Bull. Chem. Soc. Jpn., 71, 403—412 (1998)

Preparation, Ligand Substitution, and Structural Stability of (η^3-Allyl)dicarbonylnitrosyliron Complexes

Saburo Nakanishi,* Seiji Memita, Toshikazu Takata, and Keiji Itoh[†]

Department of Applied Chemistry, College of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Sakai, Osaka 599-8531

†Department of Industrial Chemistry, Osaka Prefectural College of Technology, Neyagawa, Osaka 572-0017

(Received July 3, 1997)

[Fe(η^3-allyl)(CO)$_2$(NO)] complexes were prepared by the reaction of tetrabutylammonium tricarbonylnitrosylferrate with tosylates, trifluoroacetates and phosphonates of allylic alcohols and with allylic halides. However, acetates and carbonates of the allylic alcohols are ineffective for the preparation of the complexes. The reaction of [Fe{η^3-(1-substituted allyl)}(CO)$_2$(NO)] with phosphorus ligands (L) gave a mixture of diastereomeric [Fe{η^3-(1-substituted allyl)}(CO)(NO)(L)] complexes, which have planar chirality and central chirality of the iron atom. Variable-temperature ^{1}H NMR spectroscopy revealed that no isomerization between these diastereomers occurred upon heating up to 80 °C. Also, neither *syn–anti* isomerization of the allylic ligand nor isomerization of planar chirality of the complexes took place. The unsubstituted allylic ligand rotates about the iron-allyl ligand axis at room temperature, while η^3-(1-substituted allylic) ligands do not.

η^3-Allyl transition-metal complexes have been recognized as being useful reagents for organic synthesis. They can provide versatile methods for electrophilic or nucleophilic allylation of organic compounds, depending on the properties of the transition metals.[1)] Among the η^3-allyl transition-metal complexes, η^3-allyl palladium complexes have been the most extensively studied. η^3-Allyl iron complexes mainly consist of cationic (η^3-allyl)tetracarbonyliron,[2)] (η^3-allyl)tricarbonylhalogenoiron,[3)] chelated (η^3-allyl)tricarbonyliron,[4)] and (η^3-allyl)dicarbonylnitrosyliron complexes.[5—11)] Compared to the η^3-allyl palladium complexes, the η^3-allyl iron complexes have not been well studied. We have recently reported that η^3-allyldicarbonylnitrosyliron complexes exhibit ambiphilic reactivities; that is, the allyl ligands of the complexes can function as both electrophiles and nucleophiles.[10f,10i)]

In general, η^3-allyl transition-metal complexes often exhibit some sort of isomerizations which involve an interconversion of *exo* and *endo* conformers via a rotation of the η^3-allyl ligands, *syn–anti* isomerization of the substituents in the allyl ligands, and isomerization of optically active stereoisomers having planar and central chirality.[1c,1f,12)] [Fe(η^3-allyl)(CO)$_3$X] (X = halide) complexes consist of a mixture of *exo* and *endo* conformers which are interconverted to each other by the rotation of the allyl ligands.[13)] *Syn–anti* isomerization of the substituents of the allyl ligands and isomerization of planar chiral stereoisomers occur via a π–σ–π mechanism.[14)] The structural feature of [Fe(η^3-allyl)(CO)$_2$(NO)] complexes has not yet been elucidated by ^{1}H NMR spectroscopy, because the proton signals of the η^3-allyl ligands have not been well assigned. Accordingly, little is known about the structure of the (η^3-allyl)dicarbonylnitrosyliron complexes. For the purpose of investigating the structural features concerning these isomerizations, it is necessary to assign the proton signals of the allyl ligands thoroughly and exactly. In this paper we report on the preparation of (η^3-allyl)dicarbonylnitrosyliron complexes by the reaction of allylic substrates with tricarbonylnitrosylferrate, and the ligand-substitution reaction of the produced complexes with phosphorus ligands. Further, full assignments of the allylic protons and carbons are presented, along with the structural features of the η^3-allyl iron complexes, which were investigated by NMR spectroscopy in view of the rotation and *syn–anti* isomerization of the η^3-allyl ligands. Further the stability of planar and central chirality of the η^3-allyl complexes is also discussed.

Experimental

General. The IR spectra were recorded on a JASCO IRA-16 spectrometer. The NMR spectra were measured at 270 MHz on a JEOL JNM-GX 270 and at 500 MHz on a JEOL α500 with TMS as the internal standard. Elemental analyses were carried out on a Yanaco CHN analyzer.

Materials. Tetrabutylammonium tricarbonylnitrosylferrate (TBAFe) was prepared by a previously reported method.[10f)] 3-Bromopropene, 1-bromo-2-butene, trimethyl phosphite, triphenyl phosphite, and triphenylphosphine were commercial products and purified before use. 1-Bromo-2-octene,[15)] methyl 4-bromo-2-butenoate,[15)] *t*-butyl 4-bromo-2-butenoate,[15)] 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane,[16)] tris(2,6-dimethylphenyl) phosphite,[17)] and tri-2-naphthyl phosphite,[18)] were prepared by a method from the literature. P(OCD$_3$)$_3$,[19)] were prepared using tetradueterated methanol. η^3-Allyl complexes **3a** and **3b** were prepared by a previously reported method.[10e)]

General Procedure for the Synthesis of [Fe(η^3-allyl)(CO)$_2$(NO)] 1a—e, 4, and 5. A solution of allylic substrates (3.0 mmol) and TBAFe (3.0 mmol) in CH_2Cl_2 (30 mL) was stirred at 5 °C for 3 h. After removing of the solvent, the residue was column chromatographed on silica gel using a mixture of hexane and CH_2Cl_2 as an eluent to give the products. The chemical shifts of the protons and carbons other than the allylic ligands are described below.

1a:[5)] Dark-red oil (78%). IR (neat) 2044, 1978 (CO), 1742 cm^{-1} (NO).

1b:[5,6a)] Dark-red oil (83 %). IR (neat) 2027, 1965 (CO), 1733 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 1.99$ (3H, d, $J = 6.0$ Hz, CH_3); ^{13}C NMR (67.5 MHz, $CDCl_3$) $\delta = 19.82$ (CH_3).

1c:[10e)] Dark-red oil (83%). IR (neat) 2028, 1966 (CO), 1742 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 0.93$ (3H, t, $J = 6.9$ Hz, CH_3), 1.28—1.80 (6H, m, CH_2), 2.06—2.20 (1H, m, diastereotopic CH_2C=), 2.27—2.73 (1H, m, diastereotopic CH_2C=); ^{13}C NMR (67.5 MHz, $CDCl_3$) $\delta = 14.02$ (CH_3), 22.55 (CH_2), 31.44 (CH_2), 31.47 (CH_2), 34.60 (CH_2).

1d: Dark-red oil (81%). IR (neat) 2043, 1981 (CO), 1749 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 3.81$ (3H, s, CH_3O); ^{13}C NMR (67.5 MHz, $CDCl_3$) $\delta = 52.15$ (CH_3). Found: C, 34.95; H, 2.80, N, 5.88%. Calcd for $C_7H_7NO_5Fe$: C, 34.89; H, 2.93; N, 5.81%.

1e:[9,10e)] Dark-red oil (83%). IR (neat) 2041, 1980 (CO), 1750 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 7.18$—7.46 (5H, m, arom); ^{13}C NMR (67.5 MHz, $CDCl_3$) $\delta = 127.35$, 128.55, 128.97, 139.02 (arom).

(1*R*, 3*S*)-4: Dark-red solids. Mp = 75—77 °C; (36%); IR (neat) 2040, 1980 (CO), 1750 (NO), 1711 cm^{-1} (C=O); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 0.79$ (3H, d, $J = 6.9$ Hz, CH_3), 0.90 (3H, d, $J = 6.9$ Hz, CH_3), 0.92 (3H, d, $J = 6.5$ Hz, CH_3), 1.00—2.05 (9H, m, CH, CH_2), 2.02 (3H, d, $J = 6.1$ Hz, CH_3), 4.80 (1H, dt, $J = 4.4$ and 10.9 Hz, OCH); ^{13}C NMR (67 MHz, $CDCl_3$) $\delta = 16.39$ (CH_3), 19.69 (CH_3), 20.80 (CH_3), 22.07 (CH_3), 23.52 (CH_2), 26.35 (CH_2), 31.43 (CH_2), 34.30 (CH), 40.72 (CH), 47.11 (CH), 77.53 (OCH), 172.55 (CO). Found: C, 53.77; H, 6.82, N, 3.60%. Calcd for $C_{17}H_{25}NO_5Fe$: C, 53.84; H, 6.64; N, 3.69%.

