215. ^{195}Pt-NMR. Spectroscopy. The Direct Measurement of the Values $^{1}J(^{195}Pt, ^{14}N)$ and Chemical Shift Data for the Complexes *trans*-[$PtCl_2(C_2H_4)$(substituted pyridine)]

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Summary

The values $^{n}J(^{195}Pt, ^{14}N)$ are shown to be measurable directly from the ^{195}Pt spectrum for a variety of complexes containing nitrogen ligands. The sample temperature can play an important role in determining the width of the ^{195}Pt signal. ^{195}Pt chemical shifts for the complexes *trans*-[$PtCl_2(C_2H_4)$(substituted pyridine)] have been measured. Methyl substitution at the 2- and 6-positions produces a relatively large downfield shift.

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1. Introduction. - NMR. spectroscopy of ^{195}Pt ($I = 1/2$, natural abundance $= 33.7\%$) is now recognized as a sensitive probe for molecular structure [1]. The range of ^{195}Pt chemical shifts for complexes of platinum (II) is > 5000 ppm with changes of several hundred ppm resulting when one ligand is substituted for another. Thus the chemical shift parameter is often stressed, at the expense of the platinum-ligand couplings $^{n}J(^{195}Pt, L)$, when direct ^{195}Pt measurements are under discussion. Nevertheless, platinum-ligand atom coupling constants are sensitive probes for molecular structure and in some cases these data have been obtained directly from the ^{195}Pt spectrum [2]. This type of measurement can be difficult when the ^{195}Pt line-width is large. Indeed, when the L nucleus possesses a large nuclear quadrupole moment (*e.g.* ^{14}N and ^{75}As), the ^{195}Pt spectrum can be difficult to obtain, since intermediate L relaxation-times result in broad ^{195}Pt resonances. In our previously reported [3] study of the complexes *trans*-[$PtCl_2(C_2H_4)$(amine)] we often had to cool the solutions to $-50°$ in order to obtain even moderately sharp ($\Delta\nu_{1/2} < 100$ Hz) ^{195}Pt signals. In some few cases, however, we have observed that platinum complexes containing one nitrogen donor reveal ^{195}Pt resonances which show structure due to ^{14}N ($I = 1/2$, natural abundance $= 99.7\%$) coupling. Given that the one-bond Pt,N coupling has been shown to be both a useful structural tool [2] and quite sensitive to the nature of the *trans*-ligand [4], we have attempted to explore the possibility of obtaining this coupling constant information directly from the platinum spectrum.

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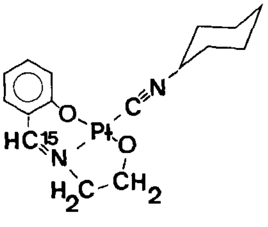

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2. Experimental. - ^{195}Pt-NMR. spectra were measured using a *Bruker*-HX 90 NMR. spectrometer operating at 19.3 MHz based on a separate frequency synthesizer. The samples were contained in 10 mm tubes. Pt chemical shifts are relative to external Na_2PtCl_6 with a negative sign indicating a higher field (lower frequency) position relative to the reference. The chemical shift data are accurate to ± 1 ppm, whereas the $^1J(^{195}Pt, ^{14}N)$ values are estimated to be ± 10 Hz.

The synthesis of the *Zeises* salt derivatives, *trans*-$[PtCl_2(C_2H_4)$(nitrogen ligand)] followed previously described methods [4]. The complex *cis*-$[PtCl_2(C_2H_4)$(hexylamine)] is prepared *via* a photochemical isomerization of the *trans*-isomer [4]. The synthesis of the *Schiffs* base derived from salicylaldehyde and ethanolamine as well as the platinum complex (I) will be described in detail at a later time.

3. Results and discussion. - 3.1. *Pt, N-coupling constants.* Our previous studies on Pt-complexes containing ^{15}N- enriched ligands have shown the $^1J(^{195}Pt, ^{15}N)$ is often of the order of several hundred Hz [4] [5]. Thus, in the event that the coordinated ^{14}N-atom is not relaxing quickly, effects due to residual ^{14}N-coupling

