



Variable-temperature one- and two-dimensional ^{13}C CP/MAS NMR studies of the dynamics of monohaptocyclopentadienyl rings of hafnium and titanium tetracyclopentadienyl in the solid state

Eric J. Munson ^{a,*}, Michelle C. Douskey ^a, Susan M. De Paul ^{b,1}, Marcia Ziegeweid ^{b,2}, Leonidas Phillips ^c, Frances Separovic ^d, Murray S. Davies ^c, Manuel J. Aroney ^c

^a Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455, USA

^b Department of Chemistry, University of California and Materials Sciences Division, EO Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^c School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

^d Department of Chemistry, University of Melbourne, Parkville, Melbourne, Vic 3052, Australia

Received 16 April 1998

Abstract

Organometallic compounds with cyclopentadienyl ligands (C_5H_5) can undergo fluxional motion. We have studied the Group IVB transition metal complexes of the formula $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$, where $\text{M} = \text{Ti}$ and Hf , in the solid state using variable-temperature ^{13}C CP/MAS NMR spectroscopy. We present data which indicate that intramolecular rearrangement proceeds via a sigmatropic shift. Using two-dimensional (2D) exchange NMR, we can follow the rearrangement of the single bonded cyclopentadienyl ligands. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 2D exchange spectroscopy; Fluxional organometallics; Solid-state NMR spectroscopy

1. Introduction

Fluxional motion in stereochemically nonrigid organometallic molecules has interested inorganic chemists ever since its discovery in $(\eta^1\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ by Piper and Wilkinson in 1956 [1]. Considerable effort has been invested in studying the fluxional motion of cyclopentadienyl rings σ -bonded to metal centers in solution [2] and in the solid state [3,4]. In these compounds, the ring has been observed to undergo either a ring flip or a sigmatropic rearrangement, which shifts the identity of the carbon atom

attached to the metal center [2]. This rearrangement may be well defined, such as a [1,2] or a [1,3] shift, or more random, such that either shift may occur with equal probability. Solution-state ^1H -NMR spectroscopy has been used extensively to determine the mechanism of exchange for monohaptocyclopentadienyl-containing compounds [2]. In the solid state, however, the problem is much more difficult, as strong dipole–dipole interactions make high-resolution ^1H -NMR extremely difficult and sites that are crystallographically inequivalent complicate peak assignments. Many of the NMR studies of fluxional motion of cyclopentadienyl groups in the solid state have primarily focused on determining the activation energy and not in determining the mechanism of reorientation [3]. Recently, two-dimensional (2D) exchange spectroscopy has been used to study fluxional motion in organometallic compounds in the solid state [5]. Two-

* Corresponding author. Fax: +1-612-6267541; e-mail: munson@chem.umn.edu

¹ Present address: Max-Planck-Institut fuer Polymerforschung, Postfach 3148, D-55021, Germany.

² Present address: Clorox Technical Center, 7200 Johnson Drive, Pleasanton, CA 94588, USA.

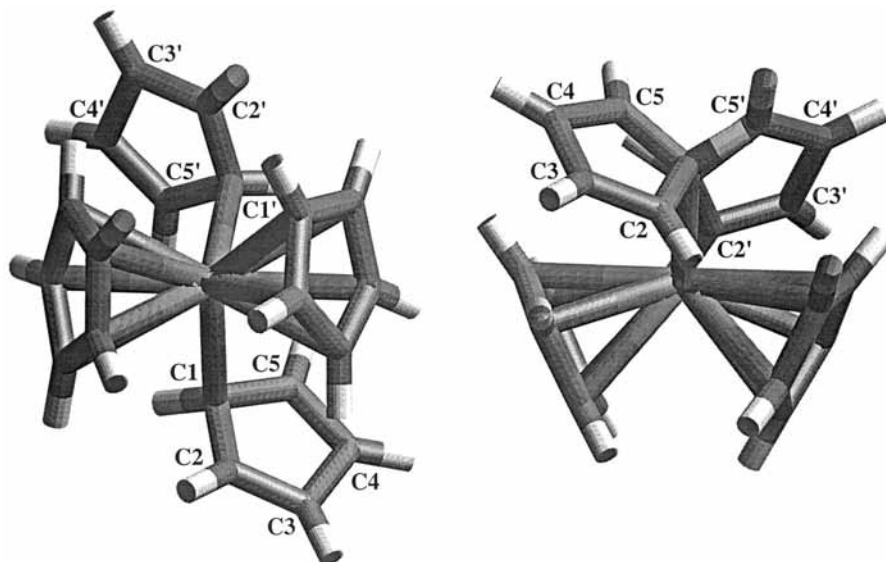


Fig. 1. Two representations of **1** ($M = \text{Hf}$) as obtained from X-ray structure determination [7]. The metal center atom resides on a crystallographic 2-fold axis. The spacegroup of **1** is $P\bar{4}2_1c$ with four molecules per unit cell. The structure of compound **2** ($M = \text{Ti}$) (not shown) is very similar [8]. The numbering scheme used in the figure is not unique.