(1*S*, 3*R*)-5: Dark-red oil (36%). IR (neat) 2040, 1980 (CO), 1750 (NO), 1715 cm^{-1} (C=O); ^1H NMR (270 MHz, $CDCl_3$) $\delta =$ 0.78 (3H, d, $J = 6.9$ Hz, CH_3), 0.91 (3H, d, $J = 6.9$ Hz, CH_3), 0.99 (3H, d, $J = 6.5$ Hz, CH_3), 1.00—2.05 (9H, m, CH, CH_2), 2.01 (3H, d, $J = 6.0$ Hz, CH_3), 4.84 (1H, dt, $J = 4.4$ and 10.9 Hz, OCH); ^{13}C NMR (67 MHz, $CDCl_3$) $\delta = 16.29$ (CH_3), 19.73 (CH_3), 20.66 (CH_3), 22.00 (CH_3), 23.66 (CH_2), 26.45 (CH_2), 31.39 (CH_2), 34.33 (CH), 40.92 (CH), 47.36 (CH), 77.55 (OCH), 172.98 (CO). Found: C, 53.59; H, 6.61, N, 3.53%. Calcd for $C_{17}H_{25}NO_5Fe$: C, 53.84; H, 6.64; N, 3.69%.

Ligand Substitution Reaction of [Fe(η^3-allyl)(CO)$_2$(NO)] Complexes with Phosphorus Ligands. A solution of **1** (2.0 mmol) and phosphorus ligand (2.0 mmol) in benzene (20 mL) was stirred at 50 °C for 20 h. After removing of the solvent, the residue was subjected to column chromatography on silica gel to give **2**. The chemical shifts of the protons and carbons other than allyic ligands are described below.

2a: Dark-red crystals. Mp 174—176 °C (lit,[5)] mp 174 °C); IR (KBr) 1920 (CO), 1692 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 7.32$—7.77 (15H, m, arom); ^{13}C NMR{^1H} (67.5 MHz, $CDCl_3$) $\delta = 128.48$ (d, $J_{cp} = 4.7$ Hz, arom), 130.12 (arom), 133.26 (d, $J_{cp} =$ 12.1 Hz, arom), 135.60 (d, $J_{cp} = 43.1$ Hz, arom).

2b: Dark-red oil (58%). IR (neat) 1918 (CO), 1686 cm^{-1} (NO); ^1H NMR (270 MHz, C_6D_6) $\delta = 0.83$ (9H, t, $J = 7.1$ Hz, CH_3), 1.16—1.39 (12H, m, CH_2), 1.54—1.63 (6H, m, PCH_2); ^{13}C NMR (C_6D_6) $\delta = 13.53$ (s, CH_3), 24.20 (d, $J = 12.1$ Hz, $PCCCH_2$), 25.76 (s, $PCCH_2$), 28.83 (d, $J_{cp} = 25.5$ Hz, PCH_2). Found: C, 53.78; H, 9.21; N, 3.88%. Calcd for $C_{16}H_{32}NO_2PFe$: C, 53.79; H, 9.03; N, 3.92%.

2c: Dark-red oil. IR (neat) 1942 (CO), 1702 cm^{-1} (NO); ^1H NMR (270 MHz, CD_3COCD_3) $\delta = 3.53$ (9H, d, $J_{Hp} = 12.5$ Hz, CH_3); ^{13}C NMR{^1H} (67.5 MHz, CD_3COCD_3) $\delta = 52.00$ (OCH_3). Found: C, 30.30; H, 5.18; N, 5.25%. Calcd for $C_7H_{14}NO_5PFe$: C, 30.13; H, 5.06; N, 5.02%.

2d: Dark-red oil. IR (neat) 1942 (CO), 1702 cm^{-1} (NO); ^{13}C NMR{^1H} (67.5 MHz, CD_3COCD_3) $\delta = 52.10$ (m, OCD_3). Found: C, 29.40; H(D), 8.11; N, 4.59%. Calcd for $C_7H_5D_9NO_5PFe$: C, 29.19; H(D), 8.04; N, 4.86%.

2e: Dark-red solids. Mp = 155—158 °C; IR (neat) 1934 (CO), 1695 cm^{-1} (NO); ^1H NMR (270 MHz, CD_2Cl_2) $\delta = 0.83$ (3H, s, CH_3), 4.30 (6H, d, $J_{Hp} = 4.6$ Hz, OCH_2); ^{13}C NMR{^1H} (67.5 MHz, CD_2Cl_2) $\delta = 15.43$ (CH_3), 32.83 (d, $J_{cp} = 33.6$ Hz, $\underline{C}CH_3$), 75.73 (d, $J_{cp} = 6.7$ Hz, OCH_2). Found: C, 35.52; H, 4.61; N, 4.73%. Calcd for $C_9H_{14}NO_5PFe$: C, 35.67; H, 4.66; N, 4.62%.

2f: Dark-red solids. Mp = 84 °C; IR (neat) 1958 (CO), 1718 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 7.10$—7.35 (15H, m, arom); ^{13}C NMR{^1H} (67.5 MHz, $CDCl_3$) $\delta = 121.54$ (d, $J_{cp} = 4.0$ Hz, arom), 124.95 (d, $J_{cp} = 57.8$ Hz, arom), 129.70 (d, $J_{cp} = 2.7$ Hz, arom), 151.43 (d, $J_{cp} = 28.3$ Hz, arom). Found: C, 56.80; H, 4.28; N, 2.90%. Calcd for $C_{22}H_{20}NO_5PFe$: C, 56.80; H, 4.33; N, 3.01%.

2g: Dark-red oil. IR (neat) 1960 (CO), 1718 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 2.32$ (18H, s, CH_3), 7.00—6.82 (9H, m, arom). Found: C, 61.36; H, 5.93; N, 2.42%. Calcd for $C_{28}H_{32}NO_5PFe$: C, 61.22; H, 5.87; N, 2.55%.

2h: Dark-red oil. IR (neat) 1958 (CO), 1717 cm^{-1} (NO); ^1H NMR (270 MHz, $CDCl_3$) $\delta = 7.90$—7.15 (21H, m, arom); ^{13}C NMR{^1H} (67.5 MHz, $CDCl_3$) $\delta = 149.4$—116.8 (m, arom). Found: C, 66.26; H, 4.36; N, 2.15%. Calcd for $C_{34}H_{26}NO_5PFe$: C, 66.36; H, 4.26; N, 2.28%.

2i:[6a)] Dark-red solids. Mp = 138—144 °C; IR (KBr) 1962 (CO), 1678 cm^{-1} (NO); For the major diastereomer; ^1H NMR (270 MHz, C_6D_6) $\delta = 1.90$ (3H, dd, $J = 6.1$, $J_{Hp} = 1.8$ Hz, CH_3), 8.00—6.85 (15H, m, arom); ^{13}C NMR {^1H} (67.5 MHz, C_6D_6) $\delta = 21.02$ (CH_3), 136.99—128.50 (m, arom). For the minor diastereomer; ^1H NMR (270 MHz, C_6D_6) $\delta = 1.80$ (3H, d, $J = 6.1$, CH_3), 8.00—6.85 (15H, m, arom).

2j: Dark-red oil. IR (neat) 1934 (CO), 1694 cm^{-1} (NO); For the major diastereomer; ^1H NMR (270 MHz, C_6D_6) $\delta = 1.88$ (3H, dd, $J = 6.3$, $J_{Hp} = 3.7$ Hz, CH_3), 3.32 (9H, d, $J_{Hp} = 12.1$ Hz, OCH_3); ^{13}C NMR{^1H} (67.5 MHz, C_6D_6) $\delta = 20.19$ (CH_3), 48.94 (d, $J_{cp} = 8.1$ Hz, OCH_3). Signals of the minor diastereomer were not assighed. Found: C, 32.71; H, 5.46; N, 4.89%. Calcd for $C_8H_{16}NO_5PFe$: C, 32.79; H, 5.50; N, 4.78%.

