

PREPARATION AND STRUCTURAL FEATURE OF (η^3 -ALLYL)DICARBONYLNITROSYLIRON COMPLEXES WITH PLANAR CHIRALITY

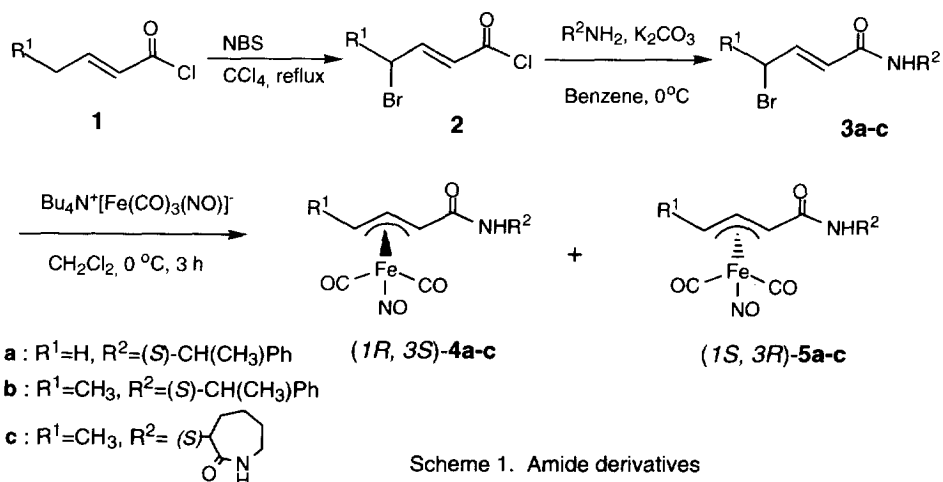
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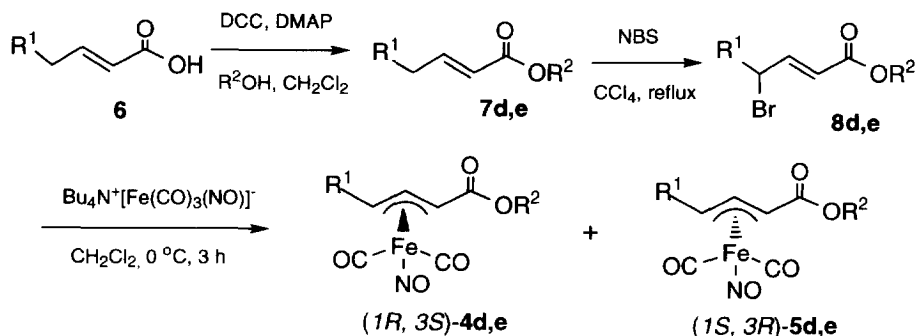
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Abstract: The preparation of novel (η^3 -Allyl)Fe(CO)₂(NO) complexes with planar chirality has been achieved via separation of the diastereomeric complexes having chiral amide and ester groups as auxiliaries. X-ray analysis and CD spectra revealed the structural assignment of the complexes thus obtained.

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(η^3 -Allyl)Fe(CO)₂(NO) complexes have been shown to be versatile reagents for organic transformations.¹⁻¹¹ We have recently reported that the η^3 -allyl ligands of the complexes exhibited ambiphilic reactivities with high regioselectivity and they can serve as both carbon electrophiles and carbon nucleophiles.⁶⁻¹¹ When the complexes have asymmetric allyl ligands, (η^3 -Allyl)Fe(CO)₂(NO) complexes are optically active molecules with planar chirality which can be expected to induce asymmetric organic transformations. However, no study has been hitherto reported on the synthesis of (η^3 -Allyl)Fe(CO)₂(NO) complexes with planar chirality. We report in this communication the preparation and the structural characterization of planar chiral (η^3 -Allyl)Fe(CO)₂(NO) complexes having chiral amide and ester groups as chiral auxiliary.





