ORGANIC
LETTERS

2001
Vol. 3, No. 2
205−207

^{195}Pt NMR Determination of the Enantiomeric Purity and Absolute Configuration of Trisubstituted Allenes by Using $[PtCl_3(C_2H_4)]^-[(S,S)\text{-}(1\text{-}NpMeCH)_2NH_2]^+$ as CDA

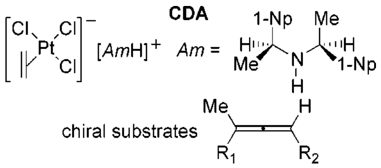
**Gloria Uccello-Barretta, Raffaella Bernardini, Federica Balzano,
Anna Maria Caporusso, and Piero Salvadori*,†**

*Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive,
Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy*

psalva@dcci.unipi.it

Received November 3, 2000

ABSTRACT



The ionic CDA $[PtCl_3(C_2H_4)]^-[(S,S)\text{-}(1\text{-}NpMeCH)_2NH_2]^+$ produces, on exchange of its coordinated ethylene by chiral trisubstituted allenes, diastereoisomeric mixtures originating distinct ^{195}Pt NMR resonances for the complexed enantiomers, thus allowing the determination of the enantiomeric purity. A reproducible correlation between relative positions of platinum signals due to the complexed enantiomers and their absolute configuration has been found.

Among nonchiroptical methods, the use of chiral auxiliaries for NMR spectroscopy[1] has offered suitable procedures for the efficient determination of the enantiomeric composition and absolute configuration of trisubstituted allenes.[2]

We have, very recently, developed[3] new CDAs (chiral derivatizing agents) based on ionic platinum(II) complexes $[PtCl_3(C_2H_4)]^-[AmH]^+$ containing chiral secondary amines, having widespread applicability for the analyses of chiral unsaturated compounds. In particular, complex **1** (Scheme 1), containing the chiral symmetrical secondary amine (1*S*,1′*S*)-bis[1-(1-naphthyl)ethyl]amine, has shown the greatest versatility.[3b]

We now report that ionic complex **1** is an efficient CDA for the complete stereochemical characterization of trisubstituted allenes **2** (Scheme 1), leading to the simultaneous determination of their enantiomeric purities and absolute configurations.

The preparation of **1** has been described elsewhere.[3b] The derivatization reaction involved in its use as CDA is the exchange of the coordinated ethylene by the enantiomeric mixture to be analyzed. This process occurs by mixing the

---

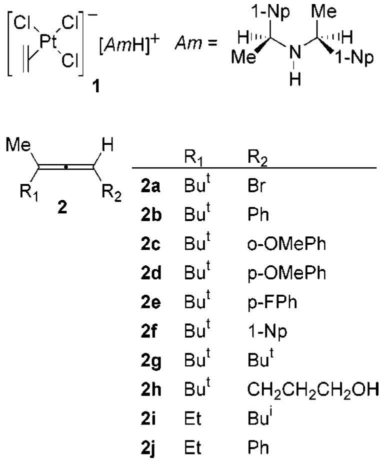
[†] Ph: +39-050-918203. Fax: +39-050-918409

(1) (a) Parker, D. *Chem. Rev.* **1991**, *91*, 1441−1457. (b) Weisman, G. R. *Asymmetric Synthesis;* Morrison, J. D., Ed.; Academic: New York, 1983; Vol.1, pp 153−171. (c) Fraser, R. R. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1983; Vol.1, pp 173−196. (d) Yamaguchi, S. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1983; Vol. 1, pp 125−152.

(2) (a) Uccello-Barretta, G.; Balzano, F.; Caporusso, A. M.; Salvadori, P. *J. Org. Chem.* **1994**, *59*, 836−839. (b) Uccello-Barretta, G.; Balzano, F.; Caporusso, A. M.; Iodice, A.; Salvadori, P. *J. Org. Chem.* **1995**, *60*, 2227−2231. (c) Uccello-Barretta, G.; Balzano, F.; Salvadori, P.; Lazzaroni, R.; Caporusso, A. M.; Menicagli, R. *Enantiomer* **1996**, *1*, 365−375. (d) Salavdori, P.; Uccello-Barretta, G.; Lazzaroni, R.; Caporusso, A. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1121−1123. (e) Mannschreck, A.; Munninger, W.; Burgemeister, T.; Gore, J.; Cazes, B. *Tetrahedron* **1986**, *42*, 399−408. (f) Parker, D.; Taylor, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1781−1783. (g) Parker, D.; Taylor, R. J. *Tetrahedron* **1988**, *44*, 2241−2248.

