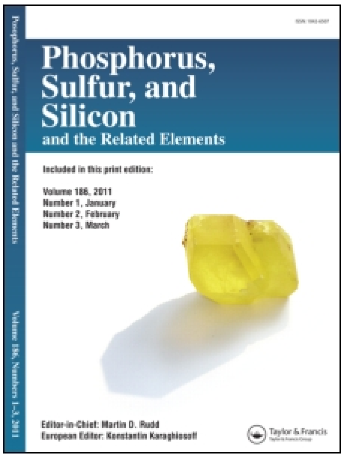

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Complete Analysis of the Phosphorus and Fluorine NMR Spectra of Mer-$(Pf_3)_3Mo(CO)_3$

Charles G. Barlow[a]; Daniel L. Miller[a]; Richard A. Newmark[a]
[a] Chemical Power Sources, 3M Company, St Paul, MN, USA

To cite this Article Barlow, Charles G. , Miller, Daniel L. and Newmark, Richard A.(1999) 'Complete Analysis of the Phosphorus and Fluorine NMR Spectra of Mer-$(Pf_3)_3Mo(CO)_3$', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 15

To link to this Article: DOI: 10.1080/10426509908053488

URL: http://dx.doi.org/10.1080/10426509908053488

Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 15-15
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Complete Analysis of the Phosphorus and Fluorine NMR Spectra of Mer-$(Pf_3)_3Mo(CO)_3$

CHARLES G. BARLOW, DANIEL L. MILLER and
RICHARD A. NEWMARK

Chemical Power Sources,3M Company, 209–2C-26, St Paul, MN 55144, USA

The original study of the complexes formed between fluorophosphines and molybdenum carbonyl relied upon IR and NMR spectroscopy to determine the structures of the products formed by displacement of organic ligands whose steric requirements fixed the structures of the starting materials[1],[2]. The trisubstituted products were assigned a mer structure on the basis of their IR spectra since the NMR spectra at 40.5 and 94.1 MHz were too complex to interpret at that time.

We have now re-examined the product from the reaction of phosphorus trifluoride and cycloheptatriene molybdenum tricarbonyl by high field ^{19}F and ^{31}P NMR.

The spectrometer used was a Varian UNITY 500 operating at 202.334 MHz and 470.268 MHz for ^{31}P and ^{19}F, respectively. The computer program "gNMR, version 4.0" by Cherwell Scientific[3] was used in the analysis of the NMR spectra.

The large number of lines in the NMR spectra and the occurrence of patterns known to occur in similar compounds suggested that there was a mixture of isomers from the reaction [4]. Detailed analysis of the spectra indicated a mixture of fac and mer isomers in a 2:3 ratio.

Several features can be seen in this limited data set. The PP' and the PP'F couplings are always found to be much larger for ligands which are trans to each other. It has been postulated [5] that the phosphorus-phosphorus coupling is determined by the s orbital contribution to the bonds between them. The trans atoms can bond to the metal through a common d orbital of the metal and therefore have larger coupling than cis atoms which bond to two different d metal orbitals. A complete fit between experimental and calculated spectra could only be achieved when a coupling between fluorines in trans ligands through the F-P-Mo-P-F bonds was set to about 6 Hz, an unusually large 4 bond coupling which must occur through the bonds. The corresponding coupling between fluorines in cis ligands is only 0.5 Hz. The final fit included the determination of all nine coupling constants (where the subscripts refer to t-trans; c-cis ligands):

$^1J(P_tF_t)$ -1311, $^1J(P_cF_c)$ -1301, $^2J(P_tP_t)$ -292, $^2J(P_tP_c)$ -59, $^3J(P_tP_tF_t)$ +36,
$^3J(P_tP_cF_c)$ +3.5, $^3J(P_cP_tF_t)$ -2.0, $^4J(F_tP_tP_tF_t)$ +5.7, $^4J(F_tP_tP_cF_c)$ -0.5 Hz.

Since the original structure was determined from the gas phase IR spectrum we measured the ^{19}F NMR of the vapour above a small sample of solid compound at 60°C. Two broad doublets were found which corresponded very well with the solution spectrum, confirming that the mixture of isomers is present in the gas phase as in solution.

References

[1] C.G. Barlow, J.F. Nixon, M. Webster, J. Chem. Soc. (A), 2692, (1968).
[2] C.G. Barlow, J.F. Nixon, J.R. Swain, J. Chem. Soc. (A), 1082, (1969).
[3] Cherwell Scientific, The Magdalen Centre, Oxford OX4 4GA, UK.
[4] R.K. Harris, J.R. Woplin, R. Schmutzler, Ber. Bunsen., **75**, 134, (1971).
[5] F. Olgilvie, R.J. Clark, J.G. Verkade, Inorg Chem., **8**, 904, (1969).