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Ferrocenes derived from isodicyclopentadiene and tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene

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Abstract

The ferrocene derivatives of isodicyclopentadiene and tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene were synthesized and studied by 2D ^{1}H NMR (COSY and NOESY). The results of the studies indicated the presence of all possible isomers (*exo,exo, exo,endo,* and *endo,endo*) in each case, although the *exo,exo* isomeric distribution was favored for each compound. This contrasts somewhat with the findings in earlier studies which predicts the *exo,exo* isomers to be the sole species formed from these cyclopentadienyl ligands.

Introduction

Recent interest in our group has focused on the synthesis and subsequent reactions of functionalized η^5-cyclopentadienylmetal compounds, because of their potential use as monomers in polymerization reactions, crosslinking agents, and polymer-bound catalysts. Paquette and coworkers have reported the results of research on ferrocene complexes of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene [1,2], which meets our criteria for further investigation of reactions of the double bond on the norbornene ring.

These compounds were initially prepared by Paquette's group to determine their structures, and so to provide evidence for electronic control of stereochemistry. Thus, even though the methano bridge provides greater steric hindrance than the ethano bridge, the ferrocene compounds derived from isodicyclopentadiene and tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene both are of the *exo,exo* configuration (compounds **1** and **2**, respectively).

This result is expected from INDO calculations, which predict that the high lying norbornyl σ-orbitals in isodicyclopentadiene are strongly coupled to π-orbitals in the cyclopentadienide part of the molecule. The effect of this orbital mixing is disrotatory tilting of the peripheral lobes toward the methano bridge, and metal complexation toward the *exo* face of the cyclopentadienide portion of the molecule should be favored [1].

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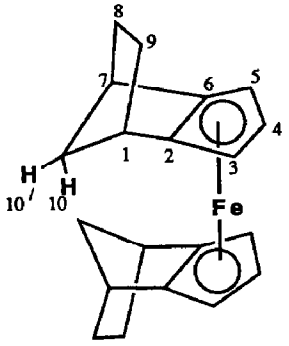
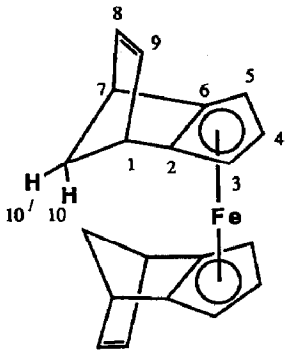


(1)



(2)

Their method of preparation of compounds **1** and **2** involved the reaction of $Fe(acac)_2py_2$ with the organic ligand and ethylmagnesium bromide. The reactions were carried out in xylene solution (2 days at 20 °C and 1 h at 65 °C) resulting in conversions to single ferrocenes in 33% yield of compound **1** and 17% yield of compound **2**. In neither case were the *exo,endo* or *endo,endo* isomers observed.

Our method of preparation yielded 72.6% of compound **2**, and upon investigation by NMR spectrometry of the structure of **2**, the existence of all three isomers of **2** was evident. This result prompted the preparation by our methods of compound **1**, which was achieved in 64.6% yield; once again, the presence of all three isomers was evident by NMR studies.

Experimental

Starting materials and solvents

Benzene (reagent) and tetrahydrofuran were purchased from Fisher, refluxed over sodium/benzophenone, and distilled under nitrogen before used. Ether (Fisher) was used as received. Anhydrous ferrous chloride was obtained from Alfa Inorganics, and used as received. n-Butyllithium was purchased from Alfa Products as a 22%, 2.4 *M* solution in hexanes.

Tricyclo[5.2.1.$0^{2,6}$]deca-2,5,8-triene was synthesized according to literature methods [3] (m.p. 43–44 °C lit., 44 °C), as was isodicyclopentadiene [4]. Elemental analyses and NMR spectra were consistent with the formulations and reported spectroscopic data, respectively.

Physical methods

^{1}H NMR spectra were collected on a Varian VXR 300 MHz spectrometer. Two dimensional NMR studies in the form of homonuclear correlation spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY) were carried out to elucidate the isomeric forms of the compounds prepared in this work.

Proton 1D-NMR spectra were collected with a 5600 Hz spectral window 2.93 s acquisition time, 6.0 μs (30 degrees) pulse width, and 0 s relaxation delay. The data were weighted with increasing exponential and Gaussian smoothing functions for

resolution enhancement, and zero filled to 128k points before Fourier transformation. Spectra were referenced relative to the residual proton signals of $CHCl_3$ (7.25 ppm) in the $CDCl_3$ lock solvent.

