A New Method for the Enantiomeric Excess Determination of Chiral Trisubstituted Allenes by ^{195}Pt NMR of *trans*-Dichloro[(*S*)-α-methylbenzylamine](allene)platinum(II) Complexes

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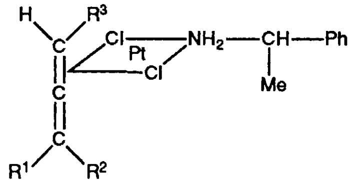
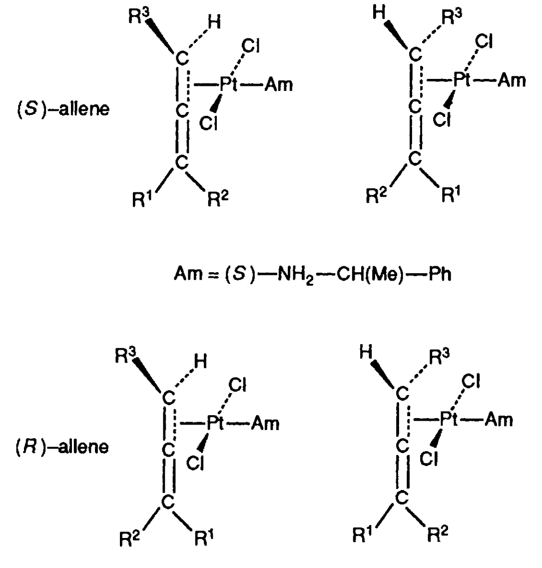
The formation of diastereoisomeric complexes *trans*-dichloro[(*S*)-α-methylbenzylamine](allene)platinum(II) and detection by ^{195}Pt NMR of their concentrations in $CDCl_3$ solution allow the enantiomeric purity of chiral trisubstituted allenes to be determined easily.

In spite of the large interest in the synthesis and reactivity of chiral allenes, there is a paucity of absolute methods for determining their enantiomeric purity.[1,2] Recently, chiral silver shift reagents[3] and transition metal complexes[4,5] have been used to convert a chiral allene into a mixture of labile or stable diastereoisomers, whose concentrations can be determined by NMR spectroscopy. These applications, although attractive, were rather limited and, to the best of our knowledge, no cases have hitherto been reported where the enantiomeric composition of chiral trisubstituted allenes has been obtained by use of such methods.

In the present paper we describe the enantiomeric purity



(1)



Am = (S)—NH₂—CH(Me)—Ph

determination of trisubstituted chiral allenes having structure $R^1R^2C{=}C{=}CHR^3$ (**a**: R^1 = Et, R^2 = Me, R^3 = Bu^i; **b**: R^1 = Bu^t, R^2 = Me, R^3 = Bu^t)[6] by ^{195}Pt NMR spectroscopy. As recently reported for the enantiomeric purity determination of chiral allyl alcohols and allyl ethers,[7] the allenes have been transformed into the corresponding diastereoisomeric complexes *trans*-dichloro[(*S*)-α-methylbenzylamine](allene)platinum(II) (**1**), and the concentration of the latter determined by detecting their ^{195}Pt resonances in $CDCl_3$.

The complexes (**1a** and **b**) were prepared by treating the allene with *trans*-dichloro[(*S*)-α-methylbenzylamine](ethylene)platinum(II)[8] in $CDCl_3$ solution. On standing at 30—40 °C for a few minutes, the allene replaces the co-ordinated ethylene and this reaction is driven to completion by removing the ethylene *in vacuo*.

Four species are present in solution, which are the four diastereoisomers arising from the binding to platinum of the two prochiral faces of the less substituted double bond[9] of the two enantiomeric allenes (Scheme 1). Therefore, in principle, each diastereoisomer formed can give a single ^{195}Pt resonance. Accordingly, the platinum spectrum of the complex (**1a**), prepared starting from racemic allene **a**, shows four resonances centred at −2601, −2606, −2589, and −2585 ppm (Figure 1).†

When (**1a**) is prepared from (*R*)-**a** having high enantiomeric excess, only the two resonances at −2606 and −2585 ppm are observed; therefore they must be assigned to the two diastereoisomers originating from co-ordination of the prochiral faces of the (*R*)-antipode. As a consequence, the other two resonances at −2601 and −2589 ppm are due to the

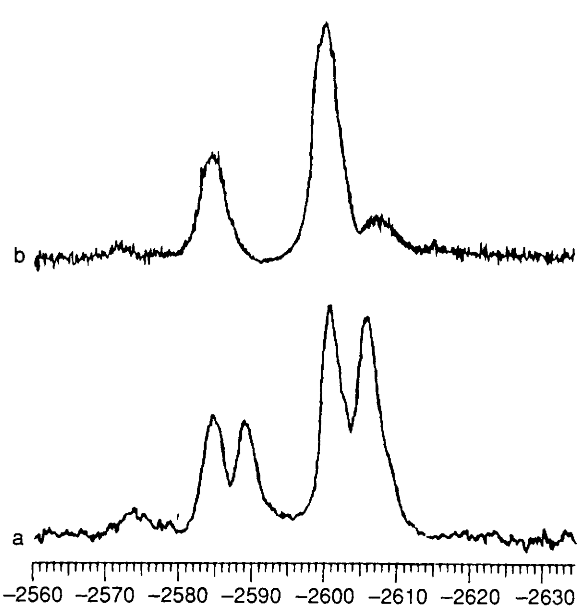


Figure 1. ^{195}Pt NMR spectra (64.3 MHz, $CDCl_3$, chemical shifts in ppm referred to Na_2PtCl_6) of complex (**1a**). (a) Spectrum of the complex containing the racemic allene. (b) Spectrum of the complex containing the allene enantiomerically enriched in the (*R*)-antipode.

