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Enantiomeric Discrimination in η^2-Olefin Complexes by Chiral Lanthanide Shift Reagents

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The optical purity of Pt(II) η^2-complexes of prochiral olefins can be determined by ^{1}H NMR spectroscopy in presence of a chiral LSR.

The use of lanthanide shift reagents has proved to be very fruitful in the elucidation of many structural problems [1], but to our knowledge very few examples have been reported on the enantiomeric discrimination of chiral complexes [2, 3]. In this field a problem arises when the optical purity of prochiral olefin complexes [4] of relevant mechanistic interest [5], has to be determined. For enantiomeric complexes this could only be achieved by using empirical rules, whose validity is limited to complexes of unsubstituted alkenes.§

We report here an investigation carried out on Pt(II) complexes containing prochiral olefin ligands. Our preliminary results show that in the presence of the optically active lanthanide shift reagent Eu(hfc)$_3$** it is possible to ascertain the optical purity of olefin η^2-complexes, making use of ^{1}H NMR at high fields. The investigated penta-coordinated Pt(II) complexes are of the type [PtCl$_2$-(L–L)(olefin)] where L–L is biacetyl-bis-N,N-dimethylhydrazone and the olefins are fumarodinitrile (*1*), acrylonitrile (*2*), acrolein (*3*), methyl acrylate (*4*) and (*E*)-2-butene (*5*)≠. A square-planar Pt(II) complex of (*E*)-2-butene was also investigated.

In the case of penta-coordinated complexes we have found that when the unsaturated ligand bears electron-rich substituents, such as C=O or C≡N, an efficient interaction with the LSR occurs. In fact all proton signals undergo a remarkable downfield shift and, even more important, a doubling of signals is always observed for the racemic complexes (see Table I).

For complex (*1*) a splitting of the olefinic CH single resonance occurs at a LSR/Pt ratio of 1:1 ($\Delta\delta$ = 7.1 Hz). At higher ratios the N-methyl signal of L–L also doubles ($\Delta\delta$ = 2.7 Hz). This is certainly due to enantiomeric differentiation since no splitting occurs with enantiomeric (–)(*1*). The same experiment carried out on (–)(*1*) with an optical purity of 60% yield splittings of the olefin signals with different intensities (4:1) as expected ($\Delta\delta$ = 21.6 Hz at LSR/Pt ratio of 4:1), see Fig. 1. The motion of the olefin ligands of complexes (*2*), (*3*) and (*4*) is restricted on the NMR time scale. Therefore the N(CH$_3$)$_2$ signal of L–L, as well as the CCH$_3$ resonance, are already split in two lines of equal intensity. In the case of (*2*) a further splitting of the N(CH$_3$)$_2$ signals occurs at high (5:1) LSR/Pt ratio, while a 1:1 ratio is sufficient to give a clear splitting of the olefinic proton multiplets. When the olefin ligand bears a C=O group, as in the case of (*3*) and (*4*), no clear indication of enantiomeric differentiation can be obtained by the olefinic protons. However, for (*4*) the COOCH$_3$ methyl resonance splits in two lines of equal intensity ($\Delta\delta$ = 60 Hz at 500 MHz, LSR/Pt ratio of 1:1, see Table I). The aldehydic

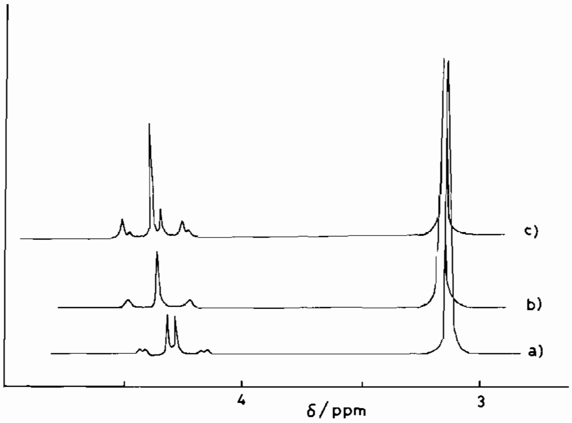

Figure 1. ^{1}H 270 MHz spectra of [dichloro(fumarodinitrile)-(L–L)Pt(II)] complex in the presence of various amounts of Eu(hfc)$_3$. Only the olefinic proton region is shown in these spectra. a) Racemic Pt(II) complex with Eu(hfc)$_3$ at a molar ratio of 1:1. b) Enantiomeric Pt(II) complex with Eu(hfc)$_3$ at a molar ratio of 1:1.5. c) 60% optically pure Pt(II) complex with Eu(hfc)$_3$ at a molar ratio of 1:2.