10.1021/ol000335l CCC: $20.00

Scheme 1

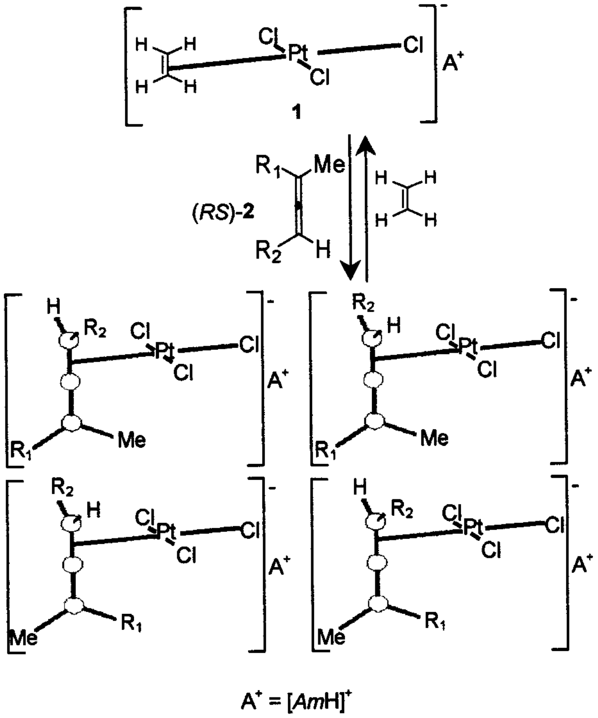


	R_1	R_2
2a	Bu^t	Br
2b	Bu^t	Ph
2c	Bu^t	o-OMePh
2d	Bu^t	p-OMePh
2e	Bu^t	p-FPh
2f	Bu^t	1-Np
2g	Bu^t	Bu^t
2h	Bu^t	$CH_2CH_2CH_2OH$
2i	Et	Bu^i
2j	Et	Ph

CDA and the unsaturated substrate in benzene and it can be driven very quickly to completion by removing the ethylene under vacuum. By using a very small excess of the CDA (CDA:**2** = 1:0.8) kinetic resolution phenomena are avoided. The complexes formed can be directly analyzed by ^{195}Pt NMR spectroscopy. The favorable properties of the nucleus observed ($I = 1/2$, natural abundance = 33.8%) allow us to record spectra suitable for the analyses in short instrumental times by using standard pulse sequences on a sample containing about 50−100 mg of the complex.

Taking into account that complexation of trisubstituted allenes occurs (Scheme 2) by the two prochiral faces of the less substituted double bond, the one bearing the hydrogen, each enantiomer can originate two diastereoisomers. Therefore, in the hypothesis that each of them produces a distinct platinum resonance, the enantiomeric composition of the mixture analyzed is obtained by comparing the areas of the signals produced by each enantiomer. For example, the complex originated by complexation of the racemic allene **2a** produced two well resolved ^{195}Pt resonances at −2391.7 and −2397.0 ppm (Table 1), having equal intensities (Figure 1). The complex containing enantiomerically enriched (*S*)-**2a**, having a known enantiomeric excess of 65% (determined by gas chromatographic analyses on CYDEX-B), showed a large prevalence of the signal at −2397.0 ppm and a minor signal at −2391.7 ppm, and the ratio between their integrated areas corresponded to the enantiomeric composition of the complexed allene. Therefore, the coordination of each enantiomer occurred with complete stereoselectivity and the two signals corresponded respectively to the two complexed enantiomers. Only two ^{195}Pt NMR signals have also been detected (Table 1) for the complexed racemic allenes **2b**−**h**, having a methyl and a *tert*-butyl group on the terminal quaternary carbon atom independently from the nature of

Scheme 2



A+ = [*Am*H]+

Table 1. ^{195}Pt NMR[a] of the Diastereoisomeric Mixtures Obtained by Using **1** as CDA and Trisubstituted Allenes **2**

allene	δ_S	δ_R	δ_S	δ_R
2a	−2397.0	−2391.7		
2b	−2432.8	−2424.8		
2c	−2438.1	−2434.1		
2d	−2412.7	−2404.6		
2e	−2426.7	−2416.9		
2f	−2455.2	−2449.7		
2g	−2444.1	−2439.7		
2h	−2553.5	−2534.9		
2i	−2531.6	−2528.6	−2507.6	−2505.3
2j	−2483.1	−2476.1	−2458.5	−2452.3

[a] NMR conditions: 64.3 MHz, C_6D_6, 25 °C. Chemical shifts (δ, ppm) are referred to Na_2PtCl_6 as external standard.

