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CO Insertion of (η^3-allyl)Fe(CO)$_2$(NO) Complexes by Diphosphines

Saburo Nakanishi,* Yasuhiro Sawai, Takeshi Yamamoto, and Toshikazu Takata

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

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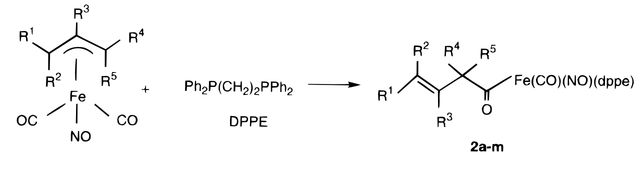
Summary: Allyl groups of (η^3-allyl)Fe(CO)$_2$(NO) complexes undergo regioselective cabonylation at the less substituted carbon of the η^3-allyl ligands in the presence of 1,2-bis(diphenylphosphino)ethane to give (β,γ-unsaturated acyl)Fe(CO)(NO)(dppe) complexes in good yields. X-ray analysis of the acyl complex thus obtained revealed that the complex has a trigonal bipyramid geometry. A characteristic substituent effect of the η^3-allyl ligands on the CO insertion reaction was observed.

Introduction

(η^3-allyl)Fe(CO)$_2$(NO) complexes have been shown as versatile reagents for organic transformations.[1−9] Carbonylation reaction of η^3-allylic metal complexes is one of the most useful reactions for the preparation of β,γ-unsaturated carbonyl compounds.[10−12] η^3-Allylic complexes of metals such as nickel, cobalt, and palladium can be employed in both catalytic and stoichiometric CO insertion reactions. In contrast to these complexes, the CO insertion reaction of (η^3-allyl)Fe(CO)$_2$(NO) complexes hardly takes place in the presence of CO and monodentate phosphines. However, bidentate phosphines such as 1,2-bis(diphenylphosphino)ethane can induce the CO insertion reaction of (η^3-allyl)Fe(CO)$_2$(NO) complexes to give β,γ-unsaturated acyliron complexes which are converted to corresponding β,γ-unsaturated carboxylic acid esters on treatment with alcohols in the presence of iodine.[9,13,14] Not only details of the CO insertion reaction of (η^3-allyl)Fe(CO)$_2$(NO) complexes but also the structures of the acyliron complexes have not been clarified. In this paper, we report on the details of the CO insertion reaction and the structures of the acyliron complexes.

Results and Discussion

Scheme 1

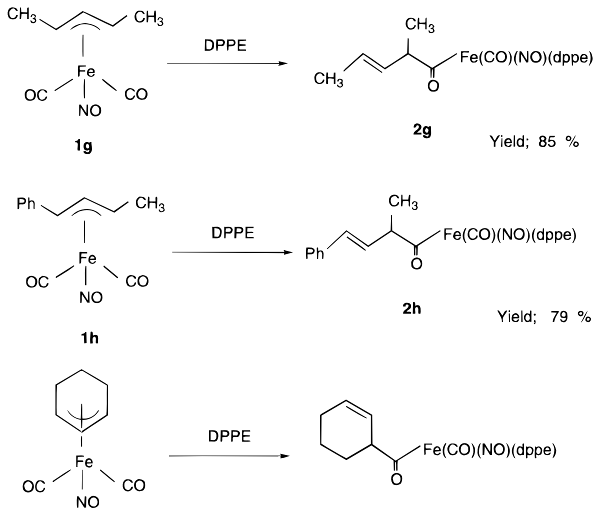


1a-m

2a-m

a: R^1=R^2=R^3=R^4=R^5=H
b: R^1=CH$_3$, R^2=R^3=R^4=R^5=H
c: R^1=C$_6$H$_5$, R^2=R^3=R^4=R^5=H
d: R^1=p-CH$_3$OC$_6$H$_4$, R^2=R^3=R^4=R^5=H
e: R^1=p-ClC$_6$H$_4$, R^2=R^3=R^4=R^5=H
f: R^1=Cl, R^2=R^3=R^4=R^5=H
g: R^1=R^4=CH$_3$, R^2=R^3=R^5=H
h: R^1=C$_6$H$_5$, R^2=R^3=R^5=H, R^4=CH$_3$
i: R^1=R^3=R^4=H, R^2,R^5=CH$_2$CH$_2$CH$_2$
j: R^1=R^2=R^4=R^5=H, R^3=CH$_3$
k: R^1=R^2=R^4=R^5=H, R^3=C$_6$H$_5$
l: R^1=(CH$_3$)$_2$C=CHCH$_2$CH$_2$, R^2=CH$_3$, R^3=R^4=R^5=H
m: R^1=CH$_3$, R^2=(CH$_3$)$_2$C=CHCH$_2$CH$_2$, R^3=R^4=R^5=H
n: R^1=CO$_2$Me, R^2=R^3=R^4=R^5=H
o: R^1=CN, R^2=R^3=R^4=R^5=H

