Convenient Sign Determination of Various Coupling Constants in Alkynylplatinum(II) Phosphine Complexes

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\[ ^{13}\text{C}/^{1}\text{H} \text{ NMR, } ^{31}\text{P}/^{1}\text{H} \text{ NMR, } ^{195}\text{Pt}/^{1}\text{H} \text{ NMR, Signs of Coupling Constants, Alkynylplatinum(II) Complexes} \]

The utilization of two-dimensional (2D) \(^{13}\text{C}/^{1}\text{H}, ^{31}\text{P}/^{1}\text{H}\) and \(^{195}\text{Pt}/^{1}\text{H}\) heteronuclear shift correlations for the sign determination of various coupling constants (e.g., \(J(195\text{Pt}^{13}\text{C}) > 0\) (trans), \(J(195\text{Pt}^{31}\text{P}) < 0\) (cis), \(J(195\text{Pt}^{13}\text{C}=^{1}\text{H}) < 0\) (trans), \(J(195\text{Pt}^{31}\text{P}) < 0\) (cis), \(J(195\text{Pt}^{13}\text{C}^{=^{1}\text{H}}) > 0, J(195\text{Pt}^{31}\text{P}) < 0, etc.\)) is demonstrated, using standard equipment. The complexes \([\text{trans-(Bu}^3\text{P})_2\text{Pt}^{3}\text{C}=^{1}\text{H}]=1\) and \([\text{cis-(Et}^3\text{P}^{2}\text{CH}^{2}\text{CH}_2\text{P}^2\text{Et})\text{Pt}^{3}\text{C}=^{1}\text{H}]=2\) serve as model compounds.

The combined application of \(^1\text{H}, ^{13}\text{C}, ^{31}\text{P}\) and metal (M) NMR measurements to transition metal chemistry has revealed a wealth of information on structure, bonding and dynamic properties in solution [1, 2]. Coupling constants of the type \(J(195\text{Pt}^{13}\text{C})\), \(J(195\text{Pt}^{31}\text{P})\) are particularly helpful in this respect. If the sign of \(J\) is known, the diagnostic value of these data is greatly enhanced. Although the signs of a large number of coupling constants are known for \(n=1\) [3], the situation is less clear if \(n>1\). The majority of sign determinations are based on selective heteronuclear double resonance experiments [4, 5], mostly \(^1\text{H}(X)\), requiring additional equipment or modifications of the spectrometers (working either in CW or in the PFT mode). With the advent of two-dimensional (2D) NMR techniques a convenient alternative is available, considering in particular the multifarious information to be gained from heteronuclear shift correlations [6, 7]. These experiments can be carried out using the standard equipment of modern PFT-NMR instruments and relatively little spectrometer time is needed. In this note the alkynylplatinum(II) complexes 1 and 2 serve as illustrative examples for such measurements.

Just by focusing on the ethyne-protons the 2D heteronuclear shift correlations of the type \(^{13}\text{C}/^{1}\text{H}\), \(^{195}\text{Pt}/^{1}\text{H}\) and \(^{195}\text{Pt}/^{1}\text{H}\) allow the comparison of the signs of the following pairs of coupling constants: \(J(195\text{Pt}^{13}\text{C}^{=^{1}\text{H}})/J(195\text{Pt}^{31}\text{P})\), \(J(195\text{Pt}^{31}\text{P})/J(195\text{Pt}^{13}\text{C}^{=^{1}\text{H}})\), \(J(195\text{Pt}^{13}\text{C})/J(195\text{Pt}^{31}\text{P})\), \(J(195\text{Pt}^{31}\text{P})/J(195\text{Pt}^{13}\text{C})\) for compound 1 are fully in agreement with previous selective \(^1\text{H}(^{31}\text{P})\) and \(^1\text{H}(^{195}\text{Pt})\) experiments, respectively [8]. The absolute signs given in Table I for the various coupling constants are consistently based on the known positive signs of \(J(=^{13}\text{C}^{=^{1}\text{H}})\), \(J(=^{13}\text{C}=^{1}\text{H})\) [9], \(J(=^{195}\text{Pt}^{31}\text{P})\) [10] and \(J(=^{195}\text{Pt}^{31}\text{P})\) [11].