All two dimensional COSY [5] and NOESY [6] NMR spectra were obtained with phase sensitive detection according to the method of States et al. [7]. 2D-NMR symmetrization techniques were not used for any of the spectra collected. COSY spectra were obtained using 19 μs 90° pulses, 3000 Hz spectral window, 0.17 s acquisition time, a 1 s relaxation delay, and 16 transients were collected for each of 512 t_1 increments. The COSY data were weighted with a shifted sinebell function and zero filled to 2k × 2k points before Fourier transformation. NOESY spectra were obtained using 19 μs 90° pulses, 1700 Hz spectral window, 0.59 s acquisition time, 1.0 s relaxation delay, 2.5 s mixing time, and 48 transients were averaged for each of 256 t_1 increments. The NOESY data were weighted with a shifted sinebell and zero filled to 4k × 1k points before Fourier Transformation.

Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were carried out by Midwest Microlab, Indianapolis, IN.

Preparation of the ferrocenes

Synthesis of bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trien-4-yl)iron (2). A solution of 1 g (7.6 mmol) of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene in 3.3 ml THF under a dry

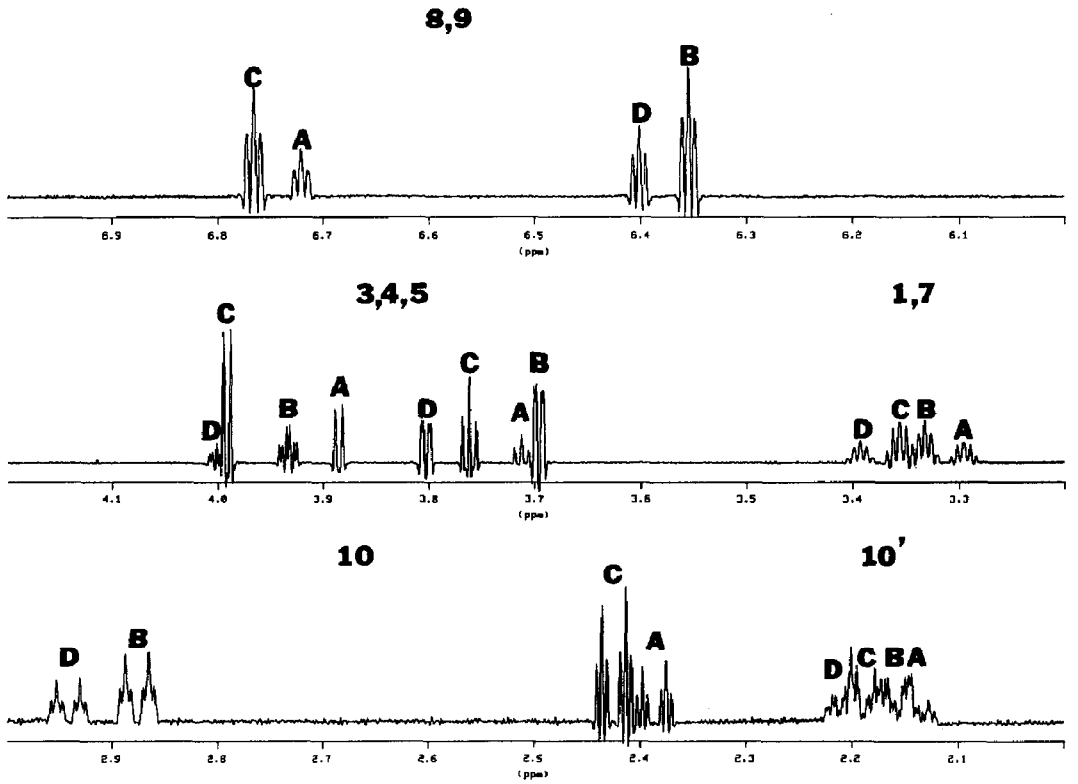


Fig. 1. 300 MHz proton NMR spectrum from a mixture of *exo,exo*-**2**, *exo,endo*-**2** and *endo,endo*-**2**. The resonances from each of the chemically nonequivalent ligand species are labelled A, B, C, and D.

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nitrogen atmosphere was treated dropwise at −78 °C with n-butyllithium in hexane (3.4 ml, 8.1 mmol). The reaction mixture was stirred at −78 °C for 0.5 h, and allowed to warm to room temperature gradually. The solution was then cooled to −78 °C and added slowly to a solution of anhydrous $FeCl_2$ (0.49 g, 3.86 mmol) in 4 ml of benzene. This solution was stirred magnetically for 20 min at 15 °C and a further 20 min at room temperature. The reaction mixture was then poured into 500 ml of rapidly stirred cold water. The organometallic compound was extracted with ether, washed with water, and dried over anhydrous sodium sulfate. The pure ferrocene was obtained after the solvent was stripped and the residue was dried under high vacuum (0.88 g, 72.6% yield). Found: C, 76.21; H, 5.77. $C_{20}H_{18}Fe$ calc.: C, 76.47; H, 5.74%.