Scheme 2



1g **2g** Yield; 85 %

1h **2h** Yield; 79 %

1i **2i** Yield; 75 %

(η^3-allyl)Fe(CO)$_2$(NO) complexes were prepared by the method previously reported.[3,8,14] Reactions of (η^3-allyl)Fe(CO)$_2$(NO) complexes with 1,2-bis(diphenylphosphino)ethane (DPPE) gave β,γ-unsaturated acyliron complexes via carbonylation of the η^3-allyl ligands.[9,14] It is demonstrated that CO insertion of monosubstituted allyl ligands in this type of iron complex occurs regioselectively at the terminal carbon of the allyl ligands and the configuration of the double bond of the allyl ligands is principally maintained during the reaction.[14] To examine the CO insertion reaction in detail, 1,3-difunctionalized η^3-allyl complexes were allowed to react with DPPE. The results are given in Scheme 2. Secondary allylic carbons in addition to the primary one were also carbonylated smoothly and regioselectively. In the case of **1h** having methyl and phenyl groups, the CO insertion occurred at the carbon bearing the methyl group.

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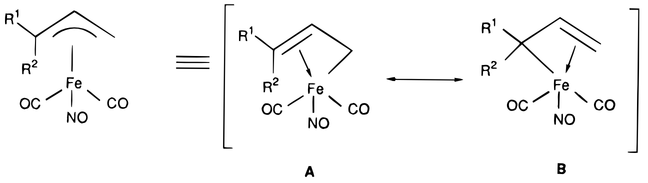
Table 1. Relative Rates of CO Insertion Reactions of η^3-Allyl Complexes

complex	R^1	R^2	R^3	R^4	R^5	rel rate[a]
1a	H	H	H	H	H	1
1b	CH_3	H	H	H	H	1.1
1c	C_6H_5	H	H	H	H	11.1
1d	p-$MeOC_6H_4$	H	H	H	H	10.9
1e	p-ClC_6H_4	H	H	H	H	9.8
1f	Cl	H	H	H	H	<0.1
1g	CH_3	H	H	CH_3	H	0.28
1h	C_6H_5	H	H	CH_3	H	0.97
1i	H	$-(CH_2)_3-$	H	H		0.48
1j	H	H	CH_3	H	H	0.42
1k	H	H	Ph	H	H	0.23
1l	$(CH_3)_2C{=}CHCH_2CH_2$	CH_3	H	H	H	2.2
1m	CH_3	$(CH_3)_2C{=}CHCH_2CH_2$	H	H	H	1.7
1n	CO_2Me	H	H	H	H	0
1o	CN	H	H	H	H	0

Scheme 3



The initial rate of the CO insertion reaction was measured by ^1H NMR spectroscopy from the viewpoint of substituent effects. Relative rates of the complexes to **1a** are summarized in Table 1.

Alkyl groups on the terminal carbon atom slightly accelerate the reaction (**1b,l,m**). Phenyl group on the terminal carbon promotes the reaction significantly (**1c**−**e**), but substituents on the benzene ring exhibit little effect (**1c-e**). On the other hand, methyl and phenyl groups on the central carbon of η^3-allyl ligands considerably retard the reaction (**1j,k**). These results can be explained in terms of the coordination structure of the η^3-allyl ligands. η^3-Allyl complexes can have both resonance structures A and B in which the allyl ligand coordinates to the iron atom in σ- and π-bonds as shown in Scheme 3. Since CO inserts into the carbon−iron σ-bond, the larger the contribution of structure A is, the more rapid the reaction is. Acceleration of the CO insertion is confirmed in the case of the complexes **1c**−**e,l,m**, presumably because of the large contribution of the structure A. When the substituent is situated at the central carbon, the η^3-allyl ligands coordinate symmetrically to the iron atom. Consequently, the CO insertion reaction would be retarded.

Electron-withdrawing groups depress the CO insertion reaction; thus the relative rate of **1f** (R = Cl) is less than unity and CO insertion does not occur in the case of **1n** ($R = CO_2CH_3$) and **1o** (R = CN). This indicates that the CO insertion is an electrophilic reaction. In contrast to $(\eta^3\text{-allyl})Fe(CO)_2(NO)$ complexes, η^3-allylic Ni and Pd complexes having a methoxycarbonyl group can easily undergo CO insertion.[15,16]

The rate of CO insertion into secondary carbon−iron bonds is smaller than that of primary carbon−iron bonds. This is probably due to steric effects.

