

^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME TRISUBSTITUTED METAL TRIFLUOROPHOSPHINE COMPLEXES. EXAMPLES OF $[\text{AX}_3]_3$ NUCLEAR SPIN SYSTEMS

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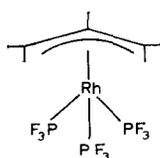
SUMMARY

The ^{19}F NMR spectra of π -allyl-tris(trifluorophosphine)rhodium(I), [A], benzene-tris(trifluorophosphine)chromium(0), [B], and nitrosyl-tris(trifluorophosphine)rhodium(-I), [C], are presented. These are examples of $[\text{AX}_3]_3$ nuclear spin systems (A = phosphorus, X = fluorine). The spectra of [A] and [B] have been completely analysed to afford values for $^1J(\text{PF})$, $^2J(\text{PP}')$, $^3J(\text{PF}')$ and $^4J(\text{FF}')$.

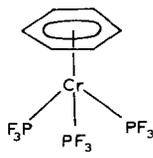
INTRODUCTION

The literature contains relatively few examples of nuclear magnetic resonance spectra of spin systems of the $[\text{AX}_3]_3$ type. Finer and Harris¹ have presented algebraic expressions for the frequencies and intensities of transitions in the X part of this type of spin system for the case where $J(\text{XX}') = 0$.

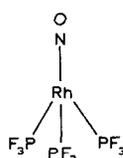
Symmetrical trisubstituted transition metal complexes of trifluorophosphine such as *cis*- $\text{Mo}(\text{CO})_3(\text{PF}_3)_3$ represent examples of the $[\text{AX}_3]_3$ spin system, (X = fluorine, A = phosphorus)², and if $J(\text{XX}') = 0$ the spectrum is defined by the three parameters $^1J(\text{PF})$, $^3J(\text{PF}')$ and $^2J(\text{PP}')$. The relative signs of $^1J(\text{PF})$ and $^3J(\text{PF}')$ can also be obtained directly from the spectrum¹.



(A)



(B)



(C)

We wish to report the ^{19}F NMR spectra of three other trisubstituted metal trifluorophosphine complexes, $[\text{A}] = \pi\text{-C}_3\text{H}_5\text{Rh}(\text{PF}_3)_3$, $[\text{B}] = \text{cis-Cr}(\text{C}_6\text{H}_6)(\text{PF}_3)_3$ and $[\text{C}] = \text{RhNO}(\text{PF}_3)_3$, which all show the expected features of $[\text{AX}_3]_3$ spin systems but in $[\text{B}]$ and $[\text{C}]$ ${}^2J(\text{PP}') > {}^3J(\text{PF}')$ whereas in $[\text{A}]$ ${}^3J(\text{PF}') > {}^2J(\text{PP}')$. The spectra of $[\text{A}]$ and $[\text{C}]$ are complicated by the presence of the ^{103}Rh nuclei ($I = \frac{1}{2}$, 100% natural abundance) which causes each line in the spectrum to appear as a 1:1 doublet due to ${}^2J(\text{RhF})$ coupling. The ^{19}F NMR spectra of $[\text{A}]$ and $[\text{B}]$ have been completely analysed.

RESULTS AND DISCUSSION

(a) π -Allyl-tris(trifluorophosphine)rhodium(I), $[\text{A}]$

The low-field half of the ^{19}F NMR spectrum of $[\text{A}]$ is shown in Figure 1(a). This is the limiting low-temperature NMR spectrum since as discussed elsewhere³ the complex readily undergoes intermolecular trifluorophosphine ligand exchange and at room temperature the ^{19}F NMR spectrum simply consists of a broad 1:1 doublet. The appearance of the spectrum is characterised by a relatively small value of ${}^2J(\text{PP}')$ which leads to a close spacing of most of the lines in the spectrum. Analysis of the spectrum of $[\text{A}]$ leads to the coupling constant parameters listed in Table 1, and the calculated ^{19}F NMR spectrum (using computer programme UEANMR BASIC)* is shown in Figure 1(b).

