Pergamon

Tetrahedron: Asymmetry, Vol. 7, No. 8, pp. 2219-2222, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0957-4166/96 $15.00 + 0.00

PII: S0957-4166(96)00276-5

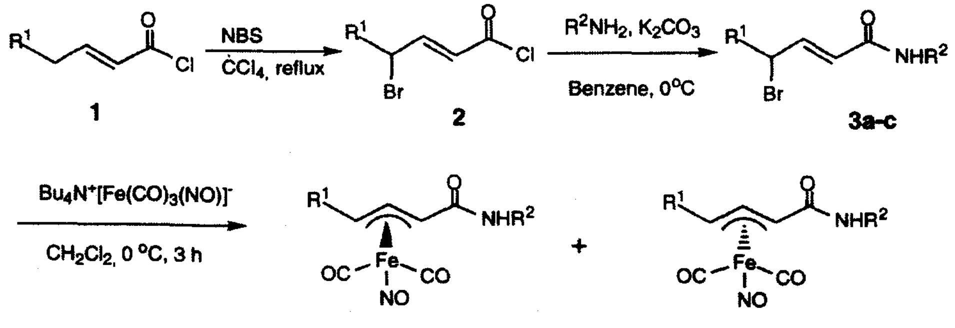
PREPARATION AND STRUCTURAL FEATURE OF (η^3-ALLYL)DICARBONYLNITROSYLIRON COMPLEXES WITH PLANAR CHIRALITY

Saburo Nakanishi,* Hiroshi Yamaguchi, Kenji Okamoto, and Toshikazu Takata

Department of Applied Chemistry, College of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Sakai, Osaka 593, Japan

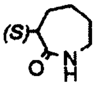
Abstract: The preparation of novel (η^3-Allyl)Fe(CO)$_2$(NO) complexes with planar chirality has been achieved via separation of the diastereomeric complexes having chiral amide and ester groups as auxiliaries. X-ray analysis and CD spectra revealed the structural assignment of the complexes thus obtained.

(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.

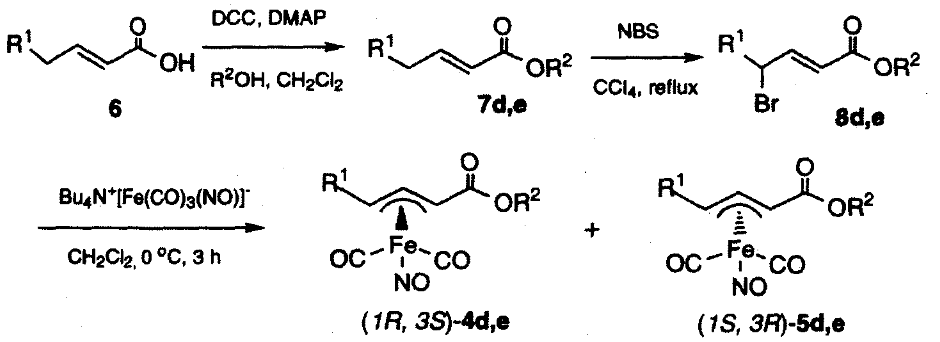


(*1R, 3S*)-**4a-c** (*1S, 3R*)-**5a-c**

a : R^1=H, R^2=(*S*)-CH(CH$_3$)Ph
b : R^1=CH$_3$, R^2=(*S*)-CH(CH$_3$)Ph
c : R^1=CH$_3$, R^2=



Scheme 1. Amide derivatives



DMAP: 4-Dimethylaminopyridine

d : R^1=CH_3, R^2=*(R)* - $CH(CH_3)$ Ph, **e** : R^1=CH_3, R^2=*(S)* - $CH(CH_3)(CH_2)_5CH_3$

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 $Bu_4N^+[Fe(CO)_3(NO)]^-$ 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] 4	 5	 Yields / %[b] 4	 5	 Ratio 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: CH_2Cl_2 for (**4a, b, d** and **5a, b, d**), CH_2Cl_2/CH_3CO_2Et (1:1) for (**4c, 5c**), CH_2Cl_2/ 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 (η^3-Allyl)Fe(CO)2(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 (*1R, 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.