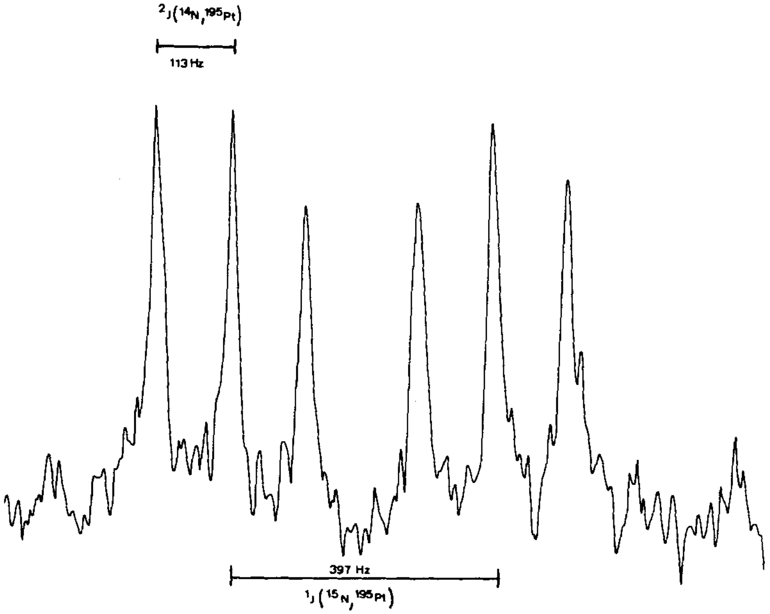

Figure. *^{195}Pt-NMR. spectrum of $[Pt(OC_6H_4{-}CH{=}^{15}NCH_2CH_2O)(C{\equiv}N{-}C_6H_{11})]$ (I) showing both ^{15}N- and ^{14}N-coupling to the metal* should be observable. To test this idea we first chose a relatively simple case. Uncoordinated isonitrile ligands show $^{14}N,^{1}H$- and $^{14}N,^{13}C$-couplings [6]. Since coordination to the platinum is through carbon the relaxation of the ^{14}N might not be strongly influenced upon complexation. That this is indeed the case may be seen in the *Figure*. The selection of the ^{15}N-enriched complex (I) stems from previous studies, and accounts for the appearance of two triplets. The 397-Hz-separation between the two triplets is $^{1}J(^{195}Pt, ^{15}N)$, whereas the 113-Hz-splitting is $^{2}J(^{195}Pt, ^{14}N)$. Thus relatively sharp lines revealing $^{195}Pt,^{14}N$-coupling can be observed in the platinum spectrum. Although Pt, N- coupling can be measured, isonitriles represent one of those few classes where coupling to ^{14}N is often observed. Indeed a collection of $^{2}J(^{195}Pt, ^{14}N)$ coupling constants in isonitrile complexes of Pt (II and IV) has recently been reported using double resonance methods [7]. We thus turned our attention to more commonly employed nitrogen ligands where ^{14}N-coupling is rarely observed.

We had previously noticed that the ^{195}Pt-spectrum of *trans*-$[PtCl_2(C_2H_4)$(4-methylpyridine)] showed a poorly resolved triplet at room temperature in $CDCl_3$. Attempts to slow the ^{14}N-relaxation by warming the sample[1]) resulted in the known [8] exchange of the nitrogen ligand (as shown by ^{1}H- and ^{13}C-studies). It is recognized, however, that 2-methylpyridine complexes of this type are kinetically more inert [9], and indeed we find triplets for both *trans*-$[PtCl_2(C_2H_4)$(2,4-dimethylpyridine)] and *trans*-$[PtCl_2(C_2H_4)$(2,4,6-trimethylpyridine)] in their ^{195}Pt-NMR. spectra (acetone-d_6, 40°). The one-bond coupling constants of 292 and 304 Hz respectively, are reasonable[2]) for this type of complex.

^{195}Pt INDOR-measurements on trimethylamine complexes of platinum have already shown [10] that the coupling of sp^3 type nitrogen to platinum should be observable. We find for *cis*-$[PtCl_2(C_2H_4)(NH_2(CH_2)_5CH_3)]$, a value of 210 Hz for $^{1}J(^{195}Pt, ^{14}N)$, thereby showing that $^{1}J(^{195}Pt, ^{14}N)$ can indeed be observed in a variety of platinum-nitrogen complexes.