Synthesis of bis(η^5-isodicyclopentadienyl)iron (1). In this procedure, which was identical in reaction conditions to that described above, 1 g (7.58 mmol) of isodicyclopentadiene was used with 0.49 g (3.85 mmol) of $FeCl_2$ to obtain 0.79 g (64.6% yield) of the ferrocene. Found; C, 75.49; H, 6.97. $C_{20}H_{22}Fe$ calc.: C, 75.51; H, 6.92%.

Attempted separation of the isomers. NMR spectra of the analytically pure compounds **1** and **2** indicated the presence of all possible isomers in each sample. Column chromatography of the compounds on silicon gel afforded no separation. Therefore, compounds **1** and **2** were subjected to selective crystallization techniques from warm acetone, wherein a sufficient amount of acetone was added to completely dissolve the samples, and the solutions were concentrated at 50 °C under high vacuum. The solutions were placed in a freezer overnight whereupon a crop of crystals of exclusively the *exo,exo* isomer was obtained in each case. A second crop of *exo,exo* isomers could be obtained by repeating the process. An NMR spectrum of the mother liquor indicated that in each case, all three isomers were still evident, although the signals due to the *exo,exo* isomers were significantly reduced.

Results and discussion

The 300 MHz proton spectrum of **2** is shown in Fig. 1. The contour plots of the COSY spectrum from this sample shown in Fig. 2 permitted us to assign the resonances of four chemically nonequivalent ligand species **A**, **B**, **C**, and **D**. The set of resonances from ligand **D** are consistent with those reported by Paquette for the *exo,exo* isomer of **2**. The COSY spectra do not provide evidence that the resonance from **B** and **C** are from chemically nonequivalent *exo*- and *endo*-coordinated ligands attached to the same disubstituted metal atom. NOESY spectra were used to obtain evidence that resonances **B** and **C** are from *exo,endo*-**2** and that resonances **A** arise from *endo,endo*-**2**.

If the two sets of proton resonances **B** and **C** are from chemically nonequivalent ligands bound to the same metal, H–H dipolar interactions between ligand fragments should produce cross peaks between the corresponding proton resonances in the 2D NOESY spectra. Specifically, H(3,5) of the *exo,endo* ligand should show cross peaks to two sets of H(1,7) resonances (those on the same ligand, and those on a second chemically nonequivalent ligand); these two cross peaks are seen between C(3,5) and B(1,7)/C(1,7) in Fig. 3a. Other H(3,5) resonances exhibit only a single cross peak to the H(1,7) region. This identifies **C** as the *endo*-coordinated triene ligand of the *exo,endo*-**2**. Similarly, other cross peaks can be observed to confirm

this assignment. All H(8,9) proton signals will produce one set of cross peaks to neighboring protons H(1,7) but only the *exo,endo* H(8,9) will show an extra cross peak to *exo,endo* H(1,7) (C(8,9) to B(1,7) and C(1,7) in Fig. 3b). Only resonances from *exo*(3,4,5) or *endo*(3,4,5) ligand protons can exhibit cross peaks to *endo* H(8,9) protons (**C**(8,9) to **B**(3,5) and **B**(4) in Fig. 3c); and only signals from *endo* H(8,9) ligand protons can produce cross peaks with resonances from *exo* H(10) ligand protons (**C**(8,9) to **B**(10) and **C**(10) in Fig. 3d). Signals from *endo*(3,4,5) or *exo*(3,4,5) ligands of **2** will only produce cross peaks with H(10) of *exo*-coordinated ligands (Fig. 3e). This evidence identifies the sets of resonances **B** and **C** as those arising from the *exo*- and *endo*-coordinated triene ligands of *exo,endo*-**2**. The relative shifts of the protons are also consistent with these assignments when the shielding anisotropy of the norbornene double bond is taken into consideration: the *endo* complexed triene should shield the 3,5 protons of the second ligand on the metal ion (*exo,endo* H(3,5) and *endo,endo* H(3,5)), and *exo*-complexed ligands should have H(10) signals shifted downfield due to the deshielding effect of the second ligand's Cp ring. The H(10′), proton resonances should be relatively insensitive to the stereochemistry of ligand substitution.

Since the *exo,endo*-**2** can be identified conclusively from the above evidence, the additional cross peak from **A**(3,5) to **A**(8,9) in Fig. 3c permits us to assign isomer **A** as *endo,endo*-**2**. This cross peak cannot arise from intraligand H–H dipolar interactions and can only result from interligand interactions between *endo*-coordinated triene ligands. Similarly, the additional cross peaks between *D*(10) and *D*(3,4,5) in Fig. 3e permit us to confirm the assignments of the **D** resonances as those of *exo,exo*-**2** as made by Paquette. Table 1 summarizes the resonance assignments of **1** and **2**.