2k: Dark-red oil. IR (neat) 1934 (CO), 1694 cm^{-1} (NO); For the major diastereomer; ^1H NMR (270 MHz, C_6D_6) $\delta = 1.88$ (3H, dd, $J = 6.3$, $J_{Hp} = 3.7$ Hz, CH_3); For the minor diastereomer; ^1H NMR (270 MHz, C_6D_6) $\delta = 1.84$ (3H, dd, $J = 6.4$, $J_{Hp} = 2.8$ Hz, CH_3). Found: C, 31.90; H(D), 8.25; N, 4.88%. Calcd for $C_8H_7D_9NO_5PFe$: C, 31.81; H, 8.34; N, 4.64%.

2l: Dark-red oil. IR (neat) 1950 (CO), 1710 cm^{-1} (NO); For the major diastereomer; ^1H NMR (270 MHz, C_6D_6) $\delta = 1.88$ (3H, dd, $J = 6.1$, $J_{Hp} = 4.5$ Hz, CH_3), 7.44—7.14 (15H, m, arom); ^{13}C NMR{^1H} (67.5 MHz, C_6D_6) $\delta = 20.41$ (CH_3), 121.55 (d, $J_{cp} = 6.7$ Hz, arom), 122.44 (d, $J_{cp} = 4.2$ Hz, arom), 130.41 (d, $J_{cp} = 6.7$ Hz, arom), 152.19 (d, $J_{cp} = 5.4$ Hz, arom); For the minor diastereomer; ^1H NMR (270 MHz, C_6D_6) $\delta = 1.91$ (3H, dd, $J = 6.4$,

$J_{\rm Hp}$ = 3.4 Hz, CH$_3$), 7.61—7.13 (15H, m, arom). Found: C, 57.74; H, 4.51; N, 2.63%. Calcd for $C_{23}H_{22}NO_5PFe$: C, 57.64; H, 4.63; N, 2.92%.

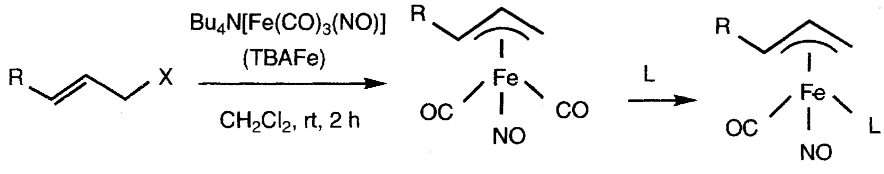
2m: Dark-red crystals. Mp = 99—103 °C; IR (KBr) 1922 (CO), 1682 cm^{-1} (NO); For the major diastereomer; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 0.91 (3H, t, J = 6.9, CH$_3$), 1.85—1.20 (6H, m, CH$_2$), 2.40—2.21 (2H, m, CH$_2$), 7.78—7.13 (15H, m, arom); ^{13}C NMR{^{1}H} (67.5 MHz, CDCl$_3$) δ = 14.4 (CH$_3$), 22.65 (CH$_2$), 31.69 (CH$_2$), 31.95 (CH$_2$), 35.23 (CH$_2$), 137.33—128.35 (m, arom); For the minor diastereomer; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 0.89 (3H, t, J = 6.8 Hz, CH$_3$), 1.85—1.20 (6H, m, CH$_2$), 2.40—2.12 (2H, m, CH$_2$), 7.78—7.13 (15H, m, arom). Found: C, 66.45; H, 6.18; N, 2.59%. Calcd for $C_{27}H_{30}NO_2PFe$: C, 66.54; H, 6.21; N, 2.87%.

2n: Dark-red oil. IR (KBr) 1942 (CO), 1710 cm^{-1} (NO); For the major diastereomer; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 0.86 (3H, t, J = 6.6 Hz, CH$_3$), 1.65—1.20 (6H, m, CH$_2$), 2.10—1.85 (2H, m, CH$_2$), 7.37—7.06 (15H, m, arom); ^{13}C NMR{^{1}H} (67.5 MHz, CDCl$_3$) δ = 22.47 (CH$_3$), 21.36 (CH$_2$), 31.42 (CH$_2$), 31.49 (CH$_2$), 34.58 (CH$_2$), 120.73 (d, $J_{\rm cp}$ = 6.8 Hz, arom), 121.58 (d, $J_{\rm cp}$ = 5.4 Hz, arom), 124.25 (arom), 129.66 (d, $J_{\rm cp}$ = 4.0 Hz, arom); For the minor diastereomer; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 0.86 (3H, t, J = 6.6 Hz, CH$_3$), 1.65—1.20 (6H, m, CH$_2$), 2.10—1.85 (2H, m, CH$_2$), 7.37—7.06 (15H, m, arom). Found: C, 60.45; H, 5.73; N, 2.55%. Calcd for $C_{27}H_{30}NO_5PFe$: C, 60.58; H, 5.65; N, 2.62%.

2o: Dark-red crystals. Mp = 158—160 °C; IR (KBr) 1937 (CO), 1734 (CO$_2$), 1690 cm^{-1} (NO); For the major diastereomer; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 3.65 (3H, s, CH$_3$), 7.68—7.24 (15H, m, arom); ^{13}C NMR{^{1}H} (67.5 MHz, CDCl$_3$) δ = 51.64 (CH$_3$), 134.66—128.35 (m, arom), 175.78 (CO$_2$); For the minor diastereomer; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 3.68 (3H, s, CH$_3$), 7.68—7.24 (15H, m, arom). Found: C, 60.80; H, 4.55, N, 2.96%. Calcd for $C_{24}H_{22}NO_4PFe$: C, 60.65; H, 4.67; N, 2.95%.

2p: Dark-red oil. IR (neat) 1964 (CO), 1730 (CO$_2$), 1703 cm^{-1} (NO); For the major diastereomer; ^{1}H NMR (270 MHz, CD$_2$Cl$_2$) δ = 3.68 (3H, s, CH$_3$), 7.40—7.20 (15H, m, arom); ^{13}C NMR{^{1}H} (67.5 MHz, CD$_2$Cl$_2$) δ = 53.05 (CH$_3$), 121.42 (d, $J_{\rm cp}$ = 5.4 Hz, arom), 125.45 (arom), 129.85 (arom), 150.85 (d, $J_{\rm cp}$ = 6.7 Hz, arom), 175.80 (CO$_2$); For the minor diastereomer; ^{1}H NMR (270 MHz, CD$_2$Cl$_2$) δ = 3.66 (3H, s, CH$_3$), 7.40—7.20 (15H, m, arom). Found: C, 55.29; H, 4.33, N, 2.44%. Calcd for $C_{24}H_{22}NO_7PFe$: C, 55.09; H, 4.24; N, 2.68%.

Single Crystal X-Ray Structure Determination. Single crystals of **2a** and **2f** were grown from a saturated dichloromethane–hexane solution. The Fe atom was found from a three-dimensional Patterson map, and the nonhydrogen atoms were located by subsequent difference Fourier syntheses. All of the hydrogen atoms

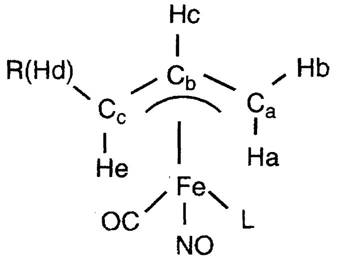


1a-e **2a-p**

1a: R=H,
1b: R=CH$_3$,
1c: R=n-C$_5$H$_{11}$,
1d: R=CH$_3$OCO
1e: R=Ph

2a: R=H, L=PPh$_3$
2b: R=H, L=PBu$_3$
2c: R=H, L=P(OCH$_3$)$_3$
2d: R=H, L=P(OCD$_3$)$_3$
2e: R=H, L=P(OCH$_2$)$_3$CCH$_3$
2f: R=H, L=P(OC$_6$H$_5$)$_3$
2g: R=H, L=P(O-2,6-(CH$_3$)$_2$C$_6$H$_3$)$_3$
2h: R=H, L=P(O-C$_{10}$H$_7$)$_3$
(C$_{10}$H$_7$=2-naphthyl)

2i: R=CH$_3$, L=PPh$_3$
2j: R=CH$_3$, L=P(OCH$_3$)$_3$
2k: R=CH$_3$, L=P(OCD$_3$)$_3$
2l: R=CH$_3$, L=P(OC$_6$H$_5$)$_3$
2m: R=C$_5$H$_{11}$, L=PPh$_3$
2n: R=C$_5$H$_{11}$, L=P(OC$_6$H$_5$)$_3$
2o: R=CH$_3$OCO, L=PPh$_3$
2p: R=CH$_3$OCO, L=P(OC$_6$H$_5$)$_3$