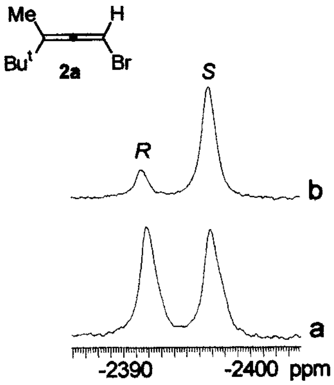


Figure 1. ^{195}Pt NMR analysis (64.3 MHz, C_6D_6, 25 °C, Na_2PtCl_6 as external standard) of the diastereoisomeric mixtures formed from **1** and (a) (*RS*)-**2a**, (b) (*S*)-**2a** (ee 65%).

the group on the less substituted double bond (an aromatic for **2b**−**f**, an alkyl for **2g**, a 3-hydroxypropyl for **2h**). The complexed (*R*)-enantiomers of **2a**−**h** produced platinum resonances high frequencies shifted with respect to those due to the corresponding (*S*)-enantiomers.

The same configurational correlation has been observed for **2i** and **2j**, in which the two substituents on the terminal quaternary carbon atom are a methyl and an ethyl. However, in these cases each complexed enantiomer produced two signals having different intensities, as a result of the fact that there is preferential complexation of one prochiral face of the double bond (the less substituted one) with respect to the other. Therefore, the enantiomeric purity of the complexed allene can be obtained by comparing the sum of the areas of the two signals produced by each enantiomer. As an example these resonances were at −2505.3 ppm (minor signal) and −2528.6 ppm (major signal) for (*R*)-**2i** and at −2507.6 ppm (minor signal) and −2531.6 ppm (major signal) for (*S*)-**2i** (Figure 2).

In conclusion, the use of CDA **1** for the derivatization of chiral trisubstituted allenes gives a simple and reliable method for their complete stereochemical characterization. This is an important result in view of the relevant role of this class of compounds in several fields of organic syntheses.[4]

The diastereoisomeric derivatives containing their enantiomers originate well separated ^{195}Pt NMR resonances. We have also found that, for all the substrates examined, the signals of the complexed (*R*)-enantiomers are shifted to higher frequencies with respect to those of complexed (*S*)-enantiomers. Therefore, the integration of the signals gives the enantiomeric purities and the determination of their relative positions the absolute configuration. The method is very practical since the procedures involved in the preparation of the CDA and its diastereoisomeric derivatives as well as their analyses are very simple and not time-consuming. Furthermore, both the CDA and the complexed allenes can be recovered by treating the diastereoisomeric derivatives with ethylene under pressure (Scheme 2). This empirical method, together with the previously reported[2a,b] one involving the use of β-permethylated cyclodextrin as a chiral solvating agent, constitutes one of the most efficient and versatile methods for the chiral analyses of trisubstituted allenes.

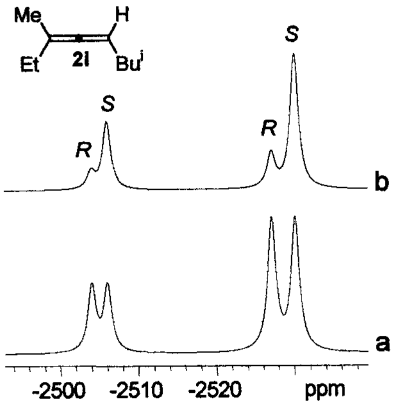


Figure 2. ^{195}Pt NMR analysis (64.3 MHz, C_6D_6, 25 °C, Na_2PtCl_6 as external standard) of the diastereoisomeric mixtures formed from **1** and (a) (*RS*)-**2i**, (b) (*S*)-**2i** (ee 66%).

Acknowledgment. This work was supported by the *Ministero della Ricerca Scientifica e Tecnologica* (*MURST*) and *CNR*, Italy.

Supporting Information Available: NMR characterization data of allenes. This material is available free of charge via the Internet at http://pubs.acs.org.

OL000335L

---

[3] (a) Uccello-Barretta, G.; Bernardini, R.; Lazzaroni, R.; Salvadori P. *Org. Lett.* **2000**, *2*, 1795−1798. (b) Uccello-Barretta, G.; Bernardini, R.; Balzano, F.; Salvadori P. *J. Org. Chem.* **2000**, in press.

[4] Schuster, H. F.; Coppola, G. H. *Allenes in oRganic Synthesis*; John Wiley & Sons: New York, 1984