We feel that these results are encouraging; nevertheless, a word of caution is required. The observed $^{1}J(^{195}Pt, ^{14}N)$ values found may be slightly too small. The ^{14}N- relaxation may be slow enough to observe fine structure in the ^{195}Pt-spectrum but still fast enough to cause partial collapse of the triplet. We have had occasion to synthesize the hexylamine complex *cis*-$[PtCl_2(C_2H_4)(^{15}NH_2(CH_2)_5CH_3)]$, enriched with ^{15}N, and thus to measure $^{1}J(^{195}Pt, ^{15}N)$. The coupling of ^{15}N ($I = 1/2$, natural abundance = 0.36%) to platinum is readily observed and, assuming no isotope effect, should be larger than the ^{14}N-coupling by the ratio of their gyromagnetic constants (a factor of 1.4). The observed $^{1}J(^{195}Pt, ^{15}N)$ coupling of 296 Hz is in agreement with the calculated value of 294 Hz, based on our observed value of 210 Hz at 323 K. However, at room temperature we observe a value of $^{1}J(^{195}Pt, ^{14}N)$ of 190 Hz, some 20 Hz smaller than at 323 K. Since we feel confident

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[1]) The ^{14}N relaxation-time is inversily proportional to the rotational correlation time, τ_C, which, for a rotating spherical molecule of radius a in a medium of viscosity η, can be estimated as $4\pi\eta a^3/3kT$. Therefore, increasing the sample temperature (and decreasing the viscosity) can slow the ^{14}N-relaxation.

[2]) Multiplication of these values by 1.4 gives values in the range found for $^{1}J(^{195}Pt, ^{15}N)$ where the N-atom is sp^2 hybridized.

Table. *^{195}Pt-NMR. data*[a]) *for the Platinum-Pyridine Complexes*

[$PtCl_2(C_2H_4)$(substituted pyridine)] Substituents in the pyridine ring	$\delta^{195}Pt(Na_2PtCl_6)$[b]) [ppm]
2,4,6-$(CH_3)_3$	−2871 (−2849)[c])
2,6-$(CH_3)_2$	−2877
2,4-$(CH_3)_2$	−2930 (−2909)[c])
2-CH_3	−2937
4-$N(CH_3)_2$	−2980[d])
4-CH_3	−2979
4-H	−2979
4-Cl	−2986
4-$COCH_3$	−2984
4-CN	−2992
piperidine	−3087
cis-2,6-dimethylpiperidine	−2953

[a]) For $CDCl_3$ solutions at −50° unless otherwise indicated. [b]) A negative sign indicates a shift to higher field (lower frequency) with respect to the reference. δ^{195}Pt is calculated using 19.34 as the divisor. [c]) Measured at 40° in acetone-d_6. [d]) Measured at −30°.

that the ^{15}N-coupling is accurate (the same value is observed in both ^{195}Pt- and ^{15}N-NMR. spectra) $^1J(^{195}Pt, ^{14}N)$ at room temperature is slightly too small. Where accurate measurements of this kind are required, an analysis of the temperature dependence of the line shape may be necessary [11]. Further, it may not always be possible to readily observe fine structure due to ^{14}N-coupling, since in some molecules the ^{14}N-relaxation will be too fast. For instance, we observe no fine structure for the complexes *trans*-[$PtCl_2L(NH_2(CH_2)_5CH_3)$], L = AsR_3, PR_3. We note, however, that there is a report on thiocyanate complexes of platinum containing $^1J(^{195}Pt, ^{14}N)$ data [12]. Since there is no obvious reason why the ^{14}N-relaxation should be slow in these thiocyanate complexes, it may prove difficult to predict which nitrogen environments are most likely to be conducive to observing this coupling.

3.2. *Platinum Chemicals Shifts.* As mentioned, δ^{195}Pt is quite sensitive to small changes within the coordination sphere. In view of our previous report [3] in which we found a steric effect on δ^{195}Pt in the complexes *trans*-[$PtCl_2(C_2H_4)$(amine)], we decided to extend our Pt-chemical-shift studies to include the case where the amine is a substituted pyridine. The ^{195}Pt-NMR. data for these *trans*-[$PtCl_2(C_2H_4)$-(substituted pyridine)] complexes are shown in the *Table.* The observed chemical shifts, which lie between 2871 and 2992 ppm to high field of Na_2PtCl_6, are reasonable for this type of complex. Interestingly, although the complexes *trans*-[$PtCl_2(C_2H_4)$(2,4-dimethylpyridine)] and *trans*-[$PtCl_2(C_2H_4)$(2,4,6-trimethylpyridine)] have similar $^1J(^{195}Pt, ^{14}N)$-values, as cited above, their ^{195}Pt chemical-shifts differ by 59 ppm (see *Table*), with the 2,4,6-trimethyl derivative at lower field.