Scheme 1.

were included at calculated positions. Lists of the observed and calculated structure factors and the anisotropic temperature factors for non-hydrogen atoms are deposited as Document No. 71003 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Preparation of (η^3-allyl)dicarbonylnitrosyliron Complexes. [Fe(η^3-allyl)(CO)$_2$(NO)] complexes are generally prepared by the reaction of allylic halides[5,6] and allylic carbonates[8] with tricarbonylnitrosylferrate. The efficiency of the leaving groups of the allylic substrates was first examined for the preparation of [Fe(η^3-allyl)(CO)$_2$(NO)] complexes by treacting allylic substrates with tetrabutylammonium tricarbonylnitrosylferrate (TBAFe) (Scheme 1). The allylic substrates were allowed to react with TBAFe in dichloromethane at 5 °C for 3 h. Column chromatography on silica gel of the reaction mixture gave the corresponding η^3-allyl iron complexes. The results are given in Table 1. Although tosylates, trifluoroacetates and phosphonates of allylic alcohols are efficient substrates for the preparation of the [Fe(η^3-allyl)(CO)$_2$(NO)] complexes, acetates and carbonates of the allyl alcohols are ineffective. The efficiency is proportional to the leaving ability of the allylic substrates. If pK_a of the conjugate acids of the leaving groups is less than 3, the allylic substrates are useful for preparing the complex.

Structural Characteristics of [Fe(η^3-allyl)(CO)(NO)(L)] Complexes. 1) Crystal Structure of [Fe(η^3-CH$_2$CHCH$_2$)(CO)(NO)(PPh$_3$)] 2a and [Fe(η^3-CH$_2$CHCH$_2$)(CO)(NO){P(OPh)$_3$}] 2f. The molecular structures of **2a** and **2f** are shown in Figs. 1 and 2. The experimental details are listed in Table 2; selected bond distances and angles are given in Tables 3 and 4, respectively. A conspicuous feature of the structure involves a *trans* conformation with respect to the H$_c$–C$_b$ and Fe–NO bonds (*endo* form in Scheme 2), and a piano chair form of the complexes. The coordination geometry of the allyl ligand is a typical η^3-allyl geometry. This structure is similar to that of the [Fe(η^3-allyl)(CO)$_2$(NO)] complex.[10a] In other words, replacement of carbon monoxide by phosphorus ligands does not change the conformation of the η^3-allyl iron complexes in the solid state.

Table 1. Formation of [Fe(η^3-allyl)(CO)$_2$(NO)] Complexes

R^1	X	Complex **1**	Yield/%	pK_a of HX
H	Br	**1a**	92	−9
H	OSO$_2$C$_6$H$_4$CH$_3$	**1a**	96	−6.5
H	OCOCF$_3$	**1a**	36	0
H	OPO(OPh)$_2$	**1a**	60	2—3
H	OPO(OEt)$_2$	**1a**	43	2—3
H	OCOCH$_3$	**1a**	0	4.8
H	OCO$_2$CH$_3$	**1a**	0	6.5
Ph	Br	**1e**	89	−9
Ph	OSO$_2$C$_6$H$_4$CH$_3$	**1e**	92	−6.5
Ph	OCOCF$_3$	**1e**	52	0
Ph	OPO(OPh)$_2$	**1e**	58	2—3
Ph	OPO(OEt)$_2$	**1e**	40	2—3
Ph	OCOCH$_3$	**1e**	0	4.8
Ph	OCO$_2$CH$_3$	**1e**	0	6.4

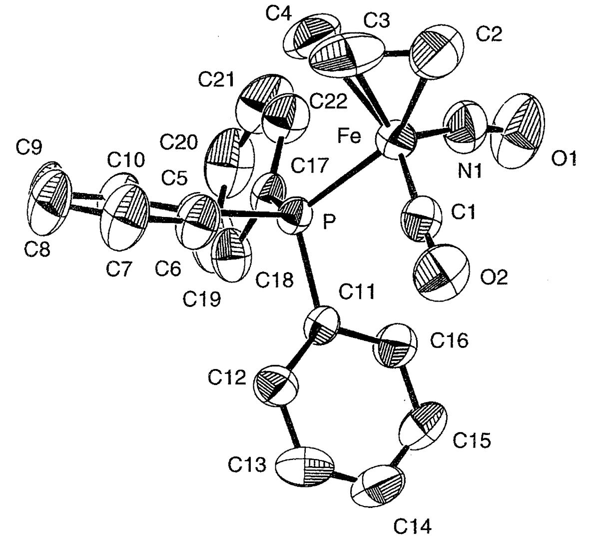


Fig. 1. Molecular structure of [Fe(η^3-CH$_2$CHCH$_2$)(CO)(NO)(PPh$_3$)] **2a**.

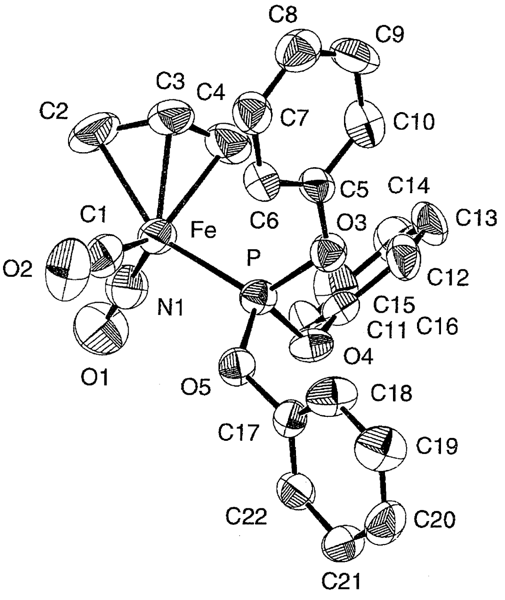


Fig. 2. Molecular structure of [Fe(η^3-CH$_2$CHCH$_2$)(CO)(NO){P(OPh)$_3$}] **2f**.

2) NMR Spectroscopic Study on Structure of the Complexes. a. [Fe(η^3-CH$_2$CHCH$_2$)(CO)(NO)(L)] Complex: The ^{1}H NMR spectrum of the [Fe(η^3-allyl)(CO)$_2$(NO)] complex **1a** exhibits A$_2$M$_2$X signals of symmetrical η^3-allyl ligands, indicating that the proton H$_a$ is equivalent to H$_e$, and H$_b$ is also equivalent to H$_d$. On the other hand, complexes **2a**—**h** with phosphorus ligands show five practically nonequivalent protons. The proton signals of **2a** having triphenylphosphine can not be assigned because they are partially overlapped.[9,11] However, allylic proton signals of **2b**—**h** are sufficiently separated to be assigned. For example, the spectrum of **2d** is shown in Fig. 3. The assignment of the protons is based on their chemical shifts and spin–spin coupling constants, as well as by proton decoupling and

Table 2. Data Collection and Processing Parameters of [Fe(η^3-CH_2CHCH_2)(CO)(NO)(PPh_3)] **2a** and [Fe(η^3-CH_2CHCH_2)(CO)(NO)(P(OPh)$_3$)] **2f**

	2a	**2f**
Formula	$C_{22}NO_2H_{20}PFe$	$C_{22}NO_5H_{20}PFe$
Formula weight	417.23	465.22
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
a/Å	10.548(2)	9.994(3)
b/Å	10.804(2)	13.671(3)
c/Å	9.357(1)	15.487(3)
α/deg	94.90(1)	—
β/deg	100.50(1)	91.23(2)
γ/deg	77.82(1)	—
V/Å^3	1023.7(3)	2115.5(8)
Z	2	4
T/°C	23	23
λ/Å(Mo $K\alpha$)	0.71069	0.71069
d (calcd)/g cm^{-3}	1.353	1.461
Crystal size/mm	$0.5\times0.2\times0.07$	$0.7\times0.3\times0.2$
μ/mm^{-1}	8.17	8.17
Max 2θ	55.1	55.1
Rflns collected	4975	5365
Indepndt rflns	4720	5085
Obsrvd rflns ($I>5.00\sigma(I)$)	2001	2594
R; R_w[a]	0.036; 0.061	0.039; 0.071
No. variables	244	271

