Journal of Organometallic Chemistry, 217 (1981) C34—C36
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

DIRECT OBSERVATION OF DIASTEREOMERS WITH OPPOSITE Mo CONFIGURATIONS BY ^{95}Mo NMR

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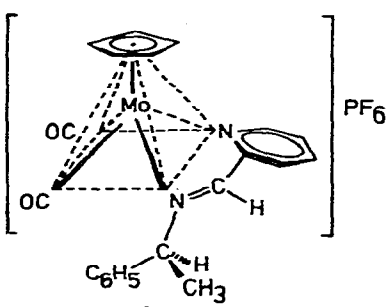
(Received June 3rd, 1981)

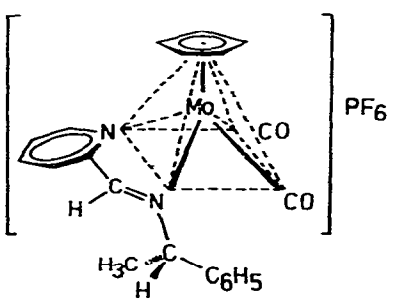
Summary

Molybdenum-95 NMR has been used to directly detect the two diastereomers differing only in the Mo configuration in the square pyramidal molybdenum(II) complex $[C_5H_5Mo(CO)_2NN^*]PF_6$, where NN^* is the chiral pyridine-2-carbaldimine ligand derived from pyridine-2-carbaldehyde and (*S*)(−)-1-phenylethylamine. The simplicity of the spectra clearly reveals the optical purity of the complex with respect to the metal center.

Chiral metal centers have been extensively studied in recent years [1]. Of particular interest are diastereomeric complexes which contain both a chiral metal center and a ligand with an optically active carbon center, such as the cations Ia and Ib of $[C_5H_5Mo(CO)_2NN^*]PF_6$ [2].



Ia



Ib

We wish to report the first direct observation of such diastereomers by ^{95}Mo NMR spectroscopy. Figure 1 shows the ^{95}Mo NMR spectrum of an equimolar mixture of Ia and Ib, and the ^{95}Mo NMR spectrum of a 4/1 mixture of the

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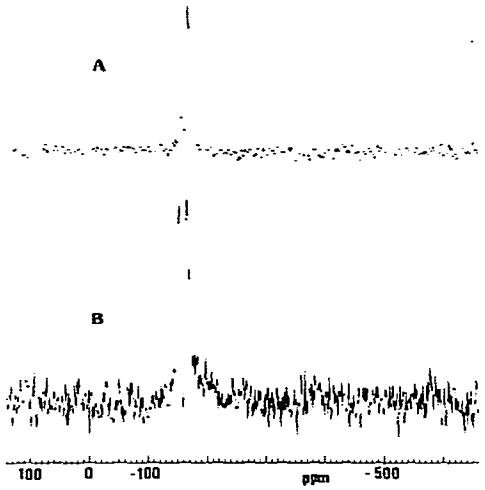

Fig. 1. ^{95}Mo NMR spectra of diastereomers Ia and Ib. Spectrum B is of an equimolar mixture; spectrum A has Ia/Ib = 4/1 and establishes that the peak of lower frequency (−168 ppm) is due to Ia. Chemical shifts are relative to 2 *M* Na_2MoO_4 at pH 11. Line widths at half-height < 100 Hz.

diastereomers. The peaks for the two diastereomers (−154 and −168 ppm) are well resolved and separated by 14 ppm. The spectrum for the 4/1 mixture clearly establishes that the peak at −168 ppm is due to Ia. Spectra were recorded in acetone at 16.3 MHz on a Bruker WM-250 MHz spectrometer as described previously [3]. Chemical shifts are relative to external 2 *M* Na_2MoO_4 at pH 11.

Complexes Ia and Ib and related diastereomers also show two sets of ^{1}H NMR peaks [1,2]. Integration of such spectra gives an indication of the optical purity of the sample provided that the multiple ^{1}H resonances from the several protons on the ligands do not overlap one another. The simplicity of the ^{95}Mo NMR spectrum (Fig. 1) reveals the optical purity of the complex at a glance.

There are only few reports on the use of ^{95}Mo NMR studying the stereochemistry of metal complexes in solution. The large chemical shift range for ^{95}Mo is well established [4] and studies of tetrahedral molybdenum(VI) complexes [5], substituted molybdenum carbonyl complexes [6,7] and dioxomolybdenum(VI) complexes [3] have been described. The chemical shifts of Ia and Ib are near the center of the known chemical shift range for molybdenum. To our knowledge only one other molybdenum(II) complex has been studied by ^{95}Mo NMR [7].

The ^{95}Mo NMR spectra of diastereomers Ia and Ib suggest that ^{95}Mo NMR will be a useful technique for stereochemical investigations. Studies of related compounds are in progress.

Acknowledgements. We thank the National Institutes of Environmental Health Sciences (ES-00966) for partial support of this research, and the National Science Foundation for a grant for the purchase of the NMR spectrometer. We thank P. Miller and Dr. K. Christensen for assistance with the NMR experiments and we are grateful to Dr. B.E. Mann for providing a preprint of ref. 7 prior to publication.

References

1 H. Brunner, Advan. Organometal. Chem., 18 (1980) 151.
2 H. Brunner and W.A. Hermann, J. Organometal. Chem., 74 (1974) 423.
3 K.A. Christensen, P.E. Miller, M. Minelli, T.W. Rockway and J.H. Enemark, Inorg. Chim. Acta, in press.
4 R.K. Harris and B.E. Mann, Eds., NMR and the Periodic Table, Academic Press, New York, 1978, p. 213.
5 (a) W.D. Kautt, H. Krüger, O. Lutz, H. Maier and A. Nolle, Z. Naturforsch., 31 (1976) 351; (b) O. Lutz, A. Nolle and P. Kroneck, ibid., 31 (1976) 454; (c) 32 (1977) 505.
6 A.F. Masters, R.T.C. Brownlee, J.D. Cotton, M.J. O'Connor and A.G. Wedd, J. Organometal. Chem., 195 (1980) C17.
7 S. Dysart, I. Georgii and B.E. Mann, submitted for publication.

JOURNAL OF ORGANOMETALLIC CHEMISTRY, VOL. 217, No. 2

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