	2.15 [-60.3] (-2.8)
$\delta^{13}C$ [$^1J(^{195}Pt,^{13}C)$] ($J(^{31}P,^{13}C)$)[c]	38.2[d] [+196.0] (+23.5)
$\delta^{31}P$ [$^1J(^{195}Pt,^{31}P)$][e]	34.9 [+3720.0]
$\delta^{195}Pt$[f] [$^1J(^{195}Pt,^{13}C)$]	-539.5 [+3720.0]

[a] In CD_2Cl_2 at 25 ± 1 °C; [b] $\Sigma^3J(^{31}P,^1H)_{trans}$ + $^3J(^{31}P,^1H)_{cis}$; [c] $\Sigma^2J(^{31}P,^{13}C)_{trans}$ + $^2J(^{31}P,^{13}C)_{cis}$; [d] Other $\delta^{13}C$ {$\Sigma^nJ(^{31}P,^{13}C)$} values: 138.1 [28.2] {43.4} C^i, 134.0 [20.3] {14.1} C^o, 128.0 {9.4} C^m, 129.2 C^p; [e] Ref. [4d]: 32.0 [3660]; [f] Ref. [4f]: -535.0.

In the case of **1** the absolute sign of $^1J(^{195}Pt,^{31}P)$ can be taken as positive as is true for all phosphane platinum complexes [8]. Thus other absolute coupling signs for **1** become accessible if the comparison of coupling signs involves $^1J(^{195}Pt,^{31}P)$. 1D $^1H\{^{31}P\}$ or 2D $^{31}P/^1H$ HETCOR experiments prove that the signs of $^1J(^{195}Pt,^{31}P)$ and $^2J(^{195}Pt,^1H)$ are opposite which means that $^2J(^{195}Pt,^1H) < 0$. An example of a 2D $^{13}C/^1H$ HETCOR which allows to compare the signs of $^1J(^{195}Pt,^{13}C)$ and $^2J(^{195}Pt,^1H)$ is shown in Fig. 1. The negative tilt of the cross peaks for the ^{195}Pt satellites indicates the opposite sign of these coupling constants. Since the negative sign of $^2J(^{195}Pt,^1H)$ was already established (vide supra), it follows that $^1J(^{195}Pt,^{13}C)$ is positive. This is also

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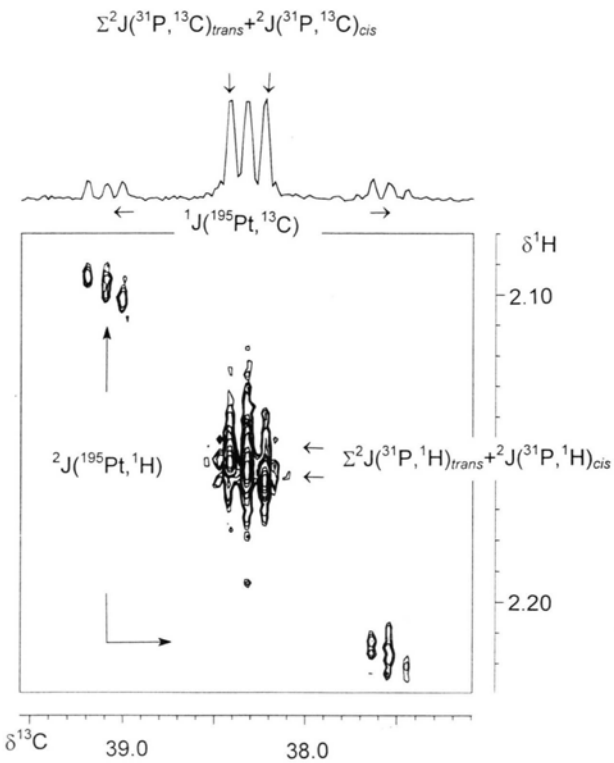

Fig. 1. Contour plot of the 2D 125.8 MHz $^{13}C/^{1}H$ HETCOR experiment, based on $^{1}J(^{13}C,^{1}H)$ = 146 Hz (digital resolution in $F_2(^{13}C)$: 2 Hz, in $F_1(^{1}H)$: 1.4 Hz, before zero filling; Gaussian multiplication in both dimensions; repetition time: 2.2 s; spectrometer time: 5 h). The region of resonance signals of the ethene ligand is shown (see text for the comparison of signs of coupling constants).

