Diastereomer Splitting in the ^{95}Mo NMR Spectra of Compounds Differing only in the Mo Configuration

HENRI BRUNNER*, PETER BEIER, ERICH FRAUENDORFER, MANFRED MUSCHIOL, DEVENDRA K. RASTOGI, JOACHIM WACHTER

Institut für Anorganische Chemie der Universität Regensburg, Universitätsstr. 31, D-8400 Regensburg, F.R.G.

MARTIN MINELLI and JOHN H. ENEMARK*

Department of Chemistry, University of Arizona, Tucson, Ariz. 85721, U.S.A.

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In a short communication we reported that the diastereomers of **1a**, differing only in their Mo configuration, give two well separated and relatively sharp signals in the ^{95}Mo NMR spectrum [1]. This result raised the question as to whether other diastereomers could also be distinguished by ^{95}Mo NMR. Therefore a general study of the ^{95}Mo NMR spectra of four different types of compounds was undertaken.

All the compounds **1a–1**, **2**, **3a**, **b**, and **4a–c** used for the study are depicted in the Scheme. For each compound that contains an optically pure ligand with (S)-configuration at the asymmetric carbon atom C*, there are two diastereomers, $R_{Mo}S_C$ and $S_{Mo}S_C$, differing only in the Mo configuration. If a racemic ligand with (R)/(S)-configuration at the asymmetric carbon atom C* is used in the synthesis then there are four isomers, two diastereomeric pairs of enantiomers $R_{Mo}S_C/S_{Mo}R_C$ and $S_{Mo}S_C/R_{Mo}R_C$. In both cases, however, the same solution NMR spectra are obtained, which arise either from the two diastereomers or from the two enantiomeric pairs of diastereomers [2]. There are examples for both cases in the compounds of the Scheme.

Table I summarizes the ^{1}H and ^{95}Mo NMR parameters of all the compounds, **1a–1**, **2**, **3a**, **b**, and **4a–c**. Column 3 of Table I gives the diastereomer ratio for each complex, determined by integration of appropriate ^{1}H NMR signals (usually C_5H_5). Columns 4–7 contain the chemical shifts and the chemical shift difference (Δ) of ^{1}H NMR signals, and columns 8–10 present the corresponding data for the ^{95}Mo NMR spectra. For each diastereomer ratio differing from 50:50 the parameters for the excess diastereomer are italicized.

Column 11 in Table I gives the references for the synthesis and characterization of the compounds incorporated in the present study. The correlation of the ^{1}H NMR and ^{95}Mo NMR parameters of individual diastereomers with solubility, chromatographic behavior and absolute metal configurations (where known) can be found in the references.

The chelate ligands in compounds **1a–i** are derived from 2-pyridine-carbaldehyde (R'' = H) and primary amines (R = methyl, ethyl, isopropyl, benzyl; R' = ethyl, phenyl, methyl ester, benzyl ester) [3, 4]. For these compounds the two diastereomers can, in all cases, be differentiated by ^{1}H NMR spectroscopy [4–7]. The chemical shift differences for the C_5H_5 resonances are large (0.3–0.4 ppm) if there is a phenyl substituent at the asymmetric center C* (nos. **1–3**, Table I). However, two alkyl groups at the asymmetric center, as in compound **1d**, usually lead to C_5H_5 signals which are not resolved for the two diastereomers (no. **4**). Sometimes, as in the case of **1d**, other signals can be used to determine the diastereomer composition. If an ester substituent is bonded to the asymmetric center C* in addition to a hydrogen atom and an alkyl group then the chemical shift differences for the C_5H_5 resonances are around 0.1 ppm (nos. **5–7**). The differences increase to about 0.4 ppm if there are benzyl substituents directly attached to the asymmetric center C* or in the ester group R' (nos. **8**, **9**). In addition to the chemical shifts for the C_5H_5 resonances and their differences (columns 4 and 5, Table I), the same parameters for other ^{1}H resonances are given in columns 6 and 7, if appropriate.