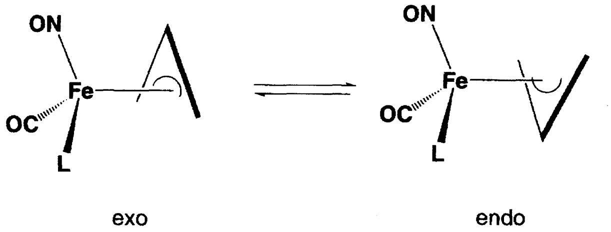
a) $R=\Sigma||F_o|-|F_c||\Sigma|F_o|$. $R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

Table 3. Selected Bond Distances (Å) of [Fe(η^3-CH_2CHCH_2)(CO)(NO)(PPh_3)] **2a** and [Fe(η^3-CH_2CHCH_2)(CO)(NO){P(OPh)$_3$}] **2f**

	2a	**2f**
Fe–C1	1.743 (8)	1.77 (1)
Fe–N1	1.660 (8)	1.670 (7)
Fe–P	2.223 (2)	2.161 (2)
Fe–C2	2.12 (1)	2.131 (8)
Fe–C3	2.08 (1)	2.093 (8)
Fe–C4	2.158 (8)	2.155 (8)
C1–O2	1.140 (8)	1.13 (1)
N1–O1	1.171 (8)	1.167 (8)
C2–C3	1.41 (1)	1.40 (1)
C3–C4	1.35 (1)	1.38 (1)

Table 4. Selected Bond Angles (°) of [Fe(η^3-CH_2CHCH_2)(CO)(NO)(PPh_3)] **2a** and [Fe(η^3-CH_2CHCH_2)(CO)(NO){P(OPh)$_3$}] **2f**

	2a	**2f**
N1–Fe–P	104.6 (3)	105.5 (2)
C1–Fe–P	90.8 (2)	91.8 (2)
C1–Fe–C2	90.1 (4)	88.0 (4)
C1–Fe–C3	99.9 (4)	100.9 (4)
C1–Fe–C4	132.6 (4)	135.3 (4)
P–Fe–C2	149.8 (3)	149.5 (3)
P–Fe–C3	111.0 (4)	111.9 (3)
P–Fe–C4	90.4 (4)	91.5 (2)
N1–Fe–C1	113.8 (3)	114.1 (4)
N1–Fe–C2	102.6 (4)	102.3 (3)
N1–Fe–C3	130.0 (4)	127.1 (3)
N1–Fe–C4	111.7 (4)	107.9 (3)
C2–C3–C4	118 (1)	119.0 (9)



Scheme 2.

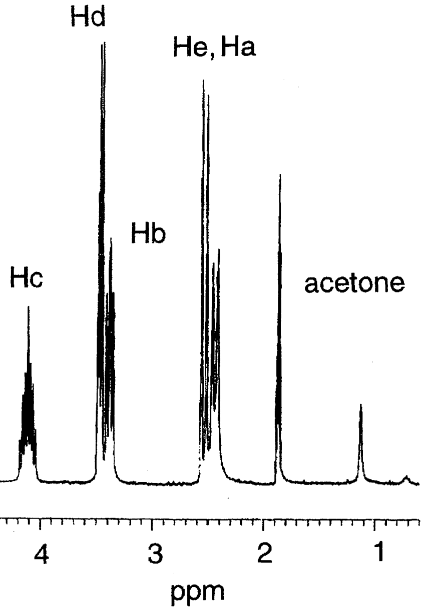


Fig. 3. ^{1}H NMR spectrum of [Fe(η^3-CH_2CHCH_2)(CO)(NO){P(OCD$_3$)$_3$}] **2d** in acetone-d_6.

two dimensional techniques. The ^{1}H NMR chemical shifts of allylic protons and carbons are listed in Tables 5 and 6, respectively. The nonequivalence of the protons ($H_a=H_e$, $H_b=H_d$) is consistent with the different chemical shifts of C_a and C_c in their ^{13}C NMR spectra. The H_a and H_e protons (also H_b and H_d) are diastereotopic due to the chiral center of the iron atom.

There is a spin–spin coupling between the phosphorus atom and some of the allylic protons. The H_b proton is always coupled to the phosphorus atom, and no coupling is observed between the phosphorus atom and both of the H_a and H_c protons. Both of the terminal carbons of the allyl ligand are also coupled to the phosphorus atom, but there is no coupling between the central carbon and the phosphorus atom.

It is well known that the η^3-allyl transition-metal complexes usually exhibit dynamic behavior which involves a rotation of the η^3-allyl ligand about the metal-allyl ligand axis,[13] *syn–anti* isomerization of the substituted η^3-allyl ligand,[12] and conversion of the planar chirality as well as the metal central chirality. Although the η^3-allyl ligand freely rotates, two conformers can sometimes exist as relatively stable

Table 5. ^{1}H NMR Data of the Allylic Parts of the Iron Complexes

Complex	Solvent	Diastereomer	H_a	H_b	H_c	H_d	H_e
1a	$CDCl_3$	—	3.23 (d, J = 12 Hz)	3.97 (d, J = 6.5 Hz)	4.24 (tt, J = 12, 6.5 Hz)	3.97 (d, J = 6.5 Hz)	3.23 (d, J = 12 Hz)
1b	$CDCl_3$	—	2.85 (d, J = 12 Hz)	3.76 (d, J = 6.9 Hz)	4.06—4.30 (m)	—	4.06—4.30 (m)
1c	$CDCl_3$	—	2.79 (d, J = 12 Hz)	3.75 (d, J = 6.4 Hz)	4.21 (dt, J = 12, 5.2 Hz)	—	3.97—4.08 (m)
1d	$CDCl_3$	—	3.20 (d, J = 13 Hz)	4.03 (d, J = 6.9 Hz)	5.13 (ddd, J = 13, 10, 6.9 Hz)	—	3.79 (d, J = 10 Hz)
1e	$CDCl_3$	—	3.00 (d, J = 12 Hz)	3.93 (d, J = 6.7 Hz)	5.08 (dt, J = 12, 6.7 Hz)	—	4.82 (d, J = 12 Hz)
2a	CD_2Cl_2	—	2.84 (d, J = 12 Hz)	2.86—2.99 (m)	3.70—3.88 (m)	3.55—3.65 (m)	2.96 (d, J = 12 Hz)
2b	C_6D_6	—	2.55 (d, J = 12 Hz)	2.96—3.07 (m)	4.00—4.20 (m)	3.42—3.47 (m)	2.55 (d, J = 12 Hz)
2c,2d	CD_3COCD_3	—	2.61 (d, J = 12 Hz)	3.55 (ddd, J = 6.8, 2.7, J_{Hp} = 8.8 Hz)	4.28 (tt, J = 12, 6.4 Hz)	3.66 (dd, J = 6.4, 2.87 Hz)	2.71 (d, J = 13 Hz)
2e	CD_2Cl_2	—	2.72 (d, J = 12 Hz)	3.72—3.82 (m)	4.06—4.20 (m)	3.72—3.82 (m)	2.80 (d, J = 12 Hz)
2f	$CDCl_3$	—	2.30 (d, J = 12.3 Hz)	3.04 (ddd, J = 6.7, 3.0, J_{Hp} = 11 Hz)	3.28 (tt, J = 12, 6.7 Hz)	3.46—3.51 (m)	2.65 (dd, J = 12, (J_{Hp} = 2.7 Hz)
2g	$CDCl_3$	—	2.46 (d, J = 13 Hz)	3.40 (dt, J = 6.0, 2.8 Hz) J_{Hp} = 2.8 Hz)	2.98 (tt, J = 1.2, 6.0 Hz)	3.55 (ddd J = 6.0, 2.8, J_{Hp} = 12 Hz)	2.70 (dd, J = 12, J_{Hp} = 4 Hz)
2h	$CDCl_3$	—	2.27 (d, J = 12 Hz)	3.41—3.52 (m)	3.23 (tt, J = 12, 6.5 Hz)	3.41—3.52 (m)	2.61 (dd, J = 12 J_{Hp} = 2.4 Hz)
2i	C_6D_6	Major	2.75 (d, J = 12 Hz)	2.64 (dd, J = 6.4, J_{Hp} = 12 Hz)	3.48 (tt, J = 12, 6.4 Hz)	—	3.94—4.07 (m)
		Minor	1.05 (d, J = 12 Hz)	3.05—3.20 (m)	4.70—4.92 (m)	—	3.05—3.20 (m)
2j	C_6D_6	Major	2.46 (d, J = 12 Hz)	3.15 (dd, J = 6.4, J_{Hp} = 11 Hz)	3.64 (tt, J = 12, 6.4 Hz)	—	3.77—3.90 (m)
		Minor	Not assigned				
2k	C_6D_6	Major	2.46 (d, J = 12 Hz)	3.15 (dd, J = 6.4, J_{Hp} = 11 Hz)	3.70 (dt, J = 11, 6.4 Hz)	—	3.87—3.96 (m)
		Minor	1.26 (d, J = 12 Hz)	3.36 (dd, J = 6.4, J_{Hp} = 4.8 Hz)	4.60—4.72 (m)	—	3.07 (dq, J = 11, 6.3 Hz)
2l	C_6D_6	Major	2.43 (d, J = 12 Hz)	3.53 (dd, J = 6.4, J_{Hp} = 12 Hz)	3.28 (dt, J = 11, 6.4 Hz)	—	3.87—4.02 (m)
		Minor	1.33 (d, J = 12 Hz)	3.48—3.53 (m)	4.63—4.75 (m)	—	2.94—3.03 (m)
2m	$CDCl_3$	Major	2.75 (d, J = 12 Hz)	2.61 (dd, J = 6.4, J_{Hp} = 12 Hz)	3.59 (dt, J = 12, 6.4 Hz)	—	3.93—4.04 (m)
		Minor	1.20—1.85 (m)	3.06 (t, J = 7 Hz)	5.08—5.15 (m)	—	3.13—3.30 (m)
2n	C_6D_6	Major	2.06 (d, J = 11 Hz)	3.15 (dd, J = 6.4, J_{Hp} = 12 Hz)	3.02 (dt, J = 11, 6.4 Hz)	—	3.72—3.83 (m)
		Minor	1.20—1.65 (m)	2.95—3.05 (m)	4.53—4.56 (m)	—	2.77—2.29 (m)
2o	$CDCl_3$	Major	3.07 (d, J = 13 Hz)	2.96 (dd, J = 6.8, J_{Hp} = 11 Hz)	4.62—4.77 (m)	—	3.57 (d, J = 12 Hz)
		Minor	1.80 (d, J = 13 Hz)	3.26 (d, J = 6.3 Hz)	5.77—5.89 (m)	—	3.27 (d, J = 10 Hz)
2p	CD_2Cl_2	Major	2.45 (d, J = 12 Hz)	3.38—3.50 (m)	4.00—4.15 (m)	—	3.38—3.50 (m)
		Minor	1.53 (d, J = 12 Hz)	3.00 (dd, J = 6.4, J_{Hp} = 10 Hz)	5.20—5.35 (m)	—	3.38—3.50 (m)
4	$CDCl_3$	(1*R*, 3*S*)	4.09—4.15 (m)	—	5.12 (t, J = 11 Hz)	—	3.55 (d, J = 11 Hz)
5	$CDCl_3$	(1*S*, 3*R*)	4.01—4.13 (m)	—	5.08 (t, J = 11 Hz)	—	3.52 (d, J = 11 Hz)