Recrystallization of compound **2** (1.0 g) afforded 0.44 g of the *exo,exo* isomer as pure crystals. Investigation of the mother liquor by integration of the NMR signals arising from corresponding protons of the three isomers indicated the following approximate distribution of isomers in the original product: 50% *exo,exo*; 33% *exo,endo*; and 17% *endo,endo*. A statistical distribution of isomers would be 50% *exo,endo*, and 25% of each of the other two isomers. Thus, while formation of the *exo,exo* isomer is clearly favored in this synthesis, it is by no means exclusive. This contrasts somewhat with the findings of Paquette et al., who obtained exclusively the *exo,exo* isomer [1,2].

These findings prompted a study on the bis(isodicyclopentadiene) compound **1**. When subjected to the same techniques of recrystallization as with **2**, only the *exo,exo* isomer was obtained separated from the other two. The distribution of isomers in the original mixture, estimated from the amount of isolated crystals and integration of the proton signals from the compounds remaining in the mother liquor was approximately: 75% *exo,exo*; 18% *exo,endo*; and 7% *endo,endo*. Once again, the *exo,exo* form is highly favored, but not to the total exclusion of the other isomers.

The isomers of compound **1** are not of equal thermal stability. We observed that during the crystallization process, the *exo,endo* and *endo,endo* isomers decomposed. Further investigation showed that in solution, even in benzene at 4°C, these two isomers slowly decomposed. This probably accounts for the fact that Paquette et al. isolated only the *exo,exo* isomer, since their preparation involved prolonged reaction times in solution.

