[16] *W. E. Morf & W. Simon*, Helv. *54*, 794 (1971).
[17] *W. E. Morf*, unpublished results.
[18] *E. M. Arnett* in Progress in Physical Organic Chemistry, Vol. 1, S. G. Cohen, A. Streitwieser, jr., & R. W. Taft (eds.), Interscience, New York 1963, p. 223.
[19] *D. Ammann, E. Pretsch & W. Simon*, Analyt. Letters *7*, 23 (1974).
[20] *A. Craggs, G. J. Moody & J. D. R. Thomas*, J. chem. Educ. *51*, 541 (1974).
[21] *J. Pick, K. Tóth, E. Pungor, M. Vašák & W. Simon*, Analyt. chim. Acta *64*, 477 (1973).
[22] *R. G. Bates & M. Alfenaar* in R. A. Durst (Ed.), Ion-Selective Electrodes, National Bureau of Standards, Spec. Publ. 314, Washington 1969.
[23] For related reactions of (a) diazoacetic ester with alcohols, SO_2 or (b) diazoketones with alcohols, see: (a) *G. Hesse & S. Majmudar*, Chem. Ber. *73*, 1129 (1960); (b) *M. S. Newman & P. F. Beal*, III, J. Amer. chem. Soc. *72*, 5161 (1950).
[24] *A. W. Archer & P. A. Claret*, J. chem. Soc. (C) *1970*, 1296.
[25] *B. Dietrich, J. M. Lehn, J. P. Sauvage & J. Blanzat*, Tetrahedron *29*, 1629 (1973).
[26] *S. A. Morell & A. H. Auernheimer*, J. Amer. chem. Soc. *66*, 792 (1944); *H. J. Lucas & H. K. Garner*, J. Amer. chem. Soc. *70*, 990 (1948).
[27] *L. M. Jackman & S. Sternhell*, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd Edition, Pergamon Press, Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris, Braunschweig 1969, p. 239.
[28] *J. D. Roberts, F. J. Weigert, J. I. Kroschwitz & H. J. Reich*, J. Amer. chem. Soc. *92*, 1338 (1970).
[29] *J. T. Clerc, E. Pretsch & S. Sternhell*, ^{13}C-Kernresonanzspektroskopie, Akademische Verlagsgesellschaft, Frankfurt a.M. 1973, p. 88.
[30] *C. Moureu*, Ann. Chim. phys. *18*, 76 (1899).
[31] *C. A. Bischoff & E. Evohlich*, Chem. Ber. *40*, 2799 (1907).

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170. Comments on the Interpretation of NMR. Parameters in Some Platinum-Olefin Complexes

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(12. VI. 75)

Summary. ^{13}C- and ^{195}Pt-NMR. parameters for the complexes *trans*-[$PtCl_2(C_5H_{10}N)(CH_3CH{=}CHCH_3)$] are presented. It is suggested that conclusions, concerning metal olefin bond strengths, drawn from NMR. studies of nuclei not directly involved in the bonding can be misleading.

Although the *Chatt-Dewar* model explaining the nature of olefin bonding in square planar complexes of Pt(II) is widely accepted [1], the more subtle aspects of this type of bond are still the subject of numerous investigations mainly by NMR. spectroscopy [2]. Although this theory predicts an energy minimum when the plane of the olefin π-system is perpendicular to the plane defined by the metal and the remaining ligand atoms, X-ray studies have shown that distortions from perpendicularity may exist [3] and attempts have been made to correlate such distortions to changes in NMR. parameters [2]. For Pt(II) complexes of the type [$PtCl_2X(RCH{=}CH_2)$], X = Cl [2a], pyridine-N-oxide [2b], pyridine [2c] it is known that the values ^2J(Pt, H) may vary in magnitude by 15–25 Hz [2]. The factors inducing these differences are not completely understood although explanations stemming from structural distortions and/or differing metal-carbon bond strengths for the CH and CH_2 have been offerred [2].

We report here the results primarily from ^{13}C- and ^{195}Pt-NMR. studies on the complexes *trans*-[$PtCl_2(C_5H_{10}N)$(*cis*-2-butene)] and *trans*-[$PtCl_2(C_5H_{10}N)$(*trans*-2-butene)] which demonstrate that when considering the relative strength of an olefin-platinum bond it is more informative to study the centers actually involved in the bonding (Pt and C_{olefin}) rather than other atoms further removed from the coordination site.