dimensional experiments are desirable because they give information about all exchanging sites in the molecule simultaneously, in contrast to other magnetization transfer experiments which only provide information about exchange occurring from a specific site to another site [6].

In this communication we report variable-temperature (VT) 1D and 2D CP/MAS NMR spectra of $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ (**1**) and $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ (**2**). The structures of **1** ($M = \text{Hf}$) and **2** ($M = \text{Ti}$) are shown in Fig. 1 [7,8]. The 1D spectra of **2** have been reported previously [4]. One-dimensional NMR spectra showed sharp resonances for carbons in the monohapto groups in **1** and **2** at temperatures below ~ 190 K. At 298 K, no signals were observed from the monohapto groups, probably due to molecular motion interfering with the ^1H high power decoupling. This phenomenon is common in systems that undergo motion on the order of the decoupler frequency [9]. Two-dimensional exchange spectra of both compounds at showed that the rings underwent a sigmatropic rearrangement rather than ring flips, and that there were only two possible assignments for the carbon resonances. The final determination of the sigmatropic rearrangement mechanism will be possible when definitive peak assignments can be made.

2. Experimental

All syntheses were performed under an inert atmosphere using standard Schlenk-line and glove-box techniques. Sodium cyclopentadienide (Aldrich) was used as

received in a supersealed bottle under argon. All solvents were distilled from Na/benzophenone under a dry argon atmosphere. $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ was prepared from the reaction of $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$ (Aldrich) and $\text{Na}(\text{C}_5\text{H}_5)$ by the method of Rogers et al. [7]. Similarly, $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ was prepared from the reaction of $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$ (Aldrich) and $\text{Na}(\text{C}_5\text{H}_5)$ by the method of Calderon et al. [8]. All NMR experiments were performed on either a Chemagnetics CMX 300MHz spectrometer operating at 75.4 MHz for ^{13}C or on a home-built 300MHz spectrometer utilizing a Tecmag data acquisition system and operating at 75.4 MHz for ^{13}C .

3. Results and discussion

The variable-temperature ^{13}C CP/MAS NMR spectra of $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ (**1**) are shown in Fig. 2. From Fig. 1, it is apparent that the carbon site pairs in the two $\eta^1\text{-C}_5\text{H}_5$ rings are magnetically equivalent. Therefore, C1 and C1' will now collectively be referred to as the C1 site. At 173 K, five peaks are evident. The largest peak at 113.0 ppm is due to carbons in the $\eta^5\text{-C}_5\text{H}_5$ rings. The four resonances at 90.0, 126.5, 127.9, and 130.7 ppm are assigned to the $\eta^1\text{-C}_5\text{H}_5$ rings. Because the four resonances all have approximately equal integrated intensity, a fifth resonance for the $\eta^1\text{-C}_5\text{H}_5$ group is likely hidden under the $\eta^5\text{-C}_5\text{H}_5$ resonance. Two-dimensional results confirm this (vide infra). Upon heating from 173 K, the peaks for the $\eta^1\text{-C}_5\text{H}_5$ groups began to broaden and then coalesce, indicating that chemical exchange is occurring on the

NMR timescale. Although the spectra are not shown, we obtained similar results for the analogous titanium compound as reported in the literature [4].

