# 210. A <sup>13</sup>C-NMR. Study of Some Arsenic Complexes of Platinum(II) and Palladium(II)

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Summary. The <sup>13</sup>C-NMR. spectra of a series of tri-n-alkyl arsenic complexes of platinum and palladium have been measured. In these complexes it is suggested that the carbon chemical shift of the atom bound directly to the arsenic is a useful structural probe. The chemical shift of the second carbon atom in the chain is interpreted in terms of interactions within the chains of any-one ligand. The values  ${}^{2}J(Pt, C)$  and  ${}^{3}J(Pt, C)$  are presented.

Introduction. – The increasing interest in the chemistry of platinum metal complexes of phosphorus and arsenic has promoted a number of <sup>13</sup>C-NMR. studies in this area [1]. These studies have, however, been concerned primarily with olefin and alkyl complexes containing these ligands. Recently [2] we have reported the <sup>13</sup>C-NMR. characteristics of a series of platinum complexes of tertiary phosphines of the type [PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] and have demonstrated that a correlation exists between the values <sup>1</sup>J(Pt,P) and <sup>2</sup>J(Pt,C). Additionally, we have shown that the carbon chemical shifts of the carbon atoms immediately adjacent to the phosphorus in the *cis*-isomers, [PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] are at consistently lower field than those for the corresponding *trans*isomers. If found to be a general characteristic this chemical shift dependence should be a useful diagnostic probe in cases where other physical techniques may not be readily brought to bear. We present here the results of <sup>13</sup>C-NMR. studies for an analogous series of arsenic complexes.

**Experimental.**-<sup>13</sup>C-NMR. spectra were measured as deuteriochloroform solutions in spinning 10 mm tubes using a *Bruker* HX-90 spectrometer operating at 22.63 MHz in *Fourier*-transform mode. Chemical shifts were measured relative to the resonance of the solvent and then corrected to TMS. The measurements were routinely performed under conditions of complete proton noise decoupling. Chemical shift assignments were made using alignatic substituent effects and proton 'off-resonance' decoupling techniques.

The complexes were all synthesized using literature methods [3] with separate preparations for each isomer.

Complexes for which we were unable to locate previous preparations were assigned structure based on their color, (the *cis*-isomers of such Pt(II) complexes of trialkyl arsenic are colorless whereas the *trans*-isomers are pale- to deep-ycllow. The analogous dimers are orange or red), nuclear magnetic resonance characteristics (the <sup>13</sup>C-spectrum of [AsPrisPr<sup>n</sup>]Br clearly shows the presence of the two different types of propyl groups in the correct proportion) and microanalytical data (see Table 1).

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Compound	Colour	m.p. <sup>a)</sup> °C	Recrystallized from		Analysis		
					c	н	Cl
[AsPr <sup>i</sup> 3Pr <sup>a</sup> ]Br <sup>b</sup> )	white	165°	ethanol/ether	Found Calc.	43.59 44.05	8.48 8.63	
t-[PdCl <sub>2</sub> (AsPr <sup>i</sup> <sub>2</sub> ) <sub>2</sub> ]	orange	203° dec.	chloroform/cther	Found Calc.	36.74 36.91	7.29 7.23	12.29 12.11
$t-[PtCl_2(AsPr_3^i)_2]$	yellow	223°	chloroform/2-propanol	Found Calc.	<b>31.8</b> 1 32.06	6.21 6.28	10.56 10.51
s-t-[Pd2Cl4(AsPr <sup>i</sup> 3)2]	red	180° dec.	dichloromethanc/ethano	l Found Calc.	28.47 28.34	5.55 5.55	18.77 18.59
<i>s-t</i> -[Pt <sub>2</sub> Cl4(AsPr <sup>i</sup> 3)2]	orange	225° dec.	chloroform/ethanol	Found Calc.	23.06 22.99	4.46 4.50	15.24 15.08
<ul> <li><sup>a</sup>) Uncorrected.</li> <li><sup>b</sup>) Hygroscopic.</li> </ul>							

### Table 1. Analytical Data for the New Compounds

With the exception of *trans*-[PtCl<sub>2</sub>(AsMc<sub>3</sub>)<sub>2</sub>], which in CDCl<sub>3</sub> solution was a mixture of *cis*and *trans*-isomers, the measurements were made on solutions containing the 'pure' isomer (The presence of small quantities (less than 5%) of the other isomer or free ligand cannot be excluded as this would have gone unnoticed). The <sup>13</sup>C-parameters of the *cis*-bis(trimethyl-arsine) derivative were, within the experimental error, unchanged in the presence of the *trans*-isomer.