In the Table are shown the ^{13}C- and ^{195}Pt-NMR. parameters for the complexes investigated. Both the C- and Pt-spectra were obtained by direct observation using a *Bruker* HX-90 spectrometer operating in *Fourier* transform mode at 22.63 and 19.34 MHz respectively. The neutral complexes were measured as deuteriochloroform solutions whereas the anionic complexes were measured in D_2O solutions.

The values for ^1J(Pt, C) fall within the range of such values reported in the literature [4]. These constants are generally smaller when the olefin is situated *trans* to a ligand with a relatively strong '*trans* influence' [5]. This is in keeping with the trends observed in other platinum-ligand coupling constants (*e.g.* ^1J(Pt, P) [5] and ^1J(Pt, N) [6]). The use of the subscripts 'c' and 't' refers to complexes containing the *cis* and *trans*-2-butenes respectively.

It may be seen that the ^{13}C chemical shifts, $\delta(^{13}CH_c)$ and $\delta(^{13}CH_t)$ for entries **1** and **2**, as well as for **3** and **4**, are similar. Additionally, ^1J(Pt, C_c) is only slightly different from ^1J(Pt, C_t). The ^{195}Pt chemical shifts for **1** and **2** are almost identical (the width at half height of these lines is greater than the difference $\Delta\delta$). In view of the recognized sensitivity of this parameter to changes in bonding [7] or medium effects [8], we conclude from these and the carbon parameters that, at least in the cases of non-strained olefin pairs, the nature of the coordinate bond is not significantly affected by olefin geometry.

The values $\delta(^{13}CH_3)$ and ^2J(Pt, C) for **1** and **2** differ significantly, as do the values ^2J(Pt, H) (66 Hz $\pm$ 1 and 60 Hz $\pm$ 1 for **1** and **2** respectively). Thus, judged solely from the two bond couplings and the position of the CH_3 carbon resonances, there would appear to be a significant difference between these complexes.

The apparent 'discrepancies' in these data are readily understood if one accepts that the basic difference in these olefins, (one example of which is given by the differences in $\delta(^{13}CH_3) = 11.2$ and 16.7 for *cis* and *trans* olefins respectively [9]) is carried over, in some part, to the complexes. Although the coordination chemical shifts, $\Delta\delta$, (= 34.1 ppm and 33.0 ppm for CH_{olefin} and -3.9 ppm and -3.6 ppm for CH_3) in **1** and **2** are similar, the differences present in the olefins are still in the complexes. ($\delta(^{13}CH_3) = 15.1$ ppm, and 20.3 ppm for **1** and **2**). Thus it would seem that, in these complexes, the differences in the ligands are manifesting themselves in variations in the NMR. parameters more remote from the bonding site. It has been suggested that, for the carbon resonances in the olefins themselves, steric factors may be important [9]. Such non-bonded interactions are known [10] to be important in determining the carbon chemical shifts in aliphatic systems. Since complexes such as these are recognized to have carbon atoms which are distorted from sp^2 towards sp^3 hybridization [3] [11] perhaps similar factors are operating here. Whatever the source it would seem that the multinuclear NMR. approach is necessary to avoid reaching conclusions about platinum-olefin bonding from one form of NMR., *e.g.* ^1H, which are rather inconsistent with data from other forms of the technique. This is especially

Table. *NMR. Parameters for Some Platinum-Olefin Complexes*

Compound	$\delta(^{13}C=)$ [a]	$\delta(^{13}CH_3)$ [a]	^1J(Pt, C) [b]	^2J(Pt, C) [b]	$\delta(^{195}Pt)$ [c]	$\Delta\delta$(C=)	$\Delta\delta(CH_3)$
1. *trans*-[$PtCl_2(C_5H_{10}N)$ [d]) (*cis*-2-butene)]	89,6	15.1	142.8	22.0	2943	34.1	– 3.9
2. *trans*-[$PtCl_2(C_5H_{10}N)$ (*trans*-2-butene)]	92.1	20.3	145.9	33.0	2941	33.0	– 3.6
3. K[$PtCl_3$(*cis*-2-butene)]	86.9	15.3	175.2			36.8	
4. K[$PtCl_3$(*trans*-2-butene)]	89.3	19.9	178.2			35.8	
5. *trans*-[$PtCl_2(C_5H_{10}N)$ ($CH_2=CH_2$)]	79.3		153.8			43.1	
6. K[$PtCl_3(CH_2=CH_2)$]	71.1		188.0		2743	51.3	
7. *trans*-[$PtCl_2(C_5H_5NO)$ [d]) ($CH_2=CH_2$)]	63.9		218.0		2853	58.5	
8. *cis*-2-butene [e])	123.7	11.2					
9. *trans*-2-butene [e])	125.1	16.7					
10. $CH_2=CH_2$ [e])	122.4						