The corresponding ^{95}Mo parameters for compounds **1a–i** are listed in columns 8–10 of Table I (nos. **1–9**). Similar to the ^{1}H NMR signals, the ^{95}Mo NMR signals are well resolved for the diastereomers of **1a–c** which have a phenyl ring at the asymmetric center C* (diastereomer splitting between 14 and 22 ppm), and the ^{95}Mo signals are not resolved for the diastereomers of **1d** with two alkyl groups at the asymmetric carbon atom C*.

Isomer enrichment shows that the diastereomers of **1a–c** with high field (shielded) C_5H_5 signals also exhibit the high field (shielded) Mo signals. The high field shift of the C_5H_5 signals in one of the diastereomers of compounds of the type **1a–c** has been attributed to a conformation around the N–C* bond in which the phenyl ring closely approaches the C_5H_5 ring [4]. The weak attraction arising from this C_6H_5/C_5H_5 interaction has been called the β-phenyl effect*. It is responsible for the high shift of the C_5H_5 signal and probably also of the Mo signal because in this conformation C_5H_5 and Mo are in the inner anisotropy region of the phenyl ring at C*.

*Authors to whom correspondence should be addressed.

*For a recent review concerning the β-phenyl effect see reference 8.

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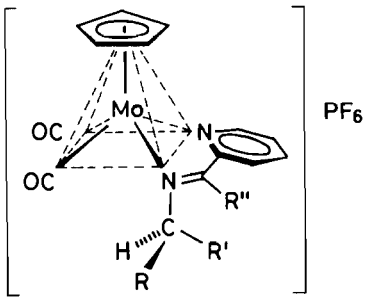
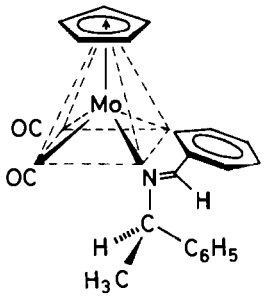
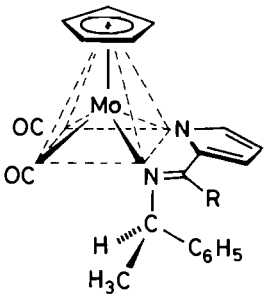


1



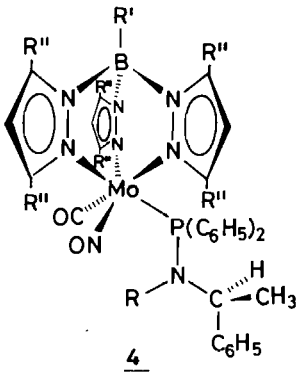
2

	a	b	c	d	e	f	g	h	i	j	k	l
R	CH_3	C_2H_5	$i\text{-}C_3H_7$	CH_3	CH_3	C_2H_5	$i\text{-}C_3H_7$	$CH_2C_6H_5$	$CH_2C_6H_5$	CH_3	CH_3	C_2H_5
R'	C_6H_5	C_6H_5	C_6H_5	C_2H_5	$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_2C_6H_5$	C_6H_5	C_2H_5	C_6H_5
R''	H	H	H	H	H	H	H	H	H	CH_3	CH_3	C_6H_5



3

	a	b
R	H	CH_3



4

	a	b	c
R	H	H	CH_3
R'	H	Bpz	Bpz
R''	CH_3	H	H

Scheme

In contrast to ^1H NMR spectroscopy there is no diastereomer splitting in the ^{95}Mo spectra if an ester group R' is bonded to the asymmetric center C* (nos. **5–9**). Even if there is an additional benzyl substituent at C* or in the ester group R' no ^{95}Mo NMR splitting is observed, whereas such changes cause additional signal separation in the ^1H NMR spectrum (nos. **8, 9**).

Derivatives **1j–l** carry methyl or phenyl substituents instead of H at the imine carbon atom of the five-membered ring. It has been argued that substitution of H by CH_3 and C_6H_5 at the imine carbon atom of the chelate ring changes drastically the conformation of the $C^*H(CH_3)(C_6H_5)$ group with respect to the Mo fragment [9]. This is obvious from the C_5H_5 signals of the two diastereomers of **1j** which are almost isochronous and from the ^{95}Mo signals, which are separated by 6 ppm (no. **10**) compared to the 14 ppm of **1a**. For compound **1j** the diastereomer splitting is much more distinct in the ^{95}Mo signals (6 ppm) compared to the C_5H_5 signals, but the diastereomer ratio is best determined by integration of the $CHCH_3$ signals, which are nicely separated.