As for 1 D \(^1\text{H}(X)\) or \(^1\text{H}(^{13}\text{C})\) experiments, the 2 D \(^1\text{H}^{1}\text{H}\) heteronuclear shift correlations require the presence of a third magnetically active nucleus for the determination of relative signs of coupling constants [4, 5]. This condition is fulfilled for an enormous number of organometallic compounds: In addition to \(^{13}\text{C}\) and \(^1\text{H}\), isotopomers with appreciable natural abundance exist with spin \(I=1/2\) nuclei such as \(^{25}\text{Si}, ^{119}\text{Sn}, ^{207}\text{Pb}, ^{199}\text{Hg}, ^{103}\text{Rh}, ^{185}\text{W}, ^{195}\text{Pt}, ^{115}\text{N}, ^{31}\text{P}, ^{79}\text{Se}, ^{125}\text{Te}\) etc. present. If four different magnetically active nuclei are present as in 1 or 2 more information can be gained in a single experiment (see Fig. 1). So far, most 2 D \(^1\text{H}^{1}\text{H}\) experiments, aiming at the sign determination of

\[
\begin{align*}
\text{Bu}_3\text{P} & \quad \text{I} \\
\text{H-C≡C-Pt-C≡C-H} & \quad \text{II}
\end{align*}
\]

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Fig. 1. Two-dimensional $^{13}$C/$^1$H heteronuclear shift correlation for $[\textit{trans}-(\text{Bu}_3\text{P})_2\text{Pt}(C\equiv\equiv C\equiv \text{H})]$ (1), showing the $^{13}$C resonance signal (the asterisk marks the position of the $^{13}$C resonance signal which is not completely suppressed) and the ethyne-proton part of the normal $^1$H NMR spectrum. The recycle delay was set to 6 s and the fixed delays in the pulse sequence correspond to $^2J(=^1\text{C}-\text{H}) = 40$ Hz; a digital resolution of $\leq 2$ Hz/pt in the $F_2$ dimension proved sufficient [spectrometer time (Bruker AC 200): 45 min]. The tilt of the cross peaks for the $^{195}$Pt satellites shows that $^1J(^{195}\text{Pt}^{13}\text{C} =)^{/}/^2J(^{195}\text{Pt}^{13}\text{C} =)^{/} > 0$. Similarly, the tilt in the triplet splitting proves that $^3J(^{13}\text{P}^{13}\text{C} =)^{/}/^6J(^{13}\text{P}^{13}\text{C} =)^{/} > 0$. Since $^6J(^{13}\text{P}^{13}\text{C} =)^{/} < 0$ (see Fig. 2) it follows that the sign of $^3J(^{13}\text{P}^{13}\text{C} =)^{/}$ is negative.

Fig. 2. Two-dimensional $^{195}$Pt/$^1$H heteronuclear shift correlation for $[\textit{trans}-(\text{Bu}_3\text{P})_2\text{Pt}(C\equiv\equiv C\equiv \text{H})]$ (1), showing the entire range of the $^{195}$Pt NMR spectrum and the ethyne-proton part of the normal $^1$H NMR spectrum. The recycle delay was set to 6 s and the fixed delays in the pulse sequence correspond to $^2J(^{195}\text{Pt}^{13}\text{C} =)^{/}/^6J(^{195}\text{Pt}^{13}\text{C} =)^{/} = 45$ Hz and coupling to two equivalent protons. A digital resolution of $\leq 1.5$ Hz/pt in the $F_2$ dimension proved sufficient [spectrometer time (Bruker AC 200): 30 min]. The low frequency and the high frequency cross peaks of the triplets in the $^1$H and $^{195}$Pt NMR spectra are related (tilt is shown by the dashed line), proving that $^1J(^{195}\text{Pt}^{13}\text{P})/^4J(^{13}\text{P}^{13}\text{C} =)^{/} < 0$. Since $^4J(^{13}\text{P}^{13}\text{P}) > 0$ [11] it follows that the sign of $^4J(^{13}\text{P}^{13}\text{C} =)^{/}$ is negative.

