A Novel Route to (η^3-Allyl)dicarbonylnitrosyliron Complexes *via* Transmetallation of η^3-Allyl Palladium Complexes

Saburo Nakanishi,* Masashi Yasui, Nobuhiro Kihara, and Toshikazu Takata
Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531

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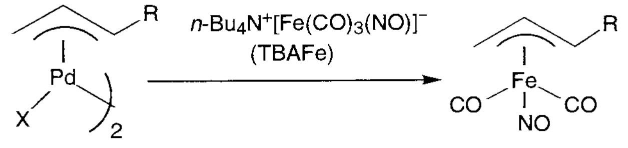
Treatment of (η^3-allyl)bromopalladium complexes with tricarbonylnitrosyl ferrate $[Fe(CO)_3(NO)]^{-1}$ afforded (η^3-allyl)-dicarbonylnitrosyliron complexes in good yields. The reaction provides a new route to (η^3-allyl)dicarbonylnitrosyliron complexes by transmetallation of the η^3-allyl ligand from palladium to iron metal.

(η^3-Allyl)dicarbonylnitrosyliron complexes are an important class of compounds among η^3-allyl transition metal complexes due to their versatile reactivity.[1] The η^3-allyl ligand of the complexes can serve as both electrophiles and nucleophiles.[2] Several methods have been developed for the preparation of the (η^3-allyl)dicarbonylnitrosyliron complexes. The most convenient method involve the reaction of tricarbonylnitrosyl ferrate $[Fe(CO)_3(NO)]^{-1}$ with allyl substrates such as allyl halides and tosylates.[3] However, the reaction of $[Fe(CO)_3(NO)]^{-1}$ with allyl acetate and allyl carbonate do not give the η^3-allyl complex. The other methods utilize the reaction of alkyl halides with the ferrate followed by treatment with 1,3-dienes[4] and vinyloxiranes[5] to give functionalized (η^3-allyl)dicarbonylnitrosyliron complexes.

It is worthwhile to develop a new route to the (η^3-allyl)-dicarbonylnitrosyliron complexes. Here we wish to report transformation of η^3-allyl palladium complexes to (η^3-allyl)-dicarbonylnitrosyliron complex by transmetallation of the η^3-allyl ligand from palladium to iron. Since η^3-allyl palladium complexes are easily prepared from palladium salt and allyl acetate or allyl carbonate, the above transmetallation would enable the synthesis of η^3-allyl iron complexes from various allyl acetate derivatives. Also transmetallation is a useful tool for coversion of the reactivity of the η^3-allyl ligand. A variety of methods have been developed for Pd,[6] Pt,[7] Sn,[8] Zn,[9] and Sm.[10]

A mixture of η^3-allylbromopalladium complex **1b**[11] (2.0 mmol) and tetrabutylammmonium tricarbonylnitrosyl ferrate (TBAFe)[2c] (4.0 mmol) in dichloromethane (10 ml) was stirred at -20 °C for 3h. (η^3-Allyl)dicarbonylnitrosyliron complex **2a** was isolated by column chromatography on silica gel of the reaction mixture. Effects of solvent and reaction temperature on the product yields are shown in Table 1. The reaction can be conducted in a variety of solvents even at -40 °C. The highest yield of the (η^3-allyl)dicarbonylnitrosyliron complex was obtained from the reaction in dichloromethane at -20 °C.



1a-f **Scheme 1.** **2a-f**

Similar treatment of several η^3-allyl palladium complexes **1** with TBAFe leads to the formation of the corresponding (η^3-allyl)dicarbonylnitrosyliron complex **2** in good yields. The results are given in Table 2. Reaction of η^3-allylchloro- and η^3-allyliodopalladium complexes underwent smoothly to give the η^3-allyl iron complex **2a** in slightly lower yields than that of the bromo derivative. η^3-Allyl iron complexes (**2d-f**) having methyl, phenyl, and ethoxycarbonyl groups on the η^3-allyl ligand were prepared in reasonable yields.