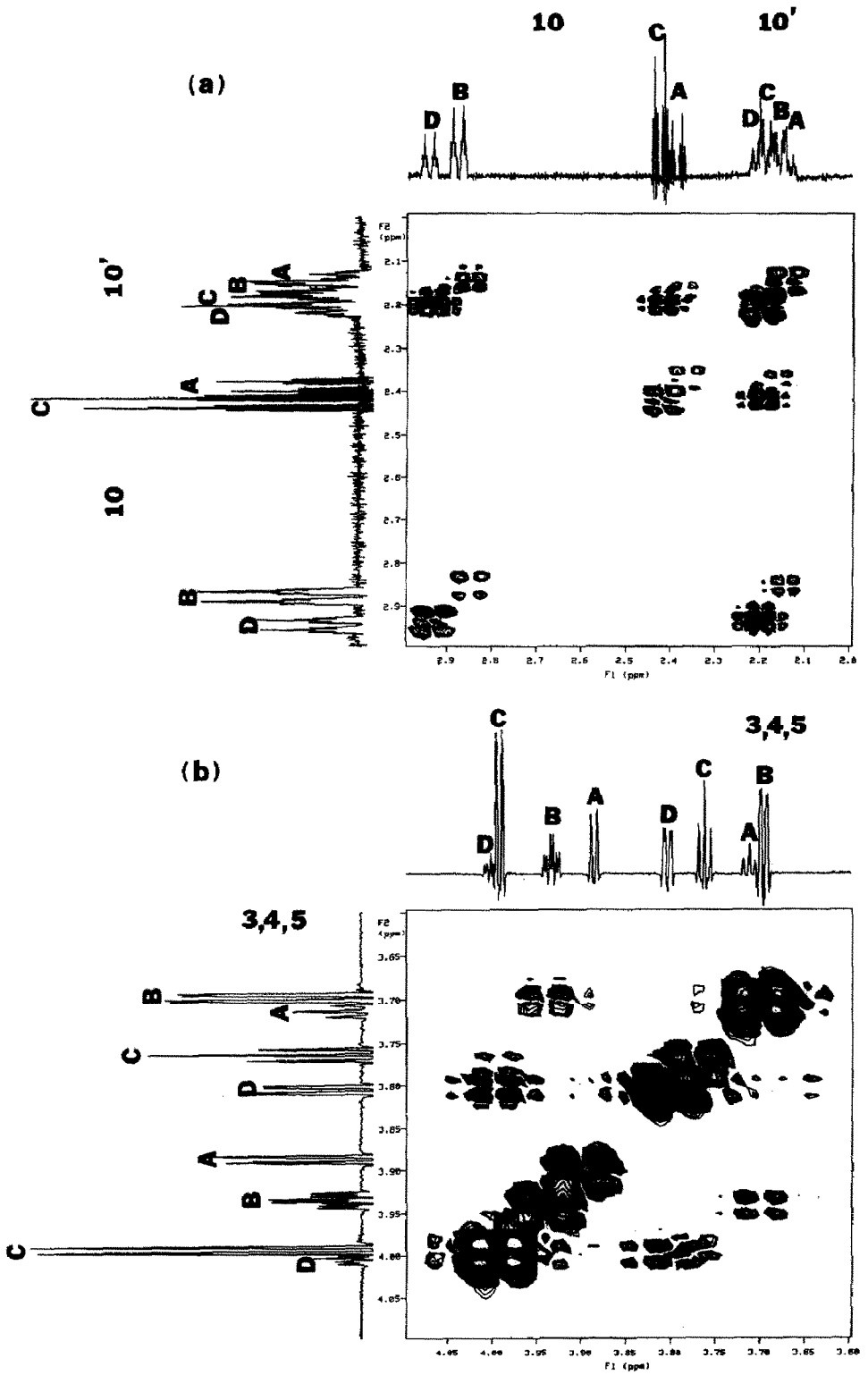

Fig. 2. Excerpts from the 300 MHz COSY spectrum of a mixture of *exo,exo*-**2**, *exo,endo*-**2** and *endo,endo*-**2**. These expansions show details of the *J*-coupling interactions between protons in the various regions for chemically nonequivalent ligands A, B, C, and D: (a) H(10)/H(10); (b) H(3,4,5)/H(3,4,5); (c) H(1,7)/H(8,9); (d) H(10′)/H(1,7).

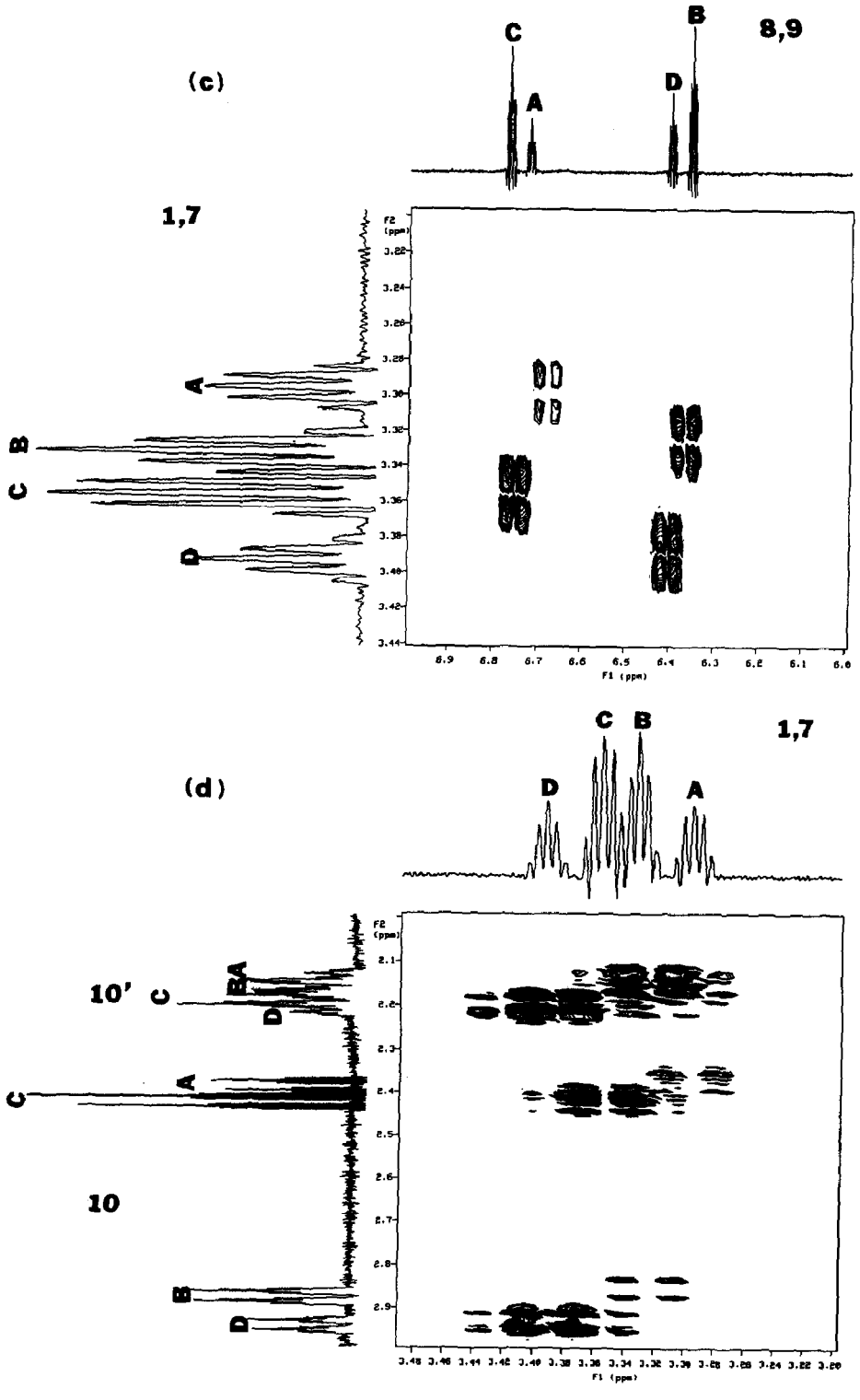

Fig. 2 (continued).