Table I. $^1$H, $^{13}$C, $^{31}$P, $^{195}$Pt NMR data$^{a,b}$ of the alkynylplatinum(II) phosphine complexes 1 and 2.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>1</th>
<th>2</th>
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<tbody>
<tr>
<td>$\delta^{13}$C (Pt-$^\equiv\equiv C-\text{H}$)</td>
<td>100.0 (a), 93.9 (b)</td>
<td>101.0 (a), 95.2 (b)</td>
</tr>
<tr>
<td>$^1J(^{195}$Pt$^{13}$C)</td>
<td>$+951.0, +268$</td>
<td>$+1062.0, +300.8$</td>
</tr>
<tr>
<td>$^1J(^{31}$P$^{13}$C)</td>
<td>$-14.5, +1.8$</td>
<td>$+137.3 (\text{trans}), +33.8 (\text{trans})$</td>
</tr>
<tr>
<td>$^1J(^{13}$C$^\equiv\equiv C-\text{H}$)</td>
<td>$+39.6, +225.0$</td>
<td>$-15.3 (\text{cis}), +1.2 (\text{cis})$</td>
</tr>
<tr>
<td>$^2$H ($^\equiv\equiv C-\text{H}$)</td>
<td>2.32</td>
<td>42.0, 229.0</td>
</tr>
<tr>
<td>$^1J(^{31}$P$^{13}$P)</td>
<td>$+44.1$</td>
<td>2.30</td>
</tr>
<tr>
<td>$^1J(^{31}$P$^{13}$C$^\equiv\equiv C-\text{H}$)</td>
<td>$-2.0$</td>
<td>$+5.7 (\text{trans}), -2.0 (\text{cis})$</td>
</tr>
<tr>
<td>$^3$P</td>
<td>$+3.5$</td>
<td>$+51.4$</td>
</tr>
<tr>
<td>$^3J(^{195}$Pt$^{31}$P)</td>
<td>$+2394.0$</td>
<td>$+2224.0$</td>
</tr>
<tr>
<td>$^3J(^{195}$Pt$^{13}$P)</td>
<td>$-273.1$</td>
<td>$-412.1$</td>
</tr>
<tr>
<td>$^1J(^{13}$C$^\equiv\equiv C$)</td>
<td>24.3, 26.7, 24.6, 14.0</td>
<td>23.9, 18.2, 8.5 (PET)</td>
</tr>
<tr>
<td>$^1J(^{195}$Pt$^{13}$C)</td>
<td>$+34.0, +22.7, &lt;2.0, &lt;2.0$</td>
<td>$+56.4, +32.0, +25.0$</td>
</tr>
<tr>
<td>$^1J(^{31}$P$^{13}$C)</td>
<td>$+35.4, +1.0, +12.8, &lt;1.0$</td>
<td>$+43.8, +35.2, &lt;1.0$</td>
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<tr>
<td>$^2$H (PR)</td>
<td>2.10, 1.62, 1.40, 0.92</td>
<td>1.75, 2.05, 1.97, 1.15</td>
</tr>
<tr>
<td>$^1J(^{195}$Pt$^{13}$H)</td>
<td>$+16.8, -1.5, &lt;1.5, &lt;1.5$</td>
<td>$+4.0, +17.0, +17.0, &lt;1.0$</td>
</tr>
<tr>
<td>$^1J(^{31}$P$^{13}$H)</td>
<td>$-7.2, +9.3, +1.5, &lt;1.5$</td>
<td>$+13.7, -10.4, -10.4, +17.5$</td>
</tr>
</tbody>
</table>

$^a$ Chemical shifts $\delta$ relative to internal Me$_4$Si ($^1$H, $^{13}$C), external 85% H$_3$PO$_4$ ($^{31}$P) and $\Xi_{195}$ = 21.4 MHz; $^b$ recorded from a solution of 1 in C$_6$D$_6$ (ca. 10%, 10 mm o.d. tube) and of 2 in CD$_2$Cl$_2$ (ca. 5%, 5 mm o.d. tube) at 25 °C; $^c$ the sign follows from the simulation of the spectra together with the results of the 2D NMR spectra; $^d$ $^3J(^{195}$Pt$^{31}$P) = $\leq 5.0 \pm 0.5$ Hz, according to the simulation of $^1$H and $^{13}$C NMR spectra; $^e$ $\Sigma [^1J(^{13}$P$^{13}$C) + $^1J(^{13}$P$^{13}$PC$^\equiv\equiv C$)] + $\Sigma [^1J(^{31}$P$^{13}$C) + $^1J(^{31}$PP$^{13}$P$^\equiv\equiv C$)]; $^f$ $\Sigma [^1J(^{31}$P$^\equiv\equiv C$) + $^1J(^{13}$P$^{13}$PC$^\equiv\equiv C$)]; $^g$ $\Sigma [^1J(^{13}$P$^\equiv\equiv C$) + $^1J(^{13}$P$^{13}$PC$^\equiv\equiv C$)]; $^h$ $\Sigma [^1J(^{31}$P$^\equiv\equiv C$) + $^1J(^{31}$PP$^{13}$P$^\equiv\equiv C$)]; $^i$ $\Sigma [^1J(^{31}$P$^{13}$C$^\equiv\equiv C$) + $^1J(^{13}$P$^{13}$PC$^\equiv\equiv C$)].
coupling constants, have been carried out for \( X = ^{13}\text{C} \) and were based on \( J(^{13}\text{C},^{1}\text{H}) \)[12, 13]. However, there is a wide selection of \( X \) nuclei, and the heteronuclear shift correlations can be based on very small coupling constants \( |\Delta J(X',H)| \), down to \( \approx 1 \) Hz, as we have shown recently [14].