Table 1. Formation of (η^3-allyl)dicarbonylnitrosyliron complex **2a** under various reaction conditions

Conditions			Yield of iron complex
Solvent	Temp / °C	Time / h	**2a** / %[a]
CH_2Cl_2	20	3	76
CH_2Cl_2	0	3	76
CH_2Cl_2	-20	3	87
CH_2Cl_2	-40	5	50
acetone	-20	3	58
THF	-20	3	53
MeOH	-20	3	53
PhH	20	3	39
CH_3CN	-20	3	20

[a] Isolated yield.

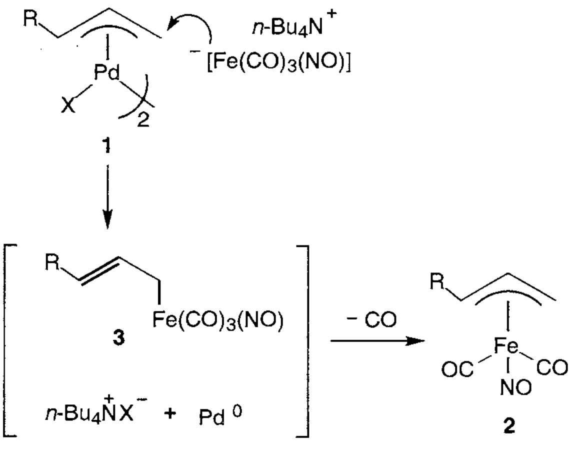
Table 2. Formation of various (η^3-allyl)dicarbonylnitrosyliron complexes **2**[a]

R	X	1	Yield of **2** / %[b]	
H	Cl	**1a**	69	**2a**
H	Br	**1b**	87	**2a**
H	I	**1c**	46	**2a**
CH_3	Br	**1d**	65	**2d**
Ph	Br	**1e**	35	**2e**
CO_2Et	Br	**1f**	88	**2f**

[a] The reaction was conducted in CH_2Cl_2 at -20°C for 3 h.
[b] Isolated yield.

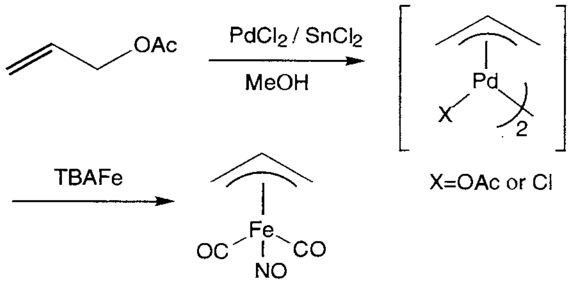
This method provides a facile route to (η^3-allyl)dicarbonylnitrosyliron complex and alteration of the reactivity of η^3-allyl palladium complex, and also presents a valuable information on the transmetallation of the ligand between two transition metals.

A possible mechanism of the transmetallation reaction is illustrated in Scheme 2. Generally, soft nucleophiles such as carbanions and amines directly attack at the allylic carbon of the complexes from the opposite site of the palladium atom with inversion of the stereochemistry in the reaction of η^3-allyl palladium complexes. On the other hand, hard nucleophiles such as Grignard reagents attack at the palladium atom followed by reductive elimination, yielding the allylated products with retention of the stereochemistry.[12] Since the ferrate is a soft nucleophile, anionic iron atom of TBAFe probably attacks at allylic carbon to form (η^1-allyl)tricarbonylnitrosyliron complex **3** which is then converted to the η^3-allyl iron complex **2** by elimination of carbon monoxide.



Scheme 2.

One pot reaction was carried out for the preparation of the (η^3-allyl)dicarbonylnitrosyliron complex from allyl acetate and TBAFe as shown in Scheme 3. Thus, reaction of allyl acetate with two equivalent of TBAFe in the presence of a mixture of equivalent $PdCl_2$ and $SnCl_2$ in methanol at -20 °C for 3 h afforded η^3-allyl iron complex **2a** in 40% yield. $PdCl_2$ is essential for the formation of the η^3-allyl iron complex. Formation of the η^3-allyl iron complex is interesting because allyl acetate is unreactive toward TBAFe.



Scheme 3.

The detailed mechanism, the stereochemistry of the transmetallation reaction and also the η^3-allyl iron complex-forming reaction catalyzed by palladium complex are now under investigation.

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