These observations suggest that, under the conditions of our measurements the equilibrium cis  $\Rightarrow$  trans is not established and/or that the rate of isomerization is relatively slow (the measurement times were generally of the order 1-10 h). A solution of trans-[PtCl<sub>2</sub>(AsBu<sup>\*</sup><sub>g</sub>)<sub>2</sub>] in propanol, containing catalytical quantities of the free arsine, precipitates a colorless solid at dry-ice acetone temperature. Slow warming produces solution of the solid. Isolation and subsequent measurement shows only the trans-isomer. In some cases the relative ease of isomerism of such platinum complexes (at least in the presence of a catalyst) has been used to synthetic advantage (see Chatt & Wilkins [3]).

**Results and Discussion.** – The <sup>13</sup>C chemical shifts for the ligands and complexes are shown in Tables 2 and 3. Typical spectra are shown in the Figure. For the remainder of this presentation the nomenclature for the various carbon atoms will be consistent with *Scheme 1*. The spectra of the platinum complexes were accompanied by <sup>195</sup>Pt (I = 1/2, natural abundance = 33.7%) satellites whose separation represent the values n J(Pt,C).

Scheme 1  

$$-M - As - C_{\alpha} - C_{\beta} - C_{\gamma} - C_{\delta}$$

Tables 2 and 3 reveal that the chemically significant differences in the <sup>18</sup>C-chemical shifts occur at the  $\alpha$ - and  $\beta$ -carbons. We note the following points of interest:

1) For the complexes  $[PtCl_2(AsR_3)_2]$ , R = n-alkyl groups, the resonance positions of  $C_{\alpha}$  appear at consistently lower field for the *cis*- than for the *trans*-isomer by more than 3.4 ppm;

R	AsR <sub>3</sub>	[AsR4]+X~b)	trans[PdCl2(AsR3)2]	sym-trans[Pd2Cl4(AsR3)3]
Ме				
Cα	11.4		9.2	11.8
Et				
C <sub>a</sub>	16.5	14.7	13.6	16.6
C <sub>f</sub>	10.8	7.8	9.7	9.5
<i>n</i> -Pr				
C <sub>a</sub>	28.1	23.4	23.4	26.1
C <sub>ø</sub>	20.6	17.2	19.0	19.0
C <sub>y</sub>	16.7	15.6	16.4	16.0
<i>n</i> –Bu				
C <sub>a</sub>	25.1	21.8	20.8	23.7
С <sub>в</sub>	29.4	25.4	27.5	27.3
Cy	25.1	24.1	24.8	24.4
Cø	13.9	13.4	13.9	13.7
í-Pr				
C <sub>a</sub>	22.6	26.50)	25.6	28.6
C <sub>ø</sub>	21.5	18.7°)	20.7	20.4

Table 2.13C Chemical Shifts<sup>a</sup>) in Trialkylarsines, Tetraalkylarsonium Salts and Palladium Complexes

<sup>a</sup>) Chemical shifts are relative to TMS and arc estimated to be correct to  $\pm$  0.1 ppm.

b) Unless otherwise specified these are Br<sup>-</sup> salts.

c) Data for [AsPra Pra]+.