The \(^1\text{H}\) NMR spectra of 1 and 2 are fairly complex except for the region of the ethyne-protons. Homonuclear \(^1\text{H}\)-decoupling by inserting a BIRD pulse [15] in the sequence for hetero- and homonuclear shift correlations simplifies the \(^1\text{H}\) NMR spectra in the \( F_1 \) dimension and makes a more straightforward comparison of the signs of coupling constants possible. Thus the \(^{195}\text{Pt}/^{1}\text{H}\) shift correlations obtained in this way show that \( J(^{195}\text{Pt},^{31}\text{P})/\Delta J(3^{1}\text{P},^{1}\text{H}) < 0 \) [1, 2 (\( \text{PET}_3 \)) and \( J(^{195}\text{Pt},^{31}\text{P})/\Sigma J(3^{1}\text{P},^{1}\text{H}) > 0 \) (2)]. Similarly, the tilt of the respective cross peaks in the \(^1\text{H}/^{1}\text{H}\) COSY spectra of 1 and 2 show that \( J(3^{1}\text{P},^{1}\text{H})/J(3^{1}\text{PC},^{1}\text{H}) < 0 \). Since the \(^{195}\text{Pt}/^{1}\text{H}\) shift correlation yields \( J(3^{1}\text{P},^{1}\text{H}) < 0 \), \( J(3^{1}\text{PC},^{1}\text{H}) \) for \( X = 2 \) (\( \text{PET}_3 \)) must be positive.

Many of the results described here can also be achieved by "inverse" 2D \(^1\text{H}(X) \) [16, 17] or \(^{31}\text{P}(X)\) experiments [17, 18], using equipment which has been implemented in the most recent generation of PFT-NMR spectrometers.

**Experimental**

The compounds 1 [8, 19] and 2 [20] were prepared following literature procedures. The NMR spectra (see also Fig. 1, 2 and Table I) were recorded using Bruker AC 200, AC 300 (\(^1\text{H},^{13}\text{C},^{31}\text{P},^{195}\text{Pt}\)) and AM 500 (\(^1\text{H},^{13}\text{C}\)) instruments at 25 ± 1 °C in 10 mm o.d. tubes (1, –10% in \( \text{C}_6\text{D}_6 \)) or 5 mm o.d. tubes (2, saturated, –5% in \( \text{CD}_3\text{Cl}_2 \)).

The 2D \(^1\text{H}/^{1}\text{H}\) heteronuclear shift correlations were based on the pulse sequence [6c] \( [\pi/2(^1\text{H})-t_1-2\pi(\text{X})-t_1/2,\pi_1/2(^1\text{H}),\pi/2(\text{X})-\pi_2,\text{FID}(\text{X})] \), with \( \pi_1 = \Delta_2 = \{2J(\text{X},^{1}\text{H})\}^{-1} \) for \( X = ^{13}\text{C} (= \text{C}) \) and \( \Delta_2 \) optimized for coupling between \( X \) and two or more protons if \( X = ^{13}\text{C} \) (other than ethynyl carbons), \(^{31}\text{P},^{195}\text{Pt}\). Owing to the significant contribution from the chemical-shift-anisotropy (CSA) mechanism (\( B_0 \) dependence!) to \(^{195}\text{Pt}\) nuclear spin relaxation [21], best results for the 2D \(^{195}\text{Pt}/^{1}\text{H}\) shift correlations were obtained at lower field strength \( B_0 \). For the same reason, the intensity of \(^{195}\text{Pt}\) satellites in all 2D spectra are much reduced with respect to 1D spectra.

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