Table 6. ^{13}C NMR Data of Carbonyl and Allylic Parts of the Iron Complexes[a)]

Complex	Solvent	CO	C_a	C_b	C_c
1a	$CDCl_3$	218.47	56.17	94.37	56.17
1b	$CDCl_3$	219.34	51.01	95.49	78.00
1c	$CDCl_3$	219.40 219.24	51.40	94.27	84.16
1d	$CDCl_3$	216.02	55.67	96.53	60.03
1e	$CDCl_3$	217.30 218.12	51.29	89.92	79.83
2a	CD_2Cl_2	222.87 (d, $J_{cp} = 22.3$ Hz)	50.25	93.53	57.45
2b	$CDCl_3$	222.60 (d, $J_{cp} = 21.5$ Hz)	47.76	93.42	52.45
2c	CD_3COCD_3	220.95 (d, $J_{cp} = 30.9$ Hz)	50.63	92.98	53.09
2d	CD_3COCD_3	220.31 (d, $J_{cp} = 32.6$ Hz)	50.66	94.25	53.86
2e	CD_2Cl_2	220.83 (d, $J_{cp} = 34.9$ Hz)	51.94 (d, $J_{cp} = 5.3$ Hz)	92.29	54.25 (d, $J_{cp} = 4.0$ Hz)
2f	$CDCl_3$	220.16 (d, $J_{cp} = 28.2$ Hz)	51.23 (d, $J_{cp} = 6.7$ Hz)	92.88	53.24
2h	$CDCl_3$	220.03 (d, $J_{cp} = 32.3$ Hz)	51.50 (d, $J_{cp} = 8.1$ Hz)	92.98	53.40 (d, $J_{cp} = 5.4$ Hz)
2i	C_6D_6	224.90 (d, $J_{cp} = 20.1$ Hz)	54.40 (d, $J_{cp} = 5.4$ Hz)	95.95	68.56 (d, $J_{cp} = 4.1$ Hz)
2j	C_6D_6	222.53 (d, $J_{cp} = 20.9$ Hz)	51.69 (d, $J_{cp} = 2.7$ Hz)	95.47	69.50 (d, $J_{cp} = 8.0$ Hz)
2l	C_6D_6	222.43 (d, $J_{cp} = 28.3$ Hz)	49.08 (d, $J_{cp} = 8.0$ Hz)	95.67	71.58 (d, $J_{cp} = 8.1$ Hz)
2m	$CDCl_3$	223.65 (d, $J_{cp} = 20.1$ Hz)	54.27 (d, $J_{cp} = 5.4$ Hz)	94.23	75.03 (d, $J_{cp} = 5.3$ Hz)
2n	$CDCl_3$	221.5 (d, $J_{cp} = 20.1$ Hz)	48.51 (d, $J_{cp} = 8.1$ Hz)	93.73	77.83 (d, $J_{cp} = 9.4$ Hz)
2o	$CDCl_3$	219.80 (d, $J_{cp} = 24.2$ Hz)	52.17	95.89	58.73
2p	CD_2Cl_2	217.22 (d, $J_{cp} = 32.3$ Hz)	51.59 (d, $J_{cp} = 4.0$ Hz)	95.63	54.95 (d, $J_{cp} = 5.4$ Hz)
(1*R*, 3*S*)-4	$CDCl_3$	216.98 217.16	56.59	97.57	74.99
(1*S*, 3*R*)-4	$CDCl_3$	216.85 217.22	56.38	97.34	74.77

a) Major diastereomer.

exo and *endo* isomers, which can be interconverted and isolated in the case of [Mo(η^3-allyl)(CO)(NO)$_{cp}$][20)] and [Re(η^3-allyl)(CO)(H)(η^5-C_5Me_5)).[21)] Scheme 2 represents the two conformers concerning the (η^3-allyl)tricarbonylnitrosyliron complexes.

To examine the dynamic behavior of complexes **2**, variable-temperature ^{1}H NMR was undertaken. The spectra of **2d** and **2f**, for example, are shown as typical examples in Fig. 4. Five allylic proton signals of both complexes appeared as sharp signals at high temperature (> 0 °C) as well as within a low-temperature range (< −60 °C); however, broadening of the signals occurred in the range from 0 to −40 °C, accompanying a migration of the signals. It seems likely that rotation and *syn–anti* isomerization of the allyl ligand induce this phenomenon. Connelly et al.[22)] and Faller et al.[13)] have utilized a spin saturation transfer technique to examine the dynamic behavior of η^3-allyliron complexes. Spin saturation transfer experiments of **2d** were carried out in order to obtain information about *syn–anti* isomerization. At 25 °C, irradiation at the *anti* proton H_a did not lead to a reduction of the intensity of the *syn* protons H_b and H_d, indicating no *syn–anti* proton exchange. Consequently, the phenomenon of these complexes may be attributed to a rotation of the allyl ligand, and not to *syn–anti* isomerization. Although the allyl ligands freely rotate beyond 0 °C, the rotation is fixed below −60 °C to form an *endo* conformer, which is the most stable conformational isomer. This is in agreement with the results of an X-ray analysis (Figs. 2 and 3). However, it is not yet clear whether another process is responsible for the dynamic behavior.