evident from the $^{13}C\{^{1}H,^{31}P\}$ triple resonance experiment, in which the signs of $^{1}J(^{195}Pt,^{31}P)$ and $^{1}J(^{195}Pt,^{13}C)$ are compared. Furthermore, the 2D $^{13}C/^{1}H$ HETCOR experiment shows a negative tilt of the cross peaks due to coupling with ^{31}P, and therefore, the signs of the sums $\Sigma^{2}J(^{31}P,^{13}C)_{trans}$ + $^{2}J(^{31}P,^{13}C)_{cis}$ and $\Sigma^{3}J(^{31}P,^{1}H)_{trans}$ + $^{3}J(^{31}P,^{1}H)_{cis}$ are opposite. Since the 2D ^{195}Pt / ^{1}H HETCOR experiment reveals a negative sign of the sum $\Sigma^{3}J(^{31}P,^{1}H)_{trans}$ + $^{3}J(^{31}P,^{1}H)_{cis}$ with respect to $^{1}J(^{195}Pt,^{31}P) > 0$, the sum $\Sigma^{2}J(^{31}P,^{13}C)_{trans}$ + $^{2}J(^{31}P,^{13}C)_{cis}$ is positive.

Although a positive sign was determined [9] for $^{1}J(^{195}Pt,^{13}C)$ in Zeise's anion $[\eta^{2}\text{-}C_2H_4PtCl_3]^-$ [relative signs of $^{1}J(^{195}Pt,^{13}C)$ and $^{2}J(^{195}Pt,^{1}H)$ were found to be opposite, and a negative sign of $^{2}J(^{195}Pt,^{1}H)$ was assumed], it was not clear whether this is also true for η^{2}-alkene platinum(0) complexes such as **1**. The experimental confirmation for $^{1}J(^{195}Pt,^{13}C) > 0$ is now presented. The comparison of the magnitude of the coupling constants $^{1}J(^{195}Pt,^{13}C) > +500$ Hz for (dialkyl)bis(triorganylphosphane)platinum(II)complexes, $^{1}J(^{195}Pt,^{13}C) = 274$ Hz for (2-butyne)bis(triphenylphosphane)platinum(0) [10] (which in the light of the present results should also be positive) with $^{1}J(^{195}Pt,^{13}C) = +196.0$ Hz for **1** rests now on a firm base, and is in support of contributions of platinacyclopropene- and platinacyclopropane structures to the respective ground states.

A negative sign of $^{2}J(^{195}Pt,^{1}H)$ for *trans*-$[(\eta^{2}\text{-}C_2H_4Pt(pyridne)Cl_2]$ has been determined previously from ^{1}H NMR spectra of the complex dissolved and partially oriented in a liquid crystalline matrix [11]. This is in agreement with the present result $^{2}J(^{195}Pt,^{1}H) < 0$ for **1**, and also for Zeise's anion [9] and η^{2}-allene-platinum(II) complexes [12].

The positive sign of the sum $\Sigma^{2}J(^{31}P,^{13}C)_{trans}$ + $^{2}J(^{31}P,^{13}C)_{cis}$ (+23.5 Hz) indicates that $^{2}J(^{31}P,^{13}C)_{trans}$ is positive and numerically larger than $^{2}J(^{31}P,^{13}C)_{cis}$ which is small and most likely negative. This conclusion is based on the $^{2}J(^{31}P,^{13}C)$ values observed for complexes of the type $(RCH{=}CH_2)(Ph_3P)_2Pt$ with $^{2}J(^{31}P,^{13}C)$ in the range of 24 to 30 Hz, assigned to the *trans* coupling pathway, and $^{2}J(^{31}P,^{13}C)$ in the range of 3 to 7 Hz, assigned to the *cis* coupling pathway [1b].

Since the sum $\Sigma^{3}J(^{31}P,^{1}H)_{trans}$ + $^{3}J(^{31}P,^{1}H)_{cis}$ is small and negative (-2.8 Hz), the sign of the coupling constants $^{3}J(^{31}P,^{1}H)$ must be opposite and their absolute magnitude similar.

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