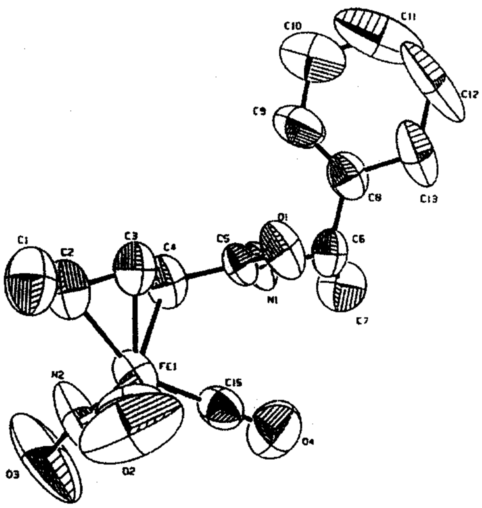


Figure 1. Molecular structure of (*1R, 3S*)-**4b**.

Table 2. CD Spectral Data of (η^3-Allyl)Fe(CO)$_2$(NO) Complexes[a]

Complex	$\lambda_1(\Delta\varepsilon_1)$[b]	$\lambda_2(\Delta\varepsilon_2)$[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, $\Delta\varepsilon$: /dm^{3}mol^{-1}cm^{-1}

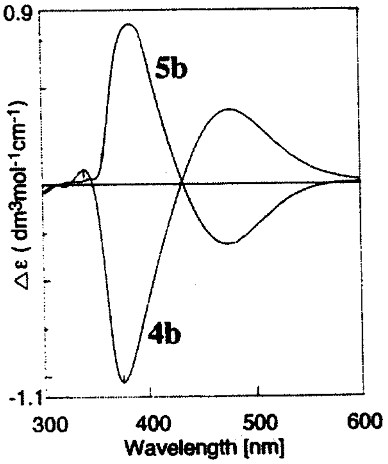


Figure 2. CD spectra of **4b** and **5b**

Acknowledgement: We are grateful to KAWASAKI STEEL 21st Century Foundation for a partial financial support.

References and Notes

1) *Iron Compounds in Organic Synthesis*, Pearson, A. J., Academic Press, London, p 46 (1994).

2) Roustan, J. L. A.; Houlihan, F.; *Can. J. Chem.*, **1979**, *57*, 2790.

3) Roustan, J. L. A.; Merour, J. Y.; Houlihan, F.; *Tetrahedron Lett.*, **1979**, *39*, 3721.

4) Xu, Y.; Zhou, B.; *J. Org. Chem..*, **1987**, *52*, 974.

5) Zhou, B.; Xu, Y.; *J. Org. Chem.*, **1988**, *53*, 4419.

6) Itoh, K.; Nakanishi, S.; Otsuji, Y.; *Chem. Lett.*, **1987**, 2103.

7) Itoh, K.; Nakanishi, S.; Otsuji, Y.; *Chem. Lett.*, **1988**, 473.

8) Itoh, K.; Nakanishi, S.; Otsuji, Y.; *Chem. Lett.*, **1989**, 615.

9) Itoh, K.; Nakanishi, S.; Otsuji, Y.; *Bull. Chem. Soc., Jpn*, **1991**, *64*, 2965.

10) Itoh, K.; Nakanishi, S.; Otsuji, Y.; *J. Organomet. Chem.*, **1994**, *473*, 215.

11) Itoh, K.; Otsuji, Y.; Nakanishi, S.; *Tetrahedron Lett.*, **1995**, *36*, 2103.

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, $CDCl_3$) 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), ^{13}C NMR (67 MHz, $CDCl_3$) 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, $CDCl_3$) 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), ^{13}C NMR (67 MHz, $CDCl_3$) 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 *(1R,3S)*-**4b**. $C_{15}H_{16}O_4N_2Fe$.

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) $Å^3$, Z=4, Dcalc=1.345 g/cm^3. 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 $I>3.00\ \sigma(I)$ converged to final agreement factors R=0.045, Rw=0.045 with GOF=3.31.

(*Received in Japan* 18 *June* 1996)