R	[PtCl <sub>p</sub> (As	5R <sub>3</sub> )2]	sym-trans[PtgCl4(AsR3)2]				
	n = 2		n == 4				
	cis	trans	cis	irans			
Ме							
C <sub>a</sub>	12.7	7.7 <sup>b</sup> )		6.6	9.2		
Et							
Ca	15.9	12.1	18.1	12.4	14.0		
C <sub>B</sub>	9.7	9.3	9.9	9.2	9.0		
n-Pr							
Ca	25.6	21.9	25.0	21.6	23.1		
C <sub>ø</sub>	19.1	18.7	18.1	18.3	18.5		
Cγ	16.1	16.3	16.2	16.1	15.8		
<i>n-</i> Bu							
C <sub>a</sub>		19.3		19.2	20.9		
C <sub>p</sub>		27.0		26.4	26.8		
C,		24.6		24.6	24.3		
C <b>o</b>		13.8		13.7	13.7		
<i>i</i> ₋₽r							
C <sub>a</sub>		24.1					
C <sub>¢</sub>		20.2					

Table 3. 13C Chemical Shifts<sup>a</sup>) in Platinum Complexes of Trialkyl Arsines

\*) Chemical shifts are relative to TMS and are estimated to be correct to  $\pm$  0.1 ppm.

b) Measured as a mixture of cis- and trans-isomers.



Fig. The 13C-NMR. spectra of a) trans-[PdCl<sub>2</sub>(AsBu<sub>3</sub><sup>n</sup>)<sub>2</sub>] and b) trans-[PtCl<sub>2</sub>(AsBu<sub>3</sub><sup>n</sup>)<sub>2</sub>]

2) When compared with the phosphine analogs [2], the arsenic complexes have  $C_{\alpha}$  at consistently higher field while  $C_{\beta}$  appears at consistently lower field;

3) Quaternization of the free ligand  $(AsR_3 \rightarrow AsR_4^+X^-)$  is accompanied by an upfield shift in the position of  $C_a^{(2)}$ ;

4) In analogous situations the complexes of palladium(II) appear at lower field than those for platinum(II);

5) The <sup>13</sup>C-positions of the  $\alpha$ -carbons in the dimers, sym-trans-[Pt<sub>2</sub>Cl<sub>4</sub>(AsR<sub>3</sub>)<sub>2</sub>] are to low field of the trans Pt(II) complexes (1-2 ppm) but to high field of the cis isomers.

The observation of a geometric dependence of the resonance position of  $C_{\alpha}$  in arsine as well as in phosphine complexes of platinum suggests that this phenomenon may have some generality. Recently a similar dependence was observed for *cis* and

<sup>&</sup>lt;sup>2</sup>) The reversal observed in the isopropyl derivative is consistent with the explanation offered by *Morishima et al* [4].

trans complexes of the type  $[PdCl_2(PR_2Ph)_2]$ ; R = n-alkyl [5]. A consideration of some platinum chemistry involving SbBu<sub>3</sub><sup>n</sup> affords an example of the utility of this chemical shift dependence. In Table 4 are shown the <sup>13</sup>C chemical shifts for a benzene solution containing *cis*- and *trans*- $[PtCl_2(SbBu_3^n)_2]$ . No <sup>195</sup>Pt satellites were observed<sup>3</sup>). The chemical shift assignments for the  $\alpha, \beta$  and  $\gamma$  carbon atoms were made by analogy. The expectation that the *cis* isomer will have a <sup>13</sup>C absorption for  $C_{\alpha}$  at lower field than will the *trans*-isomer suggests the assignment of the spectrum and an estimation of the population of each isomer (*cis/trans*  $\approx 0.8^4$ )).

While we are not capable of stating, with any certainty, the source of this geometric dependence, it seems likely that some part of it may be related to the differences in metal arsenic bonding which exist between *cis*- and *trans*-isomers. These differences have been observed using both <sup>1</sup>H [7] and <sup>195</sup>Pt [8] NMR. spectroscopy. In support of this suggestion we note that in the compounds  $[Pt(NO_2)_2(AsEt_3)_2]$  (see Table 4) where

	[PtCl <sub>2</sub> (Sb-Bu <sub>3</sub> ) <sub>2</sub> ]		[Pt(NO <sub>2</sub> ) <sub>2</sub> (AsEt <sub>3</sub> ) <sub>2</sub> ]		
	cisb)	trans <sup>b)</sup>	cis	trans	
С <u>"</u>	15.1	12.5	15.4	14.7	
C,	29.9	29.5	9.4	9.2	
с",	27.0	27.1	~	-	
Co	14.7	14.7	~		