b. [Fe(η^3-RCHCHCH$_2$)(CO)(NO)(L)] Complex: *Syn–anti* isomerization generally occurs in the case of substituted allyl metal complexes. First, *syn–anti* isomerization of substituted (η^3-allyl)dicarbonylnitrosyliron complexes was examined. The temperature dependence of the ^{1}H NMR spectra of both the *syn* complex **3a** and the *anti* complex

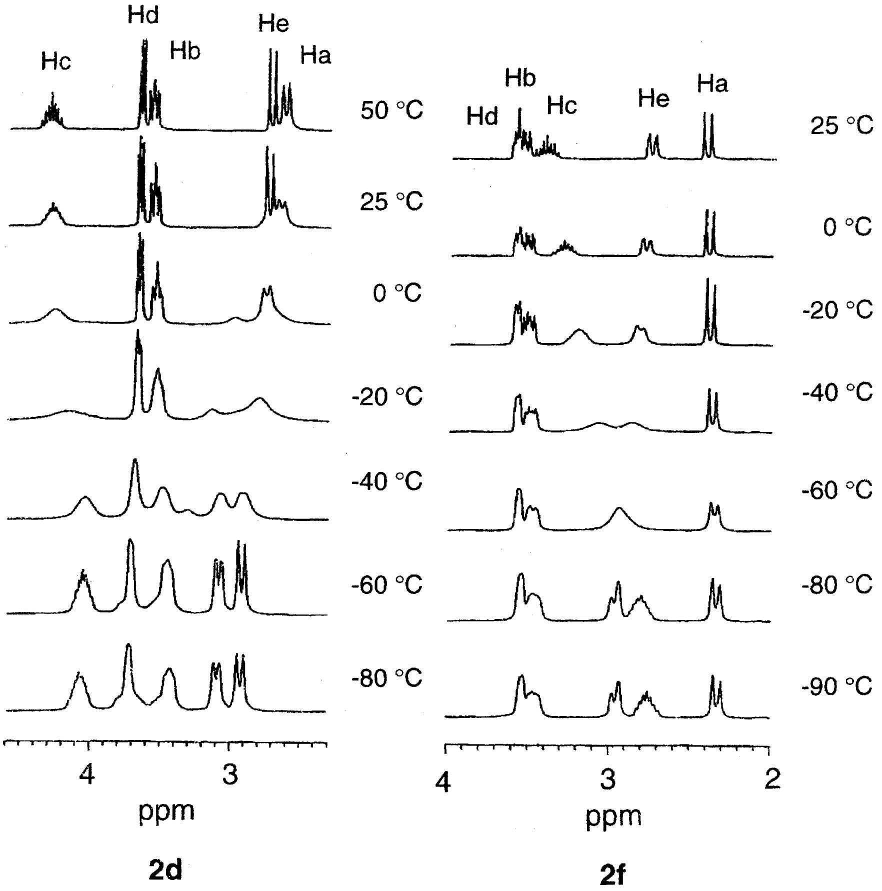
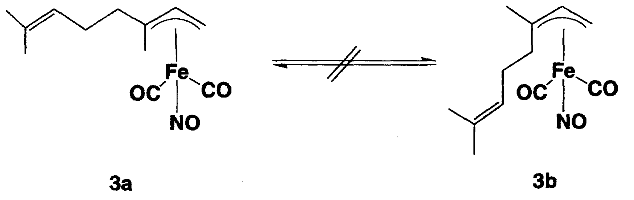


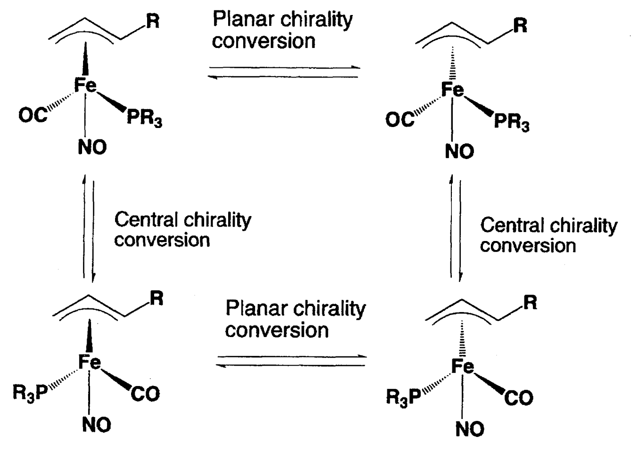
Fig. 4. Variable temperature ^{1}H NMR spectra of **2d** and **2f**.

3b[10e] were measured (Scheme 3). No *syn–anti* isomerization was observed in the range of −60—80 °C, although both the complexes gradually decomposed at 80 °C in a benzene solution.

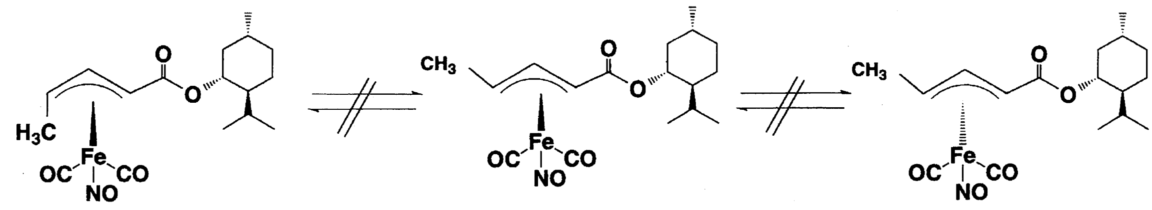
The dicarbonyl complexes **1b**—**d** having substituted allyl ligands reacted with phosphorus ligands at 50 °C to give diastereomeric complexes which have metal a center chilarity and planar chilarity due to the orientation of the η^3-allyl ligands coordinated to the iron atom. No ligand substitution proceeded upon the treatment of **1e** with phosphorus ligands, and the decomposition of **1e** occurred. The ratio of the thus-produced diastereomers was determined based on their ^{1}H NMR spectra. The proton assignment of the diastereomers was confirmed by HH COSY spectroscopy. Figure 5 shows an example of the HH COSY spectrum of complex **21**, illustrating the assignment of each proton ($H_{a\text{—}e}$ and $H_{a'\text{—}e'}$) or each diastereomer. The diastereomer ratio varied from 7 : 1 to 2 : 1, depending on the phosphorus ligands and the substituents in the allyl ligands, as shown in Table 7. Separation of the diastereomers by column chromatography and fractional recrystallization failed, although diastereomers can be separated by fractional crystallization and preparative liquid chromatography in the case of the complexes having a chiral Fe atom and an optically active phosphine ligand.[11] The dynamic behavior of the diastereomeric η^3-allyl complexes involves two kinds of isomerization of planar chirality and metal-center chirality. Scheme 4 represents the dynamic behavior. The variable-temperature



Scheme 3.



Scheme 4.



anti-(1R, 3R)-4 syn-(1R, 3S)-4 (1S, 3R)-5

Scheme 5.

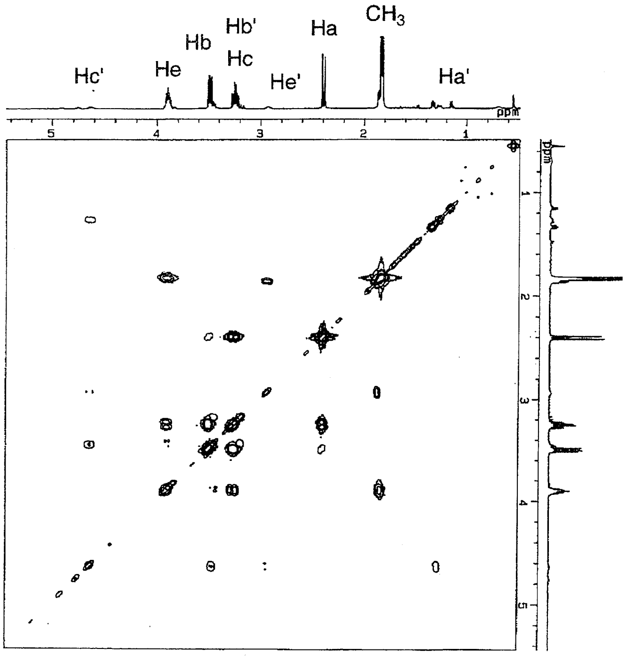


Fig. 5. HH COSY spectrum of [Fe(η^3-$CH_3CHCHCH_2$)(CO)(NO){$P(OPh)_3$}] **21**.