TABLE 1
COUPLING CONSTANTS IN SOME $[\text{AX}_3]_3$ AND $[\text{AX}_2]_2$ SPIN SYSTEMS

| Complex | ${}^1J(\text{PF})^*$ | ${}^3J(\text{PF}')^*$ | ${}^2J(\text{PP}')^*_1$ | ${}^4J(\text{FF}')^*$ | ${}^2J(\text{RhF})^*$ | $\varphi_{\text{F}}^\dagger$ |
|--|----------------------|-----------------------|-------------------------|-----------------------|-----------------------|------------------------------|
| $\pi\text{-C}_3\text{H}_5\text{Rh}(\text{PF}_3)_3$ | -1422 | +40 | 19 | 2 | 18.0 | 8.4 |
| $\text{Cr}(\text{C}_6\text{H}_6)(\text{PF}_3)_3$ | -1295 | + 5.5 | 132 | 0 | — | -12.4 |
| $\text{Rh}(\text{NO})(\text{PF}_3)_3$ | -1416§ | — | 85 ± 5 | 0 | 18.0 | 3.8 |
| $(\text{Rh}(\text{PF}_3)_2\text{Cl})_2^a$ | -1328 | +19 | 63.5 | 0 | 31.5 | 17.0 |
| $\pi\text{-C}_3\text{H}_5\text{Rh}(\text{PF}_3)_2^b$ | -1327 | + 5.2 | 147.5 | 0 | 31.2 | 3.4 |
| $\text{Mo}(\text{CO})_3(\text{PF}_3)_3^c$ | -1296 | + 2.4 | 56.0 | 0 | — | 1.2 |
| $\text{Mo}(\text{CO})_4(\text{PF}_3)_2^d$ | -1305 | $\sim + 2$ | 55.0 | 0 | — | 2.9 |

† Relative to CCl_3F as internal standard [in ppm].

* In Hz.

§ ${}^1J(\text{PF}) + {}^2J(\text{PF}')$.

^a Data from ref. 11.

^b J. F. NIXON AND A. A. PINKERTON, unpublished results.

^c Data from ref. 2.

^d Data from ref. 20.

* I am indebted to Dr. M. Kinns, University of East Anglia, for this computer programme.