The ^{95}Mo diastereomer splittings of compounds **1j–l** (R'' = CH_3, C_6H_5) are completely analogous to their counterparts **1a–i**, with R' = H. Compounds **1j** and **1l** have a phenyl substituent at C* and show diastereomer splitting, whereas **1k** has only alkyl substituents at C* and does not show diastereomer splitting (nos. **10–12**).

In contrast to the cationic complexes **1**, compounds **2** and **3** are neutral. As chelate ligands they contain an *o*-metalated benzaldimine (**2**) [10] and the anion of the Schiff base derived from (S)-(−)-1-phenylethylamine and 2-pyrrolecarbaldehyde (**3a**) [11] or 2-acetylpyrrole [**3b**] [12]. All three compounds (**2**, **3a**, **b**) contain a hydrogen/alkyl/phenyl

TABLE I. Diastereomers of Compounds 1a–l, 2, 3a, b, and 4a–c (acetone solution): ^{1}H NMR Spectra (δ, i-TMS, Bruker WM 250) and ^{95}Mo NMR spectra (δ, 2M, Na_2MoO_4 in H_2O, pH 11, Bruker WM 250).

No.	Compound	ratio	C_5H_5 δ [ppm]	Δ [ppm]	CH_3 δ [ppm]	Δ [ppm]	^{95}Mo δ [ppm]	Δ [ppm]	Line width [Hz]	Ref.
1	1a	25:*75*	6.03; *5.66*	0.37	–	–	–154; *–168*	14	<100, <100	1, 4–7
2	1b	25:*75*	6.00; *5.64*	0.36	–	–	–145; *–167*	22	150, 70	4
3	1c	30:*70*	5.94; *5.55*	0.39	–	–	–143; *–166*	20	100, 70	4
4	1d	*75*:25	*6.05*; 6.05	–	1.62; *1.57*[a]	0.05	–186	–	120	4
5	1e	50:50	6.10; 6.03	0.07	–	–	–169	–	90	4
6	1f	*60*:40	*6.09*; 6.00	0.09	3.89; *3.85*[b]	0.04	–159	–	90	4
7	1g	40:*60*	6.09; *5.95*	0.14	*3.93*; 3.85[b]	0.08	–145	–	90	4
8	1h	30:*70*	6.01; *5.56*	0.45	*3.85*; 3.78[b]	0.07	–160	–	120	4
9	1i	*55*:45	*5.92*; 5.58	0.34	–	–	–156	–	160	4
10	1j	50:50	6.02; 5.99	0.03	2.11; 1.80	0.31	–141; –147	6	90, 90	9
11	1k	40:*60*	6.05; *6.04*	0.01	–	–	–154	–	90	9
12	1l	*75*:25	6.03; *5.30*	0.72	–	–	*–128*; –160	32	*130*, 180	9
13	2	50:50	5.25; 4.87[c]	0.38	–	–	–383; –396	13	50, 150	10
14	3a	50:50	5.52; 5.24	0.28	–	–	–293; –310	17	70, 70	11
15	3b	50:50	5.57; 5.25	0.32	2.29; 2.16[d]	0.13	–293; –299	6	90, 120	12
16	4a	50:50	–	–	1.40; 1.37[a,c]	0.03	–339; –354	15	170, 220	13
17	4b	50:50	–	–	1.20; 1.07[a,c]	0.13	–355; –370	15	160, 160	13
18	4c	50:50	2.20; 2.16[e]	0.04	1.82; 1.76[a]	0.06	–298; –309	11	200, 200	13

[a] $CHCH_3$ doublets. [b] $COOCH_3$ singlets. [c] In $CDCl_3$. [d] $N{=}C(CH_3)$. [e] $PNCH_3$ doublets.

combination at the asymmetric carbon atom C* and show clear ^{95}Mo splitting of the diastereomers (nos. **13–15**), similar to compounds **1a–c**, **1j**, and **1l**.