The efficiency of bidentate phosphines for the carbonylation reaction was also examined. 1,3-Bis(diphenylphosphino)propane was as effective as DPPE. 1,4-Bis(diphenylphosphino)butane, bis(diphenylphosphino)methane, and 1,1′-bis(diphenylphosphino)ferrocene were ineffective; however, the reaction of **1a** with these diphosphines resulted in the substitution reaction of CO by the diphosphines.

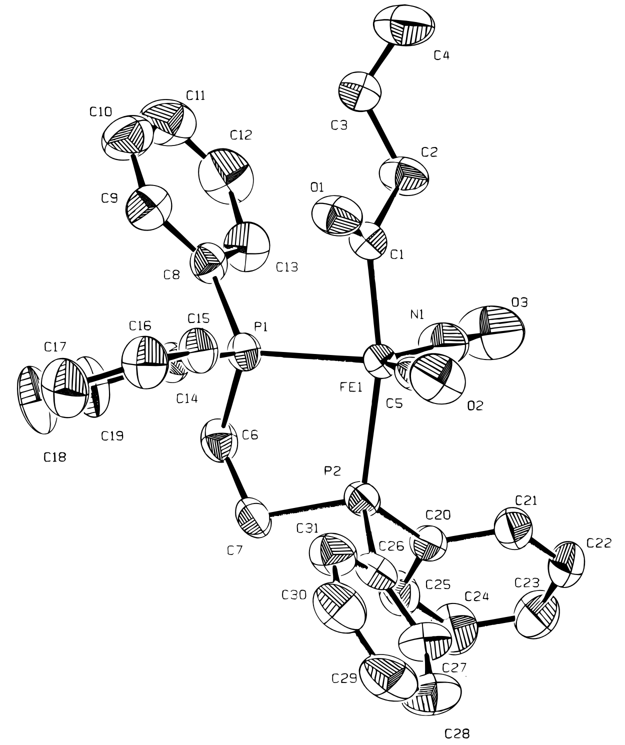


Figure 1. Molecular structure of $(\eta^3\text{-}CH_2{=}CHCH_2)Fe(CO)(NO)(dppe)$ (**2a**).

The acyliron complexes thus obtained are generally stable toward air. The structure of the complex was unambiguously determined by X-ray analysis. Figure 1 illustrates an ORTEP drawing of the molecular structure of **2a**. The complex has a trigonal bipyramid geometry where the acyl ligand is located at the axial position and two phosphorus atoms are situated at the axial and equatorial positions. The nitrosyl ligand coordinates to the iron atom in an almost linear mode (∠Fe−N−O = 173−176°). Selected bond distances and bond angles for **2a** are given in Table 2.

Since the iron atom forms a chiral center in these complexes, the complexes **2g**−**i** should be a mixture of diastereomers. This is confirmed by the ^1H and ^{13}C NMR spectra of the complexes. For example, the ^1H and ^{13}C NMR spectra of either **2g** or **2h** exhibit apparently two kinds of methyl signals based on the formation of two diastereomers.

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for (η^1-$CH_2{=}CHCH_2CO$)Fe(CO)(NO)(dppe) (2a)

Bond Distances			
Fe1−P1	2.246(2)	N1−O3	1.164(3)
Fe1−P2	2.282(2)	O1−C1	1.209(3)
Fe1−N1	1.707(3)	O2−C5	1.151(3)
Fe1−C1	2.011(3)	C1−C2	1.534(4)
Fe1−C5	1.705(3)	C2−C3	1.54(1)
P1−C6	1.834(3)	C3−C4	1.31(2)
P2−C7	1.843(3)	C6−C7	1.517(4)
Bond Angles			
P1−Fe1−P2	84.18(5)	Fe−P1−C6	107.3(1)
P1−Fe1−N1	113.2(1)	Fe1−P2−C7	109.2(1)
P1−Fe1−C1	84.1(1)	Fe−N1−O3	176.0(3)
P1−Fe1−C5	121.3(1)	Fe1−C1−O1	124.2(2)
P2−Fe1−N1	95.5(1)	Fe1−C1−C2	118.1(2)
P2−Fe1−C1	166.74(8)	O1−C1−C2	117.5(3)
P2−Fe1−C5	95.1(1)	C1−C2−C3	110.7(5)
N1−Fe1−C1	94.8(1)	C2−C3−C4	120(1)
N1−Fe1−C5	125.2(1)	Fe1−C5−O2	176.5(2)
C1−Fe1−C5	85.6(1)	P1−C6−C7	107.3(2)