Shown in Fig. 3(a) is the 2D exchange spectrum of $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ acquired at 188 K with a mixing time of 50 ms. Several conclusions about peak assignments and the dominant mechanism for rearrangement can be drawn from the location and intensity of the cross peaks in the spectrum. First, the presence of a cross peak between the large peak at 113.0 ppm and the peaks at 90.0 and 126.5 ppm, but not the peaks at 127.9 and 130.7 ppm, indicates that one of the carbon resonances of the $\eta^1\text{-C}_5\text{H}_5$ groups is hidden underneath the $\eta^5\text{-C}_5\text{H}_5$ resonance. Second, ring exchange between the monohapto and pentahapto groups as the dominant rearrangement mechanism at this temperature is ruled out by the absence of cross peaks between the 113.0 ppm and the 127.9/130.7 ppm resonances. Third, the presence of cross peaks between the 90.0 ppm resonance (due to the carbon bound to the metal center) [10] and the peaks at 113.0 and 130.7 ppm indicates that the primary rearrangement mechanism is not ring flips, because the carbon attached to the metal center would not exchange positions during a ring flip. When a longer mixing time (200 ms) was employed to allow multiple exchanges to occur, cross peaks were observed between all of the monohapto

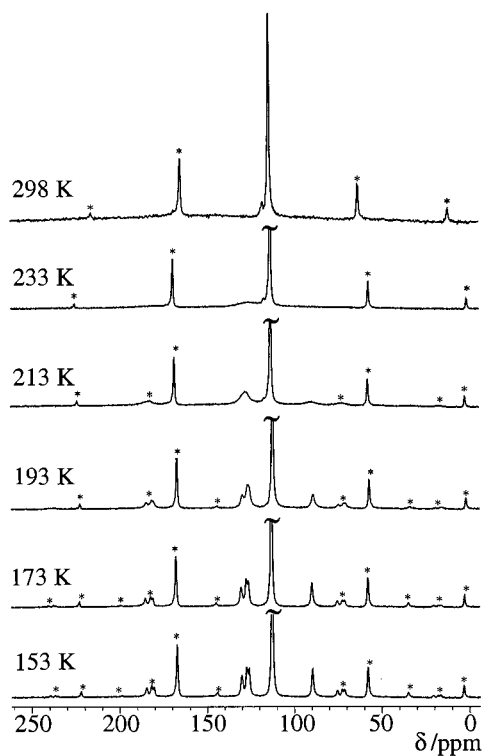


Fig. 2. Variable temperature ^{13}C CP/MAS NMR spectra of for $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$. The isotropic peak for $\eta^5\text{-C}_5\text{H}_5$ is plotted to the same height in each spectrum but is truncated in these plots. Asterisks are used to denote spinning sidebands.