Compounds **4** are polypyrazolylborato derivatives. **4a** is a trispyrazolylborate complex; **4b** and **4c** are tetrapyrazolylborate complexes. **4a** is methyl substituted in the 3,5-positions [13]. The optically active ligands are the aminophosphines $(C_6H_5)_2PN(R)CH(CH_3)(C_6H_5)$ with R = H (**4a**, **b**) and R = CH_3 (**4c**). The ligands CO and NO complete the coordination shell of the Mo atom. Although the chirality at the Mo atom is only due to the differences of the CO and NO groups, the diastereomer splitting is remarkably high (nos. **16–18**). This is in accord with other results showing that the structurally similar linear diatomic ligands CO and NO are stereochemically distinctly different [14].

The ^{95}Mo signals for the four different types of compounds appear in different chemical shift regions: **1a–l** between −130 and −185; **2** around −390; **3a, b** between −290 and −310; and **4a–c** between −300 and −370 ppm. All of these regions are in the deshielded part of the known chemical shift range for Mo(II) monomers [15, 18].

The diastereomer ratios determined from integration of the ^{95}Mo spectra are in accord with the ratios obtained from integration of the ^{1}H NMR spectra. For rapid differentiation of diastereomers ^{1}H NMR is superior to ^{95}Mo NMR because of the greater sensitivity and narrower lines in ^{1}H NMR. The spectral differences for two typical examples are shown in Fig. 1.

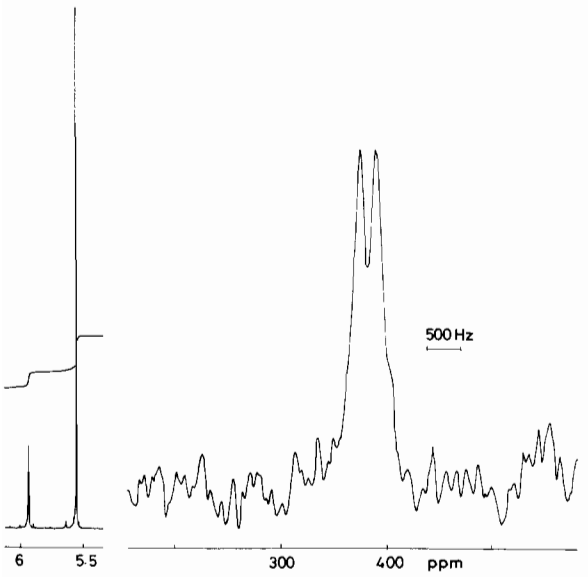


Fig. 1. Left: C_5H_5 region of the ^{1}H NMR spectrum of 1c in acetone solution (Bruker WM 250). Right: ^{95}Mo resonances of **4b**, 2 M Na_2MoO_4 in H_2O, pH 11 (Bruker WM 250).

One advantage of heteronuclear NMR studies of diastereomeric complexes is that such studies provide direct information about the transfer of chiral information among different parts of the molecule. ^{1}H NMR by itself provides information about the transfer of chiral information to other peripheral groups which contain protons. ^{95}Mo NMR of diastereomeric molybdenum complexes directly probes the transfer of chiral information from the ligands to the metal center. In some cases, *e.g.* **1e–i**, diastereomers cannot be detected at the metal center by ^{95}Mo NMR even though relatively large differences are seen in the ^{1}H NMR of the C_5H_5 rings. In other cases, *e.g.* **1j**, sizable ^{95}Mo splittings are observed, but the ^{1}H NMR of the C_5H_5 rings are nearly isochronous for the two diastereomers.

For the present study, the wealth of ^{1}H NMR data for diastereomeric molybdenum complexes provided the impetus to explore ^{95}Mo NMR as a direct probe of diastereomeric metal centers. However, for $MoO_2(L\text{-cysOR})_2$ complexes, direct observation of diastereomers in the ^{95}Mo NMR spectra prompted re-examination of the ^{1}H and ^{13}C spectra for evidence of diastereomers [19].

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