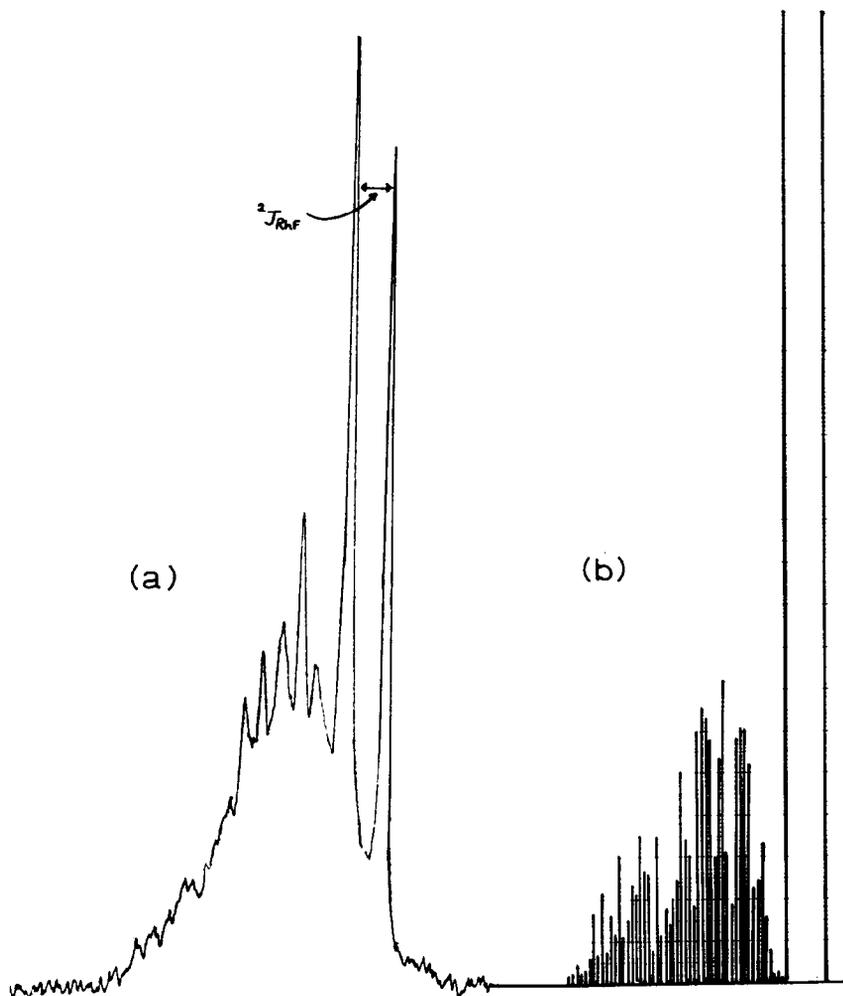


Fig. 1. (a) Observed and (b) calculated low-field ^{19}F NMR half spectrum of $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{PF}_3)_3$ (at -50°) in toluene solution, $[\text{AX}_3]_3$.

The coupling constants $^1J(\text{PF})$ and $^3J(\text{PF}')$ have *opposite* signs and by analogy with other work⁴⁻⁷ are likely to be negative and positive respectively.

The relatively large magnitude of $^3J(\text{PF}')$ is similar to earlier results obtained for a number of tetrahedral (fluorophosphine)nickel(0) complexes⁸⁻¹⁰, $\text{Ni}(\text{RPF}_2)_4$, ($\text{R} = \text{F}, \text{CF}_3, \text{CCl}_3, \text{CH}_2\text{Cl}, \text{Me}_2\text{N}$).

The value of $^2J(\text{PP}')$ found in $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{PF}_3)_3$ is much smaller than values in other (trifluorophosphine)rhodium(I) complexes we have studied, *e.g.* in $[\text{RhCl}(\text{PF}_3)_2]_2$ [$^2J(\text{PP}') = 63.5 \text{ Hz}$] and in $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{PF}_3)_2$ [$^2J(\text{PP}') = 147.5 \text{ Hz}$]^{12, 13}.

The apparent magnetic equivalence of the three trifluorophosphine ligands in $\pi\text{-C}_3\text{H}_5\text{Rh}(\text{PF}_3)_3$ at low temperature is consistent with either structure [A] if the allyl group is considered free to rotate about the threefold symmetry axis or alternatively may result from a ready *intramolecular* exchange of ligands within an approximately trigonal-bipyramid structure. This type of fluxional behaviour is known for other five-coordinated complexes containing trifluorophosphine such as $\text{CF}_3\text{Co}(\text{CO})_3(\text{PF}_3)^{14}$, $\text{C}_4\text{H}_6\text{Fe}(\text{PF}_3)_3^{15}$ and $\text{HRh}(\text{PF}_3)_4^{16}$. Recently the structure of the related $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$ complex was determined by electron diffraction¹⁷. The overall symmetry of the molecule is C_s while the local symmetry of the $\text{Co}(\text{CO})_3$ group is C_{3v}^{18} .

(b) *Benzene-tris(trifluorophosphine)chromium*, [B]

The ^{19}F NMR spectrum of [B] shown in Figure 2(a) is consistent with the molecule having C_{3v} symmetry and shows the expected widely spaced pair of quintets pattern of lines discussed previously by Finer and Harris¹ for the case where $L = |^1J(\text{PF}) - ^3J(\text{PF}')| \gg ^2J(\text{PP}')$ and $^2J(\text{PP}') > ^3J(\text{PF}')$. As expected, $^1J(\text{PF})$ and $^3J(\text{PF}')$ have opposite signs and $^3J(\text{PF}')$ has the smaller value associated with other fluorophosphine metal complexes in which the transition metal is in an approximately octahedral environment^{19,20}. The calculated NMR spectrum is shown in Figure 2(b). The overlapping of many lines partly limited the accuracy of the coupling constants listed in Table 1.

