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# $^{13}$C NMR SPECTRA OF SOME METHYLPLATINUM(IV) COMPLEXES

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## Summary

The $^{13}$C NMR spectra of some methylplatinum(IV) Schiff-base and related complexes have been recorded. The results are interpreted in terms of the differing effects of various donor atoms on a platinum—carbon bond in the *trans* position.

## Introduction

There has been considerable study of the $^1$H NMR spectra of methylplatinum compounds, particularly with a view to examining the effects of various *trans* ligands on $^2J(^{195}\text{Pt}—^1\text{H})$ for the methyl groups [1], but few corresponding $^{13}$C NMR data have been obtained [2, 3], and these almost entirely for platinum(II) complexes. Interpretation of coupling constants with platinum relies on the dominance of the Fermi contact term [4]. Although McConnell's treatment of coupling through more than one bond [5] has been applied fairly successfully to $^2J(\text{M—H})$ in methyl organometallics [6], and used to obtain information on *trans* influences in methylplatinum compounds [1], it is apparent that treatment of $^1J(^{195}\text{Pt}—^{13}\text{C})$ would be simpler and more reliable.

Therefore the $^{13}$C NMR spectra of several methylplatinum(IV) compounds, including some containing Schiff-base ligands, have been measured and are shown in Table 1. Numbering corresponds to structures in Fig. 1. Reduced coupling constants [4] given by $K(\text{Pt—C}) = (4\pi^2/h\gamma_{\text{Pt}}\gamma_{\text{C}})J(\text{Pt—C})$ are also in-

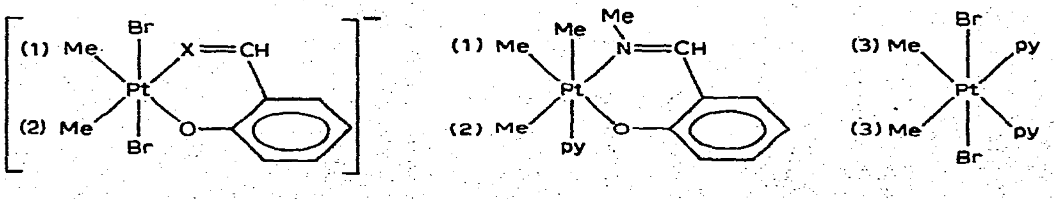

Fig. 1. Structure of methylplatinum(IV) compounds. X = N—R or O.

TABLE 1

$^{13}$C NMR SPECTRA[a]

| Compound[b] | δ values[c] (ppm downfield from TMS) |  |  |  |  |  |  | $^1J(^{195}Pt-^{13}C)$ values (Hz)[e] [$K$(Pt—C) values ($10^{-21}$ NA$^{-2}$·m$^{-3}$)] |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | Me(1) | Me(2) | Me(3) | $Bu_4N^+$ | Pyridine[d] | Salicylaldehyde residue | Others | Me(1) | Me(2) | Me(3) |
| [$Bu_4N$]<br>[$Me_2PtBr_2$(Sal=N—Me)] | −18.0 | −8.9 |  | 57.5, 23.2,<br>18.8, 13.0 |  | 166.1, 161.5, 135.0, 132.7<br>122.9, 121.1, 111.0 | N—Me 47.8 | 559<br>[8.61] | 506<br>[7.79] |  |
| [$Bu_4N$]<br>[$Me_2PtBr_2$(Sal=N—Ph)] | −15.1 | −8.1 |  | 57.9, 23.5<br>19.2, 13.4 |  | 166.7, 162.8, 136.4, 134.0<br>123.6, 121.1, 111.7 | N—Ph 151.5,<br>127.7, 125.1, 123.6 | 559<br>[8.61] | 521<br>[8.02] |  |
| [$Bu_4N$]<br>[$Me_2PtBr_2$Sal] | −16.0 | −14.5 |  | 58.1, 23.4<br>19.1, 13.1 |  | f |  | 559<br>[8.61] | 588<br>[9.06] |  |
| $Me_3$Pt(Sal=N—Me)Py | −14.6 | −4.3 | −10.7 |  | 148.4 (α)<br>137.4 (γ)<br>125.1 (β) | 166.0, 162.8, 135.0,<br>134.0, 123.4, 120.6, 113.2 |  | 756<br>[11.64] | 688<br>[10.60] | 706<br>[10.87] |
| $Me_2PtBr_2Py_2$ |  |  | − 9.7 |  | 151.0 (α)<br>138.1 (γ)<br>125.3 (β) |  |  |  |  | 512<br>[7.88] |

[a] Measured at 22.63 MHz in $CDCl_3$ solutions at a temperature of 300 K, with random noise decoupling of protons. [b] Sal=N—R$^-$ = N—R salicylaldiminato anion; Sal$^-$ = salicylaldehydato anion; Bu = n-butyl. [c] Measured relative to $CDCl_3$ and converted to TMS scale (ref. 7); ±0.1 ppm. [d] ±1.5 Hz. [e] In S.I. units. These values should be multiplied by 10 to give the equivalents in cm$^{-3}$ as generally quoted; $\pm 0.02 \times 10^{-21}$ NA$^{-2}$·m$^{-3}$ [f] As this compound was not obtained pure and displayed decomposition in solution, these peaks are not listed.