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§These rules were inferred from the optical properties of diastereomeric complexes (see G. Paiaro, *Organomet. Chem. Rev. A.*, *6*, 319 (1970), and literature therein) for which, of course, the optical purity could be in principle obtained by NMR analysis.

**hfc = 3-(heptafluoropropyl-hydroxymethylene)-*d*-camphorato.

≠The racemic complexes (*1–4*) were prepared by olefin exchange from the corresponding η^2-ethene complex reported by L. Maresca, G. Natile, M. Calligaris, P. Delise and L. Randaccio, *J. Chem. Soc. Dalton Trans.*, 2386 (1976). The racemic (*E*)-2-butene complex (*5*) was obtained with a procedure similar to that reported for the ethene complex. The optically active fumarodinitrile complex (–)(*1*), ($[\alpha]^{25}_{D}$ = –110, *c* = 0.6 chloroform), was prepared by exchange of the bidentate ligand from a diastereomeric penta-coordinated complex reported by A. De Renzi, B. Di Blasio, A. Saporito, M. Scalone and A. Vitagliano, *Inorg. Chem.*, *19*, 960 (1980).

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TABLE I. ^{1}H NMR Data for $[PtCl_2(olefin)\{(CH_3)_2NNC(CH_3)C(CH_3)NN(CH_3)_2\}]$ Complexes, Pure and in Presence of Eu(hfc)$_3$.[a]

Compound (olefin)	olefin protons[b]		chelate protons[c]	
	>C=C<	others	$N(CH_3)_2$	CCH_3
1 (*E*-CNCH=CHCN)	4.05		3.05	2.61
1 + LSR	4.31 4.28		3.13	2.64
2 (CH_2=CHCN)	3.75, 3.67, 3.47		3.11, 3.00	2.55, 2.52
2 + LSR	4.01, 3.87, 3.59 4.05, 3.89, 3.61		3.23, 3.05	2.58, 2.55
3 (CH_2=CHCHO)	4.27, 4.17, 3.72	9.79	3.08, 2.99	2.52, 2.49
3 + LSR	5.2[d], 4.51, 4.04	10.96	3.37 3.35, 3.19	2.60, 2.58
4 (CH_2=$CHCOOCH_3$)	4.59, 4.01, 3.45	3.70	3.07, 3.04	2.51, 2.49
4 + LSR	[e] 4.57 [e] 4.50	4.03 4.15	3.39, 3.34	2.82, 2.80
5 (*E*–CH_3CH=$CHCH_3$)	4.06	1.21	3.05	2.45
5 + LSR	4.10	1.25	3.09	2.49

[a] Spectra recorded in $CDCl_3$ solution at 270 and/or 500 MHz; chemical shifts are in p.p.m. relative to TMS; Eu(hfc)$_3$/Pt-complex ratio = 1:1. [b] Figures refer to the center of gravity of multiplets. [c] In all cases these resonances are singlets. [d] Partially superimposed to other resonances. [e] Obscured by other resonances.

proton doublet in (*3*) becomes increasingly broader upon LSR addition, whereas one of the two $N(CH_3)_2$ signals splits in two resonances with equal intensity at LSR/Pt ratio of 1:1.

A similar experiment on the (*E*)-2-butene complex (*5*) does not yield the expected splitting of the olefinic protons, while the downfield shift is much less pronounced than for the other complexes. However, when *trans*-[PtCl$_2$(benzylamine)(*E*-2-butene)] was investigated, two clearly resolved signals ($\Delta\delta$ = 5.4 Hz at a LSR/Pt ratio of 5:1) could be observed for the olefinic protons decoupled from the methyls. The chemical shift difference between the two signals is much less than in the case of penta-coordinated fumarodinitrile. It is interesting to note that this splitting is observed for the square-planar but not for the more crowded penta-coordinated complex (*5*).

In conclusion it is fair to say that our preliminary results suggest an easy way for the determination of the optical purity of chiral complexes of prochiral olefins. From our data on stable Pt(II) complexes it appears that the method can be of general application if electron-rich substituents are present on the coordinated double bond and/or an easy access to the chiral complex by the approaching lanthanide reagent occurs.

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5 See for instance: A. Panunzi, A. De Renzi, and G. Paiaro, *J. Am. Chem. Soc., 92,* 3488 (1970); J. K. Stille and R. Divakaruni, *ibid., 100,* 1303 (1978).