A similar difference of 40 ppm is observed for the 2,6-dimethyl and 2-methylpyridine complexes, with the ^{195}Pt-resonances for all of these *ortho*-substituted complexes appearing at lower field than the *para*-substituted analogs. The difference between the 2,6-dimethyl- and totally unsubstituted pyridine complex is

102 ppm. Since the *Table* shows no very marked change in δ^{195}Pt as a function of the substituent in the *para*-position we exclude electronic effects stemming from the methyl group as the source of this change in δ^{195}Pt. Recent X-ray structural studies for the complexes *trans*-[$PtCl_2(C_2H_4)$(pyridine)] [13] and *trans*-[$PtCl_2(C_2H_4)$-(2,4,6-trimethylpyridine)] [14] reveal no significant differences in the metal-nitrogen distances, although the angle made by the plane of the pyridine with the plane defined by the two halogen, metal and nitrogen atoms changes from ~50° to ~90° on substituting two methyl groups in the *ortho*-positions. We cannot exclude some change in the metal-to-nitrogen π-back bonding when this angle is changed; however, we find that a similar difference in δ^{195}Pt exists between the piperidine ($\delta = -3087$) and *cis*-2,6-dimethylpiperidine ($\delta = -2953$) complexes. In addition we note that these same interplane angles for the complexes *trans*-[$PtCl_2$(*cis*-2,3-dimethylpyrrolidine)(Et_3P)] and *trans*-[$PtCl_2$(*cis*-2,4-dimethylpyrrolidine)(Et_3P)] [16] are approximately 62° and 64°, respectively. Thus cyclic nitrogen ligands can be turned considerably away from the $PtCl_2N$ plane, but by less than 90°, without the necessity of invoking a π-bonding explanation. We therefore lean towards an explanation involving non-bonded interactions between the metal electron density and/or the solvation sphere and the *ortho*-methyl groups of the pyridine to explain our chemical shift data. We have observed similar changes in δ^{195}Pt for the complexes *trans*-[$PtCl_2(C_2H_4)$(amine)] [3].

A non-bonded interaction would be consistent with our own and previous [15] ^{13}C studies which show no dramatic effect on the NMR. parameters of the ethylene of substituting methyl groups in para- and ortho-positions in the pyridine ring. Since there would be no major change in the bonding at platinum no marked change with bonding to ethylene is expected.

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REFERENCES

[1] *P.S. Pregosin & L.M. Venanzi,* Chemistry in Britain *14,* 276 (1978).

[2] *S.J.S. Kerrison & P.J. Sadler,* J. chem. Soc. Chem. Commun. *1977,* 861; *I.M. Al-Najjar, M. Green, S.J.S. Kerrison & P.J. Sadler,* J. chem. Soc. Chem. Commun *1979,* 311.

[3] *P.S. Pregosin, S.N. Sze, P. Salvadori & R. Lazzaroni,* Helv. *60,* 2514 (1977).

[4] *H. Motschi, P.S. Pregosin & L.M. Venanzi,* Helv. *62,* 667 (1979).

[5] *P.S. Pregosin & E. Steiner,* Helv. *59,* 376 (1976).

[6] *T. Axenrod* in 'Nitrogen NMR' (Ed. M. Witanoski and G. Webb), Plenum Press 1973, p. 261.

[7] *J. Browning, P.L. Goggin & R.J. Goodfellow,* J. chem. Research, *5,* (1978) 328.

[8] *P.D. Kaplan, P. Schmidt, A. Brouse & M.Orchin,* J. Amer. chem. Soc. *91,* 85 (1969)

[9] *J.C. Chottard, D. Mansuy & J.F. Bartoli,* J. organomet. Chemistry *65,* C19 (1974).

[10] *P.L. Goggin, R.J. Goodfellow, S.R. Haddock, J.R. Knight, F.J.S. Reed & B.F. Taylor,* J. chem. Soc. Dalton *1974,* 523.

[11] *J.A. Pople,* Mol. Physics *1,* 168 (1958); *J. Bacon, R.J. Gillespie & J.W. Quail,* Canad. J. Chemistry *41,* 3063 (1963).

[12] *S.J. Anderson & R.J. Goodfellow,* J. chem. Soc., Dalton *1977,* 1683.

[13] *M.A.M. Meester, K. Olie, L. Sint & H. Schenk,* Crystall. Struct. Commun. *4,* 725 (1975).

[14] *F. Caruso, R. Spagna & L. Zambonelli,* submitted for publication.

[15] *M.A.M. Meester, D.J. Stufkens & K. Vrieze,* Inorganica Chim. Acta, *16,* 191 (1976).

[16] *J. Ambühl, P.S. Pregosin, L.M. Venanzi, G. Consiglio, F. Bachechi & L. Zambonelli,* submitted for publication J. organomet. Chemistry 1979.