Table 4. 13C Chemical Shifts®) in the Antimony and Nitrito-Complexes

<sup>a</sup>) Chemical shifts are relative to TMS and are estimated to be correct to 0.1 ppm.

b) Measured in  $C_6D_6$ .

the trans influences (defined [9] as the extent to which a ligand weakens the bond trans to itself in the equilibrium state) of the ligands are similar [10], the chemical shift difference  $\Delta\delta C_{\alpha}$  (=  $\delta^{cts} - \delta^{trans}$ ) decreases. Additional contributions could come from electric field effects, metal-ligand atom and/or metal-halogen anisotropic effects as well as the effects of having a formal positive charge on the arsenic. We doubt that the effects due to the anisotropy of the metal-halogen bond are dominant. Such effects are thought to be proportional to the inverse cube of the distance from the assumed point dipole to the atom in question [11]. We expect that the distance from the carbon to the center of the metal-chlorine bond should increase with both increasing carbon-ligand bond length<sup>5</sup>) and change in metal oxidation state from Pt(II) to Pt(IV)<sup>5</sup>). Since we observe little or no dependence of  $\Delta\delta C_{\alpha}$  on either substitution of arsenic for phosphorus or metal oxidation state we cannot feel that this effect is a major one.

The changes in  $\delta C_{\alpha}$  and  $\delta C_{\beta}$  resulting from substitution of arsenic for phosphorus are small in magnitude ( $\approx 1$  ppm). For  $C_{\alpha}$  the interpretation of this difference is

<sup>&</sup>lt;sup>3</sup>) This may result from metal-ligand exchange. Alternately the values  ${}^{2}J(Pt, C)$  in these compounds may be small and/or  $T_{1}$  (195 Pt) short.

<sup>4)</sup> Chatt & Wilkins [6] have reported this ratio ~ 0.25. This discrepancy could result from differences in <sup>13</sup>C-T<sub>1</sub>-values between cis- and trans-isomers.

<sup>&</sup>lt;sup>5</sup>) The mctal-ligand bond lengths in the complexes [Pt<sub>2</sub>Cl<sub>4</sub>(PPr<sup>\*</sup><sub>3</sub>)<sub>2</sub>] and [Pt<sub>2</sub>Cl<sub>4</sub>(AsMc<sub>3</sub>)<sub>2</sub>] are 2.230 and 2.308 Å respectively. These results and general data supporting an increase in the metal ligand bond length on oxidation to Pt(IV) are available from [12].

complicated by the potential for changes in several of the terms in  $\sigma_P$ , the paramagnetic screening term. The observed low field position of  $C_{\beta}$  in the arsine complexes could result from a difference in the ligand atom-carbon bond anisotropy. A second possibility involves interchain steric interactions. At this point it is useful to review, briefly, the question of aliphatic substituent effects. It is well recognized [13] from earlier studies involving a variety of organic compounds that substitution of methyl for hydrogen in a straight chain hydrocarbon skeleton, such as a in Scheme 2, affects a deshielding of  $C_{\beta}$  by greater than 9 ppm, while simultancously shielding  $C_{\gamma}$  by 2-3 ppm. These effects are commonly referred to as the  $\beta$ - and  $\gamma$ -substituent effects, respectively. That these basic effects are operating in our systems may be judged from the tables (e.g.  $C_{\alpha}$  for trans-[PdCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] = 13.6 ppm, for trans-[PdCl<sub>2</sub>(AsPr<sub>3</sub><sup>\*</sup>)<sub>2</sub>] = 23.4 ppm, the  $\beta$ -effect; for trans-[PdCl<sub>2</sub>(AsBu<sub>3</sub><sup>\*</sup>)<sub>2</sub>] = 20.8 ppm, the  $\gamma$ -effect). Perhaps somewhat less obvious is the position of C\* in **b** (Scheme 2) relative to the carbon atoms within