Table 3. Crystallographic Data for (η^1-$CH_2{=}CHCH_2CO$)Fe(CO)(NO)(dppe) (2a)

formula	$C_{31}H_{29}O_3NP_2Fe$
fw	581.37
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.922(4)
b, Å	16.667(4)
c, Å	8.502(6)
α, deg	96.22(4)
β, deg	109.75(3)
γ, deg	93.79(2)
V, Å^3	1439(1)
Z	2
T, °C	23
λ, Å (Mo Kα)	0.710 69
d(calcd), g cm^{-3}	1.341
cryst size, mm	0.8 × 0.6 × 0.1
μ, mm^{-1}	6.63
max, 2θ, deg	55.1
rflns collcd	7006
indepndt rflns	6655
obsrvd rflns ($I > 5.00\sigma(I)$)	3811
R, R_w^{a}	0.029, 0.033
no. of variables	361

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o2)]^{1/2}$.

^{31}P NMR spectra of **2a,c** show two signals of which the chemical shifts relative to $P(OMe)_3$ are 60.5 and −71.2 ppm for **2a** and −64.4 and −112.6 for **2c**. This is in good agreement with the molecular structure as depicted in Figure 1. No temperature-dependent spectral changes in the ^{1}H, ^{13}C, and ^{31}P NMR spectra of these complexes (**2a**−**c**) could be observed over temperatures ranging from −60° to 60 °C, indicating absence of dynamic behavior of **2a**−**c**.

Experimental Section

General Methods. All operations were carried out under an atmosphere of argon. All solvents were purified by standard methods and freshly distilled prior to use. NMR spectra were recorded on JEOL α500 and JEOL JNM-GX 270 instruments. The rate of CO insertion reaction was measured by the ^{1}H NMR (270 MHz) spectroscopic method. (η^3-allyl)-Fe(CO)$_2$(NO) complexes **1a**−**f,i,j,l**−**o** and (η^1-acyl)Fe(CO)-(dppe)(NO) complexes **2a**−**c,f,l,m** were prepared by literature methods.[4,8]

X-ray Structure Determination of 2a. Single crystals of **2a** were grown from a saturated dichloromethane−hexane solution. The crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC5R fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. Crystal data, data collection parameters, and results of the analyses are listed in Table 2. The Fe atom was found from a three-dimensinonal Patterson map, and the non-hydrogen atoms were located by subsequent difference Fourier syntheses. All hydrogen atoms were included at calculated positions. For **2a**, full-matrix least-squares refinement using 3811 reflections with $I > 5.00\sigma(I)$ converged to final agreement factors $R = 0.029$ and $R_w = 0.033$ with GOF = 4.07

Preparation of (η^3-allyl)Fe(CO)$_2$(NO) Complexes. General Procedure. A mixture of the corresponding allyl bromides (2.0 mmol) and tetrabutylammonium tricarbonylnitrosylferrate ((TBA)Fe, 2.0 mmol) in dichloromethane (20 mL) was stirred at 0 °C for 3 h. After evaporation of the solvent, the residue was column chromatographed on silica gel using hexane and dichloromethane (1:1) as eluent to give the (η^3-allyl)Fe(CO)$_2$(NO) complexes as red oils.

(η^3-$CH_3CHCHCHCH_3$)Fe(CO)$_2$(NO) (1g): Red oil; IR (neat) 2022, 1959 (CO), 1734 (NO) cm^{-1}. The NMR spectrum showed that the compound was a mixture of syn and anti isomers. Data for the syn isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.90 (6H, d, J = 6.1 Hz, CH_3), 3.74 (2H, m, CH=), 4.15 (1H, t, J = 11.3 Hz, CH=); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ = 18.71 (CH_3), 76.54, 96.66 (C=), 220.04 (CO). Data for the anti isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.31 (3H, d, J = 7.33 Hz, CH_3), 2.01 (3H, d, J = 6.1 Hz, CH_3), 3.74 (1H, m, CH=), 4.58 (1H, m, CH=), 4.88 (1H, m, CH=); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ = 16.82, 20.61 (CH_3), 71.10, 73.51, 99.07 (C=), 220.04 (CO).