Table 7. Diastereomer Ratio of the Complexes **2i**—**p**

Complex	R	L	Ratio of diastereomers/%
2i	CH_3	PPh_3	88 : 12
2k	CH_3	$P(OCD_3)_3$	75 : 25
2l	CH_3	$P(OPh)_3$	83 : 17
2m	C_5H_{11}	PPh_3	86 : 14
2n	C_5H_{11}	$P(OPh)_3$	88 : 12
2o	CH_3OCO	PPh_3	67 : 33
2p	CH_3OCO	$P(OPh)_3$	60 : 40

^{1}H NMR spectra of substituted η^3-allyl complexes **2i**—**2p** exhibited no significant change over the range from 80 to −80 °C, indicating that the diastereomer ratio remains constant over this temperature range. Further, the diastereomer ratio is independent on solvents such as benzene, dichloromethane, acetonitrile, acetone and methanol. These results suggest that epimerization of planar chirality and metal central chirality does not occur. Brunner et al.[11] reported that configurational stability at the Fe center of the (η^3-allyl)carbonylnitrosylphosphineiron is noticed; that is, conversion of the configuration at the Fe center does not occur up to 120 °C.

In order to obtain further insight into the isomerization of *syn–anti* and of the planar chirality, the temperature-dependence ^{1}H NMR of the diastereomeric planar chiral complexes, **4** and **5**, was taken over the range of −60—60 °C (Scheme 5). The diastereomeric complexes, **4** and **5**, are distinctly discriminated by their ^{1}H NMR spectra.[10a)] No spectral change in their temperature-dependence ^{1}H NMR was observed, indicating no isomerization of the *syn–anti* and planar chirality. From the above results, it is inferred that (η^3-allyl)dicarbonylnitrosyliron and their phosphine complexes possess high structural stability with respect to *syn–anti* isomerization and epimerization of the planar and central chirality.

The high structural stability is advantageous for applying the (η^3-allyl)dicarbonylnitrosyliron and their phosphine complexes to asymmetric organic synthesis.[23)]

We are grateful to Kawasaki Steel 21st Century Foundation for a partial financial support.

References

1) a) A. J. Pearson, "Iron Compounds in Organic Synthesis," Academic Press, London (1994), p. 44; b) Y. Masuyama, in "Advances in Metal-Organic Chemistry," ed by L. S. Liebeskind, JAI Press Inc., Connecticut (1994), p. 255; c) J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, California (1987), p. 175; d) R. F. Heck, in "Palladium Reagents in Organic Syntheses," Academic Press, London (1985), Vol. 1, p. 117; e) J. Tsuji, in "The Chemistry of the Metal–Carbon Bond," ed by F. R. Hartley and S. Patai, John Wiley and Sons, New York (1985), Vol. 3, p. 163; f) A. J. Deeming, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford (1982), Vol. 4, p. 413; g) B. M. Trost and T. R. Verhoeven, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, Pergamon Press, Oxford (1982), Vol. 8, p. 802.

2) a) D. Enders, S. Berg, and B. Jandeleit, *Synlett*, **1996**, 18; b) J. C. P. Hopman, H. Hiemstra, and W. N. Speckamp, *J. Chem. Soc., Chem. Commun.*, **1995**, 617; c) T. Zhou and J. R. Green, *Tetrahedron Lett.*, **34**, 4497 (1993); d) M. C. P. Yeh and S. I. Tau, *J. Chem. Soc., Chem. Commun.*, **1992**, 13; e) Z. Li and K. M. Nicholas, *J. Organomet. Chem.*, **402**, 105 (1991); f) A. Hafner, W. Philipsborn, and A. Salzer, *Helv. Chim. Acta*, **69**, 1757 (1986); g) A. J. Pearson, *Tetrahedron Lett.*, **1975**, 3617; f) T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *J. Am. Chem. Soc.*, **95**, 5792 (1973).

3) a) R. Hüttel and H. Christ, *Chem. Ber.*, **97**, 2037 (1964); b) M. Brookhart, T. M. Whitesides, and J. M. Crockett, *Inorg. Chem.*, **15**, 1550 (1976).

4) a) P. Eilbracht and A. Hirshfelder, in "Advances in Metal-Organic Chemistry," ed by L. S. Liebeskind, JAI Press Inc., Connecticut (1996), p. 55; b) K. Khumtaveeporn and H. Alper, *Acc. Chem. Res.*, **28**, 414 (1995); c) S. T. Ley, L. R. Cox, and G. Meek, *Chem. Rev.*, **96**, 423 (1996).

5) F. M. Chaudhari, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, **1967**, 2255.

6) a) G. Cardaci and A. J. Foffani, *J. Chem. Soc., Dalton Trans.*, **1974**, 1808; b) G. Cardaci, *J. Chem. Soc., Dalton Trans.*, **1974**, 2452; c) G. Cardaci, S. M. Murgia, and A. J. Foffanil, *J. Organomet. Chem.*, **37**, C11 (1972); d) G. Cardaci and S. M. Murgia, *J. Organomet. Chem.*, **25**, 483 (1970).

7) a) J. L. A. Roustan and A. Forgues, *J. Organomet. Chem.*, **184**, C13 (1980); b) J. L. A. Roustan, J. Y. Merour, and F. Houlihan, *Tetrahedron Lett.*, **39**, 3721 (1979); c) J. L. A. Roustan and F. Houlihan, *Can. J. Chem.*, **57**, 2790 (1979).

8) a) B. Zhou and Y. Xu, *J. Org. Chem.*, **53**, 4419 (1988); b) Y. Xu and B. Zhou, *J. Org. Chem.*, **52**, 974 (1987).

9) T. Ueda, M. Kawakita, and Y. Otsuji, *Nippon Kagaku Kaishi*, **1985**, 271.

10) a) S. Nakanishi, H. Yamaguchi, K. Okamoto, and T. Takata, *Tetrahedron*: *Asymmetry*, **7**, 2219 (1996); b) S. Nakanishi, Y. Sawai, T. Yamamoto, and T. Takata, *Organometallics*, **15**, 5432 (1996); c) K. Itoh, Y. Otsuji, and S. Nakanishi, *Tetrahedron Lett.*, **36**, 5211 (1995); d) K. Itoh, S. Nakanishi, and Y. Otsuji, *J. Organomet. Chem.*, **473**, 215 (1994); e) S. Nakanishi, T. Yamamoto, N. Furukawa, and Y. Otsuji, *Synthesis*, **1994**, 609; f) K. Ito, S. Nakanishi, and Y. Otsuji, *Bull. Chem. Soc. Jpn.*, **64**, 2965 (1991); g) K. Ito, S. Nakanishi, and Y. Otsuji, *Chem. Lett.*, **1989**, 615; h) K. Ito, S. Nakanishi, and Y.Otsuji, *Chem. Lett.*, **1988**, 473; i) K. Ito, S. Nakanishi, and Y. Otsuji, *Chem. Lett.*, **1987**, 2103.

11) H. Brunner, H. Weber, I. Bernal, and G. M. Reismer, *Organometallics*, **3**, 163 (1983).

12) H. L. Clarke, *J. Organomet. Chem.*, **80**, 155 (1974).

13) J. W. Faller and M. A. Adams, *J. Organomet. Chem.*, **170**, 71 (1979).

14) R. W. Fish, W. P. Giering, D. Marten, and M. Rosenblum, *J. Organomet. Chem.*, **105**, 101 (1976).

15) K. Ziegler, A. Spath, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann. Chem.*, **551**, 80 (1942).

16) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

17) H. N. Rydon and B. L. Tonge, *J. Chem. Soc.*, **1956**, 3043.

18) L. Anschutz, H. Kraft, and K. Schmidt, *Ann.*, **542**, 14 (1939).

19) T. Milobendzki and A. Sachnowski, *Chem. Pol.*, **15**, 34 (1917).

20) J. F. Faller and A.M. Rosan, *J. Am. Chem. Soc.*, **98**, 3388 (1976).

21) R. J. Batchelor, F. W. B. Einstein, R. H. Jones, J. M. Zhuang, and D. Sutton, *J. Am. Chem. Soc.*, **111**, 3469 (1989).

22) P. K. Baker, S. Clamp, N. G. Connelly, M. Murray, and J. B. Sheridan, *J. Chem. Soc., Dalton Trans.*, **1986**, 459.

23) H. Yamaguchi, S. Nakanishi, K. Okamoto, and T. Takata, *Synlett*, **1997**, 722.