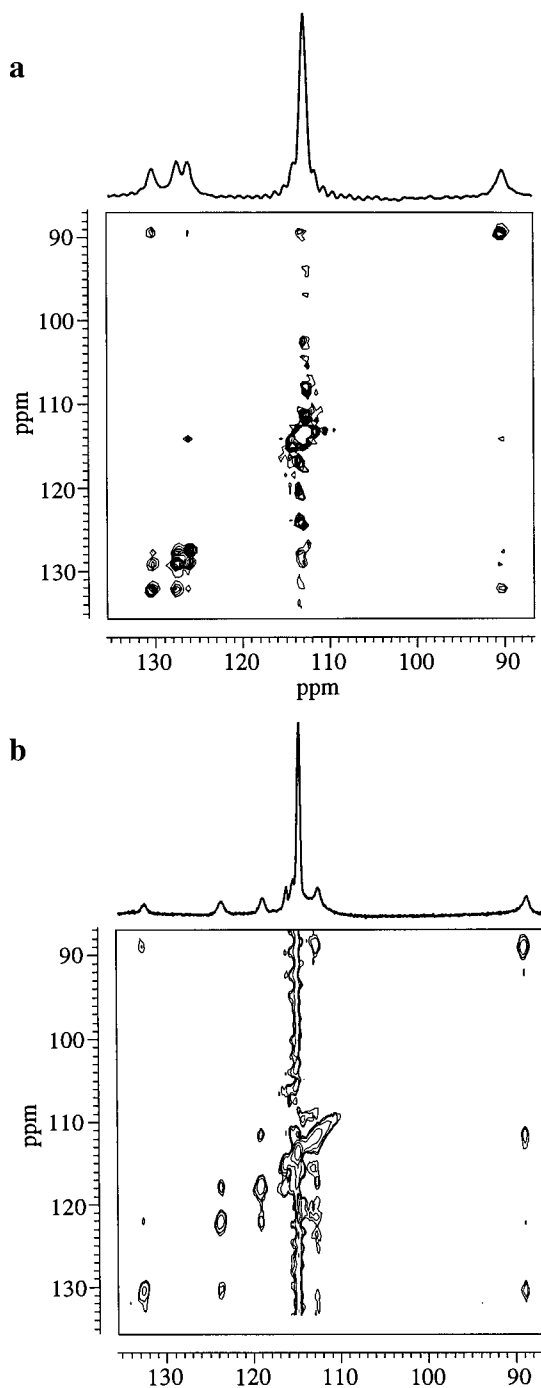


Fig. 3. (a) 2D 75.739 MHz ^{13}C CP/MAS exchange spectrum of $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ at $T = 188$ K. The size of the data matrix was 128×256 before zero filling. The mixing time was 50 ms. The cross peaks indicate exchange between the resonances at 90.0 and 113.0, 113.0 and 126.5, 126.5 and 127.9, and 127.9 and 130.7 ppm. Cross peaks between the resonances at 90.0 and 113.0 ppm, and at 113.0 and 126.5 ppm, are more intense than indicated in the spectrum due to a negative intensity ridge at 113 ppm. (b) 2D 75.425 MHz ^{13}C CP/MAS exchange spectrum of for $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ at $T = 183$ K. The size of the data matrix was 32×256 before zero filling. The mixing time was 50 ms. The cross peaks indicate exchange between resonances at 89.5 and 115.3, 115.3 and 122.1, 122.1 and 127.2, 127.2 and 136.5 ppm. In both spectra, t_1 noise is associated with the large pentahapto resonance.

resonances (spectrum not shown). This further indicates that the rearrangement mechanism was not ring flips. Fourth, the absence of equal intensity cross peaks between all of the sites in Fig. 3(a) ruled out a sigmatropic rearrangement mechanism based upon either random shifts or an equal probability of [1,2] and [1,3] sigmatropic rearrangements. We therefore conclude that the dominant mechanism is either a [1,2] or [1,3] sigmatropic rearrangement.

Shown in Fig. 3(b) is the 2D exchange spectrum of $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$. In the 1D spectrum a large peak was observed at about 117.6 ppm, which is attributed to the $\eta^5\text{-C}_5\text{H}_5$ carbons. It is clear that there is a correspondence in pattern of cross peaks of compounds **1** and **2**, and that all of the conclusions drawn for $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ can also be made for $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$. The slight discrepancies in the chemical shifts of the carbons in **1** and **2** are probably due, in part, to the differences in the packing geometry of the compounds.

Fig. 4 is a schematic diagram of the cross peak patterns observed for the 2D NMR spectra acquired for compounds **1** and **2**. Cross peaks exist between the resonances of the carbon atoms on the monohaptocyclopentadienyl groups. Because the 2D results have shown unambiguously that the shift mechanism is a sigmatropic rearrangement, the cross peaks must correspond to one shift or rearrangement of the monohaptocyclopentadienyl groups. A connectivity pattern between the peaks has been established that validates such a rearrangement.

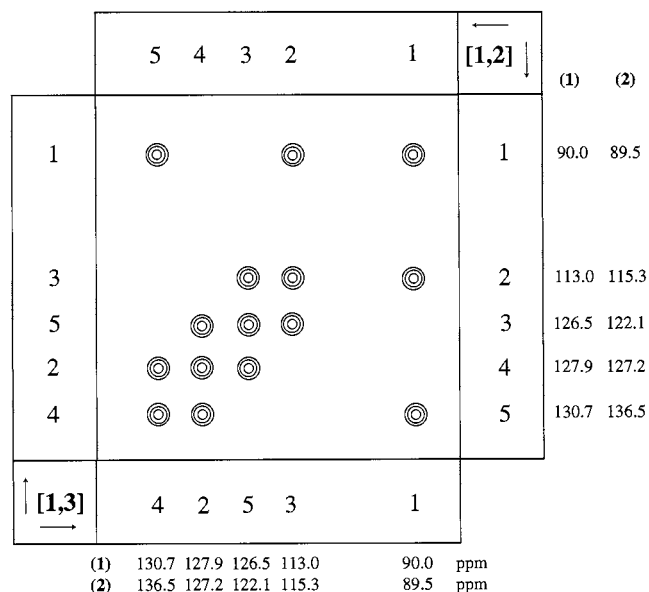


Fig. 4. Diagram shows a schematic of the cross peak patterns observed for the 2D exchange experiments for $\text{Hf}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ (**1**) and $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ (**2**). The corresponding chemical shifts for the monohaptocyclopentadiene groups of compounds **1** and **2** are shown on the lower and right axes. Both [1,2] and [1,3] shift mechanisms are shown.