the same ligand but on a different chain. From this point of view it is obvious that C\* exercises a  $\beta$ -effect on the carbon atoms bound directly to arsenic and a  $\gamma$ -effect on the immediately adjacent ( $C_{n}$  in **b**, Scheme 2) carbon atoms of a neighboring chain. The presence of an interchain  $\gamma$ -effect is clearly illustrated by a comparison of the  $C_{\alpha}$ chemical shifts in cis-[PtCl<sub>2</sub>(AsMe<sub>3</sub>)<sub>2</sub>], 12.7 ppm and cis-[PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>], 15.9 ppm. Direct substitution of a methyl group in straight chains, denoted as the  $\alpha$ -effect, normally induces a low field shift of approximately 9-10 ppm at the substituted carbon atom [13] (approximately the same magnitude as the  $\beta$ -effect); however, we observe only a 3.2 ppm change. The explanation for this is readily forthcoming if we accept the presence of two shielding y-effects whose source are the CH<sub>3</sub> groups on the other chains. Since the  $\gamma$ -effect is known [14] to have its source in steric interactions, it is not too surprising to discover that the arsenic complexes show resonance positions for the second carbon atom in the chain at lower field than do the corresponding phosphorus complexes (e.g.  $C_{\beta}$  for cis-[PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] = 9.7 ppm, for cis-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] = 8.7 ppm). Since the arsenic-carbon bond should be longer than the phosphoruscarbon bond<sup>6</sup>), less steric compression may be experienced by  $C_d$  (source = C\*) within the ligand. This relief of compression, or negative  $\gamma$ -effect, should bring with it a slightly lower field position and this is what is observed. The source of the general  $\beta$ -effect is not well understood, although it has been suggested [17] that molecular strain may be involved. Such an explanation, in combination with an argument similar to that advanced above (negative  $\beta$ -effect with increasing arsenic carbon bond length) could account for the relative high field positions of the  $C_{\alpha}$  carbon atoms in the arsenic complexes if the change in the  $\beta$ -effect was larger than the change in the  $\gamma$ effect. While not mentioned in their report, the <sup>13</sup>C data of Spiesecke & Schneider [18] for the compounds  $(CH_3)_4M$  and  $(CH_3CH_2)_4M$ , (M = C, Si, Sn, Pb) are consistent

<sup>6)</sup> The As—C bond length in sym-irans-[Pt<sub>2</sub>Cl<sub>4</sub>(AsMe<sub>3</sub>)<sub>2</sub>] is ≈ 1.948 Å [15]. The P—C bond length in cis-[PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] is ≈ 1.830 Å [16].

with our formulation of interchain interactions. The differences  $\Delta \delta = [\delta(CH_3CH_2)_4M - \delta(CH_3)_4M]$  have the values -6.5, +2.3, +8.8 and +10.7 for C. Si, Sn and Pb respectively, with a positive sign indicating the  $^{13}CH_2$  of the ethyl group is at lower field. Additionally the  $^{13}CH_3$  group of the ethyl group appears at progressively lower field (4.2, 6.0, 10.8 and 15.7 ppm respectively). While the absolute positions of the CH<sub>3</sub> and CH<sub>2</sub> groups in the Me<sub>4</sub>M and Et<sub>4</sub>M derivatives, respectively, may be caused by anisotropic and both paramagnetic and diamagnetic contributions to the total screening,  $\sigma$ , the change in the relative effects scem to reflect the changes in  $\sigma_P$  in-

duced via the  $\gamma$ -substituent effect?). Thus in the molecules with central atoms higher in the Periodic Table we have the largest  $\gamma$ -effects and thus the smallest differences in  $\Delta \delta$ . (When the  $\gamma$ -effect is large the difference ( $\beta$ -effect- $\gamma$ -effect) is small).

The observation that quaternization at arsenic results in an upfield shift at  $C_{\alpha}$  is consistent with previous reports concerned with ammonium [4] and phosphonium ions [19].