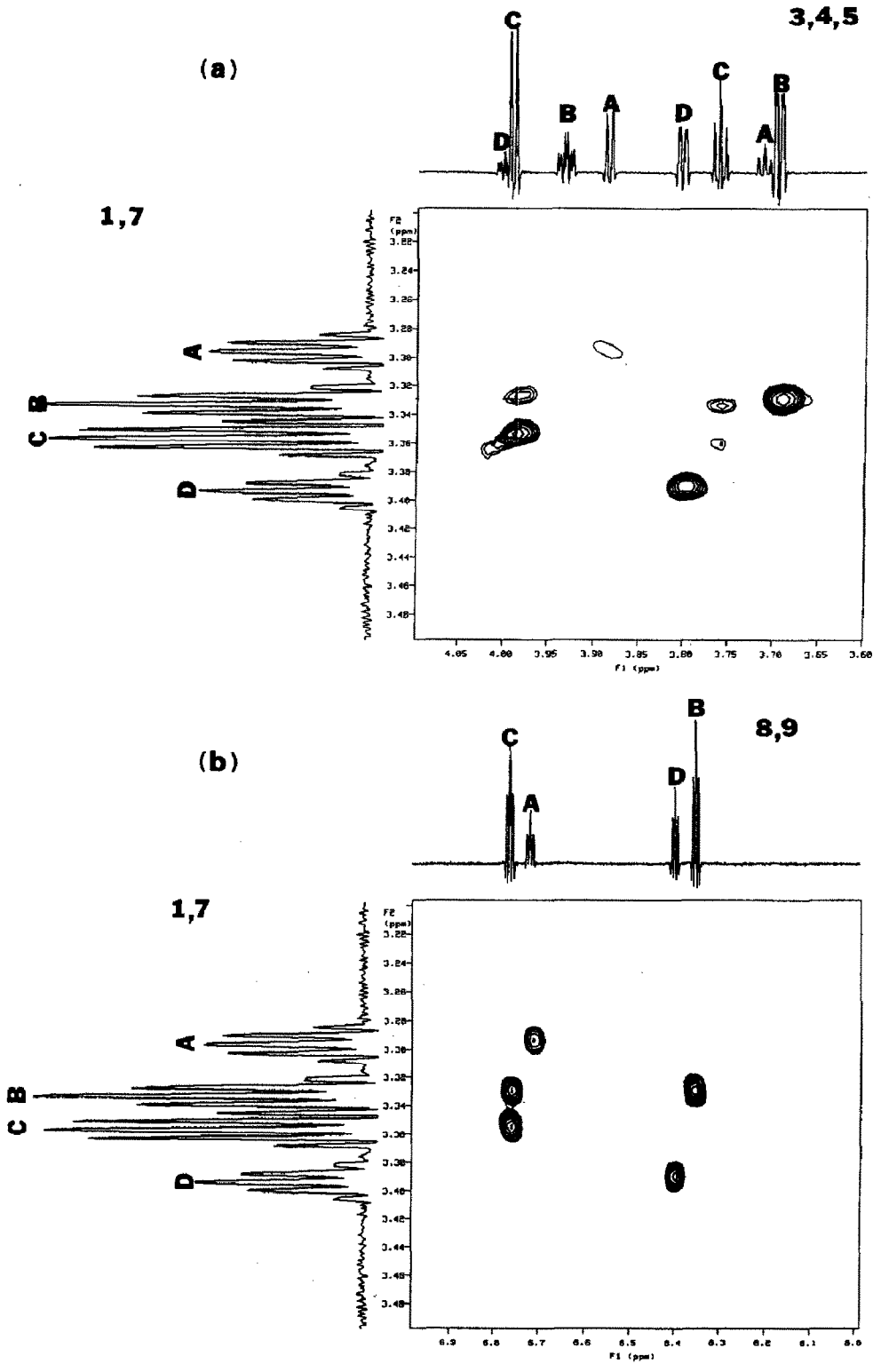

Fig. 3. Excerpts from the 300 MHz NOESY spectrum from a mixture of *exo,exo*-2, *exo,endo*-2, and *endo,endo*-2. These expansions show details of through space dipole–dipole interactions (1–3 Å) between protons in the various regions: (a) H(1,7)/H(3,4,5); (b) H(1,7)/H(8,9); (c) H(8,9)/H(3,4,5); (d) H(8,9)/H(10,10′); (e) H(3,4,5,)/H(10,10′).