[a]) In ppm from TMS. [b]) Measured in Hz. Estimated to be correct to $\pm$ 2. [c]) In ppm from the platinum resonance of Na_2PtCl_6 (aq).
[d]) $C_5H_{10}N$ = piperidine, C_5H_5NO = pyridine-N-oxide. [e]) Data from ref. [9]. Corrected to TMS using $\delta(CS_2) - \delta(TMS) = 192.8$ ppm.

important when the nucleus under consideration is not directly involved in the bonding. In fact a meaningful interpretation of the NMR. data in complexes is not possible unless intra-ligand interactions are also taken into account.

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REFERENCES

[1] *M. J. S. Dewar*, Bull. Soc. chim. France *18*, 79 (1951); *J. Chatt & L. A. Duncanson*, J. chem. Soc. *1953*, 2939.

[2] a) *H. D. Fritz, K. E. Schwartzhans & D. Sellman*, J. organometal. Chemistry *6*, 551 (1966); b) *P. D. Kaplan & M. Orchin*, Inorg. Chemistry *6*, 1096 (1967); c) *R. Lazzaroni & C. A. Veracini*, J. organomet. Chemistry *33*, 131 (1971); d) *D. G. Cooper, R. P. Huges & J. Powell*, J. Amer. chem. Soc. *94*, 9244 (1972); e) *J. Ashley-Smith, I. Douek, B. F. G. Johnson & J. Lewis*, J. chem. Soc. Dalton, *1972*, 1776 and references therein; f) *J. Lewis et al.*, submitted for publication, 1974.

[3] *C. Pedone & E. Benedetti*, J. organometal. Chemistry *29*, 443 (1971); *E. Benedetti, P. Corradini & C. Pedone*, J. organometal. Chemistry *18*, 203 (1969); *J. R. Holder & N. C. Baenziger*, J. Amer. chem. Soc. *77*, 4987 (1955).

[4] *M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers & J. E. H. Ward*, J. Amer. chem. Soc. *97*, 721 (1975); *D. G. Cooper, G. K. Hamer, J. Powell & W. F. Reynolds*, Chem. Commun. *1973*, 449; *M. H. Chisholm, H. C. Clark, L. E. Manzer & J. B. Stothers*, J. Amer. chem. Soc. *94*, 5087 (1972).

[5] *A. Pidcock, R. E. Richards & L. M. Venanzi*, J. chem. Soc., (A) *1966*, 1707.

[6] *P. S. Pregosin, H. Omura & L. M. Venanzi*, J. Amer. chem. Soc. *95*, 2047 (1973).

[7] *A. Pidcock, R. E. Richards & L. M. Venanzi*, J. chem. Soc. (A) *1968*, 1970; *A. v. Zelewsky*, Helv. *51*, 803 (1968); *D. W. W. Anderson, E. A. V. Ebsworth & D. W. H. Rankin*, J. chem. Soc., Dalton *1973*, 2370; *W. McFarlane*, J. chem. Soc., Dalton *1974*, 324.

[8] *P. S. Pregosin*, unpublished results.

[9] *D. E. Dorman, M. Jautelat & J. D. Roberts*, J. org. Chemistry *36*, 2757 (1971).

[10] *D. M. Grant & B. V. Cheney*, J. Amer. chem. Soc. *89*, 5315 (1967); *B. V. Cheney & D. M. Grant*, J. Amer. chem. Soc. *89*, 5319 (1967).

[11] *L. J. Guggenberger & R. Cramer*, J. Amer. chem. Soc. *94*, 3779 (1972).

171. Piperaceae Alkaloids: Part I. Structure of Piperstachine; ^{13}C- and ^{1}H-NMR. Studies[1])

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Dedicated to Prof. *T. R. Govindachari* on the occasion of his 60th Birthday

(22. V. 75)

Summary. From the stem of *Piper trichostachyon C. DC.* a new alkaloid designated piperstachine (VII) has been isolated. Its structure is derived on the basis of spectral data and synthesis of hexahydropiperstachine (X).

[1]) Contribution No 392 from *Ciba-Geigy Research Centre*; ^{13}C-NMR.-Spectroscopy, Part 7. Part 6 see [1].