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Preliminary communication

DIRECT OBSERVATION OF DIASTEREOMERS WITH OPPOSITE Mo CONFIGURATIONS BY ⁹⁵Mo NMR

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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 $[C_{\varepsilon}H_{5}Mo(CO)_{2}NN^{*}]PF_{6}$, 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].



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

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Fig. 1. ⁹⁵Mo 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 Na₂MoO₄ 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 Na₂MoO₄ at pH 11.

Complexes Ia and Ib and related diastereomers also show two sets of ¹H NMR peaks [1,2]. Integration of such spectra gives an indication of the optical purity of the sample provided that the multiple ¹H resonances from the several protons on the ligands do not overlap one another. The simplicity of the ⁹⁵Mo 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 ⁹⁵Mo NMR spectra of diastereomers Ia and Ib suggest that ⁹⁵Mo NMR will be a useful technique for stereochemical investigations. Studies of related compounds are in progress.

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