(η^3-PhCHCHCHCH$_3$)Fe(CO)$_2$(NO) (1h): Red oil; IR (neat) 2024, 1966 (CO), 1729 (NO) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 2.04 (3H, d, J = 6.1 Hz, CH_3), 3.80−3.86 (1H, m, CH=), 4.46 (1H, d, J = 11.6 Hz, CH=), 5.07 (1H, t, J = 11.6 Hz, CH=), 7.24−7.33 (5H, m, C_6H_5); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ = 19.91 (CH_3), 72.42, 74.45, 92.49 (C=), 125.69−139.15 (C_6H_5), 218.74, 219.45 (CO).

(η^3-$CH_2C(Ph)CH_2$)Fe(CO)$_2$(NO) (1k): Red oil; IR (neat) 2034, 1974 (CO), 1742 (NO) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 3.44 (2H, s, CH_2=), 4.48 (2H, s, CH_2=), 7.47−7.20 (5H, m, C_6H_5); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ = 54.25, 105.39 (C=), 124.94, 125.99, 127.83, 128.54 (C_6H_5), 217.60 (CO).

Preparation of (η^1-acyl)Fe(CO)(dppe)(NO) Complexes. General Procedure. A solution containing **1** (1.0 mmol) and 1,2-bis(diphenylphosphino)ethane (1.2 mmol) in dichloromethane (15 mL) was stirred at room temperature for 15 h. Column chromatography of the reaction mixture gave the acyl complexes as red solids from the dichloromethane eluent. The red solids were recrystallized from hexane−CH_2Cl_2 solution.

(η^1-$CH_3CH{=}CHCH(CH_3)CO$)Fe(CO)(dppe)(NO) (2g): Red solids; mp 52−55 °C; IR (neat) 1924 (CO), 1707 (NO), 1622 (C=O) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 0.86 (3H, d, J = 6.7 Hz, diastereomeric CH_3), 0.91 (3H, d, J = 6.7 Hz, diastereomeric CH_3), 1.51 (3H, d, J = 4.9 Hz, CH_3), 2.10−2.60 (4H, m, CH_2 (dppe)), 3.91−4.04 (1H, m, CH), 5.26−5.33 (2H, m, CH=), 7.32−7.77 (20H, m, C_6H_5); ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$) δ = 17.27, 17.34, 18.11 (CH_3), 29.0−31.4 (m, CH_2 (dppe)), 69.71 (t, J_{CP} = 11.9 Hz, CH), 124.3−136.4 (m, C_6H_5, C=), 218.1−218.6 (m, CO), 261.7−262.5 (m, C=O).

(η^1-PhCH=CHCH(CH_3)CO)Fe(CO)(dppe)(NO) (2h): Red solids; mp 62−65 °C; IR (neat) 1922 (CO), 1700 (NO), 1617 (C=O) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.01 (3H, d, J = 6.7 Hz, diastereomeric CH_3), 1.07 (3H, d, J = 6.7 Hz, diastereomeric CH_3), 2.10−2.60 (4H, m, CH_2 (dppe)), 4.10−4.28 (1H, m, CH), 5.98−6.24 (2H, m, C=), 7.10−7.77 (25H, m, C_6H_5); ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$) δ = 17.53 (diastereomeric CH_3), 17.67 (diastereomeric CH_3), 28.90−31.96 (m, CH_2 (dppe)), 70.31 (dd, J_{CP} = 25.5, 9.6 Hz, CH), 125.25−138.00 (m, C=, C_6H_5), 217.90−218.42 (m, CO), 261.09−262.26 (m, C=O).

(η^1-CH_2=CH(Ph)CH_2CO)Fe(CO)(dppe)(NO) (2k): Red solid; mp 62−64 °C; IR (neat) 1924 (CO), 1703 (NO), 1620 (C=O) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ = 2.13−2.58 (4H, m, CH_2 (dppe)), 4.12 (2H, dd, J_{HP} = 23.2, 17.1 Hz, CH_2), 4.60 (1H, d, J = 1.61 Hz, CH_2=), 5.34 (1H, d, J = 1.61 Hz, CH_2=), 7.06−7.75 (25H, m, C_6H_5); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ = 29.19 (dd, J_{CP} = 28.6, 17.5 Hz, CH_2 (dppe)), 30.59 (dd, J_{CP} = 27.0, 19.0 Hz, CH_2 (dppe)), 68.77 (d, J_{CP} = 12.8 Hz, CH_2), 114.37−143.45 (m, C=, C_6H_5), 218.39 (dd, J_{CP} = 16.7, 11.9 Hz, CO), 255.29 (t, J_{CP} = 21.5 Hz, C=O).

Supporting Information Available: Tables of positional and thermal parameters and bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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