The relatively large value of $^2J(\text{PP}')$ (= 132 Hz) found for $\text{Cr}(\text{C}_6\text{H}_6)(\text{PF}_3)_3$ is consistent with other data on *cis* complexes of Group VI metals where it is usually found that $|^2J(\text{PP}')|$ decreases in the order $\text{Cr} > \text{Mo} > \text{W}^{19,21-24}$.

(c) *Nitrosyl-tris(trifluorophosphine)rhodium(-I)*, [C]

The ^{19}F NMR spectrum of [C] which is temperature independent (shown in Figure 3) exhibits the similar quintet line pattern found in [B], but is complicated by the presence of the ^{103}Rh nucleus which makes each line in the ^{19}F NMR spectrum appear as a 1:1 doublet. The poorer quality of the spectrum precluded a full analysis, however the distance between the strongest lines in the two halves of the ^{19}F NMR spectrum gives $^1J(\text{PF}) + 2^3J(\text{PF}')$ accurately and $^2J(\text{PP}')$ is found to be approximately 85 Hz.

The solution ^{19}F NMR spectrum of [C] is thus entirely consistent with the known C_{3v} geometry found for the vapour by an electron diffraction study²⁵.

EXPERIMENTAL

π -Allyl-tris(trifluorophosphine)rhodium(I) was prepared as described elsewhere³ and carefully purified in the high-vacuum manifold before use. Benzene-tris(trifluorophosphine)chromium(0), which was a gift from Dr. P. L. Timms,