Given that the resonance at ca. 90 ppm is the carbon attached to the metal center, an assignment of the peaks can be made which justifies either a [1,2] or [1,3] shift. Fig. 4 illustrates both possibilities, showing which chemical shift assignments would give rise to each of the two shift mechanisms.

It is interesting to compare our results with a previous solid-state NMR study of $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2$ [4]. In that study, the peak at ca. 90 ppm (assigned to C1 in this study) was also assigned to the carbon of the $\eta^1\text{-C}_5\text{H}_5$ that is attached to the metal center. The four remaining resonances at 114.9, 121.8, 126.8 and 136.3 ppm were assigned to carbons C3, C4, C2, and C5, respectively, based on chemical shift anisotropy (CSA) tensors for each of the resonances and comparisons to solution-state NMR data of related compounds. Magnetization transfer experiments were then used to elucidate the mechanism of rearrangement. From these results the authors concluded that the [1,2] shift mechanism was predominant. However, these chemical shift assignments are inconsistent with our 2D exchange results [4].

We have shown that the rearrangement mechanism of the monohaptocyclopentadienyl groups in these compounds proceeds via a single sigmatropic rearrangement. Our results indicate that the mechanism must be that of a [1,2] or a [1,3] shift. We are confident in our 2D exchange results because the data do not require one to make assumptions about chemical shifts. Future areas of work include establishing the correct assignments of the $\eta^1\text{-C}_5\text{H}_5$ resonances by determining connectivity between neighboring carbons as is done in an INADEQUATE experiment. We are currently synthesizing ^{13}C labeled **1** containing $^{13}\text{C}\text{-}^{13}\text{C}$ pairs in order to perform a 2D experiment in which spin-spin exchange between neighboring carbons is monitored rather than chemical exchange. These results should provide the definitive evidence required to correctly assign the peaks.

Acknowledgements

We are very grateful to Professor Alexander Pines for his advice and encouragement of this work. We would also like to thank Professor Jerry L. Atwood for X-ray crystal structure data, and Drs Matthias Ernst, Jonathan Jones, Andrew Kolbert, Russell Larsen, Klaus Schmidt-Rohr, and Jay Shore for helpful suggestions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the US Department of Energy under contract no. DE-AC03-76SF00098, and by the University of Minnesota. S.M. De Paul thanks the National Science Foundation for a graduate fellowship.

References

- [1] (a) T.S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.* 3 (1956) 32. (b) T.S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.* 3 (1956) 104.
- [2] (a) F.A. Cotton, *Acc. Chem. Res.* 1 (1968) 257. (b) F.A. Cotton, in: *Dynamic Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1975.
- [3] (a) A.J. Campbell, C.E. Cottrell, C.A. Fyfe, K.R. Jeffrey, *Inorg. Chem.* 16 (1976) 1326. (b) A.J. Campbell, C.A. Fyfe, R.G. Goel, E. Maslowsky, C.V. Senoff, *J. Am. Chem. Soc.* 94 (1972) 8387.
- [4] S.J. Heyes, C.M. Dobson, *J. Am. Chem. Soc.* 113 (1991) 463.
- [5] (a) J. Kummerlen, A. Sebal, *J. Am. Chem. Soc.* 115 (1993) 1134. (b) R. Benn, H. Grondey, R. Nolte, G. Erker, *Organometallics* 7 (1988) 777. (c) R. Benn, R. Mynott, I. Topalovic, F. Scott, *Organometallics* 10 (1989) 2299. (d) R. Benn, H. Grondey, G. Erker, R. Aul, R. Nolte, *Organometallics* 9 (1990) 2493.
- [6] (a) K. Takegoshi, C.A. McDowell, *J. Am. Chem. Soc.* 108 (1986) 6852. (b) C. Conner, A. Naito, K. Takegoshi, C.A. McDowell, *Chem. Phys. Lett.* 113 (1985) 123.
- [7] R.D. Rogers, R. Vann Bynum, J.L. Atwood, *J. Am. Chem. Soc.* 103 (1981) 692.
- [8] J.L. Calderon, F.A. Cotton, J. Takats, *J. Am. Chem. Soc.* 93 (1971) 3587.
- [9] W.P. Rothwell, J.S. Waugh, *J. Chem. Phys.* 74 (1981) 2721.
- [10] The assignment of the resonance at 90.0 ppm to the atom σ -bonded to the metal center is a reasonable assumption given that it is the only sp^3 hybridized carbon in the cyclopentadienyl ring and that sp^2 hybridized carbons typically resonate above 100 ppm.