DMAP: 4-Dimethylaminopyridine

d : $\text{R}^1=\text{CH}_3$, $\text{R}^2=(R)\text{-CH}(\text{CH}_3)\text{Ph}$, **e** : $\text{R}^1=\text{CH}_3$, $\text{R}^2=(S)\text{-CH}(\text{CH}_3)(\text{CH}_2)_5\text{CH}_3$

Scheme 2. Ester derivatives

Preparations of a mixture of diastereomeric (η^3 -Allyl)Fe(CO)₂(NO) complexes (**4** and **5**) with planar chirality having chiral amide and ester groups are illustrated in Schemes 1 and 2. The complexation of chiral allyl bromides **3** bearing chiral amide groups with $\text{Bu}_4\text{N}^+[\text{Fe}(\text{CO})_3(\text{NO})]^-$ proceeded with low diastereoselectivity, but no diastereoselectivity was observed in the case of the complexation of allyl bromides **8** having chiral ester groups. The diastereomers thus obtained can be easily separated by silica gel column chromatography.¹² Among the chiral auxiliaries employed, the amide groups are more effective than the ester groups for the separation of the diastereomers and 2-amino-6-hexanelactam is the most effective. Structural assignments are based on an X-ray crystal structure determination of the crystalline diastereomer of **4b**, which was unequivocally shown to have the (*1R,3S*)-configuration (Figure 1).¹³

Table 1. Preparation of η^3 -Allyl Fe(CO)₂(NO) Complexes with Planar Chirality

Substrate	Products				
	Rf values ^a		Yields / % ^b		Ratio 4 : 5
	4	5	4	5	
3a	0.36	0.25	42	28	60 : 40
3b	0.38	0.31	40	31	57 : 43
3c	0.17	0.34	44	19	70 : 30
8d	0.88	0.94	36	36	50 : 50
8e	0.58	0.55	38	37	50 : 50

a) Eluent: CH₂Cl₂ for (**4a, b, d** and **5a, b, d**), CH₂Cl₂/CH₃CO₂Et (1:1) for (**4c, 5c**), CH₂Cl₂/Hexane (1:1) for (**4e, 5e**).

b) Isolated yields based on allyl bromides (**3** and **8**) used.

To get an insight into the configuration of the $(\eta^3\text{-Allyl})\text{Fe}(\text{CO})_2(\text{NO})$ fragment, CD spectra of the diastereomeric complexes were measured. As an example, those of **4b** and **5b** are shown in Figure 2. The complex **4b** having (*IR*, *3S*)-configuration exhibits a negative band at short wavelength (around 350 nm) and a positive band at long wavelength (around 450 nm). Configuration of the other complexes was assigned on the basis of their CD spectra. The results are given in Table 2.

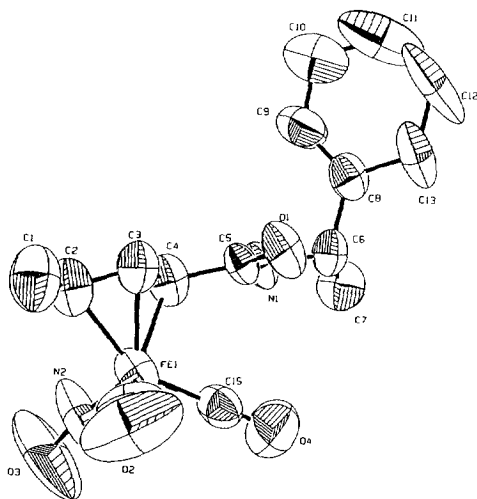


Figure 1. Molecular structure of (*IR*, *3S*)-**4b**.

