Distinction of Diastereomeric Amine Derivatives of η^5-$C_5H_5V(CO)_4$ by ^{51}V NMR Spectroscopy

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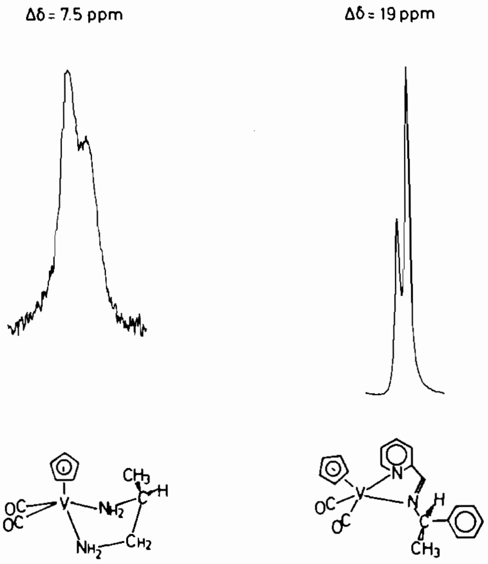
Complexes of the type *cis*-$[CpV^*(CO)_2NN^*]$ (1) and $CpV(CO)_3N^*N^*$ (2) with two centers of chirality situated at the vanadium and the carbon backbone of the bidentate nitrogen ligand (1) or solely in the ligand system (2) give rise to two pairs of enantiomers (*R,R* and *S,S*; *R,S* and *S,R*); these are diastereomeric to each other and hence exhibit differing spacial conditions of the kind which should result in two distinct signals in the ^{51}V NMR spectrum with the more sterically crowded diastereomer at lower field (higher frequency). The low-field shift of vanadium NMR signals with increasing steric strains had been established in the series $CpV(CO)_3P(alkyl)_3$ and *cis*-$[CpV(CO)_2Ph_2P(CH_2)_nPPh_2]$, $n = 1-4$ [1, 2]. The diastereomer splitting has previously been reported for, *inter alia*, the ^{95}Mo resonances of *cis*-$[CpMo^*(CO)_2NN^*]^+$ [3, 4] and the ^{31}P NMR signals of *cis*-$[CpNb^*(CO)_2Ph_2P(CH_2)_2P^*\text{-}Cy(CH_2)_2PPh_2]$ [5].

We have investigated the complexes **1a** (NN* = 1,2-diaminopropane), **1b** (NN* is the Schiff base formed by condensation of 2-formylpyridine and 1′-amino-1′-methyltoluene [6]) and **2a** (N*N* = 1,2-diaminocyclohexane, 1,2-DACH). The complexes were prepared according to eqns. (1) and (2), using racemates of the ligands or, in the case of **2a**, a mixture of (*meso*)-*cis*-[1,2-DACH] and (±)-*trans*-[1,2-DACH]. For the generation and substitution reactions of $CpV(CO)_3THF$, see also ref. 7.

$$CpV(CO)_4 + NN^* \xrightarrow{h\nu\,(THF)} CpV^*(CO)_2NN^* \qquad (1)$$

$$CpV(CO)_4 + THF \xrightarrow{h\nu,\,195\,K} CpV(CO)_3THF \xrightarrow{+N^*N^*,\,250\,K} CpV(CO)_3\,N^*N^* \qquad (2)$$

The results are displayed in Figs. 1 and 2. The signal positions are typical [7] of disubstituted $CpV(CO)_4$ derivatives containing two amine functions (**1a**: −302 and −309; **1b**: −194 and −213 ppm), and tricarbonyl species with one amine ligand occupying the fourth position of the tetragonal pyramid (**2a**: −615 and −649 ppm; all $\delta(^{51}V)$ relative to $VOCl_3$ and at room temperature). In the latter case, the disubstitution product is also formed by simultaneous loss of THF and CO (*cf.* eqn. (2)), evidenced by the low-field signal at −345 ppm (Fig. 2).



1a **1b**

Fig. 1. ^{51}V NMR spectra of **1a** (left) and **1b**. The spectra were obtained as THF solutions on a Bruker WH 90 spectrometer at 23.66 MHz in 7.5 mm diameter vials fitted into 10 mm vials containing acetone-d_6 as external lock. Measuring temperature was 300(1) K.

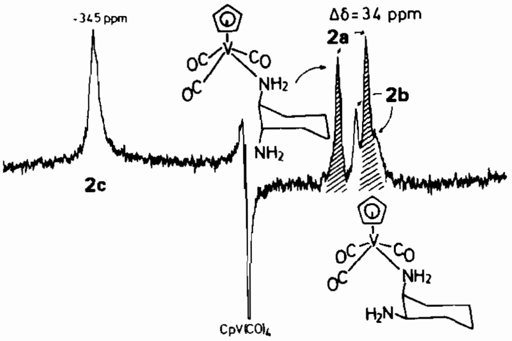


Fig. 2. ^{51}V NMR spectrum of the reaction mixture obtained from $CpV(CO)_3THF$ and diaminocyclohexane (DACH). The shaded signals correspond to the two diastereomers **2a**; the lower field signal is the *R,R* isomer. The superimposed, weaker pair of signals (**2b**) is probably due to the two diastereomers formed with 1,3-DACH; the signal at −345 ppm (**2c**) is associated with disubstituted product. The off-phase signal, folded into the shift range for this NMR experiment, corresponds to $CpV(CO)_4$ (correct position: −1534 ppm). The shifts are quoted relative to neat $VOCl_3$. Measuring conditions as in Fig. 1.

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For all three compounds, there are two distinct signals corresponding to the diastereomeric pairs of enantiomers, and it is also evident that they are in non-equivalent proportions. In the case of **2a**, the low-field signal could be assigned to the *R,R* (*trans*-[1,2-DACH]) enantiomer by employing the *R,R* form of the ligand in eqn. (2).

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