In Table 5 are shown the two and three bond couplings of platinum to carbon. In all cases the values  ${}^{2}J(Pt,C)$  and  ${}^{3}J(Pt,C)$  are larger for the *cis*-isomers than for the

		[sym-irans[Pt2X4(AsR3)2]	$[PtX_n(AsR_3)_2]$			
R X	х		n 2		n = 4	
			cis	trans	cis	trans
			<sup>2</sup> J <sub>E</sub>	't,C		
Me	Cl	55.7	54.2	41.0		19.0
$\mathbf{Et}$	Cl	51.3	49.1	35.1	27.1	17.6
n-Pr	Cl	47.6	44.7	31.5	23.4	16.8
n-Bu	Cl	49.1		32.2		17.6
i-Pr	Cl	45.4		31.5		
Et	NO2		41.0	<del>44</del> .7		
			۶ <b>3</b> - ۲	ኪር		
Et	Cl	17.6	19.8	13.2	8.1	5.1
n-Pr	Cl	18.3	19.6	12.5	7.3	4.4
n-Bu	Cl	16.1		10.8		5.1
i-Pr	Cl	13.9		9.5		
Et	$NO_2$		19.0	16.8		
a) Co	oupling	Constants are estimated to be corre	cted to $\pm 1.0$ H	7		

Table 5. Two Bond and Three Bond Platinum-Carbon Coupling Constants<sup>a</sup>) in the Complexes

trans analogs. Additionally, we note that there seems to be a marked dependence of both the two and three bond couplings on metal oxidation state, with the Pt(II) complexes having larger magnitudes in all cases. These trends in metal-ligand coupling are not novel and have been noted previously in the proton spectra of some platinum complexes of trimethyl arsine [7] as well as in the NMR. spectra of platinum complexes of a variety of ligands [9] [20]. These differences are thought to be related to changes in the s-character of the orbital which is used by the metal to form the platinumligand bond [9]. The magnitudes of the ratios  ${}^{2}J(Pt,C)_{eis}/{}^{2}J(Pt,C)_{trans}$  and  ${}^{3}J(Pt,C)_{-eis}/{}^{3}J(Pt,C)_{trans}$  are of the order of 1.3-1.6 in good agreement with previous studies [2] [9].

<sup>7)</sup> The comparison of the cases  $(CH_3CH_2)_4M+X^-$  and  $(CH_3)_4M+X^-$  (M = N, P, As) is complicated by ion pairing. A similar trend in  $\Delta \delta$  is observed for  $(CH_3CH_2)_3M$  and  $(CH_3)_3M$  (M = N, P, As).

There appears to be a finite effect of the size of the alkyl group in *both cis-* and *trans-*isomers on the values  ${}^{2}J(Pt,C)$ , and to a smaller extent,  ${}^{3}J(Pt,C)$ , with the largest values observed for the smallest group. This suggests as does the chemical shift data discussed earlier, that steric interactions between neighboring chains, while small, are finite, and should be considered in evaluating the chemistry of these molecules.

Interestingly, the ratios  ${}^{n}J(Pt(II),C)/{}^{n}J(Pt(IV),C)$  are of the order 1.8–2.0. This is somewhat larger than that found for these same coupling constants in the analogous phosphine complexes [2].

While the values  ${}^{3}J(\text{Pt,C})$  in the arsenic complexes are generally smaller than those observed for the phosphine analogs (e.g. = 19.8 Hz for cis-[PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] and 27.8 Hz for cis-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]), a reversal is observed for the values  ${}^{2}J(\text{Pt,C})$  (e.g. = 51.3 Hz for cis-[PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>] and 41.0 Hz for cis-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]). The sense of the relative magnitudes of the platinum-proton couplings through three bonds is in agreement with the values  ${}^{3}J(\text{Pt,C})$  [7]. It is difficult to evaluate the significance of this inversion in relative magnitudes in the absence of information concerning their absolute signs. We note that phosphorus is generally accepted to have a stronger 'trans influence' [10] than arsenic and that the platinum-phosphorus bond is shorter than the platinum-arsenic analog<sup>5</sup>). Additionally, in cases where the sign of a one bond interaction involving platinum, is known, a larger NMR. 'trans influence' has usually been associated with an enhanced coupling constant (e.g. both  ${}^{1}J(\text{Pt,H})$  [21] and  ${}^{1}J(\text{Pt,P})$  [22] are positive and larger when the group trans to the coupled ligand has a relatively small 'trans influence' [10]).