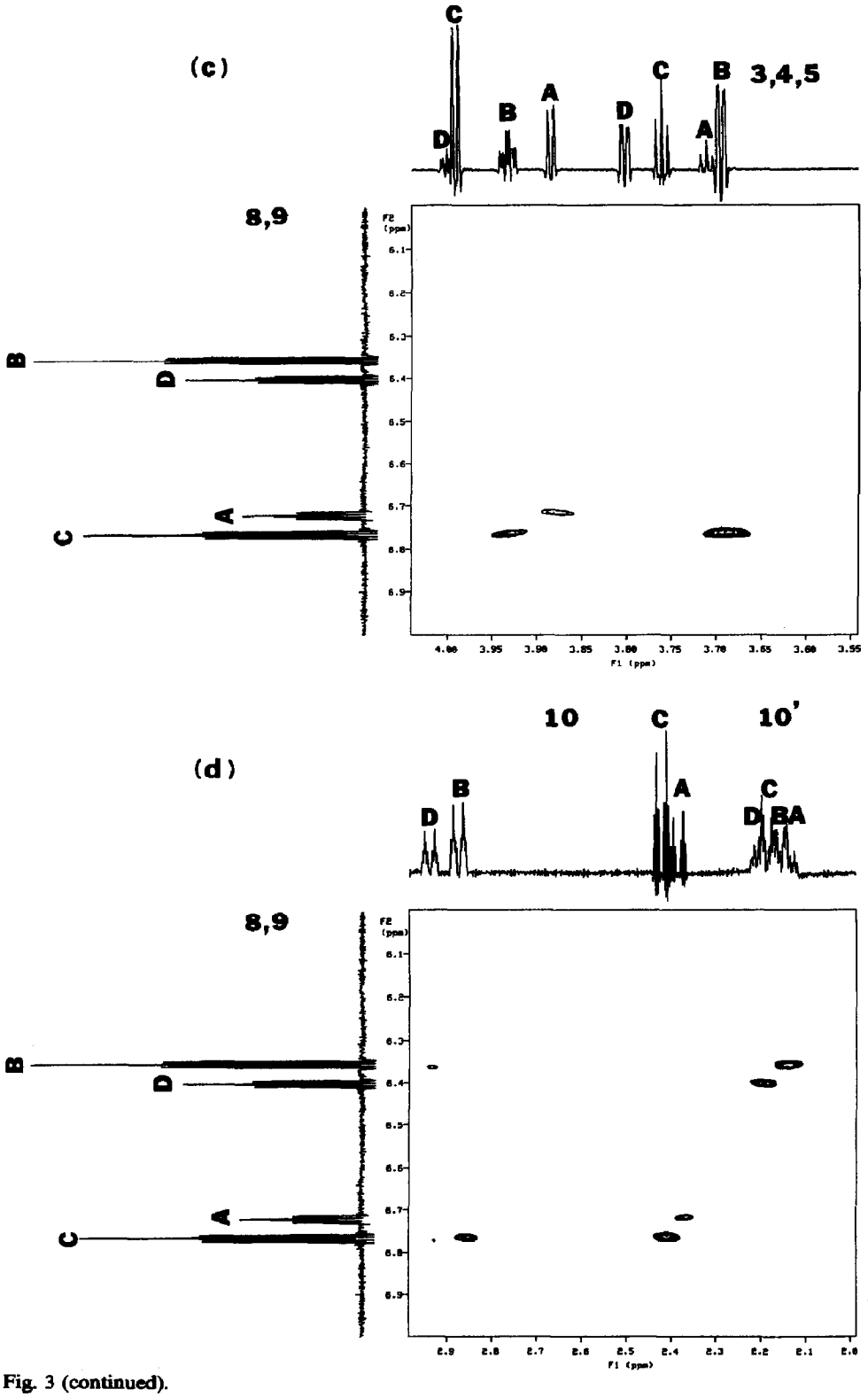

Fig. 3 (continued).