TABLE 2

$^1$H NMR SPECTRA$^a$

| Compound | δ values (ppm downfield from internal TMS) | | | $^2J(^{195}Pt—^1H)$ values (Hz) | | |
|---|---|---|---|---|---|---|
| | Me(1) | Me(2) | Me(3) | Me(1) | Me(2) | Me(3) |
| $[Bu_4N]$ $[Me_2PtBr_2(Sal{=}N—Me)]$ | 1.83 | 1.99 | | 73.1 | 67.3 | |
| $[Bu_4N]$ $[Me_2PtBr_2(Sal{=}N—Ph)]$ | 1.27 | 2.02 | | 73.0 | 69.1 | |
| $[Bu_4N]$ $[Me_2PtBr_2Sal]$ | 2.04 | 2.15 | | 74.1 | 78.6 | |
| $Me_3Pt(Sal{=}N—Me)Py^b$ | 0.86 | 0.95 | 0.85 | 71.5 | 65.5 | 71.7 |
| $Me_2PtBr_2Py_2$ | | | 2.06 | | | 70.1 |

$^a$Measured at 100 MHz in $CDCl_3$ solutions at 306 K. $^b$Assignments of Me(1) and Me(3) are arbitrary.

cluded. $Me_2PtBr_2Py_2$ and $[Bu_4N]$ $[Me_2PtBr_2(Sal{=}N—R)]$ were synthesized by reported methods [9, 10], while $[Bu_4N]$ $[Me_2PtBr_2Sal]$ was made analogously to the Schiff-base complexes and $Me_3Pt(Sal{=}N—Me)Py$ by reaction of $[Me_3PtI]_4$ with $TlSal{=}N—Me$ [11] then treating the $[Me_3Pt(Sal{=}N—Me)]_2$ obtained with pyridine. The $^1$H NMR spectra of some of these complexes have been reported elsewhere [10], however the chemical shifts and $^2J(^{195}Pt—^1H)$ values for the platinum methyl resonances are shown in Table 2 for comparison.

From the equation of Pople and Santry [4] for the dominant contact contribution to the reduced coupling constant, this can, if overlap integrals are neglected, be expressed as:

$$K\,(Pt—C) = (\text{constant})\,(\Delta E^{-1})\,\alpha_{Pt}^2\alpha_C^2\,\langle 2s_C|\delta|2s_C\rangle\,\langle 6s_{Pt}|\delta|6s_{Pt}\rangle$$

where $\Delta E$ is a mean excitation energy for the bonding electrons, $\alpha_x^2$ are the *s* orbital contributions to the bonding orbital from the appropriate atoms (i.e. *s* characters of the hydrid orbitals) and the last terms are integrals giving electron densities of the bonding *s* orbitals at the indicated nuclei. This type of expression has been widely used in the discussion of coupling constants involving platinum, particularly direct $^{195}Pt—^{31}P$ couplings, to investigate *trans* influences in reduction of covalency and hence $\alpha_{Pt}^2$ [1]. These studies have generally assumed constancy of $\Delta E$ and the electron density integrals, and although one should be wary about these assumptions they appear to be generally satisfactory.

The results presented here indicate, following this same approach, that the nitrogen donor of a salicylaldimine has a considerably stronger *trans* influence than the oxygen, and is stronger in the alkyl salicylaldimine than in the aryl analogue. The aldehyde oxygen of salicylaldehyde, on the other hand, has a much weaker effect, while pyridine appears to be slightly weaker than the nitrogen of *N*-methyl salicylaldimine. These results parallel those suggested by the $^1$H NMR data.

The assignments for the anionic dimethylplatinum complexes have been made on the basis of a constant $K$(Pt—C) value for one $^{13}$C nucleus and this is therefore assigned *trans* to the oxygen donor. For the trimethylplatinum complex it has been assumed that the ratio of the $K$(Pt—C) values for Me(1) and Me(2) will be the same as in $[Bu_4N][Me_2PtBr_2(Sal{=}N{-}Me)]$, the assignments shown both give ratios of 1.10. It is quite notable that the $K$(Pt—C) values are much larger in $Me_3Pt(Sal{=}N{-}Me)Py$ than in the dimethyl complexes. The ratios of $K$(Pt—C) for Me(1), Me(2) and Me(3) in the trimethyl compound to the corresponding values in $[Bu_4N][Me_2PtBr_2(Sal{=}N{-}Me)]$ and $Me_2PtBr_2Py_2$ are 1.35, 1.36 and 1.38 respectively, i.e. they are virtually equal. This suggests that the effect is due to the bromine, rather than the charge on the complex. It may be that the bromine atoms, which are very strongly bound [10], exert a *cis* influence by reducing $\alpha^2_{Pt}$ for the platinum carbon bond, they themselves using a large part of the Pt 6*s* orbital in bonding.

Another noteworthy feature is the lack of any appreciable coupling of platinum to other $^{13}C$ nuclei (less than 20 Hz) while the protons of the CH=N and N—Me groupings in the salicylaldimine complexes have couplings approximately 1/3 and 1/4 respectively of the directly bonded methyls. This strongly suggests that $\pi$ contributions are important in these couplings and the contact term does not give an adequate approximation to their values.

Further studies should provide more information about these and related complexes.

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