In summary we have shown that <sup>13</sup>C-NMR. may be a useful structural tool for bis-arsine complexes of type  $[PtCl_2(AsR_8)_2]$ . In these cases, where the *trans* influence of Cl<sup>-</sup> differs considerably from that for arsenic, there is a marked dependence of both the chemical shift of  $C_{\alpha}$  and its coupling to the metal, upon molecular geometry. There seems to be evidence that the carbon chains within the ligand interact.

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# 211. Horminon, Taxochinon und weitere Royleanone aus 2 abessinischen *Plectranthus*-Spezies (*Labiatae*)

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Horminone, taxoquinone and other royleanones, obtained from two Abyssinian **Plectranthus species** (Labiatae). Summary. From the coloured glands on the leaves of two botanically unclassified **Plectranthus sp.** from Abyssinia, a series of royleanones has been isolated, namely royleanone (1) and 6,7-dehydroroyleanone (2) from one species, and 6,7-dehydroroyleanone, horminone (3), taxoquinone (4),  $6\beta$ ,  $7\alpha$ -dihydroxyroyleanone (5),  $7\alpha$ -acetoxy- $6\beta$ -hydroxyroyleanone (6) and 7-oxoroyleanone (7) respectively, from the other.

Royleanone sind diterpenoide Benzochinone mit Abietanskelett und p-chinoidem C-Ring<sup>2</sup>). Man hat sie aus einer Composite [1], einer Taxodiacee [5] und zahlreichen Labiaten [2] [8] isoliert. Im folgenden wird die Isolierung von Royleanon (1), 6, 7-Dehydroroyleanon (2), Horminon (= 7 $\alpha$ -Hydroxyroyleanon, 3), Taxochinon (= 7 $\beta$ -Hydroxyroyleanon, 4), 6 $\beta$ , 7 $\alpha$ -Dihydroxyroyleanon (5), 7 $\alpha$ -Acetoxy-6 $\beta$ -hydroxyroyleanon (6) und 7-Oxoroyleanon (7) aus Blattdrüsen von zwei bisher nicht identifizierten, bzw. nicht klassifizierten *Plectranthus*-Arten beschrieben. Die Verbindungen 1-4 waren bereits bekannt, 5-7 sind neu.

1. Die erste Art (Bally 8087) stammt aus Abessinien, jedoch sind leider weder Fundstelle noch Sammler bekannt<sup>3</sup>). Für die vorliegende Untersuchung dienten getrocknete Blätter und Zweige<sup>4</sup>).

Plectranthus B. 8087 ist eine robuste, aufrechte, ca. 1,2 m hohe Staude mit fascriger Wurzel, vielstämmig, Stengel etwa fingerdick, sukkulent, auch im Alter nur schwach verholzt. Die Blätter sind schwach fleischig, 10-12 cm lang, 6-7 cm breit,

<sup>1)</sup> Aus der geplanten Dissertation von M. Hensch.

<sup>&</sup>lt;sup>2)</sup> Benannt nach Royleanon (1), dem ersten Vertreter dieser Stoffgruppe [1]; Tanshinone sind o- oder p-Naphthochinone mit nor- oder bisnor-Abietanskelett [2]; Coleone sind meist Drüsenfarbstoffe und strukturell Hydrochinone, Cyclohexendione oder Methylenchinone der Abietanreihe [3]; zu dieser Gruppe sind auch das Naphthochinon Coleon A [4], die Methylenchinone Taxodion und Taxodon [5], Fuerstion [6] und Maytenochinon [7] zu zählen.

<sup>3)</sup> Dr. h.c. P. R. O. Bally schrieb uns am 12, 2, 1972: \*Die Pflanze wurde mir vor einer Reihe von Jahren von Lady Muriel Jez-Blake gegeben, die sie in ihrem Garten hatte und von einem Bekannten aus Abessinien bekam, ohne aber den Standort in Erfahrung zu bringen.»

<sup>4)</sup> Von P. R. O. Bally in scinem Garten in Nairobi, Kenya, aufgezogen.