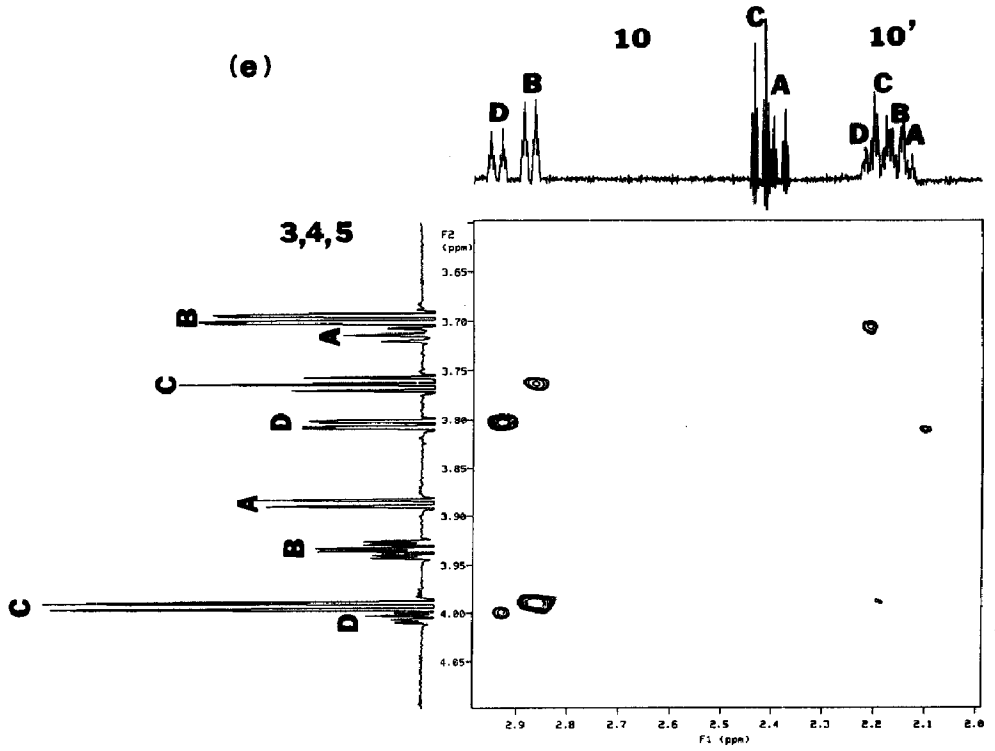

Fig. 3 (continued).

Table 1 ^{1}H chemical shift assignments of **1** and **2** [a]

Compound	Ligand	^{1}H Assignment						
		H(1,7)	H(3,5)	H(4)	H(8,9)*exo*	H(8,9)*endo*	H(10)	H(10′)
exo,exo-**1**	*exo*	2.84	3.70	3.91	1.69	0.96	2.30	1.36
		(q–)	(d2.1)	(–)	(–)	(d2.5,5.1,–)	(–)	(d8.3,–)
exo,endo-**1**	*exo*	2.05	3.95	3.80	1.67	0.94	2.22	1.34
		(–)	(–)	(t–)	(–)	(d2.2,5.4,–)	(–)	(d8.3,–)
	endo	2.74	3.87	3.75	1.80	1.68	2.10	1.73
		(–)	(d1.7)	(–)	(–)	(–)	(–)	(–)
endo,endo-**1**	*endo*	2.84	3.75	3.95	[b]	[b]	[b]	[b]
		(q–)	(d2.1)	(–)				
exo,exo-**2**	*exo*	3.38	3.80	3.99	6.39		2.94	2.20
		(p1.7)	d2.1)	(t2.1,d0.7)	(t1.7)		(d6.7,t1.4)	(–)
exo,endo-**2**	*exo*	3.32	3.69	3.93	6.35		2.86	2.15
		(p1.7)	(d2.0)	(t2.0,d0.75)	(t1.8)		(d6.7,t1.4)	(–)
	endo	3.35	3.98	3.7	6.76		2.42	2.18
		(p1.7)	(d2.0)	(t2.0)	(t.19)		(d6.8,t1.5)	(–)
endo,endo-**2**	*endo*	3.29	3.88	3.70	6.71		2.38	2.12
		(p1.7)	(d2.0)	(t2.0)	(t1.9)		(d6.7,t1.5)	(–)

[a] Resonance assignments for **1** are based on COSY spectra and the 1D ^{1}H spectrum from a sample of > 90% *exo,exo*-**1**. Resonance assignments for **2** are based on the COSY and NOESY 2D NMR spectra. Shifts are reported relative to the signal from residual $CHCl_3$ in the $CDCl_3$ solvent. Values in parentheses are resolved *J* couplings (Hz) ± 0.1; a dash in parentheses indicates additional coupling which could not be measured. [b] These resonances are obscured by signals from the other three chemically nonequivalent ligands in the isomer mixture, and could not be assigned.

Compound **2** was hydrogenated in 88% yield using 10% Pd on charcoal as the catalyst. The distribution of isomers of the resulting compound **1** was the same as that of compound **2**, but in solution, only the *exo,exo* isomer remained stable, while the others slowly decomposed. The isomers of **2** were subjected to reflux in THF for 6 h to examine the thermodynamic vs. kinetic stabilities of these isomers. After removal of the THF and recrystallization from acetone to afford only the *exo,exo* isomer, the mother liquor exhibited, by NMR spectral investigation, an approximate distribution of isomers as follows: 50% *exo,endo* and 25% of each of the other isomers. Further recrystallization from acetone afforded more of the *exo,exo*-**2** accompanied by slow decomposition of the other two isomers. It appears, therefore, that the *exo,endo* and *endo,endo* isomers of compounds **1** and **2** do not convert to the *exo,exo* form upon standing in warm solution.

The fact that *exo,exo* isomers of both compounds **1** and **2** are stable and are favored in the synthesis of these compounds, whereas the other isomers are relatively unstable and are formed in minor amounts, tends to support the prediction of the theoretical calculations that the *exo* face of the ligand should form the strongest bond upon metal complexation. However, the *exo,exo* isomer is not favored to the exclusion of the others.

Acknowledgments

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