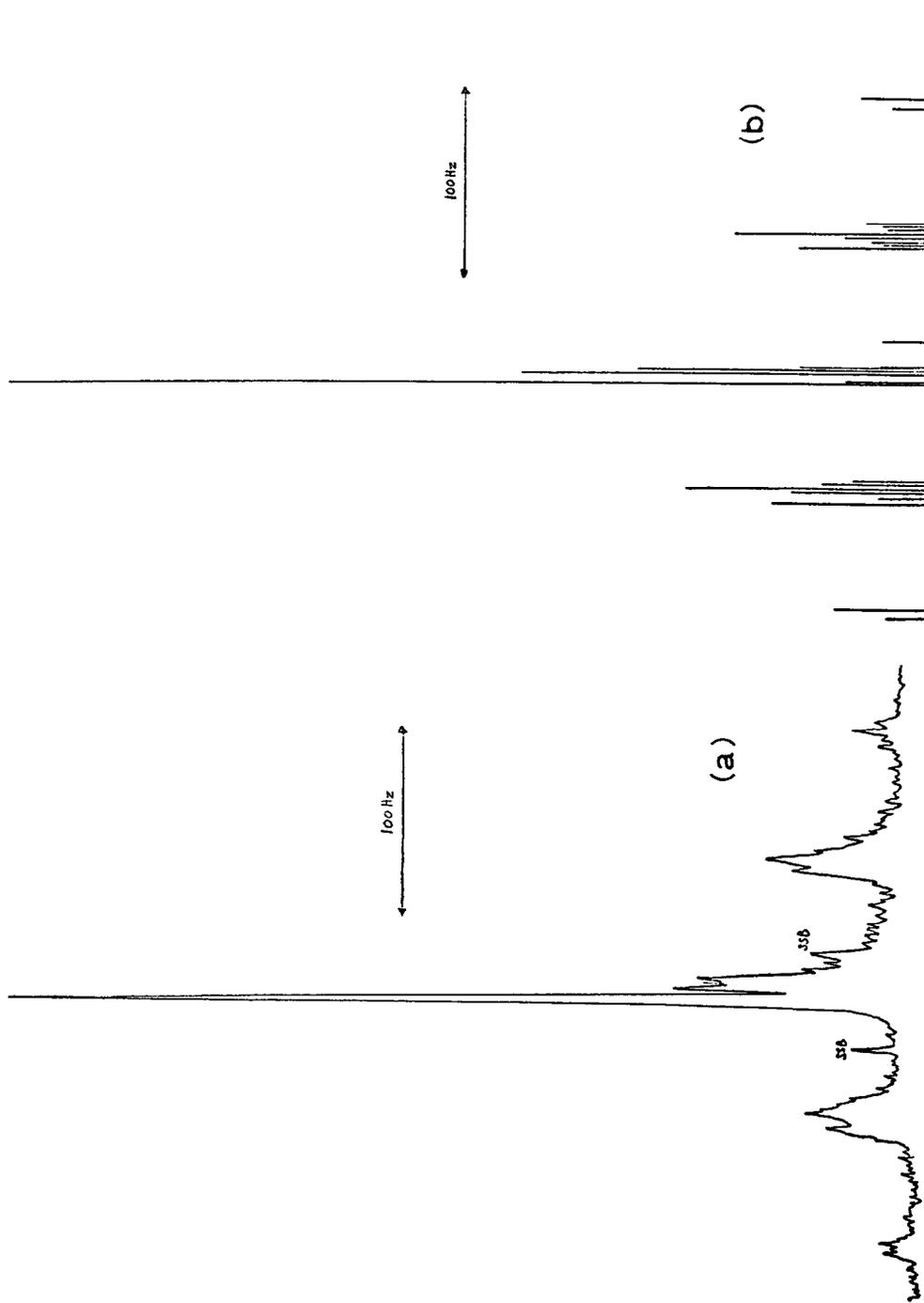


Fig. 2. (a) Observed and (b) calculated ^{19}F NMR half spectrum of $\text{C}_6\text{H}_6\text{Cr}(\text{PF}_3)_3$ in benzene solution (SSB = spinning side-band).

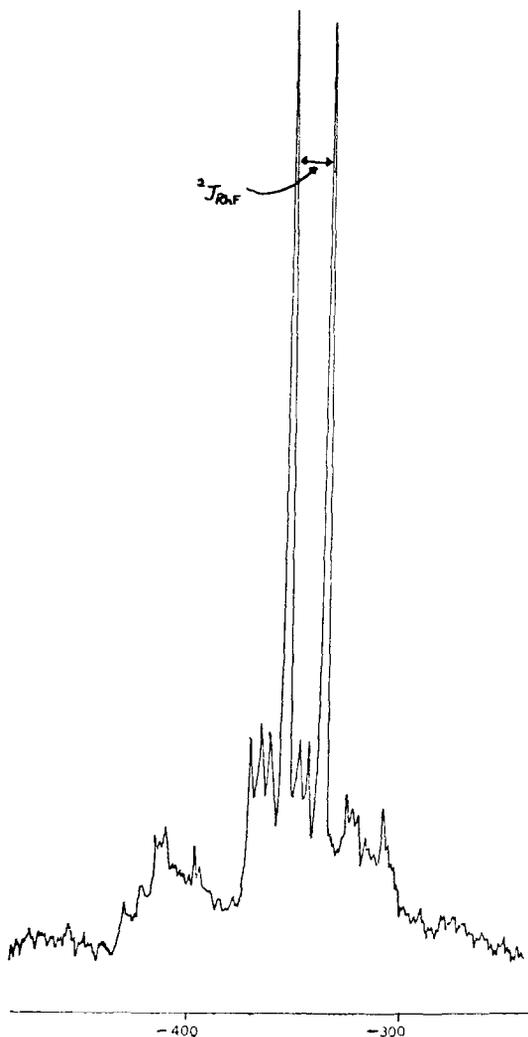


Fig. 3. The low-field half of the ${}^{19}\text{F}$ NMR spectrum (at 94.1 MHz) of $\text{RhNO}(\text{PF}_3)_3$ in CCl_3F solution.

University of Bristol, was purified by high-vacuum sublimation. The preparation of nitrosyl-tris(trifluorophosphine)rhodium(-I) is described elsewhere²⁶.

${}^{19}\text{F}$ NMR spectra were recorded using a Varian HA-100 NMR spectrometer operating at 94.1 MHz.

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