Table 2. CD Spectral Data of $(\eta^3\text{-Allyl})\text{Fe}(\text{CO})_2(\text{NO})$ Complexes^a

Complex	$\lambda_1(\Delta\epsilon_1)^b$	$\lambda_2(\Delta\epsilon_2)^b$
4a	451 (1.12)	376 (- 0.96)
5a	449 (- 0.52)	361 (1.25)
4b	477 (0.38)	373 (- 1.00)
5b	473 (- 0.31)	383 (0.83)
4c	472 (0.19)	344 (- 0.96)
5c	476 (- 0.36)	350 (1.61)
4d	474 (0.68)	351 (- 2.66)
5d	480 (- 0.45)	355 (1.52)
4e	482 (0.12)	348 (- 0.62)
5e	460 (- 0.20)	378 (0.52)

a) Solvent : CH_2Cl_2 .

b) λ : /nm, $\Delta\epsilon$: / $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$

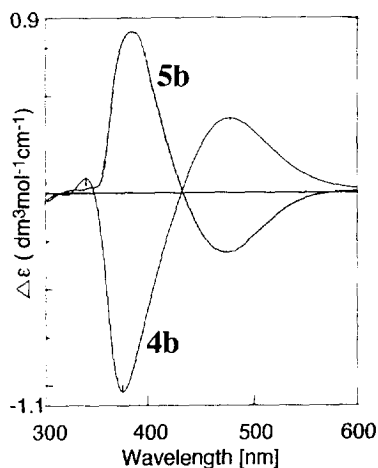


Figure 2. CD spectra of **4b** and **5b**

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- 12) All new compounds were characterized by their spectral data and X-ray analysis.
Selected data: **4b**: Red Solids. mp (dec) 136-139 °C. IR (KBr) 2036, 1974 (CO), 1744 (NO), 1638 (C=O) cm⁻¹. ¹H NMR (270 MHz, CDCl₃) δ 7.39-7.24 (m, 5H), 6.16 (d, J = 7.3 Hz, 1H), 5.24-5.12 (m, 1H), 5.00 (dd, J = 10.9 and 11.3 Hz, 1H), 4.25-4.10 (m, 1H), 3.57 (d, J = 9.8 Hz, 1H), 1.99 (d, J = 6.1 Hz, 3H), 1.56 (d, J = 6.7 Hz, 3H), ¹³C NMR (67 MHz, CDCl₃) δ 217.72, 217.04, 142.97, 128.78, 127.57, 126.45, 126.29, 96.70, 76.93, 49.34, 21.50, 19.72.
5b: Red oil. IR (Neat) 2036, 1974 (CO), 1744 (NO), 1638 (C=O) cm⁻¹. ¹H NMR (270 MHz, CDCl₃) δ 7.36-7.24 (m, 5H), 6.27 (d, J = 6.7 Hz, 1H), 5.24-5.12 (m, 1H), 5.01 (dd, J = 10.9 and 11.0 Hz, 1H), 4.25-4.09 (m, 1H), 3.61 (d, J = 9.8 Hz, 1H), 1.98 (d, J = 6.1 Hz, 3H), 1.55 (d, J = 7.3 Hz, 3H), ¹³C NMR (67 MHz, CDCl₃) δ 217.76, 216.47, 142.77, 128.68, 127.47, 126.43, 96.54, 76.75, 49.19, 21.44, 19.6.
- 13) X-ray crystal structure determination of the complex (*IR,3S*)-**4b**. C₁₅H₁₆O₄N₂Fe.
F.W.=344.15. **4b** was crystallized in space group P2₁ with lattice parameters: a=9.53(1) Å, b=11.75(2) Å, c=15.56(1) Å, β=102.574(8)°, V=1699(3) Å³, Z=4, Dcalc=1.345 g/cm³. From a crystal dimensions 0.150 x 0.150 x 0.500 mm, 4366 independent reflections were measured over a 2θ range of 6-55.2° using Mo-Kα radiation (λ=0.71069 Å) at 23°C. The Fe atom was found from a three dimensional Patterson map, and the nonhydrogen atoms were located by subsequent difference Fourier syntheses. All hydrogen atoms were included at calculated positions. Full matrix least-squares refinement using 1643 reflections with I>3.00 σ (I) converged to final agreement factors R=0.045, Rw=0.045 with GOF=3.31.

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