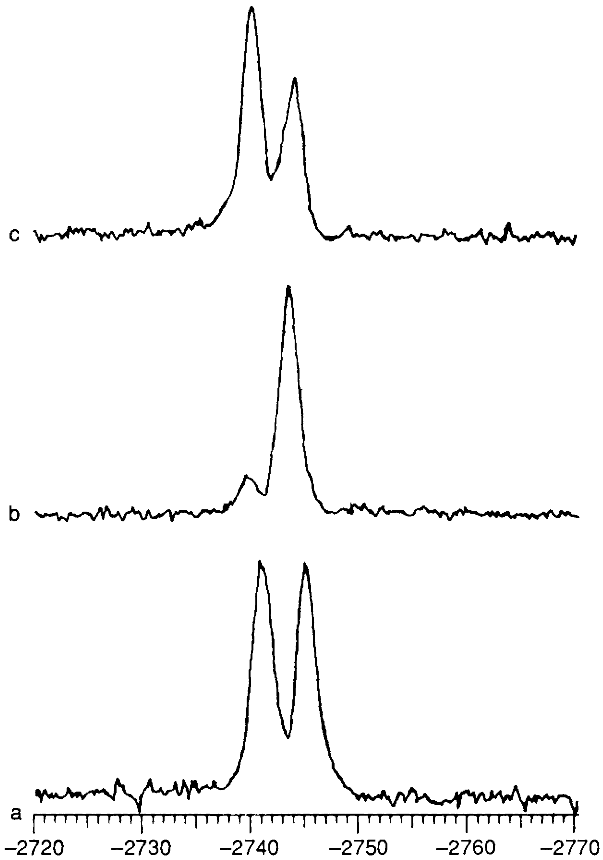


Figure 2. ^{195}Pt NMR spectra (64.3 MHz, $CDCl_3$, chemical shifts in ppm referred to Na_2PtCl_6) of complex (**1b**). (a) Spectrum of the complex containing the racemic allene. (b) Spectrum of the complex containing the allene enriched in the (*R*)-form. (c) Spectrum of the complex containing the allene enriched in the (*S*)-form.

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† NMR spectra were recorded in $CDCl_3$ on a Varian VXR-300 spectrometer operating at 64.3 MHz for ^{195}Pt. All ^{195}Pt NMR chemical shifts were referenced to Na_2PtCl_6 as external standard.

co-ordination of the (*S*)-antipode. In addition, when the complex (**1a**) is prepared starting from an excess of the ethylene complex‡ with respect to the allene (molar ratio 3—4 : 1), the allene is quantitatively co-ordinated and enantioselectivity in the co-ordination of the allene is avoided. Thus the enantiomeric composition of the allene used in the formation of the complex can be easily obtained by comparing the sum of the areas of the two peaks assigned to the (*R*)-antipode with the sum of the areas of the two peaks assigned to the (*S*)-antipode. As expected, these two values are equal for the complex prepared from the racemic allene. It is of note that the different intensity of the two resonances given by each co-ordinated antipode indicates that one face preferentially co-ordinates for both the antipodes.

Accordingly, in the case of the complex (**1b**), only one ^{195}Pt NMR signal originates from each antipode (Figure 2). Indeed only one face of each enantiomer can bind to the metal, because of the remarkable steric hindrance that arises from the t-butyl group pointing towards the Pt atom.

In conclusion, ^{195}Pt NMR spectroscopy of diastereoisomeric complexes *trans*-dichloro[(*S*)-α-methylbenzylamine](allene)platinum(II) has been successfully employed to determine, for the first time, the enantiomeric composition of trisubstituted allenes *via* an absolute method.

This method has practical and economic advantages: (i) the allene complex is rapidly and readily formed starting from the corresponding easily obtainable ethylene complex;[8] (ii) ^{195}Pt NMR spectra are recorded in a few minutes by using 50—100 mg of complex in 0.6 ml of $CDCl_3$ in a 5 mm tube; (iii) once the analysis has been performed, the co-ordinated allene can be quantitatively displaced from the complex by treating the solution with an excess of ethylene. As the *trans*-dichloro[(*S*)-α-methylbenzylamine](ethylene)platinum(II) formed is insoluble in the reaction mixture, the allene and the ethylene complex can be easily recovered and the latter can be used for further enantiomeric purity determinations.

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‡ The ^{195}Pt resonance of *trans*-dichloro[(*S*)-α-methylbenzylamine](ethylene)platinum(II) is at higher field (−3016 ppm) than the absorptions due to the complexes (**1a** and **b**).